Comparison Between Electrochemical Noise and Electrochemical Frequency Modulation Measurements during Pitting Corrosion

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Abstract: *The electrochemical noise (EN) and electrochemical frequency modulation (EFM) techniques have been compared for their use to detect pitting corrosion. To do this, experiments on different corroding systems showing passivation and pitting corrosion were carried out. These corroding systems were: (1) Aluminum in borate buffer solution with and without chlorides (pitting corrosion + passivation behavior), (2) AISI 304SS in 0.3 wt.% FeCl₃ solution and 6 wt.% FeCl₃ solution at room temperature (passivation behavior + pitting and/or crevice corrosion), and (3) AISI 304SS in 6 wt.% FeCl₃ at elevated temperature of 57 °C (pitting corrosion). Both EN and EFM were measured on-line meanwhile changing the corrosive environment by adding chlorides or by increasing the temperature.*

A potential perturbation composed of two sine waves is applied with the help of EFM to get current response at various frequencies. As the corrosion process is nonlinear in nature, the ac-response contains components at harmonic and intermodulation frequencies. Analysis of current components at different frequencies yields the information about the corrosion behavior under investigation. EFM may be considered to detect pitting initiation and its further development due to the results obtained by measuring the so-called "causality factors", which are the ratio of the current components in the ac-response.

Keywords: EN and EFM techniques, AISI 304SS, pitting, causality factors

1. INTRODUCTION

Electrochemical noise (EN) may be defined as the random fluctuations in current or potential, which are associated with corroding metals and can be measured. Iverson [1] and Tyagai [2] were the first to explain the EN measurements associated with corroding metals in 1968 and 1971 respectively. Only the potential noise was given importance in the beginning but later on the workers found that current noise alone or combined with potential noise can give valuable information about corrosion process as well. Several workers [3-6] have investigated the EN associated with pitting and crevice corrosion.

One of the main features of electrochemical frequency modulation (EFM) as a new electrochemical technique [7] is the measurement of corrosion rate, Tafel parameters and causality factors in a single set of data. To get the current response, EFM employs a potential perturbation signal composed of two sine waves to a corroding system. Due to nonlinear nature of corrosion process, more and higher frequencies are observed for the ac-response than the applied signal. Like harmonic method, EFM measures corro-

sion parameters with the help of nonlinearity in the voltage-current response of electrochemical interface. Both EFM and harmonic method apply lower amplitude (20 mV) sinusoidal perturbation signal where as the later one uses one sine wave instead of two. EFM is better than harmonic method due to abilities like data validations, larger current response and insensitive to harmonics in the perturbation signal. The results obtained by Kuş and Mansfeld [8] show that EFM can be applied successfully but in case of high corrosion rates. Khaled [9] and Abdel-Rahim [10] showed that EFM is a nondestructive technique to measure corrosion rate without prior knowledge of Tafel parameters. They have demonstrated good comparison of EFM with other electrochemical techniques.

Sometimes it is not easy to identify the type of localized corrosion from potential or current noise without further analysis and interpretation of EN data. Girija and Kamachi Mudali [11] have found for AISI type 304L SS immersed in 0.1 M FeCl₃ that the standard deviation of current noise increased with time while the localization index was found to be in the range between 0.5 and 0.7. This range is reported for pitting corrosion. However, the localization index for type 304L SS in H₂SO₄ did not reflect the observed uniform corrosion. The pitting index, which is the ratio of the standard deviation of the current noise to the root mean

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square of the coupling current, has been found not to correlate with the onset of pitting [12, 13]. Furthermore, the noise signal between two identical electrodes is not highly sensitive to localized corrosion events in systems containing powerful redox agents [12]. In the previous work of Cottis [14], it has been suggested that a large value of q indicates localized corrosion. However, it has been shown that uniform corrosion of steel in NaCl solution exhibits a relatively large value of q, but coupled with a large value of f_n [3]. These two parameters are interrelated by $I_{corr} = q\,f_n$, where I_{corr} is corrosion current, q is charge and f_n is frequency of events. Shot noise analysis can be applied to transient events that are observed during different types of localized corrosion providing that the current associated with these transient events is dominant over the I_{corr}. In brief, different conflicting statements and results can be found in the literature for the EN to detect different types of localized corrosion.

In the present investigation, a detailed comparison between EN and EFM measurements has been presented to analyze the effectiveness of both techniques to detect pitting corrosion at room and elevated temperatures. To do this, experiments on different corroding systems showing passivation and pitting corrosion were carried out. These corroding systems were: (1) Aluminum in borate buffer solution without and with chlorides (passivation behavior + pitting corrosion), (2) AISI 304SS in 0.3 wt.% FeCl$_3$ solution and 6 wt.% FeCl$_3$ solution at room temperature (passivation behavior + pitting and/or crevice corrosion), and (3) AISI 304SS in 6 wt.% FeCl$_3$ at elevated temperature of 57 °C (pitting corrosion).

1.1. Causality factors

EFM works [7, 15] on the principle of applying a potential perturbation signal composed of two sine waves to get the current response. Mathematical analysis of current components at various frequencies yields the corrosion parameters and causality factors. The ratio between current components at specific intermodulation frequency and harmonic frequency defines the causality factor. Causality factor 2 and causality factor 3 are generally used for the data validation purpose. Both theoretically and experimentally [16], causality factors deviate from their normal values of 2 (causality factor 2) and 3 (causality factor 3) during pitting corrosion.

2. EXPERIMENTAL

2.1. Materials and samples preparation

Aluminum alloy used in this study was UNS A96151 (Cu: 0.2% to 0.6%, Mg: 0.45% to 0.90%, Si: 0.5% to 1.2%, Mn: 0.15% to 0.35%, Fe: 0.50%, Ti: 0.15%, Zn: 0.05%, Al: balance). The samples were cut from the bar of aluminum alloy with a diameter of 8 mm and were embedded in an epoxy resin. All the samples were grounded and then polished to 1 μm finish, cleaned with soap and water, rinsed with distilled water and ethanol (C$_2$H$_6$O), and finally dried with air.

Similarly cylindrical shaped samples of AISI 304SS were cut and embedded in an epoxy resin with an exposed surface area of 1 cm^2. Before each experiment, the electrodes were mechanically polished with silicon carbide (SiC) emery papers from grade 300 to 4000, and then polished to 1 μm finish with diamond paste. The electrodes were then cleaned with soapy water, rinsed with distilled water and dried with C$_2$H$_6$O and hot air.

2.2. Equipment

The potential noise was measured versus silver/silver chloride (Ag/AgCl) reference electrode with the help of solartron equipment and Gamry's CMS100 (corrosion measurement system). CMS recorded the data at a scan rate of 1 pt/s where as 4 pts/s with the help of solartron equipment.

The EFM measurements were made by using Gamry potentiostat along with Gamry Framewrok that contains EFM 140. With the EFM technique, two frequencies of 2 and 5 Hz were used with a base frequency of 0.1 Hz due to three arguments [7, 10]. The amplitude of the applied voltage fluctuation was set at 20 mV [7, 17].

2.3. Corroding systems
2.3.1. Aluminum in borate buffer with and without chlorides

0.2 M sodium tetraborate (Na$_2$B$_4$O$_7$.H$_2$O) also known as borax was mixed with 0.2 M boric acid (H$_3$BO$_3$). The pH of this new solution was brought nearly equal to 6.5 by adding and mixing boric acid until the required pH is achieved. 0.1 M NaCl and 0.5 M NaNO$_3$ were also prepared for using during these experiments.

First, the aluminum sample was immersed into borate buffer solution to obtain passivation. Few readings were recorded in this solution and then 0.1 M NaCl was added in borate buffer solution without stopping the experiment to observe the change in the response of the signal during pitting. Similarly the third solution 0.5 M NaNO$_3$ was added to previous two solutions to observe the effect on output signal during repassivation. This procedure was performed with both EFM technique and potential noise measurement.

2.3.2. AISI 304SS in 0.3 wt.% and 6 wt.% FeCl$_3$ at room temperature

To monitor pitting and crevice corrosion for AISI 304SS in 0.3 wt.% FeCl$_3$, potential noise was measured. The crevice corrosion was studied by keeping the Teflon block over the metal surface. In a same manner, pitting and crevice corrosion were investigated by the potential noise measurements in 6 wt.% FeCl$_3$.

Long-term joint measurements by EN and EFM were performed for pitting corrosion in 6 wt.% FeCl$_3$. This aggressive solution has been used to create pitting on the surface of AISI 304SS sample at open circuit potential. The sample was immersed into the electrolyte for duration of more than three days. During this period, different EFM and EN measurements were recorded and then analyzed with respect to the metallic surface at the end of the experiment.

2.3.3. AISI 304SS in 6 wt.% FeCl$_3$ at elevated temperature of 57 °C

Pitting occurs certainly for AISI 304SS in 6 wt.% FeCl$_3$ solution at higher temperature quickly even if the metallic surface is polished up to 1 μm finish, so EFM and EN measurements have been compared at a temperature of 57 °C.

2.4. Test set-up

The usual connections of three electrodes were made according to fig. 1 for comparing the response of EN and EFM measurements during pitting. The working and reference electrodes were connected to both data acquisition unit and EFM potentiostat but the counter electrode was connected only to the EFM potentiostat.
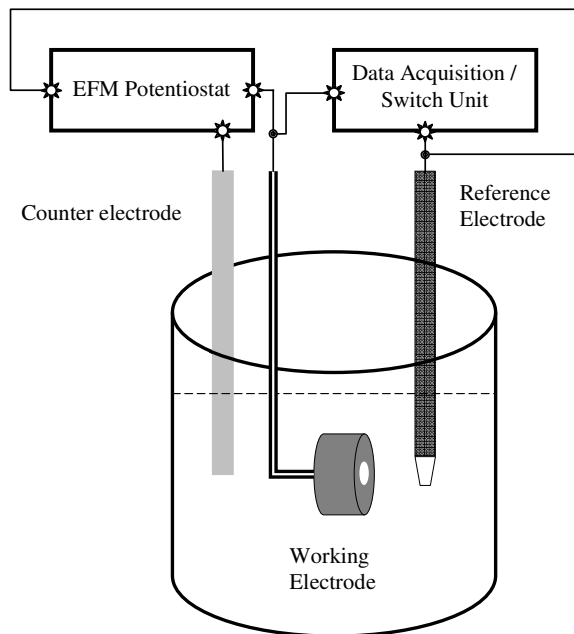
Figure 1. Setup arrangement to perform combined experiments to get electrochemical noise and EFM data
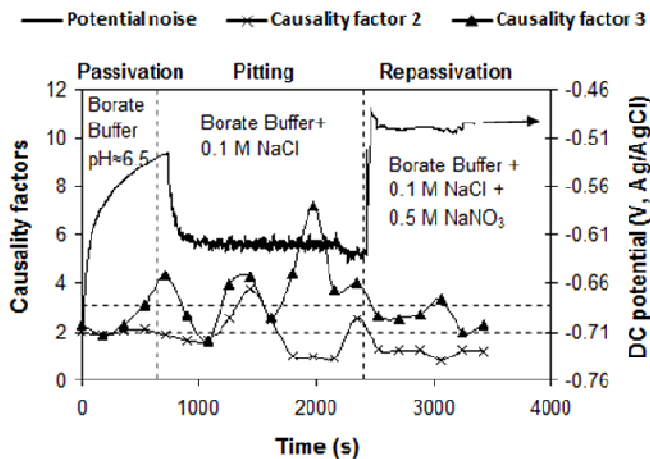

Figure 2. The change in the behavior of potential noise due to pitting and repassivation for aluminum is shown along with the response of causality factors of EFM.
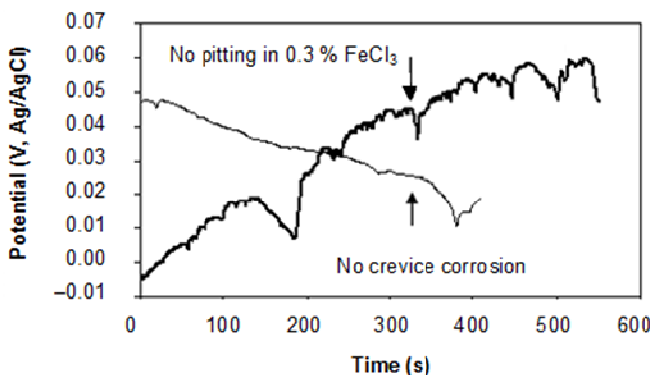

Figure 3. No pitting was observed after immersing AISI 304SS in 0.3 wt.% $FeCl_3$ for 9 minutes. Similarly, under the cylindrical TFE-fluorocarbon block no crevice corrosion was observed in 0.3 wt.% $FeCl_3$ after 6.8 minutes.

3. RESULTS AND DISCUSSIONS

3.1. Potential noise and EFM measurements for aluminum

Three regions of passivation, pitting and repassivation for aluminum are observed (fig. 2). The surface of aluminum alloy starts to passivate in the presence of borate buffer solution and voltage rises towards positive values but this passivation is broken due to the addition of 0.1 M NaCl that promotes pitting corrosion and the voltage drops down sharply and starts to fluctuate. During pitting initiation, the voltage drops sharply from -0.53 to -0.61 (V, Ag/AgCl) with many upward and downward fluctuating peaks indicating the pitting corrosion. Similarly the sudden addition of 0.5 M $NaNO_3$ to the previous solution caused the voltage to increase sharply from -0.63 to -0.49 (V, Ag/AgCl) due to repassivation of the aluminum surface.

No fluctuation is observed in potential signal during passivation and thus a steady state potential response is obtained. The sharp decrease and then fluctuations in the voltage occur due to pitting phenomena (fig. 2).

Few transients in the potential signal can be linked to incomplete repassivation of aluminum in the presence of chlorides, but overall shifting of potential noise towards positive values can be attributed to passivation (fig. 2). The potential noise clearly distinguishes different regions of passivation, pitting and repassivation (fig. 2).

A similar experiment was performed with EFM to observe the response during pitting and passivation of aluminum sample. The response of EFM shows clearly that causality factor 3 gives higher values indicating stable pitting (fig. 2) although causality factor 2 gives few lower values due to passivation behavior. During repassivation, the potential noise is slightly fluctuating due to incomplete passivation in the presence of $NaNO_3$ and chlorides. Generally

causality factor 3 gives values around 3 during uniform corrosion but for this particular case in which borate buffer solution passivates/covers aluminum surface, causality factor 3 during passivation and repassivation gives lower values, but higher values during pitting. In most cases both causality factors must be considered for better judgment about localized corrosion. Three regions for passivation, pitting and repassivation have been easily distinguished in a continuous fashion with the help of both EFM and potential noise measurements for aluminum in borate buffer and other accompanying solutions.

3.2. Short term potential noise measurements for AISI 304SS

Potential noise was measured for AISI 304SS immersed in 0.3 wt.% $FeCl_3$ for 9 minutes (fig. 3). The response of potential noise shows an increase of the potential towards more positive values with downward spikes. Similar behavior was observed by Sasaki
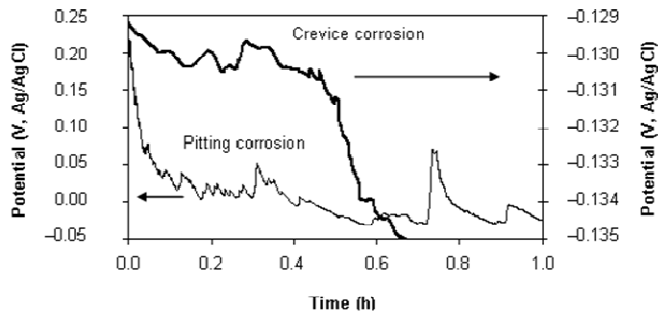
Figure 4. During pitting in 6 wt.% $FeCl_3$, the potential signal is becoming more negative with many fluctuating peaks. Crevice corrosion in 6 wt.% $FeCl_3$ can also be detected by the potential noise due to the fluctuations in the signal.

[18] for 304L stainless steel in sodium chloride solution. These spikes have been associated with meta-stable pitting because meta-stable pits repassivate rapidly and overall potential rises towards more positive value. The spikes are downwards towards more negative value due to the activation of meta-stable pits but these pits quickly repassivate and potential returns back towards rising trend. Similarly, no crevice corrosion was observed under the Teflon block on the surface of AISI 304SS sample in 0.3 wt.% $FeCl_3$ but still a couple of downward spikes can be seen (fig. 3).

After the immersion of AISI 304SS sample in 6 wt.% $FeCl_3$ for 1 h, the fluctuations in the potential signal were recorded (fig. 4) and two pits were observed. The sharp fall in the potential is caused by stable pit growth and subsequent large fluctuations indicate the pitting propagation in a destructive way. A permanent fall in potential is due to stable pitting.

In proceeding experiment, central part of the stainless steel sample was covered with the Teflon block to create crevice corrosion under this block. The metallic sample was immersed in 6 wt.% $FeCl_3$ for 2 hr and severe crevice corrosion under the block was achieved. The potential signal shifted towards more negative values progressively with many slow upward fluctuations (fig. 4). This observation is in agreement with the conclusions of Conde and Williams [19]. They have found that the predominant nature for the crevice corrosion process is a continuous rise of the current at the same time a shift towards negative values in voltage is taking place during crevice corrosion. Without pitting and crevice corrosion, the potential signals also show some downward spikes. On the other hand, during pitting and crevice corrosion the potential signal provides upward spikes.

3.3. Long term joint measurements by EN and EFM

The dc potential has been measured in a continuous way for AISI 304SS sample immersed in 6 wt.% $FeCl_3$ for 76 hrs. During alternative potential measurements (fig. 5), four EFM measurements were also performed.

The very first data of potential noise shows a decrease and many fluctuations due to pitting initiation whereas other measurements are also shown in this fig. 5 separately illustrating some fluctuating potentials during the pitting phenomenon.
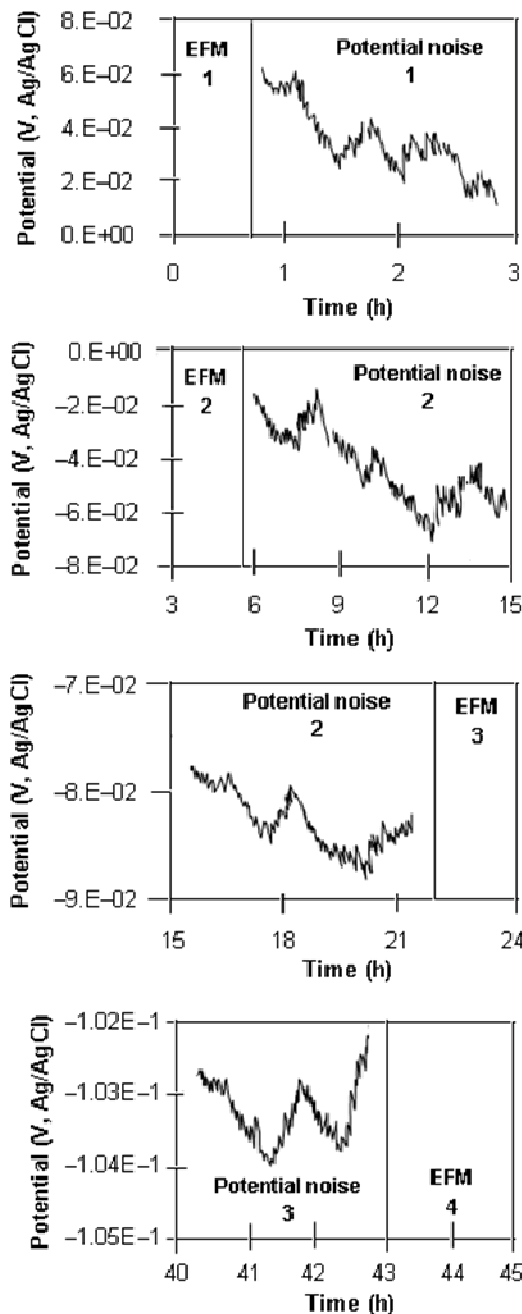

Figure 5. Three potential noise measurements combined with four alternative EFM results

In the case of $FeCl_3$, overall the potential noise moves progressively towards more negative values in the first two measurements. This trend suggests the domination of crevice corrosion because during stable pitting propagation the noise usually remains stable at specific potential base line. The last measurement is different than the first two because the potential falls as well as rises due to pitting and crevice corrosion. At the end of the experiment, the surface of the sample was visually analyzed and the crevice corrosion was found to be more dominant than pitting.

Comparison Between Electrochemical Noise and Electrochemical Frequency Modulation Measurements during Pitting Corrosion
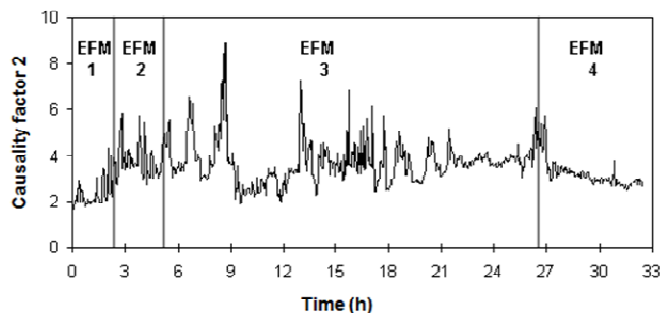*/ J. New Mat. Electrochem. Systems*

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Figure 6. Four results obtained by EFM for causality factor 2 as joint measurements shown in above fig. 5.
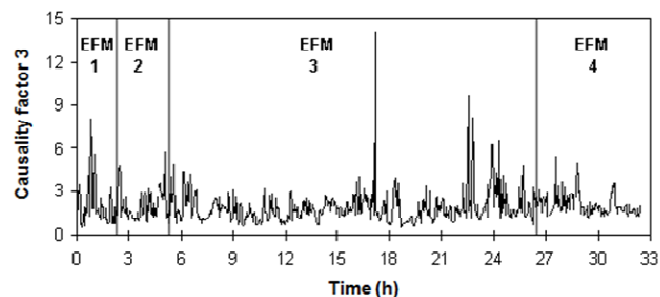

Figure 7. High peaks of causality factor 3 are due to the pitting where as lower values are due to crevice corrosion as investigated in case of crevice corrosion. These results for causality factor 3 are shown separately having a link with fig. 5.

The causality factor 2 and causality factor 3 measured with EFM are shown separately in fig. 6 and fig. 7. In general, the response of both causality factors with higher values but particularly only few higher values of causality factor 3 is a weak indication of pitting corrosion. Furthermore it can be seen that EFM provides noisier data than EN to detect localized corrosion. Detailed analysis of causality factors shows that all values of causality factor 2 are higher than its normal value of 2 where as causality factor 3 also provides many lower values than 3 and this type of collective response indicates crevice corrosion. High peaks of causality factor 3 are due to pitting initiation but the majority of causality factor 3 is showing lower values than 3, which indicates the prevalence of crevice corrosion (between the edges of metal and epoxy) over the pitting corrosion.

3.4. EFM and EN measurements at elevated temperature of 57 °C

In this experiment, temperature of the solution was first raised to 57 °C and then the heating was stopped. Many pits were observed in 6 wt.% $FeCl_3$ and the data was recorded by the Solartron at a scan rate of 4 pts/s (fig. 8). The potential noise first decreases with fluctuations due to the pitting initiation and then stabilizes during pitting propagation. This behavior of potential noise is similar to our previous result (fig. 4) during pitting.

In the test with the EFM, the surface of AISI 304SS sample was prepared with 1μm diamond paste. Again the temperature of 6
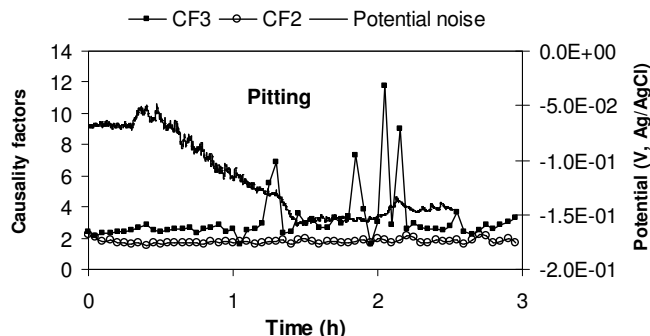

Figure 8. Many pits were observed at the metal surface of AISI 304SS in 6 wt.% $FeCl_3$ at 57 °C. Noise measurements were performed with the help of solartron. The causality factors were also measured with the help of EFM

wt.% $FeCl_3$ solution was raised to 57 °C and then heating was stopped. EFM measurements were performed for 3 hours. At the end, the sample was visually analyzed and pitting was observed. The higher peaks of causality factor 3 indicate the pitting corrosion (fig. 8). In the first hour of the experiment, causality factors remained stable showing uniform/passive corrosion; mainly due to the better surface quality of the metallic sample.

4. CONCLUSIONS

Three regions of passivation, pitting and repassivation were successfully distinguished by both EN and EFM techniques for aluminum in borate buffer solution due to the addition of chloride and then inhibitor in a continuous experiment.

The EN measurements gave satisfactory indications to distinguish crevice and pitting corrosion.

During pitting initiation, the potential noise sharply drops down and then gives fluctuating peaks during stable pitting propagation.

Without pitting in 0.3 wt.% $FeCl_3$, the potential noise grows towards more positive values with downward peaks. The downwards peaks are due to the short term activation of meta-stable pits.

The overall rise of the potential towards more positive value is due to the passivation of the meta-stable pits.

Pitting causes noisy data both for EN and EFM results.

The results obtained by both techniques can be well compared with each other during pitting at room and elevated temperatures.

5. ACKNOWLEDGEMENT

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