

Institute of Paper Science and Technology Atlanta, Georgia

# **IPST Technical Paper Series Number 950**

A Review and Application of Electrochemical Noise (ECN) Measurements As a Corrosion Monitoring Tool

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July 2002

Submitted to Corrosion Reviews

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# A REVIEW AND APPLICATION OF ELECTROCHEMICAL NOISE (ECN) MEASUREMENTS AS A CORROSION MONITORING TOOL

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# ABSTRACT

The present article reviews electrochemical noise (ECN) measurement as a probe for ECN test methods as well as data analysis and monitoring corrosion changes. interpretation have been demonstrated by using a model system where stainless steel 304L (UNS 30403) samples were tested in 10% NaCl solution at room temperature. Controlled tests for weight loss measurements were also conducted to verify ECN measurements. Corrosion behavior was established by comparing and analyzing ECN signals, from both time and frequency domains, to weight loss and visual observations. Conventional data treatment of the ECN parameters in both time and frequency domains yielded the same results, which related to physical weight loss and pitting observations. According to the findings of this study, electrode biasing occurred in tested conditions. The source of biasing is unclear at the moment. However, it is believed that minor differences between the two "nominally identical" electrodes (e.g., surface finish, size, microstructure, temperature variations, solution composition) may be responsible for its occurrence. No definite explanation is available at this time to justify the persistency of biasing throughout the test

### Keywords:

Electrochemical Noise, Time Domain, Frequency Domain, Pitting, Stainless Steel, Sodium Chloride.

# 1. INTRODUCTION

All corrosion processes cause spontaneous fluctuations of the free corrosion potential and current associated. These fluctuations, named electrochemical noise (ECN), can be further analyzed to interpret corrosion processes in a system. Typically, the events take place at frequencies less than 1 Hz and show small currents ( $\mu$ A to mA) and small voltages ( $\mu$ V to mV). The magnitude, duration, and frequency of the fluctuations can be used to determine the prevailing corrosion mechanism. The technique gained recognition in industrial applications by showing some promising results [1-3]. Another reason for its recent development is that digital signals, data acquisition, and storage techniques, have evolved in the past forty years since the use of the ECN technique was first proposed [4-5].

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### Parameters Used for ECN Analysis

Electrochemical noise (ECN) is understood as fluctuations in electrochemical potential and current with time of a three-electrode system in a liquid medium. Two of the electrodes are of the same material as well as geometry, whereas the third one is a standard reference electrode (Figure 1). The measurements are carried out such that the potential is measured between the reference electrode and the two working electrodes with a high impedance voltmeter, while the current between the two identical working electrodes is measured with a zero resistance ammeter (ZRA) [6]. Typically, the events take place at frequencies less than 1 Hz and show small currents ( $\mu$ A to mA) and small voltages ( $\mu$ V to mV). The magnitude, duration, and frequency of the fluctuations can be used to determine the prevailing corrosion mechanism.



Fig. 1. ECN cell configuration.

ECN measurements are not new. They were firstly proposed in 1961 [4] and subsequently used in 1968 [5]. Due to the technological revolution of computer performance in terms of speed, processing, and data storage in the past decade, ECN has regained interest from both the scientific and technical communities and has even gotten attention for commercialization for industrial applications. In theory, the absence of disturbance of the electrodes has appealed to many individuals. ECN data analysis can provide mechanisms and to some extent quantify corrosion in a large variety of materials, environments and conditions.

There exist many technical articles and publications that describe the principles and characteristics of ECN techniques. Especially the information available through the work sponsored by NACE and ASTM [6, 8] is worth reviewing. There are several parameters that can be obtained in the time and frequency domain analyses to assess corrosion through ECN. The time domain reflects the current and potential changes in a time scale, whereas the frequency domain represents a function --power spectrum- of both current and potential with the frequency at which the corrosion events are happening. Among the parameters commonly used for analysis are:

### Time Domain Analysis [6-8]

# Mean

It is the average of values of potential  $(\overline{E})$  or current  $(\overline{I})$  measurements in the time record according to Eq. (1),

$$\overline{X} = \frac{1}{N} \sum_{k=1}^{N} X[k]$$
<sup>(1)</sup>

Where X[k] is either the potential or current value of a sample corresponding to the time t.

#### Variance

It is a measure of the noise power and it is represented by the square of the standard deviation,

$$\overline{X}_{n}^{2} = \frac{1}{N} \sum_{k=1}^{N} (X_{n}[k])^{2}$$
<sup>(2)</sup>

### Standard Deviation

It represents the spread from the average in the population of a normal distribution.

### **Root Mean Square**

It is the square root of the average value of the square of potential or current (without subtraction of the mean). It is a measure of the power available from the signal.

$$X_{rms}^2 = \overline{X}^2 + \overline{X}_n^2 \tag{3}$$

Skew

It is a measure of the symmetry of a distribution. It is a nondimensional parameter. A zero value means that the distribution is symmetrical about the mean, a positive value indicates there is a tail in the positive direction, and a negative one implies a tail in the negative direction. A time record consisting of unidirectional transients will be typically heavily skewed, and this may be useful to detect transients associated with metastable pitting. If the current noise is measured between two identical electrodes, it is possible

for the transients to be unidirectional if only one electrode happens to be active or bi directional if both electrodes are active, and in this case the skew will be a rather unpredictable parameter.

$$skew = \frac{1}{N} \sum_{k=1}^{N} \left( \frac{X_n[k] - \overline{X}}{\sqrt{X_n[k]^2}} \right)^3$$
(4)

# Kurtosis

It is a measure of the shape of the distribution with respect to a normal one and it is also nondimensional. A zero value indicates a distribution equal to a normal one though it does not prove that it is in fact a normal distribution. A positive kurtosis indicates a spiked distribution whereas a negative value implies a flatter one.

$$kurtosis = \frac{1}{N} \sum_{k=1}^{N} \left( \frac{X_n[k] - \overline{X}}{\sqrt{X_n[k]^2}} \right)^4$$
(5)

# Coefficient of Variation

Coefficient of variation is the standard deviation divided by the mean for current or potential signal. This may be used as an indicator of localized corrosion when the mean is small and the standard deviation is large.

# Noise Resistance

It is calculated as the standard deviation of potential divided by the standard deviation of current.

$$R_n = \frac{\sqrt{E_n^2}}{\sqrt{I_n^2}} \tag{6}$$

### Pitting Index

1

Also named localization index, this parameter is somewhat similar to the coefficient of variation. However, the root mean square value of current is used instead of the mean (see Eq. (7)) [8].

$$PI = \frac{\sqrt{I_n^2}}{I_{rms}} \tag{7}$$

The reasoning behind this parameter is that pitting occurs on initially passive electrodes, which exhibit small coupling currents, and the initiation of localized corrosion attack can be detected by the relatively large current transients, which lead to a large standard deviation. The root mean square of the current signal is used instead of the mean current to account for all current passing between the two electrodes, independent of its direction. Eden et al. [9] have proposed that PI will have a value between 0 and 1 according to the following classification:

PI	Type of Corrosion
0.001 <i><pi< i="">&lt;0.01</pi<></i>	Uniform
0.01 <pi <0.1<="" th=""><th>Mixed</th></pi>	Mixed
0.1 <pi <1.0<="" td=""><td>Localized</td></pi>	Localized

### Charge Transient

Cottis et al. [6-7] have proposed that for the case of localized corrosion, where bursts in current records are observed, a shot analysis may be used. This leads to the calculation of average charge in the individual transients that make up the electrochemical noise using the Eqs. [6-7],

$$q = \frac{\sqrt{E_n^2}\sqrt{I_n^2}}{4bB} \tag{8}$$

$$f_n = \frac{I_{corr}}{q} \tag{9}$$

$$I_{corr} = \frac{B}{R_p}$$
(10)

where b is the bandwidth measurement (or Nyquist frequency) and B is the Stern-Geary factor given in Eq. (12). Again, a large value of q is indicative of localized corrosion.

Providing that  $I_{corr}$ , is dominated with the transient events, then  $I_{corr}$ , q, and  $f_n$ , can be estimated using the shot analysis. While these three parameters are interrelated through Eq. (9), they can also be used to identify the type of corrosion. A large value of  $f_n$ , (typically >1 kHz/cm<sup>2</sup>) indicates that many events are occurring, and this may be taken to indicate that the type of corrosion is uniform. Conversely, a smaller value of  $f_n$ , indicates a localized process. The charge q indicates the magnitude of the individual events (amount of material removed in the event). Passive systems will typically exhibit a very small value of q and a high value of  $f_n$ . The shot noise analysis applies strictly to a process that produced pulses of charge.

# **Corrosion Rate Calculations**

# Noise Resistance Parameter

According to Cottis et al. [6, 10], the parameter noise resistance,  $R_n$ , is essentially the same as that obtained by conventional linear polarization resistance (LPR) methods though ECN is claimed to be superior to LPR for high-resistance systems. This parameter may ultimately be used to yield a corrosion rate measurement. Then, the

electrochemical noise resistance,  $R_n$ , can be obtained by means of the following Eq. (6) [6, 10],

$$R_n = \frac{\sqrt{E_n^2}}{\sqrt{I_n^2}} \tag{6}$$

where,  $\sqrt{E_n^2}$  and  $\sqrt{I_n^2}$  are the standard deviations of potential and current in a given time record segment in mV and  $\mu$ A/cm<sup>2</sup>, respectively. To actually obtain a noise resistance parameter in kohm cm<sup>2</sup>, the current density should be used as opposed to the absolute value of current. Assuming that  $R_p$  is similar to  $R_n$ , as stated previously,  $i_{corr}$  may be obtained using Eq (13). and substituting  $R_p$  by  $R_n$  as shown in (11) [10-13],

$$i_{corr} = \frac{B}{R_n} \tag{11}$$

where  $i_{corr}$  is in  $\mu$ A/cm<sup>2</sup>,  $R_n$  in kohm cm<sup>2</sup>, and B is in mV. B is the so-called Stern-Geary factor obtained by using the anodic and cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ , respectively) in V/dec, obtained from potentiodynamic scans according to Eq. (12),

$$B = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)}$$
(12)

By calculating a corrosion current density, a corrosion rate may also be obtained using Faraday's law as shown below [14],

$$CR = 0.129 \frac{ai_{corr}}{n\rho} \tag{13}$$

where CR is in mpy, a is the atomic weight of the corroding species in g/mol,  $i_{corr}$  is the exchange current density obtained above in  $\mu$ A/cm<sup>2</sup>, n is the number of electrons freed per mol of cat ions produced during the corrosion reaction, and  $\rho$  is the density in g/cm<sup>3</sup>.

# Weight Loss

Corrosion rate measurements by weight loss may be performed in accordance to the standard [15],

$$CR = (3.45)I0^6 \frac{W}{At\rho} \tag{14}$$

where CR is in mils per year, mpy, W is the weight loss in g, A is the area of the electrode exposed in cm<sup>2</sup>, t the time in hours, and  $\rho$  is the density in g/cm<sup>3</sup>.

### Coulombic Integration of Current (Faraday's Law)

Current noise records may be related to a corrosion rate by using Faraday's law according to [14],

$$W = \frac{Ita}{nF} \tag{15}$$

where W is the mass reacted in grams (or weight loss), I is the current in Amperes, t is time in seconds, a is the atomic weight of the corroding species in g/mol, n is the number of electrons freed per mol of cat ions produced during the corrosion reaction, and F is the so-called Faraday's constant (96,500 coulombs/equivalent). Note that if Eq. (15) is divided by time and area, it will yield an equivalent result to that shown on Eq. (14). The application of this approach is not widespread but it has been claimed to have relatively good success [1].

# Frequency Domain Analysis [6-8, 16]

One of the tools often used individually or in conjunction with the time domain analysis of ECN is the frequency domain [6-7, 16]. In this type of analysis, first the data from the time record measurement are converted into a frequency equivalent by means of either a Fast Fourier Transformation (FFT) or Maximum Entropy Method (MEM). The essence of the former is to represent the time record as a waveform that can be decomposed into a sum of sinusoids of different frequencies and specific amplitudes and phases. MEM computes the coefficients of a particular class digital filter that would give the observed time record when applied to white noise input signal. MEM mathematically ensures that the fewest possible assumptions are made about unmeasured data by choosing the spectrum that is the most random or has the maximum entropy for the process under investigation.

So, every time domain function has a counterpart in the frequency domain. The counterpart function is called Power Spectra Density (PSD) and indicates how the sequences of power or energy are distributed in the frequency domain. Communication engineers initially developed Power Spectra, and the results are typically plotted using a unit named "bel". One bel corresponds to a change of one unit in  $\log_{10}(PSD)$ . So units of db (decibels) per decade are often used to specify slopes, which may be in turn related to corrosion phenomena. Researchers have found [16-19] a correlation between the parameters and the corrosion type of mechanism. In a typical spectrum plotted on a logarithmic scale a high magnitude of noise amplitude occurs at low frequency. This remains constant at very low frequencies and then rolls off at higher frequencies to much lower amplitudes of noise. The slope of the roll-off suggests the type of corrosion taking place. Slopes that are in absolute values less than 20 db/decade are related to pitting corrosion, whereas slopes larger than 40 db/decade are attributed to uniform corrosion. Slopes in between are of a mixed mechanism.

### **Concerns with ECN Data Interpretation**

#### Uniform Corrosion

Despite the reputed equivalency (or similarity) shown experimentally [6-10, 16-20] and mathematically [21] between noise resistance  $(R_n)$  and linear polarization resistance  $(R_p)$ , some authors [22-27] have found discrepancies in the measurements of both parameters, typically  $R_n$  being larger than  $R_p$ . Some researchers have related those differences to several sources of error, namely, instrument noise, current and voltage trends not being removed, sampling rate, and sampling duration period [25-28].

According to Tan el al. [25], for systems in stagnation, the instrument noise may be larger than real corrosion-related potential and currents measured. This will drown the signal measured within the instrument noise. This is particularly a concern with systems with relatively low corrosion rates. However, they suggested that this might be corrected by testing the noise level of the equipment and adding digital filters as needed.

DC trend or drift may also cause some problems in measuring the standard deviations of both current and voltage for noise resistance calculation [25, 27-28]. Drift has been defined as the change of the mean potential or current divided by time [7]. This definition is in fact very similar to that of ECN and it is clear that there are some fundamental questions about the difference between what is drift and noise. Though corrections of noise resistance by trend removal techniques have been claimed to work in terms of the equivalency to linear polarization resistance, it is not clear whether linear trend or moving average removal (MAR) methods work for all conditions [27]. Also, drift as been blamed for causing  $1/f^2$  slopes in power spectra density plots in the frequency domain analysis of ECN, data which may lead to wrong interpretation of results [29-31]. Another problem with drift is that its existence implies that the signal is not stationary, and virtually all standard analysis become invalid [7]. If the drift consists of a linear change in the mean divided by time, it can be removed by simply subtracting the linear regression from the data according to Mansfeld et al. [27],

$$E = E_0 + at \tag{16}$$

$$I = I_0 + bt \tag{17}$$

where "a" and "b" are the slopes of the observed drift. From the above Eq.s (16) and (17) it follows that the potential and current fluctuations should result in a straight line given by,

$$E = E_0 + a(I - I_0)/b \tag{18}$$

A similar result has been obtained by using a high-pass filter to the signal prior to sampling [7].

An additional method, namely the moving average removal (MAR) has been proposed to correct for DC drifting [32] and described as follows: a series of voltage-time records (k data points),  $\{E_n\}_{n=1,2,3,d,i+1,d+2,\dots,k}$  is experimentally recorded. Any individual data point in the group  $\{E_n\}$ ,  $E_i$ , is a combination of the random noise component and the DC component which are functions of time, t,

$$E_i(t) = E_{i,noise}(t) + E_{i,DC}(t)$$
<sup>(19)</sup>

where  $E_{i,noise}(t)$  is the real noise required for further analysis.  $E_{i,DC}(t)$  is the DC trend component which has to be removed. The central assumption is that an average value of adjacent data points of  $E_i$  can be taken as an estimation of  $E_{i,DC}(t)$ :

$$\overline{E}_{i}(p) = \left\{ \sum_{i=p}^{i+p+1} E_{i} \right\} / (2p+2)$$
(20)

where p, can be 1, 2, 3 or more. The DC trend in the voltage-time record can be therefore removed and the random fluctuation  $E_{i,noise}(t)$  could be deduced as,

$$E_{i,noise} = E_i - \overline{E}_i \tag{21}$$

The same argument is also followed for the current drift.

More complex drift functions, such as exponential decays, can potentially be removed after measurement in a similar way (by using regression procedures to fit the drift function to the data and then subtracting it from the noise data). However, as the drift function becomes more complex, concerns about the possibility of subtracting real frequency noise increase, and it has been suggested that drift removal should be limited to straight lines unless there is sound evidence of the existence of an alternative drift function [7].

As far as sampling rate goes, it has been recommended to use high sampling frequencies (>1 Hz) as well as large noise sampling duration. The highest noise signal that can be resolved in the frequency domain is determined by the sampling interval  $\Delta t$  also named the Nyquist frequency [6],

$$f_N = \frac{1}{2\Delta t} \tag{22}$$

whereas the smallest frequency measured is determined by the noise sampling duration  $N\Delta t$ ,

$$f = \frac{1}{2N\Delta t} \tag{23}$$

Other authors [26] have mathematically shown that  $R_n$  and  $R_p$  may differ and that the usefulness of  $R_n$  is limited by the requirement of very long time periods to satisfy the equivalency of the two parameters.

Another problem arises when the open cell potential of the corroding system is close to the reversible electrode potential of the anodic or cathodic reactions, or near the reversible electrode potential of any other redox process; then the corrosion rate is likely to be overestimated because other reactions are taking place at the same time as metal dissolution. A way to test the system is by using a non corroding electrode, e.g., platinum, where it will assume a redox potential governed by the reduction-oxidation reactions in the system. If the corrosion potential of the corroding metal is very close to the redox potential of such electrode, then  $E_{corr}$  may be close to a reversible electrode potential which may in turn cause problems during corrosion rate estimations [33-34].

Electrode asymmetry has also been an issue in the interpretation of ECN data. Much of the theoretical work assumes that the two working electrodes used for ECN have to be "identical". However, this is not usually found to be the case as one electrode may become more active than the other at certain time periods [7]. An explanation for pitting of one electrode while the other remains passive has been offered by Cottis [7]. He explains that small pH changes as a result of the net current between the two electrodes. The non pitting electrode will act as a cathode, and the neighboring solution becomes more alkaline as a consequence of this behavior; this is thought to inhibit pitting. The pitting electrode is said to be a net anode causing the pH to drop, facilitating pitting. Again, in general one electrode may be more active than other even for other mechanisms than uniform corrosion [6]. Some authors [35] have discerned the complications of ECN analysis when the two electrodes are dissimilar, while others [36] have proposed new mathematical correlations to account for the dissimilarity in intentionally different electrodes.

### Localized Corrosion

Metastable pitting consists of a slow current rise followed by a sharp current fall (for stainless steel) or a moderate current rise followed by a slower fall (for carbon steel and aluminum alloys) [7]. The current change was also associated with a sharp potential change, but with a slower recovery rate due to the slow discharging of the capacitance of the electrode [37]. However, corrosion in acids with hydrogen evolution has been reported to cause transient currents associated with the growth of bubbles followed by the subsequent separation [7]. Many parameters have been proposed to assess pitting through ECN analysis. It can be shown that both the coefficient of variation (standard deviation divided by the mean [6]) and the localization index (standard deviation of current divided by the root mean square current [9]) are mathematically related [6]. They both suffer the fundamental problem that the expected value of the mean current between two identical electrodes is zero (even more so if DC drift has been corrected [27]) and it is possible for a large coefficient of variation to be obtained even if the standard deviation is small [7].

Other parameters such as skew and kurtosis have a number of limitations. One of them is related to the increase in the number of transients. If so, the current and potential values will tend towards a normal distribution, and the skew and normal distribution will tend to zero. Again, those parameters are also sensitive to drift and long-term transients [7]. In regards to roll-off slopes in power spectra density plots [16-19], there are arguments as to what can be clearly and reliably said about a particular type of corrosion mechanism [38]. It is believed that for a narrow set of well-characterized corrosion conditions, those parameters will correlate well with the type of corrosion.

Other mechanisms of corrosion may be identified through ECN [6-7]. In particular, crevice corrosion may be identified when drastic potential drops occur in the potential record.

# 2. EXPERIMENTAL PROCEDURE

Work on this study was conducted to test the field equipment used for ECN measurements. Tests were designed to understand the signals collected from a threeelectrode array in relation to physically measurable parameters. The current noise and flow between two identically coupled electrodes is monitored through a zero resistance ammeter. The potential noise and corrosion potential is also measured with respect to a third electrode (in this case a standard Calomel reference electrode, SCE) with high impedance voltmeter. The experimental setup used was a commercially available system, a concerto CIS400<sup>TM</sup> Corrosion Monitoring Rack from Petroleum Research Production, UK. This device is interfaced to a personal computer where data collection is carried out with a database program, namely AMULET<sup>TM</sup>, developed by Corrosion and Condition Control Ltd (C<sup>3</sup>). Data sampling and storage were carried out at 1Hz time intervals.

In this set of experiments, stainless steel (SS304L (UNS 30403)) electrodes were exposed to 10% NaCl solution at room temperature in a glass cell. Electrodes were polished to 600 grit finish, degreased with acetone, and rinsed with double-distilled water. Electrode dimensions and weight were recorded prior and after exposure. Current and potential data were recorded every second. Relevant ECN parameters were calculated for both time and frequency domains include: mean potential and current, standard deviation of potential and current, noise resistance, pitting index, impedance at low frequency, and roll-off slopes of power spectra density plots. Power spectra density plots were calculated from current and voltage records using a commercially available software [6]. Additionally, current integration through Faraday's law was used to yield a corrosion rate. Physical evaluation of the samples was also performed to corroborate measured parameters, i.e., weight loss for general corrosion rates, and physical observations for pitting and film formation. ASTM G1 standard procedure with inhibited acid cleaning solutions was followed [39].

### 3. RESULTS AND DISCUSSION

Figure 2 depicts both the current (lower line) and voltage (upper line) time records for the stainless steel in sodium chloride solution over seven days. The current record starts out with some biasing (theoretically the average current should be zero). Then the current decreases over two days, but some biasing is still observed. Over the seven-day exposure, current bursts are observed accompanied by voltage changes. Current bursts have been attributed to pitting activity on the surface of the electrode [6]. The sign of the current burst indicates which of the two electrodes is undergoing active pitting. So it can be inferred that both electrodes are active at different time intervals. Figure 3 shows how the application of Eq. (7) predicts pitting activity as a function of time since the pitting

index indicates values greater than 0.1 [9]. By using the roll-off slope approach of both current (lower line) and voltage (upper line) power spectra densities, as shown in Figure 4, a similar prediction is obtained. In this case the slopes are more positive than -20 db/decade criterions, which have been claimed to indicate pitting [16-19]. Upon physical inspection of the electrodes, pitting was evidenced (Figure 5). However, the extent of pitting varied between the two working electrodes. This is associated with biasing. The source of biasing is unclear at the moment. However, it is believed that minor differences between the two "nominally identical" electrodes (e.g., surface finish, size, microstructure, temperature variations, solution composition) may be responsible for its occurrence. It is unclear whether the explanation offered by Cottis [7] will describe the current observations.

An additional calculation that may also yield some important information is the noise resistance  $(R_n)$ . Again, this parameter as its equivalent, polarization resistance,  $R_p$ , might be used to yield corrosion rates. However, it requires the Stern-Geary constant as well. On this regard, assumptions as to Tafel constant approximations are often made by making them approximately 100 mV for both anodic and cathodic slopes, which will give an error of about 2 in the worst case. This is well within the experimental error of the technique [16]. In the case of stainless steel 304L (UNS 30403) in 10% NaCl,  $R_n$ calculations were carried out in both, time and frequency domains. As can be depicted in Figure 6, noise resistance can be averaged either over time segments or over the entire time record. In this case the overall average is in the order of ~590 kohm. A similar result is obtained [6] when power spectra density plots for impedance are used (Figure 7). The low-frequency limit of the impedance for both FFT (noisy line) and MEM (smooth line) calculations is in the order of ~530 kohm. Using the above parameters a corrosion rate estimation was carried out by using Eqs. (6) and (11)-(13) above and assuming a Stern-Geary factor of 26 mV. The calculation yields a value of ~0 mpy. This result was also confirmed by weight loss measurements (Eq. (14)) and current integration calculations using Faraday's law (Eqs. (14) and (15)). Based on the model system tested here, there seems to be a correlation, both quantitatively and qualitatively, in terms of corrosion rate behavior between physical observations and estimated parameters using ECN.

#### 4. CONCLUSIONS

Experimental results obtained in this study suggest that ECN may be used as a corrosionmonitoring tool for industrial applications. Distinctive signatures for current (and voltage) that represent pitting and general corrosion were obtained. Weight loss measurements and surface inspection of the electrode surface coincided with the traditional ECN data interpretation in both time and frequency domains.

Biasing was always observed in the conditions tested in this study. However, the source of a permanent bias is not clear at the moment.

Well-behaved systems, where corrosion mechanisms are well understood, may be modeled by using ECN traditional calculations. That is the case of stainless steel 304L (UNS 30403) in NaCl. However, in industrial settings and in systems where other redox reactions may participate on the electrode surfaces, interpretation of ECN data and its correlation to corrosion behavior may require further investigation.



Fig. 2. Voltage and current records in the time domain for stainless steel 304L (UNS 30403) in 10% NaCl at room temperature.



Fig. 3. Pitting index as a function of time for stainless steel 304L (UNS 30403) in 10% NaCl at room temperature.



Fig. 4. Power spectra density in the frequency domain for stainless steel 304L (UNS 30403) in 10% NaCl at room temperature.



Fig. 5. Physical appearance of stainless steel 304L (UNS 30403) electrode after testing in 10% NaCl at room temperature for seven days. Note the presence of pits.



Fig. 6. Noise resistance,  $R_n$ , in the time domain for stainless steel 304L (UNS 30403) in 10% NaCl at room temperature.



Fig. 7. ECN impedance,  $Z_n$ , in the frequency domain for stainless steel 304L (UNS 30403) in 10% NaCl at room temperature.

# REFERENCES

- 1. S.J. Pawel, D.W. Townley, D.F. Wilson, M.E. Gorog, N.J. Stead, 10<sup>th</sup> International Symposium on Corrosion in the Pulp and Paper Industry, Helsinki, Finland, 1, p. 227 (2001).
- D. Townley, S.J. Duranceau, 56<sup>th</sup> NACE Annual Conference, Houston, TX, No. 01287 (2001).
- 3. G.L. Edgemon, E.E. Barr, 56<sup>th</sup> NACE Annual Conference, Houston, TX, No. 01283 (2001).
- 4. T. Hagyard, J.R. Williams, Transactions of Faraday Society, 57, p. 2288 (1961).
- 5. W.P. Iverson, Electrochemical Society, 115, p. 617 (1968).
- 6. R. Cottis, S. Turgoose, "Corrosion Testing Made Easy: Electrochemical Impedance and Noise", Vol. 7, Houston, TX, NACE (1999).
- 7. R.A. Cottis, Corrosion, 57, p. 265 (2001).
- J.R. Kearns, J.R. Scully, P.R. Roberge, D.L. Reichert, J.L. Dawson, "Electrochemical Noise Measurement for Corrosion Applications," ASTM STP 1277, Philadelphia, PA, ASTM (1996).
- D.A. Eden, D.G. John, J.L. Dawson, International Patent WO 87/07022, World Intellectual Property Organization, 1987.
- R.A. Cottis, S. Turgoose, J. Mendoza-Flores, "The effects of solution resistance on Electrochemical Noise Resistance Measurements: A theoretical analysis", ASTM STP 1277, Philadelphia, PA, p. 93 (1996).
- 11. M. Stern, R. Roth, Journal of the Electrochemical Society, Vol. 104, p. 390 (1957).
- 12. M. Stern, Corrosion, 14, p. 440 (1958).
- F. Mansfeld, "The polarization resistance technique for measuring corrosion currents", Corrosion Science and Technology, New York, NY, Vol. VI, p. 173 (1976).
- D.A. Jones, "Principles and Prevention of Corrosion", MacMillan, New York, NY, 1<sup>st</sup> Edition, p. 75 (1992).
- ANSI/ASTM G1 72, Standard Recommended Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens, ASTM Book of Standards, p. 781 (1979).
- A.A. Alawadhi, R.A. Cottis, "Electrochemical noise signature analysis using power and cross-spectral densities", 54<sup>th</sup> NACE Annual Conference, Houston, TX, No. 207 (1999).
- 17. K. Hladky, J.L. Dawson, Corrosion Science, 21, p. 317 (1981).
- 18. P.C. Searson, J.I. Dawson, J. of Electrochemical Society, 135, p. 1908 (1988).
- Y.P. Deva, M. Gopal, W.P. Jepson, "Use of electrochemical noise to monitor multiphase flow and corrosion", 51<sup>st</sup> NACE Annual Conference, Houston, TX, No. 337 (1996).
- 20. G. Gusmano, G. Montesperelli, S. Pacetti, A. Petitti, A. D'Amico, Corrosion, 53, p. 860 (1997).
- 21. J.F. Chen, W.F. Bogaerts, Corrosion Science, 37, p. 1839 (1995).
- 22. F. Mansfeld, H. Xiao, J. Electrochem. Soc., 140, p. 2205 (1993).

- R.G. Kelly, M.E. Inman, J.L. Hudson, "Analysis of Electrochemical Noise for Type 410 SS in Chloride Solutions", ASTM STP 1277, Philadelphia, PA, p. 101 (1996).
- 24. D.L. Reichert, "Electrochemical Noise Measurement for Determining Corrosion Rates", ASTM STP 1277, Philadelphia, PA, p. 79 (1996).
- 25. Y.J. Tan, S. Bailey, B. Kinsela, Corrosion, 55, p. 469 (1999).
- 26. A. Aballe, A. Bautista, U. Bertocci, F. Huet, Corrosion, 57, p. 35 (2001).
- 27. F. Mansfeld, Z. Sun, X.H. Hsu, A. Nagiub, Corrosion Science, 43, p. 341 (2001).
- 28. Y.J. Tan, S. Bailey, B. Kinsela, Corrosion Science, 38, p. 1681 (1996).
- 29. C. Gabrielli, F. Huet, M. Keddan, Electrochim. Acta, 31, p. 1025 (1986).
- 30. U. Bertocci, J. Frydman, C. Gabrielli, F. Huet, M. Keddan, J. Electrochem. Soc., 145, p. 2780 (1998).
- 31. F. Huet, U. Bertocci, C. Gabrielli, M. Keddam, Topical Research Symposium, NACE, p. 11 (1997).
- 32. Y.J. Tan, S. Bailey, B. Kinsella, Corrosion Science, 38, p. 1681 (1996).
- 33. F. Mansfeld, K.B. Oldham, Corrosion Science, 27, p. 434 (1971).
- 34. J.R. Scully, Corrosion, 56, p. 199 (2000).
- 35. F. Mansfeld, C. Chen, C.C. Lee, H. Xiao, Corrosion Science, 38, p. 497 (1996).
- 36. J.F. Chen, W.F. Bogaerts, Corrosion, 52, p. 753 (1996).
- 37. Y.F. Cheng, M. Wilmott, J.L. Luo, Corrosion Science, 41, p. 1245 (1999).
- 38. G. Bagley, "The Measurement and the Analysis of Electrochemical Noise" (Ph.D. thesis, UMIST, 1998).
- 39. ASTM G 1 00, "Preparing, Cleaning and Evaluating Corrosion Test Specimens", ASTM Book of Standards, West Conshohocken, PA, 03.01, 781 (2001).