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ELECTROCHEMICAL NOISE ANALYSIS OF UNIFORM CORROSION IN WATER SUPPLY SYSTEM

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Abstract – The results of electrochemical noise measurements and their analysis for evaluation of corrosion intensity in the water supply system are presented. The polarization resistance R_p is calculated for corrosion evaluation, estimated by applying the proposed method of noise analysis. The method includes trend removal and impedance calculation by dividing power spectral densities of the detrended voltage and current fluctuations. The estimated impedance at low frequencies is used for R_p value calculation. The applied algorithm of electrochemical noise detrending is based on its decomposition and after trend removal reconstruction using wavelet transform.

Keywords: noise, corrosion, wavelet transform

1. INTRODUCTION

Uniform corrosion processes can be evaluated by measuring polarization resistance R_p of the corroding metal. The Stern-Geary equation directly relates R_p to its corrosion rate [1]. The different electrochemical methods, like linear polarization or electrochemical impedance spectroscopy, can be used for estimation of R_p . These methods apply small voltage signals to the electrodes that may affect the corrosion processes. The technique that does not disturb electrochemical processes at electrode surface is observation of the spontaneous current and voltage fluctuations (electrochemical noise) caused by processes of charge flows between metal (electrode) and electrolyte.

The method is well known and even applied in industry [2,3]. Though, its significant limitations, caused by presence of other noise sources (inner noise of measurement instrumentation, outside distortion) have to be taken into consideration. The mentioned problems of the presented real data analysis have to be investigated in detail to secure unambiguous measurement results and exclusion of any doubtful noise data.

The registered electrochemical noise is a $1/f$ type noise that is usually observed at frequencies lower than a few Hz. Visible trends are observed in current and voltage time records. They are caused by presence of some inevitable differences between nominally identical electrodes (mainly caused by their surface treatment) and hydrodynamic

conditions around their surfaces. The trends have to be effectively removed before the further analysis.

Electrochemical processes, that take place in boundary layer between electrode and electrolyte can be characterised by an equivalent noise circuit (Fig. 1). The current noise source having spectral density $S_{iRp}(f)$ represents intensity of fluctuations caused by corrosion processes. The source of current spectral density $S_{iRe}(f)$ represents thermal noise of electrolyte resistance R_e . The capacitor C_p represents capacity of the boundary layer. The proposed circuit is limited only to a few most crucial elements but its usage for description of random fluctuations present in metal-electrolyte boundary layer is sufficient.

The standard system for electrochemical noise measurement consists of a three-electrode set (Fig. 2) [4]. The current and voltage fluctuations are registered separately. Two, identically prepared, working electrodes are short-circuited and current fluctuations are observed there. The voltage fluctuations are measured between the potential of the working electrodes and potential of the reference electrode. The impedance of the reference electrode should be relatively low so the observed voltage fluctuations are not affected by its presence. Very often in practice, the reference electrode can be prepared in the same way as the working electrode. The same solution was applied when the presented measurements were performed.

Authors propose a method of noise analysis for evaluation of R_p value. The method of analysis removes trend from the observed noise records and estimates their power spectral densities.

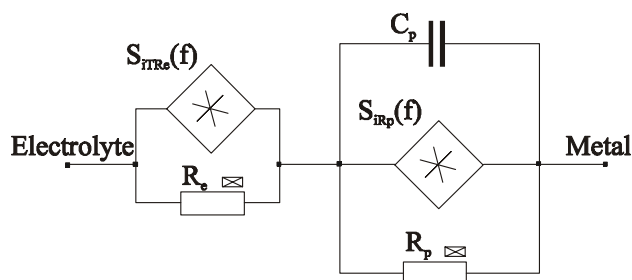


Fig. 1. The equivalent circuit of metal-electrolyte boundary layer

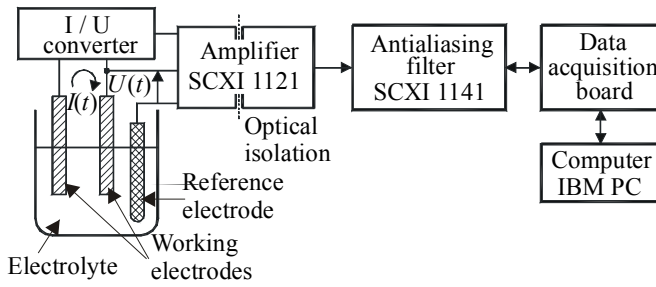


Fig. 2. The measurement setup

The estimated power spectral densities of the current $i(t)$ and voltage $u(t)$ noise after trend removal are divided and squared module of the impedance value is obtained. The R_p value is calculated by averaging the mentioned impedance at low frequencies.

2. METHOD OF NOISE ANALYSIS

The registered electrochemical noise is caused by fluctuations that take place inside electrolyte, at surfaces of the both working electrodes (current fluctuations) and also at surface of the reference electrode (voltage fluctuations). The observed current $I(t)$ and voltage $U(t)$ time series have visible trends that are caused also by the other reasons than corrosion processes (e.g. changes in water flows and some unavoidable differences between the identically prepared electrodes) and have to be removed before further analysis. Authors propose to use the algorithm described in [5]. The algorithm, based on wavelet transform is prepared in MatLab software. The fluctuations $i(t)$, $u(t)$, obtained after detrending $I(t)$, $U(t)$ are used for estimation of the impedance module

$$\begin{aligned} |Z(f)| &= \left| R_p / (1 + j2\pi f R_p C_p) \right| \approx \\ &\approx \sqrt{1/3} \cdot \sqrt{S_u(f) / S_i(f)} \end{aligned} \quad (1)$$

The power spectral densities $S_i(f)$, $S_u(f)$ of the fluctuations $i(f)$, $u(f)$ are estimated by applying Welch's method [6]. The coefficient $\sqrt{1/3}$ in (1) is obtained from the detailed analysis of the equivalent noise circuits of the observed current (Fig. 3a) and voltage noise (Fig. 3b). Equation (1), that directly relates $|Z(f)|$ to the polarization resistance $R_p \approx |Z(f)|$ at low frequencies, is valid when:

- the thermal noise of the electrolyte is negligible,
- the reference electrode is prepared in the same way as working electrodes,
- the trend components $I_t(t)$, $U_t(t)$ of the observed current and noise are removed,
- the module of impedance $|Z(f)|$ does not depend on frequency at least at low frequencies.

When $|Z(f)|$ depends on frequency at low frequencies, it can be supposed that the other noise sources than $S_{irp}(f)$ or capacitor C_p have substantial influence on the observed electrochemical noise. In such cases the proposed algorithm cannot be used for unambiguous R_p value estimation.

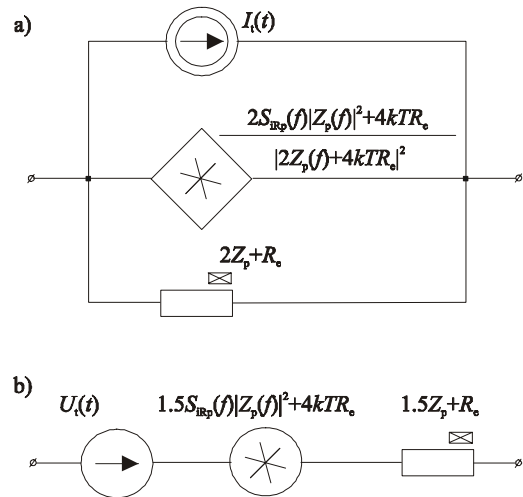


Fig. 3. Equivalent noise circuit of the observed (a) current and (b) voltage noise sources between terminals of the three-electrode set

The estimated power spectral densities $S_i(f)$, $S_u(f)$ should have dominant $1/f$ noise component at low frequencies. The absence of such component suggests that the observed electrochemical noise is not caused by corrosion processes but is overwhelmed by the other noise sources like e.g. inner noise of the measurement system.

Different methods of detrending are suggested [6-8]. Authors propose to apply the method that is proposed by Donoho [5]. The observed random discrete signal $x(t_n)$ is treated as a sum of a discrete deterministic function $a(t_n)$ that represent trend and Gaussian noise $e(t_n)$, having $1/f$ like spectrum (non-white noise)

$$x(t_n) = a(t_n) + e(t_n) \quad (2)$$

The algorithm of detrending means subtraction from the observed signal samples $x(t_n)$ the identified trend function $a(t_n)$. Trend is recognized by decomposition of the analysed signal into vector of detail coefficients and approximation (Fig. 4). At each level of decomposition k , the detail coefficient $x_{D,k}$ is obtained by high-pass filtering and down-sampling (throwing away every second data point) of approximation $x_{A,k-1}$, calculated at the previous decomposition level $k-1$. Approximation $x_{A,k}$ at level k is calculated by low-pass filtering and down-sampling of the previous level approximation $x_{A,k-1}$. Only the detail coefficients are threshold. The method of soft threshold and assumption of non-white noise samples $e(t_n)$ is applied. The detail coefficient $x'_{D,k}$ after operation of soft threshold is equal to:

$$x'_{D,k} = \begin{cases} \text{sign}(x_{D,k}) (|x_{D,k}| - A) & \text{if } |x_{D,k}| > A \\ 0 & \text{if } |x_{D,k}| \leq A \end{cases} \quad (3)$$

A rule of selection of the threshold A , rescales it at each level of decomposition separately, using a level-dependent estimation of the level noise [9].

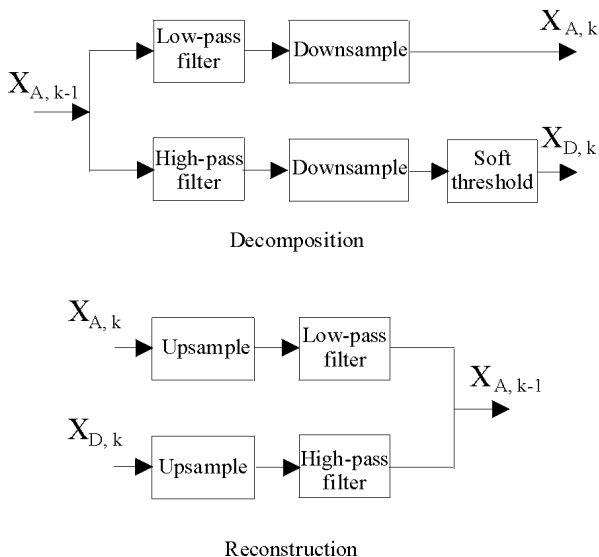


Fig. 4. One-dimensional fast wavelet transform decomposition and reconstruction step with soft-threshold of the detail coefficients

The detail coefficients after threshold and approximation are assembled back by inverse wavelet transform to obtain trend function $a(t_n)$. The inverse wavelet transform is performed by operations of up-sampling (inserting zeros between samples) and high-pass or low-pass filtering the adequate approximations and detail coefficients after threshold (Fig. 4). The four mentioned filters, used within wavelet and inverse wavelet transform, are called quadrature mirror filters and are specified by the chosen wavelet functions [10].

The presented method of detrending needs to establish the level K of wavelet decomposition and wavelet function. Only the orthogonal wavelet functions can be considered.

The whole algorithm is available in MatLab software, in wavelet toolbox and is described in detail [9].

3. EXPERIMENTAL RESULTS

The electrochemical noise measurements were done in water supply system by placement of the three-electrode set inside the pipe that supplied water. The applied measurement system was optimised for minimizing its low frequency inner noise and was separated from computer by optical isolation barrier limiting outside distortion generated mainly by computer.

The flow of water was changeable due to the temporary demand but was stopped within a period when electrochemical noise had been recorded. All the three electrodes were prepared in the same way, made of carbon steel of area about 1 cm^2 . The noise records were registered at sampling frequency $f_s=1 \text{ Hz}$. The observed voltage and current fluctuations had visible trends (Fig. 5a, 5c). The fluctuations after detrending (Fig. 5b, 5d) were used for estimation of its power spectral densities $S_u(f)$ (Fig. 6a) and $S_i(f)$ (Fig. 6b).

The example estimated impedance module $|Z(f)|$ (Fig. 6c) does not show evident dependence at low frequencies, so its averaged values were used for evaluation of R_p . The results obtained within a few following days of measurements

presents tab. 1. The most doubtful results $R_p=1140 \Omega$ and $R_p=950 \Omega$ were obtained when $|Z(f)|$ values started to depend slightly on frequency.

All the presented results were obtained for $K=8$ or $K=11$ and for Daubechies family wavelet of the first order. The K value was set arbitrary when the detrended current and voltage noise records have not any visible and predictable dependency on time.

4. CONCLUSIONS

The experimental results of uniform corrosion evaluation by estimation of resistance R_p using electrochemical noise analysis are presented. The obtained results confirm that the proposed method of noise analysis can be applied for real data corrosion rate monitoring - water supply pipe. It considers different problems appearing when the real data are analysed.

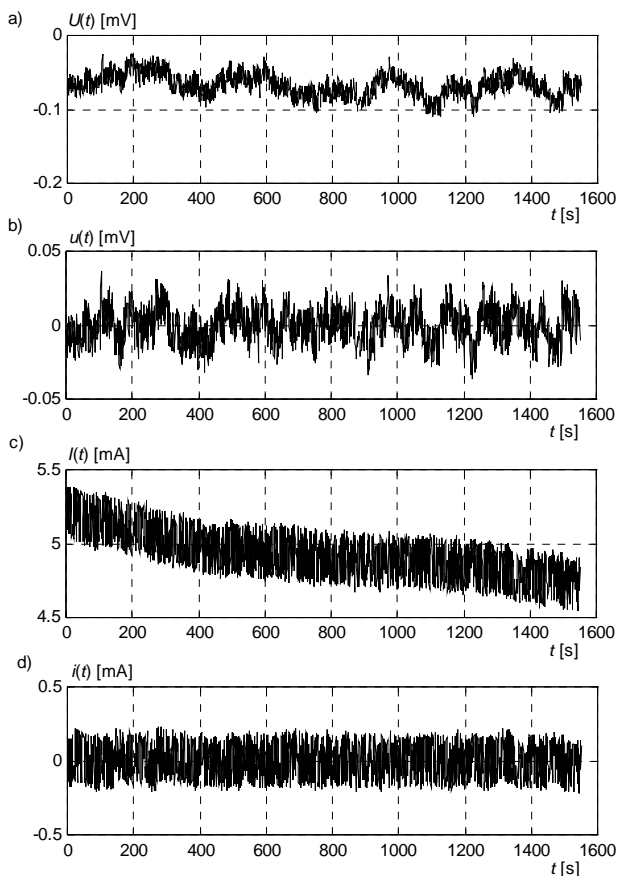


Fig. 5. Example of the observed: (a) voltage $U(t)$, (b) its noise component $u(t)$ after detrending, (c) current $I(t)$, (d) its noise component $i(t)$ after detrending

TABLE I. The estimated R_p values

Day	R_p [Ω]
1	630
2	1140
3	950
4	134
5	82
6	118

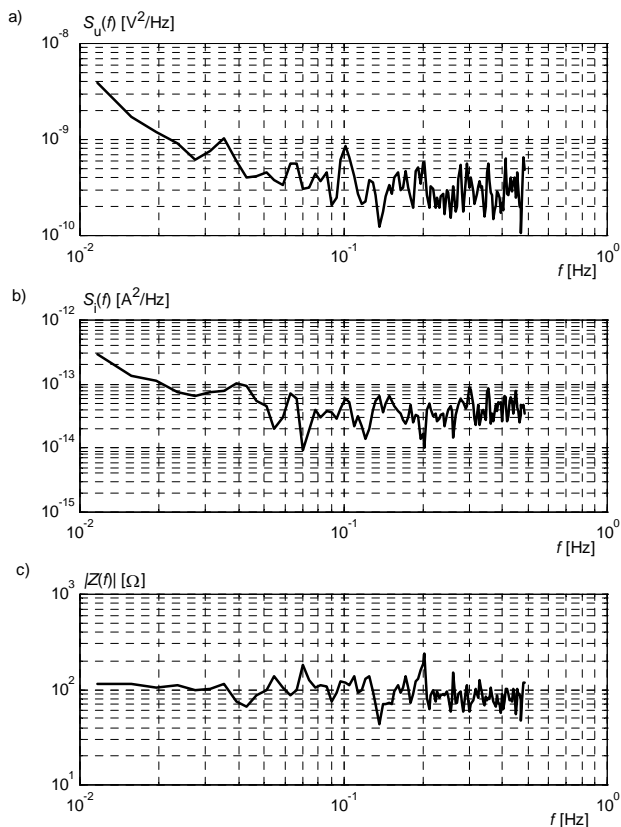


Fig. 6. Example of estimated: (a) voltage power spectral density $S_u(f)$, (b) current power spectral density $S_i(f)$, (c) module of impedance $|Z(f)|$

The additional investigation has to be undertaken for more rational recognition of the detrending procedure parameters (selection of wavelet function and level of decomposition).

The tentatively proposed method of R_p calculation can be included into the virtual instrument that controls process of noise measurements (controls data acquisition board) and can be estimated continuously for corrosion intensity monitoring in real corroding systems.

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