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CORROSION MONITORING BY FREQUENCY INTERMODULATION TECHNIQUE EMPLOYING GABOR TRANSFORMATION

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Summary: A process of ST3S steel corrosion in neutral environment has been monitored. Harmonic measurements employing frequency intermodulation technique have been carried out. A new time-frequency method, so-called Gabor transformation, has been introduced in harmonic analysis. It has been proved that Gabor transformation can be useful in corrosion monitoring in dynamic conditions. Gabor transformation provides good representation of the investigated signal in joint time-frequency domain. Application of Gabor method enables determination of instantaneous value of corrosion current. A technique of corrosion risk assessment based on on-line analysis of the harmonic components containing frequency intermodulations has been presented.

Key words : *harmonic analysis, Gabor transformation, corrosion monitoring*

INTRODUCTION

Corrosion monitoring is of great importance from the standpoint of corrosion risk assessment. It provides the information about the scope of risk, so appropriate prevention measures against the negative impact of environment can be taken. There is no monitoring technique, which univocally describes the process of corrosion. Several techniques should be employed simultaneously. Most frequently the rate of corrosion is determined for fixed DC potential corresponding to corrosion potential. Application of direct current to polarization allows analysing of obtained current-potential characteristics. Non-linearity of investigated systems makes evaluation difficult. The polarization resistance and Tafel slopes extrapolation techniques are based on the assumption of partial linearity of the characteristics. DC measurements are burdened with errors connected with the presence of ohmic resistance and diffusion polarization. The drawback of these techniques is their degradative character in case of the investigation carried out in wide range of potential. Determination of corrosion current on the basis of Stearn-Geary equation requires the knowledge of Tafel coefficients and the value of polarization resistance. Very often these parameters are unknown or they cannot be determined. In low-amplitude investigations the values of Tafel coefficients are assumed but they can change with temperature, aeration and pH of corrosive environment. Because of these reasons a tendency to elaborate the investigation method, which does not induce significant changes in the examined process is currently observed. It is meant to provide reliable information about Tafel coefficients and the magnitude of corrosion current. Harmonic analysis fulfils this condition connecting the advantages of non-destructive character and ability to determine several kinetic parameters during one measurement [1, 2, 3, 4]. It is one of only few methods that take into account real non-linearity of corrosion processes. Theoretical bases of harmonic analysis were elaborated by Rao and Mishra [5] as well as by Devay and Meszaros [6]. Devay and Meszaros defined the relations describing harmonic components of current enabling determination of the corrosion parameters. These relations were verified during examination of iron in sulphuric acid [5] and in hydrochloric acid [6]. Gill and co-workers [4] investigated the process of steel corrosion in sodium chloride with the use of harmonic analysis. Bosh and co-workers [7] as well as Meszaros and co-workers [5] put an attention to the problem of application of harmonic analysis in examination of steel corrosion in the solution of sodium sulphate occurring with mixed control. Literature describes the possibility of utilization of harmonic analysis in corrosion monitoring in field conditions [9]. Laboratory tests exhibit good correlation with the results obtained by the other monitoring methods [8, 9, 10, 11]. A modification of harmonic analysis is the

method employing the phenomenon of intermodulation. It can be considered as a development of Faraday distortion technique. The pioneers of intermodulation technique were Meszaros and Devay. In the paper [12] Meszaros and Devay investigated the dependence between potential and harmonic components of the current flowing through the electrode polarized by the sum of overlapped sine-changing potential and constant potential. Intermodulation method did not meet with high interest as a technique useful in corrosion research and it was not developed.

The aim of this paper is to present practical application of frequency intermodulation technique in corrosion monitoring in conditions when kinetically controlled corrosion potential is often subjected to time drift. A new technique of spectral analysis of joint time-frequency type, so-called Gabor transformation [13], was used in the investigation.

GABOR TRANSFORMATION

In harmonic analysis the algorithms of Fourier transformation are often applied [14, 15]. However, this method gives significantly better results for stationary systems where frequency composition does not change during the investigation. In reality most corrosion processes are connected with natural potential drift. If the system is unstable so-called short time Gabor transformation can be applied in the analysis by intermodulation technique [13, 16]. General formula of Gabor transform is given by the expression:

$$G(f, t) = \int i(\tau)g(\tau - t)\exp(-j\omega\tau) d\tau \quad (1)$$

where:

$(t-\tau)$ - window function,

t - time location of analysing window

Gabor transformation is one of the non-stationary methods of signal analysis. This transformation is of joint time-frequency type. The formula contains a fragment dependent on time; in the STFT theory it is called window function. In our case window function has a shape of Gauss curve. In practice windows of various shapes are applied [13]. Gabor transformation is based on a shift of the analysing window $g(t-\tau)$ along time axis. The window is moved in a different manner along examined signal. The analysing window cuts out a fragment of register for time location equal t and then this fragment is subjected to classical Fourier transformation. In case of Gabor transformation the analysing window is of Gauss curve shape. Fourier transform of Gauss window is described by the following relation:

$$\int \exp\left[\frac{\lambda}{2}(\tau - t)^2\right] \exp(-j2\pi f\tau) d\tau = \sqrt{\frac{2\pi}{\lambda}} \exp\left[-\frac{2\pi^2 f^2}{\lambda} + j2\pi ft\right] \quad (2)$$

where:

λ - parameter of Gauss window

Due to this operation instantaneous amplitude characteristic is obtained. Analysed signal is well characterized in time (potential) domain and frequency domain. Time selectivity and frequency resolution of joint time-frequency analysis depends on the width of the window. This problem was discussed by Quian and Chen [16] as well as by Darowicki [17].

THEORETICAL DESCRIPTION OF DYNAMIC INTERMODULATION DISTORTION

In investigations by dynamic intermodulation method the perturbation signal is a superposition of two sine signals of frequencies ω_1 and ω_2 and amplitudes $U_1=U_2$. For simplification the amplitude of the signal will be denoted as U_0 .

Application of two sine perturbation signals gives the amplitude composition described by formula 3:

$$\begin{aligned}
 i = & i_{\text{cors}} \left(1 + \frac{U_0^2}{2b_A} \right) + i_{\text{sort}} \left(\frac{U_0}{b_A} + \frac{3U_0^3}{8b_A^3} \right) \cos \omega_1 t + i_{\text{ors}} \left(\frac{U_0}{b_A} + \frac{3U_0^3}{8b_A^3} \right) \cos \omega_2 t + i_{\text{ors}} \left(\frac{U_0^2}{2b_A^2} \right) \cos(\omega_1 - \omega_2) t + \\
 & + i_{\text{ors}} \left(\frac{U_0^2}{2b_A^2} \right) \cos(\omega_1 + \omega_2) t + i_{\text{ors}} \left(\frac{U_0^3}{8b_A^3} \right) \cos(\omega_1 - 2\omega_2) t + i_{\text{ors}} \left(\frac{U_0^3}{8b_A^3} \right) \cos(\omega_1 + 2\omega_2) t + i_{\text{sort}} \left(\frac{U_0^2}{4b_A^2} \right) \cos 2\omega_1 t + \quad (3) \\
 & + i_{\text{sort}} \left(\frac{U_0^2}{4b_A^2} \right) \cos 2\omega_2 t + i_{\text{sort}} \left(\frac{U_0^3}{8b_A^3} \right) \cos(2\omega_1 - \omega_2) t + i_{\text{sort}} \left(\frac{U_0^3}{8b_A^3} \right) \cos(2\omega_1 + \omega_2) t + i_{\text{sort}} \left(\frac{U_0^3}{24b_A^3} \right) \cos 3\omega_1 t + \\
 & + i_{\text{sort}} \left(\frac{U_0^3}{24b_A^3} \right) \cos 3\omega_2 t + \dots
 \end{aligned}$$

Obtained expression describes basic harmonic components of anodic current as well as intermodulation components. An influence of capacitive current on the basic harmonic components is neglected in the considerations. Corrosion current will be determined by comparison of appropriate intermodulation components. By comparing suitable intermodulation components a magnitude of current can be found and then related to the corrosion current. The relations enable determination of i_k parameter without the knowledge about amplitude of the perturbation signal. They also allow elimination of IR component, which has an influence on the effective value of the perturbation signal amplitude. Consideration of bigger number of elements in the expression enables determination of the current by comparing the intermodulation amplitudes of higher orders. However, the analysis of intermodulation components of higher orders is burdened with more significant error. Description of harmonic components is limited to activation controlled processes. In natural environment the majority corrosion processes occur with mixed control.

EXPERIMENTAL

Harmonic analysis of freely corroding system was performed. Three-electrode system consisting of identical electrodes, each of an area $S = 5,94 \text{ cm}^2$, was employed during the investigation. The electrodes were manufactured from construction steel ST3S. The measuring system consisted of EP-20 Elpan potentiostat and two FZ-7002C sine signal generators. Electrochemical measurements were conducted in 0.5 M solution of sodium sulphate. The solution was prepared from pure reagent and threefold distilled water. Additionally to determine the corrosion current potentiodynamic measurements were carried out. They were correlated with the results obtained by harmonic analysis technique. Potentiodynamic measurements were performed with the use of Gamry Instruments card for the rate of potential change equal to 1 mV/s. While conducting measurements the pH and electrode potential changes during the exposure were monitored. In case of investigation in neutral solution sine-changing signals of the frequencies $f_1=3 \text{ Hz}$ and $f_2=34 \text{ Hz}$ were overlapped on DC signal. In order to simplify the analysis the amplitude of both perturbation signals was equal to $U_1 = U_2 = U_0 = 50 \text{ mV RMS}$. The results of measurements were registered with National Instruments DAQ PCI-MIO-16XE-50 card. Lab-View software made by the National Instruments was used to analyse obtained results.

RESULTS AND DISCUSSION

Harmonic analysis was performed by the technique of corrosion system intermodulation. Time characteristics was registered during the experiment. Time characteristics presented on exemplary Fig. 1. are analysed by Lab-View software. The amplitude analysis was performed.

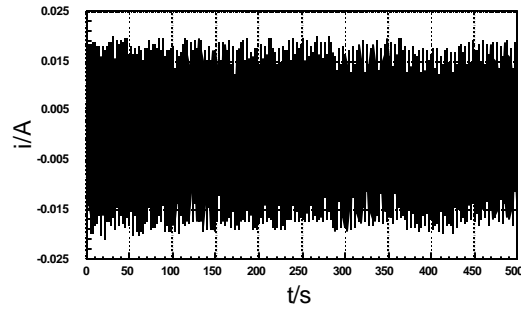


Fig. 1. An exemplary time register and corresponding Gabor spectrogram obtained for the sampling frequency of 320 Hz.

A current signal registered with the measuring card was subjected to computer processing during which Gabor transformation was performed. Gabor transformation of current response of the investigated system can be presented as a sum of transforms of particular harmonic components.

$$\begin{aligned}
 G\{i(f, t)\} \approx G\{i_f(f, t) + i_{nf}(f, t)\} = & G\{i_0(f_1, t) + G\{i(f_1, t)\} + G\{i(2f_1, t)\} + \\
 G\{i(3f_1, t)\} + G\{i(f_2, t)\} + G\{i(2f_2, t)\} + G\{i(3f_2, t)\} + G\{i(f_{1f_1-f_2}, t)\} + & \\
 G\{i(f_{f_1+f_2}, t)\} + G\{i(f_{f_1-2f_2}, t)\} + G\{i(f_{f_1+2f_2}, t)\} + G\{i(f_{2f_1-f_2}, t)\} + & \\
 G\{i(f_{2f_1+f_2}, t)\} + \dots &
 \end{aligned} \quad (4)$$

As a result the spectrogram in join time-frequency domain is obtained. Fig. 2 presents Gabor spectrogram of the current changes in investigated system. The spectrogram corresponds to the time register presented on Fig. 1 and it results from overlapping of two sine signals of frequency $f_1=3$ Hz and $f_2=34$ Hz on freely corroding system. Gabor spectrogram was determined for the parameter λ , characterizing the width of the window, equal to 256.

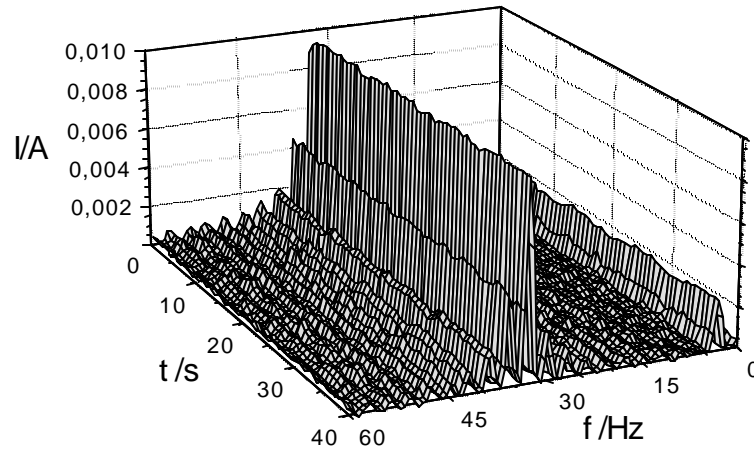


Fig. 2. Gabor spectrogram corresponding to time register presented on Fig. 1.

The harmonic components of perturbation signals f_1 , f_2 and suitable intermodulation components of frequencies $f_1 \pm f_2$, $f_1 \pm 2f_2$ are visible on Gabor spectrogram. The spectrogram is presented in 3D manner where time domain describes the change of harmonic components in the entire time of signal registration. No rapid amplitude variations of particular harmonic components, characteristic for local corrosion, are visible on the spectrogram. 3D representation of the results can be considered in more details by analysing particular amplitude characteristics for a given moment of measurement. Analysis of instantaneous amplitude characteristics allows finding the corrosion current

in any moment of the measurement. Determined rate of corrosion will correspond to its instantaneous value. During the experiment the magnitude of current obtained by harmonic analysis was correlated with corrosion current determined by the analysis of potentiodynamic curves. In case of activation control the interpretation of the results is univocal. If the process of corrosion is characterized by mixed control one can correlate the magnitude of current employing empirical relations. Description of harmonic components is very difficult in case of mixed control – too many parameters influence the process of corrosion. Monitoring of corrosion in natural environment with harmonic analysis technique enables registration of only time-dependent changes in corrosion activity. In majority of corrosion processes a natural potential drift appears. The change in character and intensity of corrosion process will be reflected in the spectrogram determined with the use of Gabor transformation. This technique has certain advantages over classical harmonic method where measurement and analysis of fundamental harmonic components is burdened with an error resulting from the existence of capacitive component. The correctness of the results depends on selection of appropriate amplitude and frequency of perturbation signal. Presented method supplies satisfactory description of the parameters of electrode process in the field of kinetics. The technique can be successfully applied in corrosion monitoring. On-line analysis of harmonic components enables observation of corrosion process in dynamic conditions.

CONCLUSIONS

A new approach to the utilization of intermodulation technique and Gabor transformation in determination of corrosion parameters has been presented in this paper. Harmonic analysis in conjunction with Gabor transform applied in the stationary conditions allows determination of the instantaneous amplitude characteristics, which enable evaluation of the parameters characterizing corrosion process. On-line analysis is very promising in the field of corrosion monitoring in industrial conditions. In some circumstances, when Tafel coefficients are not known, satisfactory assessment of corrosion intensity is possible. Investigations by frequency intermodulation method can be carried out in wide range of frequency. Moreover the necessity of additional impedance measurement aimed at selection of appropriate perturbation signal is eliminated. Due to this technique intermodulation harmonic components cleared from the capacitive component can be analysed. Intermodulative amplitude spectrum supplies broad range of data concerning investigated system. Application of Gabor transformation can be an alternative to classical spectrum analysis in frequency domain, that is to Fourier transformation which averages the results and in this way makes identification of subtle time-variations of observed signal more difficult.

Acknowledgement: This work was financed by BW 2001 grant.

REFERENCES

1. J. Devay, L. Meszarosz, Acta Chim. Acad. Sci. Hung.,100(1979)183.
2. L. Meszaros, J. Devay, Acta Chim. Acad. Sci. Hung.,109(1982)241.
3. S. Sathinarayanan, K. Balakrishnan, Brit. Corosion J., 291(994)152
4. J.S. Gill, L.M. Callow, J.D. Scanlebury, Corrosion, 39(1982)241
5. L. Meszaros, E. Fekete, Acta Chim. Acad. Sci. Hung.,129(1992)83.
6. A. Pirnat, L. Meszarosz, B. Lengyel, J. Electrochemical. Soc.141(1994)2068
7. R.W. Bosch, W.F. Bogaerts, J. Electrochemical Soc., 143(1996)4033
8. M.C.H McKubre, F.L.Tanzella, B.C. Syrett, The Determination of Rates and Mechanisms of Localized Corrosion Using Harmonic Impedance Spectroscopy, SRI International, California 1983
9. A. Pirnat, L. Meszaros, G. Meszaros, B. Lengyel, Corrosion Sci., 34(1993)1147
10. M.I. Jafar,J.L., Dawson, D.G. John, Electrochemical Impedance Analysis & Interpretation,(Eds.)J.R. Scully, D.C. Silvermann, M.W. Kendig, ASTM STP 1188,Philadelphia 1993,384
11. M. Kendig, D. Anderson, Corrosion, 48,1992,178

12. L. Meszarosz, J. Devay, Acta Chim. Acad. Sci. Hung.,105(1980)1
13. L. Cohen, Time – Frequency Analysis, Prentice Hall, Englewood Cliffs, N. Y, 1995
14. R.W.Ramirez, The FFT fundamental and Concepts, Engelwood, New York,1985
15. A.G. Piersol, J.S. Bendat, Measurement and Analysis of Random Data, John Willey & Sons, 1966
16. D.Chen, S. Quian, Joint – Time Frequency Analysis, Method & Applications, Prentice Hall PTR,1996
17. K. Darowicki. J of Electroanal. Chem. 394(1995)81