Proceedings of International Conference on Heat Exchanger Fouling and Cleaning - 2011 (Peer-reviewed)
June 05 - 10, 2011, Crete Island, Greece
Editors: M.R. Malayeri, H. Müller-Steinhagen and A.P. Watkinson

Published online
www.heatexchanger-fouling.com

STUDY ON SRB INDUCED CORROSION BASED ON ELECTROCHEMICAL NOISE ANALYSIS AND SIGNAL PROCESSING

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ABSTRACT

Corrosion of 304 stainless steel induced by sulfate-reducing bacteria was investigated by electrochemical noise (EN) in this paper. The electrochemical noise data were processed by wavelet denoising. These data were analyzed by time domain analysis and frequency domain analysis. Electrochemical noise signal after wavelet denoising could show the magnitude and the density of the noise fluctuations more clearly. Standard deviation, local factors, and noise resistance were received by time domain analysis. The standard deviation focuses on the characterization of the corrosion rate, local factors can show the type of corrosion under strict conditions, and noise resistance is able to reflect the type of corrosion and the corrosion rate. Electrochemical power spectral density curve was received by frequency domain analysis. It also can characterize the level of corrosion. The analysis results of electrochemical noise data was similar with the corrosion occurred on the surface of 304 stainless steel. Electrochemical noise measurement is non-destructive and non-intrusive electrochemical method, and its analysis method is reliable and convenient. It can be used as theoretical guidance in field application of power plants and other industrial sectors.

INTRODUCTION

Industrial cooling water normally is used in the circulating water system of power plants, petroleum, chemical, metallurgical and construction industries (Aballe *et al.*, 2001). It can exchange heat through the heat exchanger or directed contacting means, and can be used circularly after entering the cooling tower. So, it can save water (Huet *et al.*, 2002).

In general, the temperature of cooling water is 30℃ -40 ℃. It contains a variety of organic and inorganic substances in cooling water, and the environment is ideal for microbial growth and reproduction. The microbial life activities may directly or indirectly impact the electrochemical process of the heat exchanger in the cooling water system, eventually leading to microbiologically influenced corrosion (MIC) (Hamilton, 1998). MIC in cooling water system can cause corrosion and sticky mud deposition of heat transfer equipment, thereby reduce cross section and heat transfer efficiency of the device. In serious cases, it can lead to localized corrosion of equipment and perforation of pipes. Finally, the factory was forced to suspend production, resulting in considerable economic losses (Santana Rodr guez *et al.*, 2006). The sulfate-reducing bacteria (SRB) is the main bacteria in industrial cooling water, and it is one of the main factors of MIC (Abedi *et al.*, 2007). Therefore, studying SRB which induces corrosion of heat transfer equipment in industrial cooling water is important.

Traditional research technology of MIC is corrosion coupon weight loss. Modern research techniques of MIC are resistance probe method, chemical analysis and electrochemical methods (including the potential, linear polarization, polarization resistance, electrochemical impedance spectroscopy, galvanic current, field imaging, constant power charging curves, electrochemical noise, etc.). Most of the electrochemical measurement techniques apply a disturbance signal on the surface of working electrode. It can lead to distortion and even losing useful information. The electrochemical noise (EN) is produced in the electrochemical system itself, rather than from the controlling instruments or external interference（Padilla-Viveros *et al.*, 2005）. Electrochemical noise measurement is the electrode detection method of in situ, nondestructive, non-interference, and it is the forefront of the current electrochemical measurement (Sykes, 1991).

The research material in this paper was 304 stainless steel which commonly used as heat exchange equipment in industrial cooling water system. It was soaked in two different culture mediums which one contained SRB and the other did not contain any bacteria. Electrochemical noise was monitored by electrochemical workstation. The electrochemical noise data was processed by wavelet denoising, and then analyzed by time domain and frequency domain. So, the information can characterize the type and degree of MIC.

Experiment

Electrochemical system:

Electrochemical noise was measured by CHI660C electrochemical workstation produced by Shanghai Chen Hua Instrument. Measurement circuit was composed of two working electrodes and a reference electrode. Reference electrode was the saturated calomel electrode (SCE).The working electrode was 304 stainless steel(its chemical composition is shown on Table 1) ,and it was cut into small cylindrical area of 1 cm^2 . Using 320 # to 1000 # water mill grinding sandpaper polished the surface of working electrode step by step. After the electrode was prepared, the two working electrodes and a reference electrode were fixed on the white rubber plug which was drilled. The white rubber plug was used to close off the tapered bottle with culture medium (one contained SRB, the other did not contain any bacteria), so it could prevent oxygen to enter, creating the anaerobic environment suitable for the growth of SRB. Figure 1 shows the experimental system.

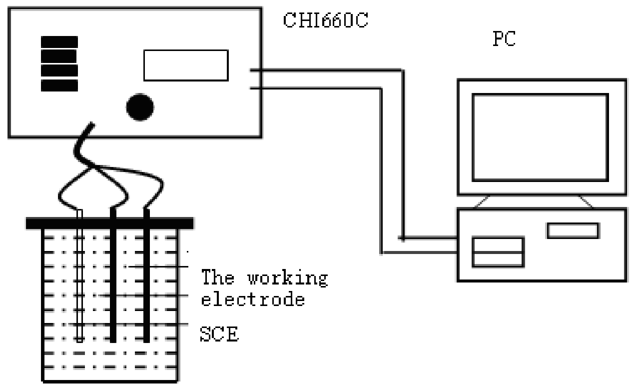


Fig.1 The experimental system

Table 1. The chemical composition and the proportion of 304 stainless steel

element	C	Si	Mn	Cr	Ni	Mo	Fe
Wt%	0.07	0.48	1.55	18.5	9.35	-	Bal

Media and biofilm growth conditions

In this experiment, sulfate-reducing bacteria was took from the Songhua River of China, and then put in incubator after enrichment and purification(29 ± 1 ℃). API-RP38 medium was used in this experiment (Mansfeld *et al.*, 1993), and its components were shown in Table 2.

Table 2. The components of API medium

Molecular Formula	Na_2SO_4	NH_4Cl	$CaCl_2$	$K_2HPO_4\cdot 3H_2O$	$MgSO_4\cdot 7H_2O$	$C_3H_5NaO_3$
Content	0.5g/L	1.0 g/L	0.1 g/L	0.5g/L	2.0g/L	3.5g/L

The configured media was placed in two erlenmeyer flask (the height of the media basically could provide a strict anaerobic environment for SRB).After the high-pressure sterilization, one of the erlenmeyer flask inoculated with SRB, the other did not contain any bacteria as control. The vaccination process was carried out in a clean bench to ensure the entire process sterility interference. After the inoculation process, the two conical flask placed in incubator.

Experimental steps:

1 The measurement was carried out at a constant temperature water bath, and the experimental technology was electrochemical noise. The test parameter sampling interval was 1 second, and the measuring time was 2048 seconds.
2 The temperature of the constant temperature water bath is 30 ℃.
3 There are four measuring electrode chuck on the electrochemical workstation. The red and green chuck, respectively, connected with two working electrodes, and reference electrode connected with the white chuck. The black chuck was vacant to reduce static interference.
4 Allowed the instrument set aside for 30min after measuring.
5 The test period was 30 days. The electrochemical noise was tested twice one day, and each time was 4096 seconds.
6 The electrochemical noise data were analyzed.

RESULTS

Signal Processing

In the electrochemical noise tests, all kinds of interference often exist, and they can not be ignored. These disturbances seriously affected the electrochemical noise data reliability and authenticity, even flooding the real signal. But it is hard to eliminate interference of the instrument itself. In filtering noise and information extraction, the wavelet function has a prominent role, and it can not only overcome limitations using the traditional approach to process non-stationary signals, but also it is expected to extract true information in the response signal as the same frequency with the excitation signal(Wharton *et al.*, 2003).

Using wavelet denoise the original signals of the electrochemical noise. Through observing the signal fluctuations before and after denoising, the denoising data can indicate the corrosion occurring information on the electrode more clearly and more accurately (Fig.2).

Domain Analysis

Spectrum Analysis

There are obvious current noise peaks after 304 stainless steel had been soaked in sterile medium for one day (Fig.3a), and it is because various ions in the medium could induce corrosion (Bradley *et al.*, 1998). While the current noise has not obvious noise peaks when immersed in the culture medium which contained SRB (Fig.3b). This is due to form a thin layer of passive film on the surface of electrode, and this layer of protective passive film protected the electrode from corrosion (Anita *et al.*, 2006).

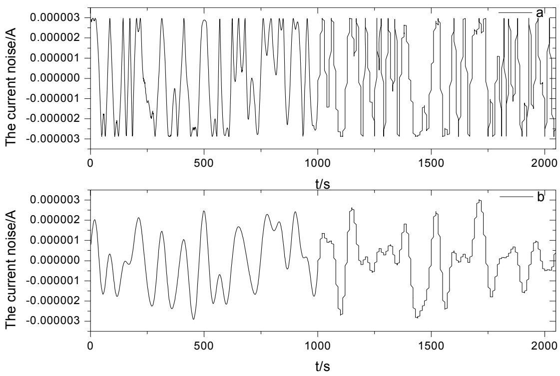


Fig.2 a.The original signal of current noise after stainless steel had been immersed in sterile medium for seven days

b. The denoising signal of current noise after stainless steel had been immersed in sterile medium for seven days

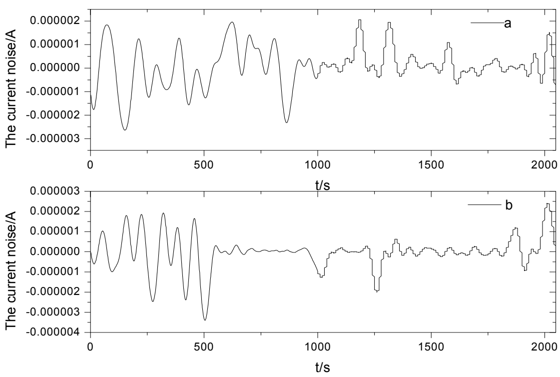


Fig.3 a.The current noise after stainless steel had been immersed in sterile medium for one day

b.The current noise after stainless steel had been immersed in the culture medium which contained SRB for one day

There are strong noise peaks after 304 stainless steel had been soaked in the culture medium which contained SRB for 7 days than in a sterile solution (Fig.4).Current apparent transient peaks are observed from the amplification chart (Fig.5).It represented the induction period of pitting corrosion occurred on the surface of the stainless steel. So metastable pitting corrosion of nucleation process had begun. This is because the metabolism of SRB were more and more active, causing the thin layer passivation membrane damaged following strong current noise peaks and big density. The time domain diagram of the current noise and potential noise revealed potential noise relatively lags than current noise fluctuation, and it had a character of sharply rise and slowly drop, and it may become the beginning of pitting corrosion of stainless steel (Fig.5 and Fig.7).

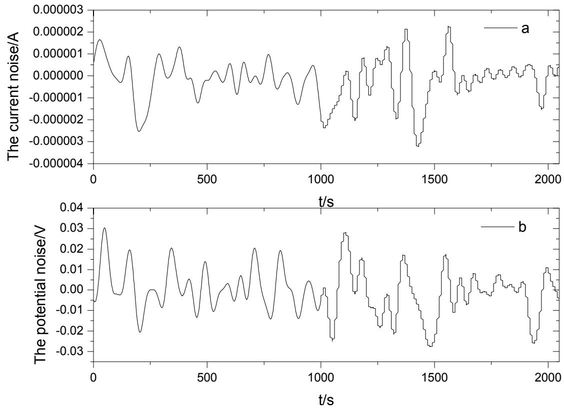


Fig.4 a.The current noise after stainless steel had been immersed in the culture medium which contained SRB for seven days

b. The potential noise after stainless steel had been immersed in the culture medium which contained SRB for seven days

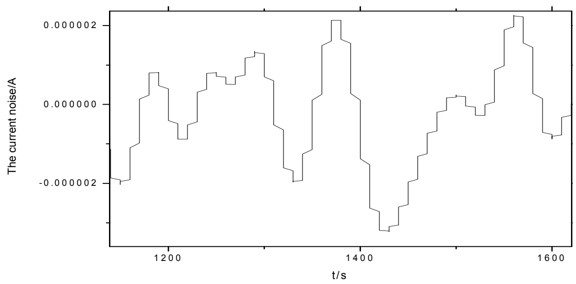


Fig.5 Enlarged picture of the current noise after stainless steel had been immersed in the culture medium which contained SRB for seven days

The current noise peaks which 304 stainless steel had been soaked in the culture medium contained SRB for three weeks was less than a week, and peak fluctuate also greatly narrowed (Fig.8). During the development of pitting corrosion, the corrosion hole on the surface of stainless steel electrode was gradually covered by the metabolites of SRB because the role of SRB metabolism (Darío Achá *et al.*, 2010). So, the surface of the electrode produced passivation membrane again, and tend to flat. Current noise peaks dramatically weakened, and corrosion rates were close to zero.

Statistical analysis

Using mathematical statistics and probability to study electrochemical data can reflect the objective nature, the inherent randomness and chance of electrochemical noise.

Standard deviation

$$\overline{X} = \frac{1}{n}\sum_{i=1}^{n} X_i \qquad (2)$$

$$\sigma = \frac{1}{n-1}\sum_{i=1}^{n}\left(Xi-\overline{X}\right)^2 \quad (3)$$

$$S = \sqrt{\sigma} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(Xi-\overline{X}\right)^2} \quad (4)$$

With the corrosion rate increasing, the standard deviation of current noise (S_I) (Fig. 6) increased, but the standard deviation of potential noise(S_E) decreased. The standard deviation of current noise when 304 stainless steel soaked in the culture medium which contained SRB increased, indicating that the corrosion rate was accelerated, and the potential noise was gradually reduced. Derived from experimental data, S_I increased and the corrosion rate increased after stainless steel had been immersed in the culture medium which contained SRB for two days. During three weeks the corrosion rate had remained been at a high level, and it was max on the twelfth day. After three weeks, S_I had a downward trend. Three weeks later, there were two fluctuations. But sulfate-reducing bacteria was lifeless, so these two fluctuations could be ignored. Observing the potential noise, it declined during two weeks, and fluctuated after three weeks. So, the potential noise and current noise had the opposite state into characterization of the corrosion rate.

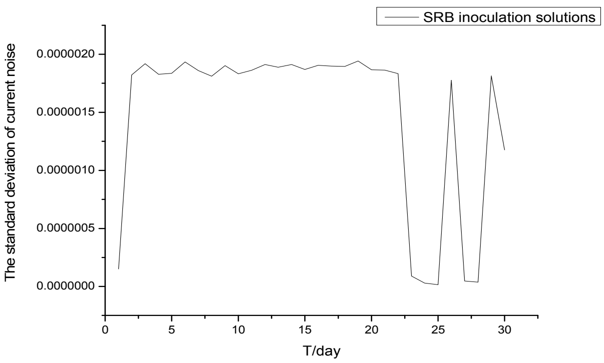


Fig.6 The standard deviation of current noise (S_I) when stainless steel immersed in the culture medium which contained SRB

Local factors LI

$$RMS = \sqrt{\frac{1}{n}\sum_{i=1}^{n} X_i^2} \quad (5)$$

$$LI = \frac{S_I}{RMS_I} \quad (6)$$

When the LI value is close to 0, indicating the electrode occurs uniform corrosion or is in passive state; when the LI value is close to 1, the researched electrode occurs pitting; when the LI value is between 0 and 1, it characterizes the occurrence of localized corrosion. It is observed that the LI value fluctuates between 0 and 1 value after the stainless steel had been immersed medium containing SRB for three days, indicating the occurrence of localized corrosion (Fig.7).The LI value is 1 on the fifth day, and it shows that pitting occurred on the surface of the electrode. Z. Sun (Sun *et al.*, 1999)studied that the LI value did not apply to localized corrosion, and it could only reflect the differences between the two worked electrodes. And if the current drift near zero, it may result in the LI value increasing. Despite uniform corrosion occurred on the surface of the electrode, the LI value is close to 1, indicating localized corrosion. Therefore, local factors should be used carefully, and it should be combined with other methods.

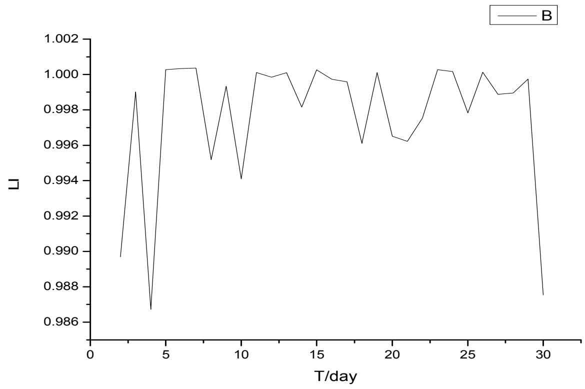


Fig.7 The value of LI when stainless steel immersed in the culture medium which contained SRB

Noise resistance

$$R_n = \frac{S_E}{S_I} \quad (7)$$

The noise resistance is inversely proportional to corrosion rate of metals（Girija *et al.*,2007）. The passive film formed on the surface of stainless steel electrode on the early time after stainless steel electrode immersed in the culture medium containing SRB. It leaded to relatively large noise resistor. The metabolism of SRB speeded up, and the passive film on the surface of the electrode broken down after 5 days(Fig.8). So, noise resistance dropped sharply, and the corrosion rate increased. After soaking three weeks, noise resistance began to increase. Then SRB gradually died, there was uniform corrosion on the surface of the electrode.

Frequency domain analysis

Electrochemical noise signal is a very complex nonlinear signal, and it is very random. Just using time-domain analysis is difficult to reflect its essential characteristics fully. Generally, the current or potential signal changes over time is converted to electrochemical power spectral density curve, and it is better to explore the process of electrode corrosion. The potential noise data after removing DC drift was transformed through the Fast Fourier Transform (FFT) (Bertocci *et al.*,2002). The received noise power spectral density potential curves (PSD, Power Spectral Density)was analyzed.

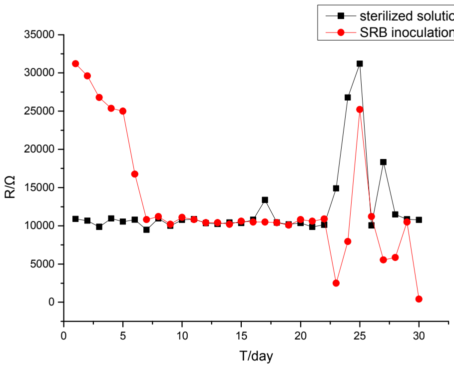


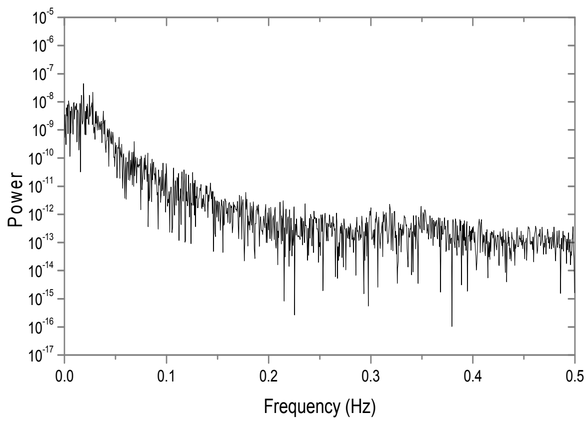
Fig.8 Noise resistance when stainless steel immersed in the culture medium which contained SRB

The high-frequency of the PSD curves of the potential noise(0.1Hz to 0.2Hz) after the stainless steel had been immersed medium containing SRB for 7 days linear fit, and the slope is -3.59362 (Fig.9a).This illustrates that the electrode occurred pitting. The PSD curves of the potential noise after the stainless steel immersed medium containing SRB 12 days began to appear white noise(there is a constant value during 0Hz to 0.5Hz), and metastable pitting points developed as steady pitting points(Fig.9b).

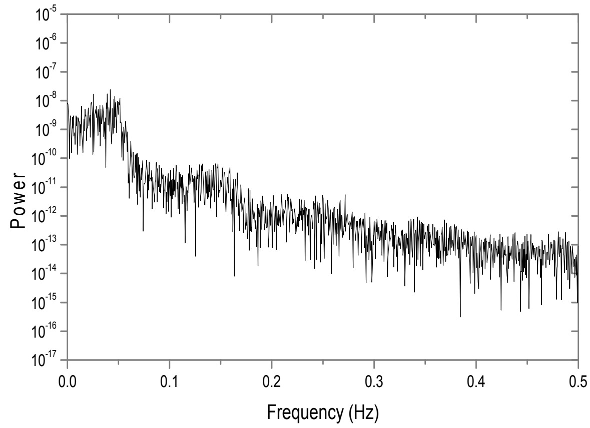
The value of the PSD curves of the potential noise after the stainless steel immersed medium containing SRB 27 days is close to a constant value in the whole frequency domain(Fig.9c), and this characterize the occurrence of uniform corrosion(Uruchurtu *et al.*,1987).

DISCUSSION

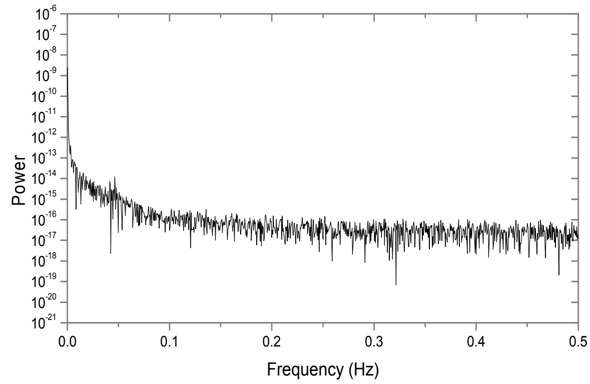
SRB metabolism affects the corrosion process on the surface of the stainless steel electrode. Using electrochemical workstation measured electrochemical noise, and the noise data were processed by wavelet denoising. The intensity of the noise peak and the size of fluctuations by observing the denoising spectra could reflect the occurrence of pitting and the formation of metastable pitting point or steady pitting point. The facts prove that the spectrum after wavelet denoising can be a good characterization of MIC.



(a) 7 days



(b) 12 days



(c) 27 days

Fig.9 The PSD curves of the potential noise after stainless steel had been immersed in the culture medium which contained SRB for different days

The standard deviation, local factors, noise resistance, and other information of electrode corrosion were received by monitoring the electrochemical noise of electrode system. The results indicate that just one way does not accurately characterize the process of electrode corrosion. The standard deviation just focus on the characterization of the corrosion rate, local factors can show the type of corrosion under strict conditions, and noise resistance is able to reflect the type of corrosion and the corrosion rate. The potential noise power spectral density curve was received through FFT. When the slope of high-frequency part is less than -20dB/Hz, it is indicated that uniform corrosion occurs. After stainless steel electrodes had been immersed in the culture medium containing SRB for three weeks, the potential noise power spectral density curve tended to a constant value, and it indicates that uniform corrosion occurred.

The life activities of SRB is complex, and the corrosion process of stainless steel electrodes induced by SRB is also very complex. The corrosion is very serious and with large destructive, so, it needs strict treatment.

CONCLUSIONS

1. Electrochemical noise measurement is non-destructive and non-intrusive electrochemical method, and its analysis method is reliable, convenient. It can be used as theoretical guidance in field application of power plants and other industrial sectors.
2. The extent of corrosion and other useful information are obtained by measuring electrochemical noise of 304 stainless steel, and we can combine the surface analysis techniques to carry out more precise study on microbial corrosion.

NOMENCLATURE

LI Local factors
n sample size, the number of analysis data
R_n Noise resistance
RMS Root mean square
RMS_I Root mean square of current noise
S Standard deviation
S_E Standard deviation of potential noise
S_I Standard deviation of current noise
X_i a electrochemical noise data, which measured the transient value of current or potential, A/V
$\overline{X}$ Average of n noise data
σ Variance

Acknowledgement

This work is supported both by National Basic Research Program of China (973 Program, NO.2007CB206904) to H. Men and Z. Xu.

REFERENCES

A. Aballe, A. Bautista, U. Bertocci and F. Huet, 2001, Measurement of the noise resistance for corrosion applications, *Corrosion*, Vol.57, pp. 35-42.

A. Padilla-Viveros, E. Garcia-Ochoa, D. Alazard,2005, Comparative electrochemical noise study of the corrosion process of carbon steel by the sulfate-reducing bacterium Desulfovibrio alaskensis under nutritionally rich and oligotrophic culture conditions, *Electrochimica Acta*, Vol .51, pp. 3841-3847.

Darío Achá,Holger Hintelmann and Janet Yee,2011，Importance of sulfate reducing bacteria in mercury methylation and demethylation in periphyton from Bolivian Amazon region, *Chemosphere*, Vol.82, pp.911-916.

F. Huet, N. Monfort Moros, R. P. Nogueira and B. Tribollet, 2002, Electrochemical noise analysis applied to SRB-induced corrosion of carbon steel, *Corrosion*, paper NO.02449.

F. Mansfeld, H. Xiao, 1993, Electrochemical Noise Analysis of Iron Exposed to NaCl Solutions of Different Corrosivity,*Electrochemical Soc*, Vol.140, pp. 2205-2207.

J. A. Wharton, R. J. K. Wood and B. G. Mellor, 2003, Wavelet analysis of electrochemical noise measurements during corrosion of austenitic and superduplex stainless steels in chloride media, *Corrosion Science*, Vol.45, pp.97-122.

J.C Uruchurtu, J.L Dawson, 1987, Noise analysis of pure aluminum under different pitting conditions, *Corrosion*, Vol.43, pp.19-26.

J. J Santana Rodr guez, F. J Santana Hem ández, J. E González González, 2006, Comparative study of the behaviour of A ISI 304 SS in a natural seawater hopper in sterile media and with SRB using electrochemical techniques and SEM, *Corrosion Science*, Vol.5, pp.1265-1278.

J. M Sykes, 1991, Electrochemical Noise:the technique for the “90s”, *British corrosion*, Vol.4, pp. 238.

M. Bradley, Tebo, Anna Ya, Obraztsova, 1998, Sulfate-reducing bacterium grows with Cr(VI), U(VI), Mn(IV), and Fe(III) as electron acceptors, *FEMS Microbiology Letters*, Vol.162, pp.193-198.

S. Girija, U. Kamachi Mudali, H. S. Khatak and Baldev Raj, 2007, The application of electrochemical noise resistance to evaluate the corrosion resistance of AISI type 304 SS in nitric acid, *Corrosion Science*, Vol.49, pp. 4051-4068.

S. Sh Abedi, A. Abdolmaleki, N. Adibi, 2007, Failure analysis of SCC and SRB induced cracking of a transmission oil products pipeline, Engineering Failure Analysis, Vol.1, pp. 250-261.

T. Anita, M.G Pujar, H. Shaikh, et al, 2006, Assessment of stress corrosion crack initiation and propagation in AISl type 316 staiuless steel by electrochemical noise technique, *Corrosion Science*, Vol.48, pp. 2689-2710.

U. Bertocci, F. Huet, R. P Nogueira, et al, 2002, Drift removal procedures in the analysis of electrochemical noise, *Corrosion*, Vol. 58, pp. 337-347.

W. A Hamilton, 1998, Bioenergetics of sulphate-reducing bacteria in relation to their environmental impact, *Biodegradation*, Vol.12, pp.201-212.

Z. F Sun, Mansfeld, 1999, Localization index obtained from electrochemical analysis, *Corrosion*, Vol.55, pp. 915-918.

APPENDIX

Wavelet analysis is the development of Fourier analysis. Wavelet analysis is a local time-domain analysis method. Its window size is fixed, but its shape is variable. There is high frequency resolution and low time resolution in the low frequency part, and there is high time resolution and low frequency resolution in the high frequency part. So, wavelet analysis is called as mathematical microscope. Wavelet transform is self-adaptive for the signal.

Wavelet transform means: a basic wavelet function $\psi(t)$ moves τ , and then it does the inner product with the analyzing signal in different scales a .

$$WT_x(a,\tau)=\frac{1}{\sqrt{a}}\int_{-\infty}^{+\infty}x(t)\psi*(\frac{t-\tau}{a})dt \qquad a>0 \quad (1)$$

Equivalent frequency domain is expressed as:

$$WT_x(a,\tau)=\frac{\sqrt{a}}{2\pi}\int_{-\infty}^{+\infty}X(w)\psi*(aw)e^{jw\tau}dw \qquad (2)$$

$X(w)$ is fourier transform of $x(t)$, $\psi(w)$ is fourier transform of $\psi(t)$.

The time-domain window features of wavelet transform is different from the time-frequency window of short-time. Because τ only impacts the position of window on the timeline in the phase plane, and a affects not only the position of the window in the frequency axis, but also the shape of the window. The sampling step size for different frequencies in the time domain after wavelet transform is adjustable. It is that the time resolution of wavelet transform at low frequencies is low while the frequency resolution is high; the time resolution of wavelet transform at high frequencies is high while the frequency resolution is low. This is consistent with the characteristics of low-frequency signal which changes slowly and high-frequency signal which changes rapidly. Generally speaking, the time-frequency window features of wavelet transform is better than the short time Fourier transform.

Wavelet transform has the following features and functions:

(1) Multi-resolution is contained in wavelet transform, and it is possible to observe the signal from coarse to fine.

(2) Wavelet transform can be seen as doing the filtering to the signal at different scales a using the band-pass filter of the basic frequency characteristics $\psi(w)$. If the Fourier transform of $\psi(t)$ is $\psi(w)$, the Fourier transform of $\psi(\frac{t}{a})$ is /a / $\psi(aw)$ because the scaling properties of the Fourier transform. So this set of filters has a constant quality factor, and it is constant relative bandwidth; (3) Selecting the basic wavelet appropriatly, so that $\psi(t)$ is supportted limitedly in the time domain,and $\psi(w)$ is relatively concentrated in the frequency domain. The ability of characterizing local characteristics of the signal is contained in time and frequency domains after wavelet transform, and it is a good test for signal transients or singularities.

One of the important applications of wavelet analysis is denoising of the signal. One-dimensional signal model which contains noise can be expressed as follows:

$$s(k)=f(k)+\varepsilon\cdot e(k), k=0,1,\cdots,n-1 \qquad (3)$$

$s(k)$ is the original signal, $f(k)$ is a useful signal, $e(k)$ is the noise signal.

Noise energy is concentrated in the high frequency part. The noise reduction process of one-dimensional signal can be divided into three steps:

(1) Wavelet decomposition;

(2) The threshold of high-frequency coefficients after wavelet decomposition is quantified;

(3) Reconstruction of one-dimensional wavelet.