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APPLICATION OF ELECTROCHEMICAL NOISE TECHNIQUE IN MULTIPHASE FLOW

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ABSTRACT

This paper presents the experimental results for CO_2 corrosion of carbon steel in a 101.6 mm ID multiphase flow loop using electrochemical noise measurement. ZRA mode electrochemical noise technique with three nominally identical electrodes was utilized to study the corrosion processes and inhibitor performance in the stationary slug flow. Comparable corrosion rates were obtained from EN, EIS, and ER tests, suggesting EN technique with a “noisy” RE a practical measurement for investigating CO_2 corrosion in multiphase slug flow condition. Results from EN signals showed that addition of 100 ppm inhibitor could retard the corrosion process to a satisfied level for stationary slug flow pattern at Fr 6 in the flow loop tests.

Keywords: ZRA mode, multiphase, flow loop, slug flow, electrochemical noise (EN), noisy RE

INTRODUCTION

In oil and gas industry, various flow regimes in multiphase flow pipeline have encountered, depending upon the pipeline diameter, the composition of the phases and their velocities. High gas and liquid velocity in transportation pipelines would result in slug flow [1, 2] with associated high turbulence and bubble impact mechanism in the mixing zone. Slug flow can be characterized by the Froude Number (Fr), which is a dimensionless parameter measuring of the ratio of the inertia force on an element of fluid to the weight of the fluid element - the inertial force divided by gravitational force. The study by Jepson [2, 3] showed that higher Froude Number of slug flow is always associated with higher turbulence, higher mass transfer rate and stronger bubble impact. Therefore, CO_2 corrosion of carbon steel pipeline in the slug flow condition is always one of the major concerns for corrosion engineers. Many techniques have been used to monitor the corrosion rate and study the corrosion and inhibition mechanisms.

Spontaneous fluctuation of the current and potential of a corroding electrode, which is commonly referred to as electrochemical noise (EN), has been extensively studied in the past two decades in order to better understand the corrosion and inhibition mechanism in various environments[4-7], especially for pitting corrosion[8,9]. The major sources of electrochemical noise observed in corrosion can be ascribed to random phenomena[10], including, partial faradaic currents, adsorption or desorption processes, and particularly the initiation of pitting. Noise data are typically acquired by monitoring the evolution of the corrosion process on two electrodes coupled through a zero resistance ammeter (ZRA) without the application of external signal. By using ZRA, current between these two electrodes is measured while the coupled electrodes are maintained with negligible potential difference. The voltage is measured simultaneously between one of the working electrodes and a reference electrode (RE). Together with some other electrochemical techniques, (e.g., linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS)), electrochemical noise measurement without externally applied voltage has shown great potential on investigating the corrosion mechanism and inhibitor performance[7]. Stochastic noise data have been interpreted in either time domain[7] or frequently domain[10, 11] and attempts of correlating the proposed noise resistance (Rn) and noise impedance (Rsn) with polarization resistance from EIS or LPR tests were carried out broadly. However, controversy on DC drift removal [12] of long term noise monitoring and consequent scattered data and non-deterministic explanation also brings up application difficulties for the noise techniques.

Several previous publications[13-16] have addressed the applications of EN to monitor CO_2 corrosion in the large scale multiphase flow loop using EN techniques. In this effort, EN signals acquired using a “noisy” RE in the Fr 6 slug flow condition (with and without inhibitor addition) were continuously monitoring for several hours by using 100 Hz sampling rate and the results particular noise resistance from the time domain analysis were compared with these obtained from electrical resistance (ER) and EIS techniques.

EXPERIMENTAL SETUP

The flow loop experiments were carried out in a 101.6 mm (4 inch) I.D., 15 m long Plexiglas pipeline. The schematic layout of the flow loop system is shown in Figure 1. The prepared test solution (ASTM saltwater with or without 2 cp@40^{o}C light oil LVT-200) was placed in a 1.4 m^3 stainless steel tank A. The liquid from the tank was pumped into the 76 mm I.D. PVC pipe by a 1.5 kW centrifugal pump. The flow rate of the liquid was controlled by a bypass line B and measured using a calibrated orifice meter D. The liquid was passed into the 76 mm I.D. PVC pipe and then forced under gate E into the 101.6 mm I.D. Plexiglas pipe, where it formed a fast moving liquid film. The carbon dioxide gas was introduced into the system at port F. The gas/liquid mixture passed through the Plexiglas pipeline and entered the tank where liquid and gas were separated using a de-entraining plate inside the tank. Liquid was recycled and gas was exhausted to atmosphere at the top of the tank.

The carbon dioxide gas was also used to pressurize the system. The pressure inside the tank was indicated by a gauge I, installed at the top of the tank. All the measurements were taken in the test section G located 8 m downstream from the gate. The liquid inside the tank was heated by two 1.5 kW heaters positioned at K. A temperature control system was used to maintain a constant temperature in the tank during tests by starting or stopping the heaters. During experiments, solution temperature in the test section was checked regularly by thermocouple.

The slug flow, or the hydraulic jump, was generated and moved to the test section by controlling the gas flow at the inlet F. This was accomplished by using a needle valve in conjunction with a gas flow control system. The EN, ER, and EIS probes were inserted into the test section G, and were flush mounted with the pipe wall. The EN probe (Figure 2) consists of three nominally identical C-1018 carbon steel electrodes: two for working electrodes (WE) and one for reference electrode (referred to as a noisy RE [17]). The exposed surface area of each electrode is 71 mm^2. The EIS probe consists of three electrodes: one C-1018 carbon steel rod as working electrode, and two S316 stainless steel rods as reference and counter electrodes. The area of each electrode of EIS probe is 78 mm^2. ER probe used in this study was also constructed using C1018 carbon steel. The principal of ER probe is that the change in the electrical resistance of a metal sheet over an adequate period of time gives the change in thickness of the metal during that time period [18,19]. The resolution of the ER probe was 0.1%.

Before each experiment, the system was de-oxygenated with carbon dioxide for several hours until the concentration of the dissolved oxygen in the solution was measured less than 10 ppb using colorimetric analysis. Once the de-oxygenation process was completed, the ER, EN and EIS probes, which were polished by 600-grit sandpaper and washed with acetone, were quickly inserted into the test section. Noise measurements were started instantly after a stable stationary slug flow was generated. The system temperature and pressure were maintained constant at 40°C and 0.136 MPa respectively for all the experiments. The test matrix is shown in Table 1.

The EN data acquisition and analysis were carried out using ESA400®™ (Electrochemical signal analyzer system), which achieves 1 µV and 100 fA resolution. Data integrity was maintained by using filters tuned to the sampling rate according to the Nyquist antialiasing criterion, which states that signals at frequencies greater than ½ the sampling frequency will appear as lower frequencies. High frequency computer noise is effectively eliminated by a series of analog and digital filters. The filters are designed to be linear in phase, insuring that peak shapes and higher order statistical moments are not distorted. EIS experiments are carried out using CMS300 EIS system®™. The AC voltage applied using EIS tests was 4 mV and frequency ran from 100K toward 0.01 Hz.

RESULTS AND DISCUSSIONS

Current and Voltage Fluctuations

Since electrochemical noise signals were continuously monitored during the experiments with high sampling rate (100Hz), a large amount of random noise data were acquired during the experiments. Figure 3 shows, as an example, the original time domain voltage and current noise signals collected in the 80% water cut solution with 50 ppm inhibitor at different experimental times. Two working electrodes were coupled through a ZRA and thus the current transients in Figures 3(a) to (h) were consequently the galvanic currents due to the surface condition and local chemistry differences between two WEs. The presence of nonstationary DC current in order of several µA (non-zero) also indicates that there existed a potential difference between two working electrodes even though a ZRA was used. A drift of the so-called DC current[7, 12] was particularly observed in the early period of immersion of the EN probe. Figure 3(b) illustrates as an example of this DC drift which might cause difficulties in interpretation of noise data. Typically, the drift of DC current was less than 1 µA as shown in Figure (c) to (h).

Compared to the noise signals during the first two hours (Figures 3a to 3d), sharp current peaks (peak height ~1µA) were observed in Figures 3(e) to (h). The sharp current transients were all positive in direction, indicating that only one working electrode experienced the transients. Transients of current and voltage took place within 1 second. In the galvanic coupling, the net current generated in one working electrode from the corrosion process was gradually consumed on the other working electrode, accompanying a drop of potential on the electrode due to the electrons accumulation. However, in Figures 3(e) to (f), most of the sharp potential peaks are associated with a sharp current peak suggestive of different mechanisms other than localized corrosion involved in generating current noise. Bertocci[17] and his coworkers indicated that the noise sources might be quite dissimilar for different corrosion systems: for Fe in weakly acidic solution (pH 3) the principle source of fluctuations is uniform corrosion accompanied by hydrogen bubble formation and detachment, while for Al in chloride solution, the source is pitting. Bertocci[13] also suggested that the origin of the fluctuations for Fe in pH 4 solutions is

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likely natural convection in solution, which varies the transport rate of the reactants. In a slug flow characterized by strong turbulence, beside hydrogen bubbles formation and detachment, CO_2 gas bubbles and oil drops are constantly brought onto the steel surface, changing the properties of the local chemistry of solution. Adsorption and desorption of inhibitor molecules due to the shear stress and turbulence might also contribute to the concurrence of the potential and current spikes.

However, the current peaks are not observed in Figures 3 (a) to (d) at the early stage of immersion of the noise probe. It was then hypothesized that it might be due the frequent detachment of corrosion productive film formed on the steel surface after 4 hour immersion. Corrosion product films would not form at the beginning immersion period with the presence of 50 ppm inhibitor. This hypothesis was partially valid because similar “pitting” phenomenon was not observed for blank test (corrosion productive film exists since the very beginning) and higher concentration 100 ppm (no corrosion product film) tests. Since uniform current fluctuations with small amplitudes dominate the corrosion process within all the 100s time intervals, uniform corrosion activity was then assumed with occasional localized corrosion phenomenon. Whether the galvanic coupling would accelerate this localized phenomenon was also not known at this moment.

As seen in these diagrams, the potential differences between two working electrodes which were made using nominally identical C1018 steel are within 8 mV. This so-called DC voltage was also due to the slight differences of the local chemistry in the slug head from location to location and the steel surface conditions between RE and WEs. Most of time, no significant drifts of DC potential trend were observed within each 100s time interval. Bearing in mind that the local chemistry and surface conditions might change simultaneously at “noisy” RE and WEs, the potential fluctuations around a mean value (DC trend) therefore might not represent the real magnitude of noise amplitudes happened on the WEs, either exaggerating or depreciating the noise magnitude. Bertocci[20] mathematically calculated and reported that the voltage PSD measured with a noisy RE (Fe made RE) was three times the voltage PSD measured with a noiseless RE (e.g. saturated calomel electrode) when assuming the noise level on RE was the same that of the two WEs. They also cast doubts on this assumption because of the non-zero mean current flowing through the two WEs. This is then considered as a disadvantage of using unstable reference electrode for noise measurement even though RE of the same material as WE is more practical for field tests. Uniform corrosion was visually inspected for C1018 steel in the synthetic sea water solution after the tests.

Comparison

Figure 4 (a) shows the changes of the mean voltage and current (DC trend) along the exposure time of EN probe in the slug flow of 100% water cut and no inhibitors. Noise resistance (Rn) was calculated using the standard deviation of voltage signals divided by the standard deviation of current signals in each 100s interval, while the corrosion rate was calculated by simply assuming that typical cathodic and anodic Tafel slopes for CO_2 corrosion process were 120 [22,23] and 40 [21] mV/decades, respectively. Noise resistances and corrosion rates calculated with 100s (10000 points) interval and 1s (100 points) interval are compared in Figure 4 (b) and (c), respectively. By using smaller time interval (or less data points) for calculating noise resistance, the amplitudes of the fluctuating curve in Figure 4 (c) are slight higher than those in Figure 4 (b). However, the trend lines of noise resistance or corrosion rate remain almost unaffected by the number of the original data points used for calculation.

The voltage difference between RE and WEs changed slightly within 2mV while the mean current continuously decreased and reached relatively stable (approximate $30\mu A/cm^2$) after 3 hour immersion. The decrease of this galvanic current also shows indicative of reduced corrosion rate due to the formation of corrosion product on the steel surface. The initial corrosion rate (first 100s) was calculated as high as 6.3 mm/yr for the bare surface and then the corrosion rate quickly reduced to less then 2 mm/yr and kept relatively stable at ~1.5 mm/yr.

Figure 5 shows the corresponding EIS responses at 2nd and 4th hours. It is shown in Nyquist diagrams that the origin of the semi-circle locates below the real axis of impedance. This depression of the semicircle may be due to the changing of surface roughness and the effect of geometry on the current distribution, which was also observed by other researchers [7, 24]. The polarization resistance (Rp) value estimated from EIS plots at 4th hour was about ~120 ohm-cm^2, which is very close to the noise resistance in the Figure 4(b).

EN signals and EIS Nyquist plots obtained from 80% water cut solution without inhibitor are shown in Figures 6 and 7, respectively. The mean voltage along the test period shown in Figure 6 (a) was always less than 2 mV and the mean current kept decreasing from ~40 μA/cm^2 at the very beginning to ~1 μA/cm^2 after 3 hours exposure to the solution. The corrosion rates calculated from the noise resistance data increased slightly in the first 2 hours and reached relatively stable around 0.7 mm/yr. However, Nyquist plots obtained at 1st, 2nd, 3rd, and 4th hour showed only very slight changes in Rp values, indicating the WE in the flow loop system reached relatively stable condition within 1 hour. Since a complete EIS measurement usually took 30 minutes, the Rp extracted from the EIS curve indeed represents an averaged value within 30 minutes. EN measurement in this aspect would thus catch more information on corrosion activities, especially when the transition of corrosion mechanism or flow pattern happens during this period. Compared to the Rp values obtained in 100% water cut slug flow condition, EIS results indicated that the addition of 20% LVT light oil decreased the corrosion rate by approximate 0.2 mm/yr, while EN result indicated a 0.6 mm/yr reduction in the corrosion rate.

As shown in Figures 8 and 9, the addition of 50 ppm imidazoline based inhibitor into 80% water cut slug flow decreased the corrosion rate to ~0.2 mm/yr. Continuous decrease of the mean current along the exposure time is again noticed in Figure 8(a). The noise resistances fluctuated broadly from 400 to 1200 ohm-cm2. Figure 10 shows the noise results with 100 ppm inhibitor. The trend line of noise resistances continuously increased during the first hour and then became relatively stable, waving around 5000 ohm-cm^2. Continuous adsorption of inhibitor onto the steel surface also decreased the galvanic corrosion activities. No rust on WEs and RE surfaces was observed through visual inspection after the tests for 100 ppm inhibitor tests, indicating a good performance of imidazoline based inhibitor in slug flow. Previous studies[7, 25] in a rotating cylinder electrode system (RCE) using similar imidazoline based inhibitor showed that a concentration of 5 to 25 ppm would already reach the same inhibition efficiency. Clearly, slug flow which is characterized by strong turbulence and bubble disturbance in the present flow loop study required much higher inhibitor concentration to reduce the corrosion rate to the satisfied level.

Comparison of corrosion rates from ER, EIS and EN tests at relatively steady state are illustrated in Figure 11. It is clear that all three corrosion monitoring methods showed similar trend of decrease in corrosion rate when increasing the inhibitor concentration. Comparable corrosion rates were obtained from ER, EIS, and EN techniques, especially in the blank tests without inhibitor. ER and EIS techniques showed more comparable corrosion rates in the tests with 50 ppm inhibitor while EIS and EN techniques showed similar corrosion rates in 100 ppm inhbitor conditions. This also suggested that the ER system used in the current study was not sensitive enough when corrosion rate was extremely low due to the presence of high concentration inhibitor.

CONCLUSIONS

1) Comparable corrosion rates were obtained from EN, EIS, and ER tests, suggesting EN technique with a “noisy” RE a practical measurement for investigating CO_2 corrosion in multiphase slug flow condition.

2) Results from EN tests showed that addition of 100 ppm inhibitor could retard the corrosion process to a satisfied level in the stationary slug flow of Fr 6.

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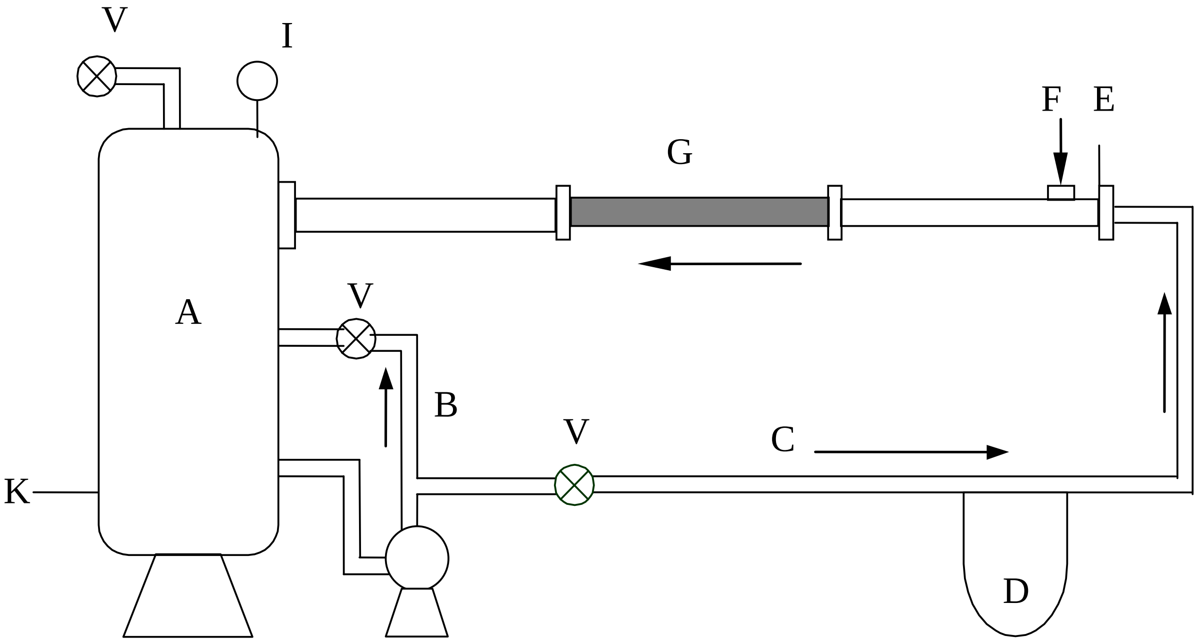
TABLE 1 TEST MATRIX

Parameter	Conditions
Temperature, °C	40
CO_2 partial pressure, MPa	0.136
Water cut, %	100 & 80
Inhibitor type	Imidazoline based
Inhibitor concentration, ppm	0, 50, 100
Oil	Viscosity: 2 cp at 40 °C
Flow pattern	Stationary slug flow: Fr=6
Liquid velocity, m/s	0.8
Noise Sampling rate, Hz	100



A. Liquid tank
B. Bypass
C. Liquid feed
D. Orifice plate with mercury meter
E. Flow height control gate
F. Gas input
G. Test section
H. Gas outlet
I. Pressure gauge
K. Heater
V. Valves

Figure 1. Layout of the Horizontal Low Pressure Experimental System

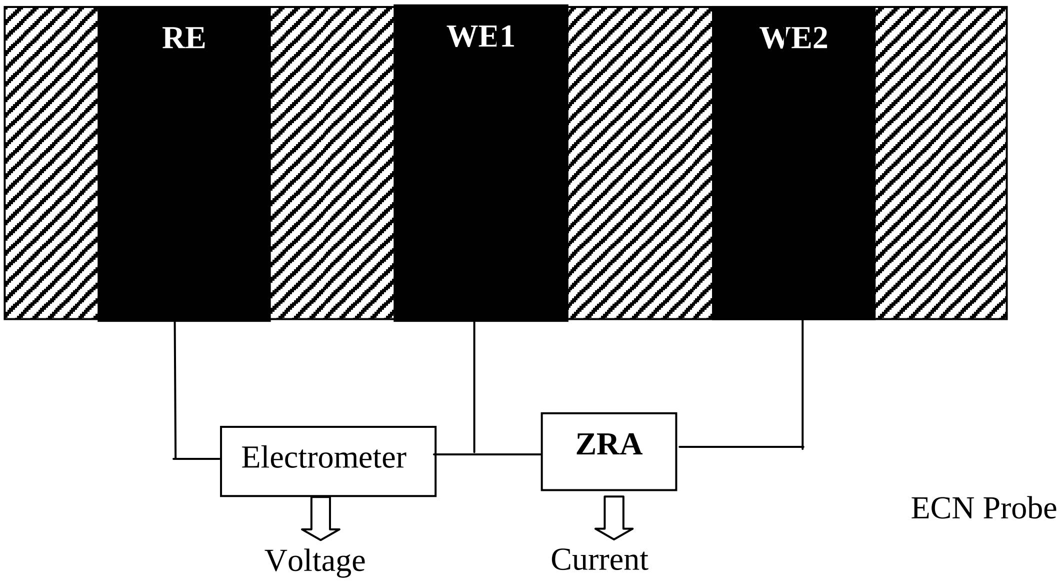


Figure 2. Schematic of three-electrode ZRA mode EN measurement

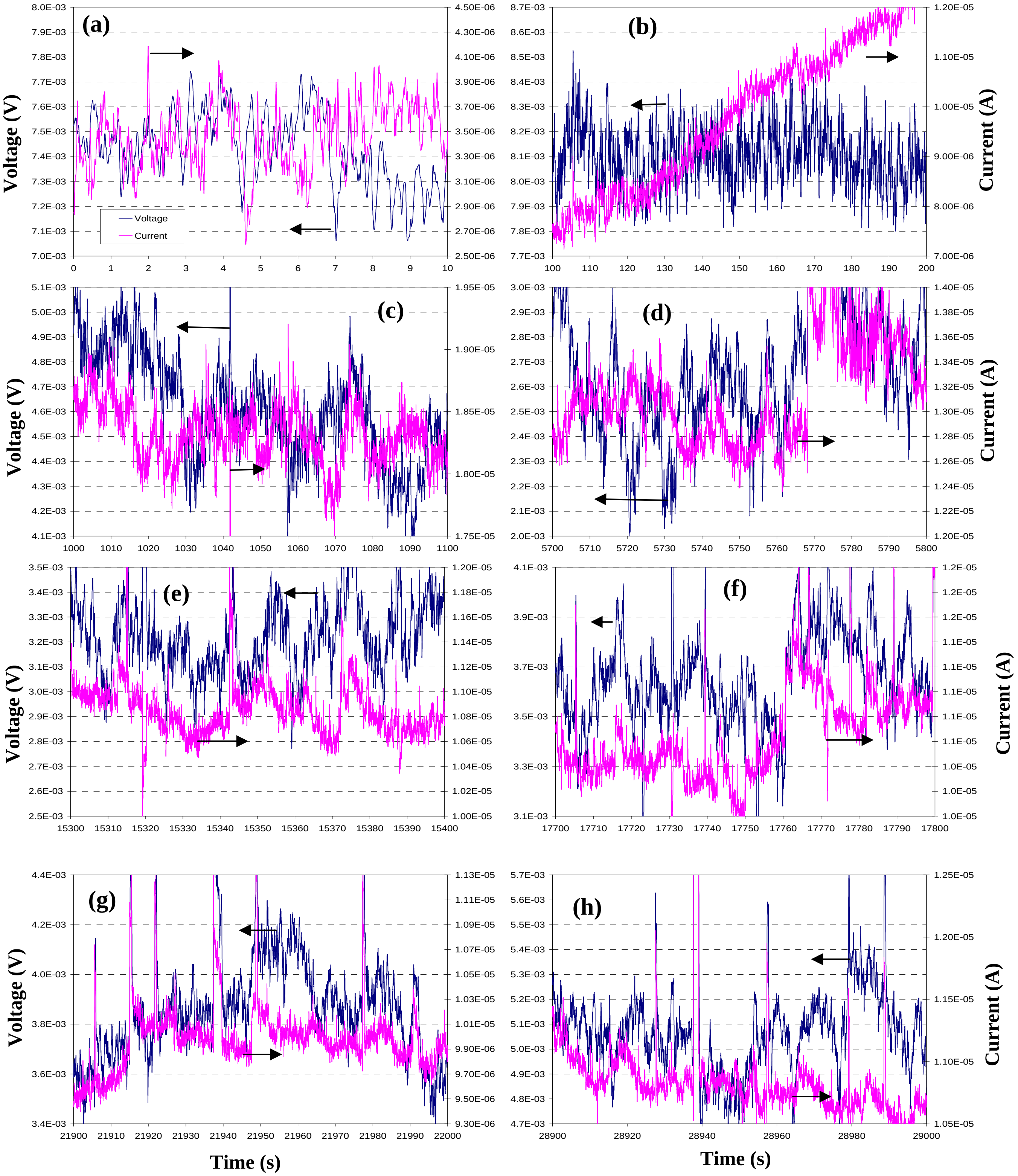


Figure 3. Continuous Monitoring of Electrochemical Noise Signals
Slug Flow, Froude Number=6, 80% water cut, 50 ppm inhibitor, 100 Hz sampling rate
Time at 0 s indicates the start of the experiment; current peaks were noticed after 4 hours exposure to the solution.

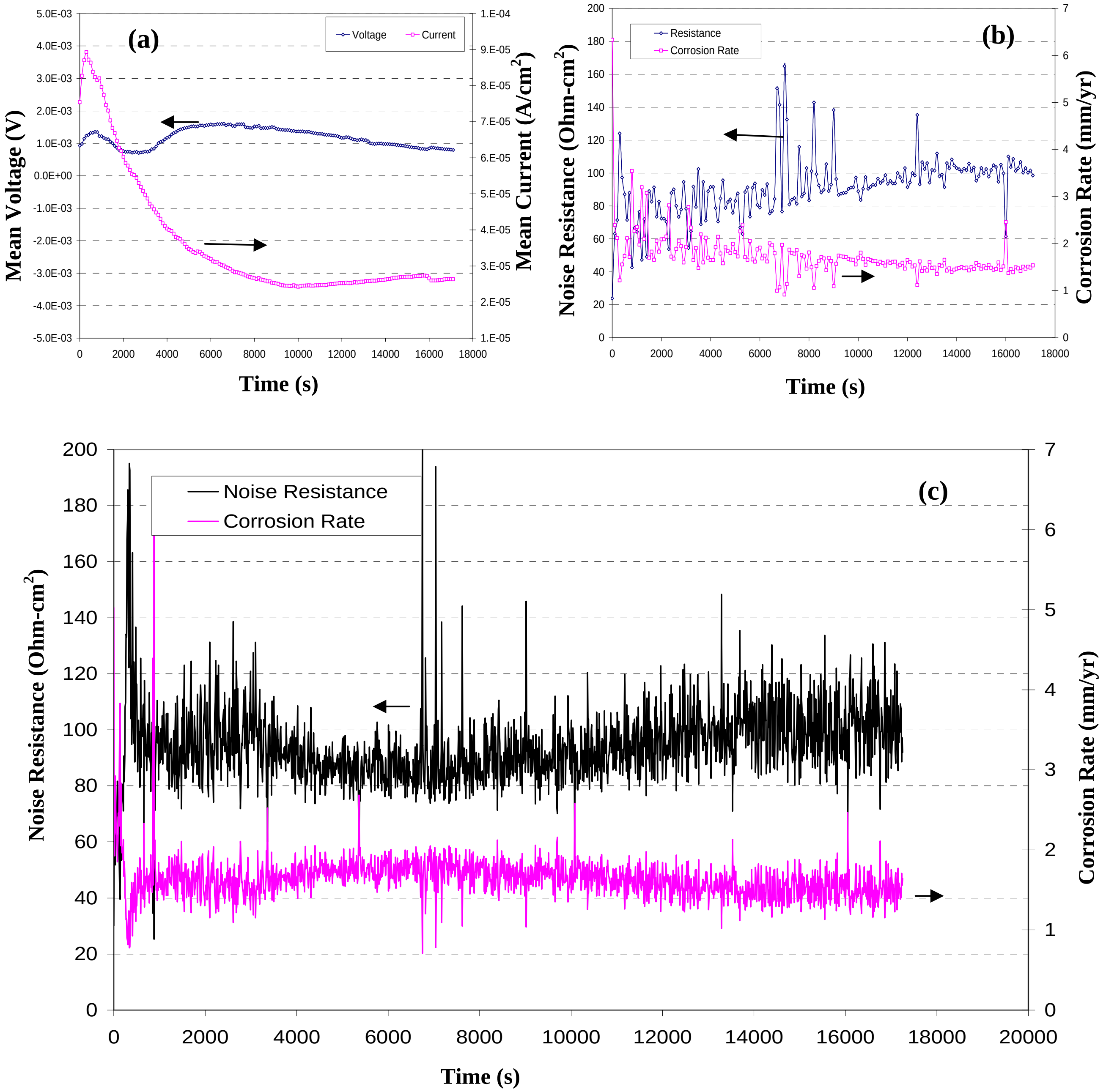


Figure 4. Electrochemical Noise Signals along the exposure time

Slug Flow, Froude Number=6, 100% water cut, 0 ppm inhibitor, 100 Hz sampling rate
Time at 0 s indicates the start of the experiment; the mean voltage and current were calculated using 100s interval for (a) and (b), 1s interval for (c); in corrosion rate calculation, cathode and anode tafel slope were 120 and 40 mV/decade, respectively.

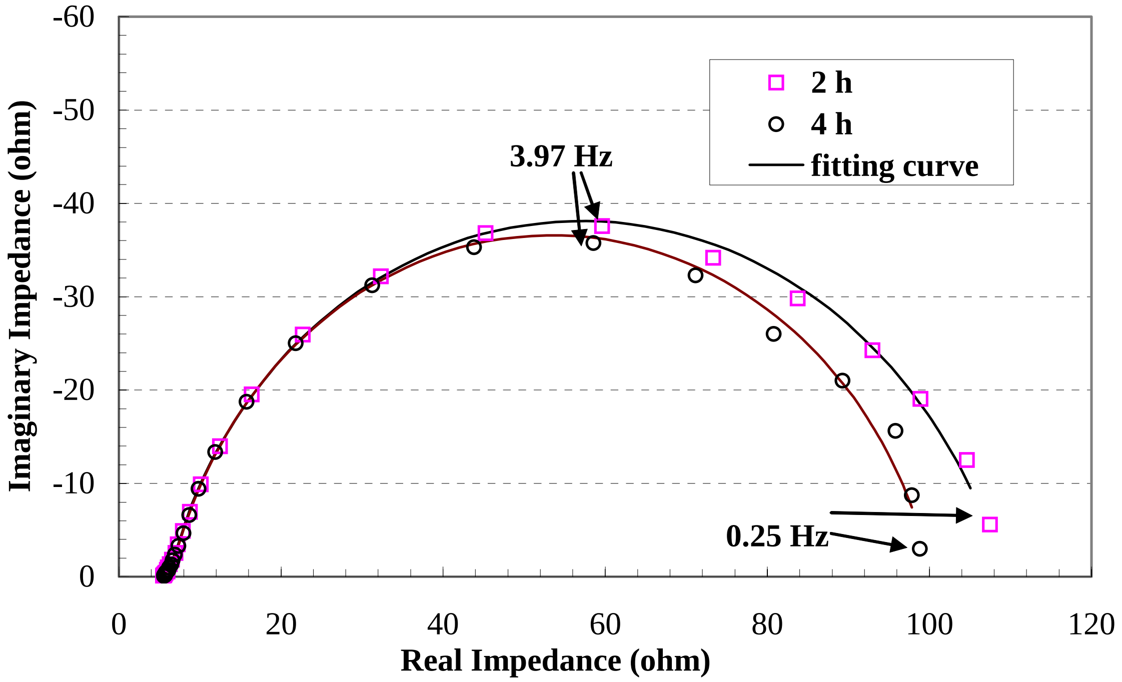


Figure 5. EIS Nyquist plots at different exposure times
Slug Flow, Froude Number=6, 100% water cut, 0 ppm inhibitor

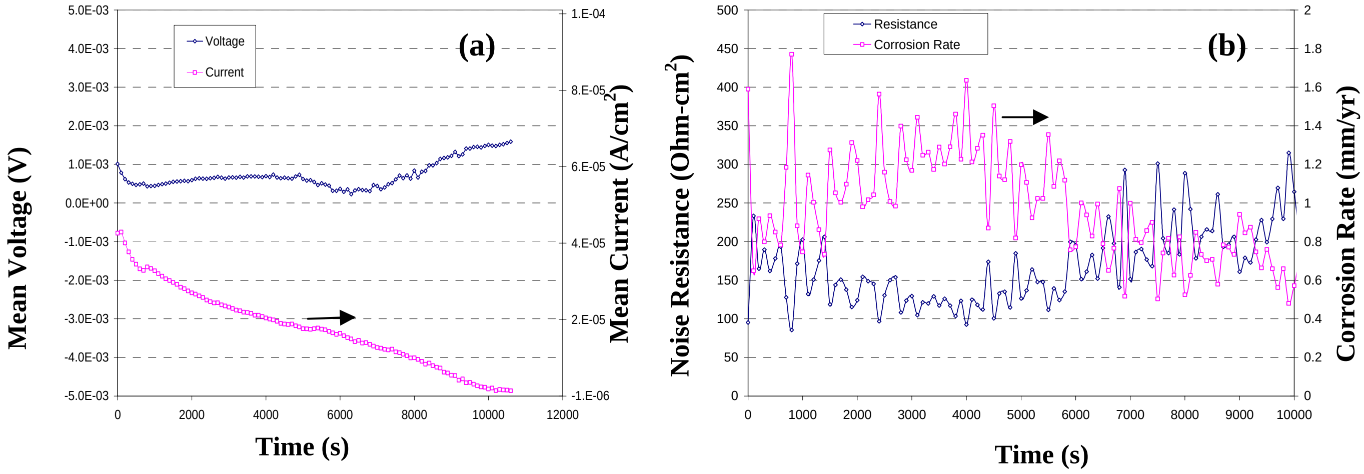


Figure6. Electrochemical Noise Signals along the exposure time
Slug Flow, Froude Number=6, 80% water cut, 0 ppm inhibitor, 100 Hz sampling rate
Time at 0 s indicates the start of the experiment; the mean voltage and current were calculated using 100s intervals; in corrosion rate calculation, cathode and anode tafel slope were 120 and 40 mV/decade, respectively.

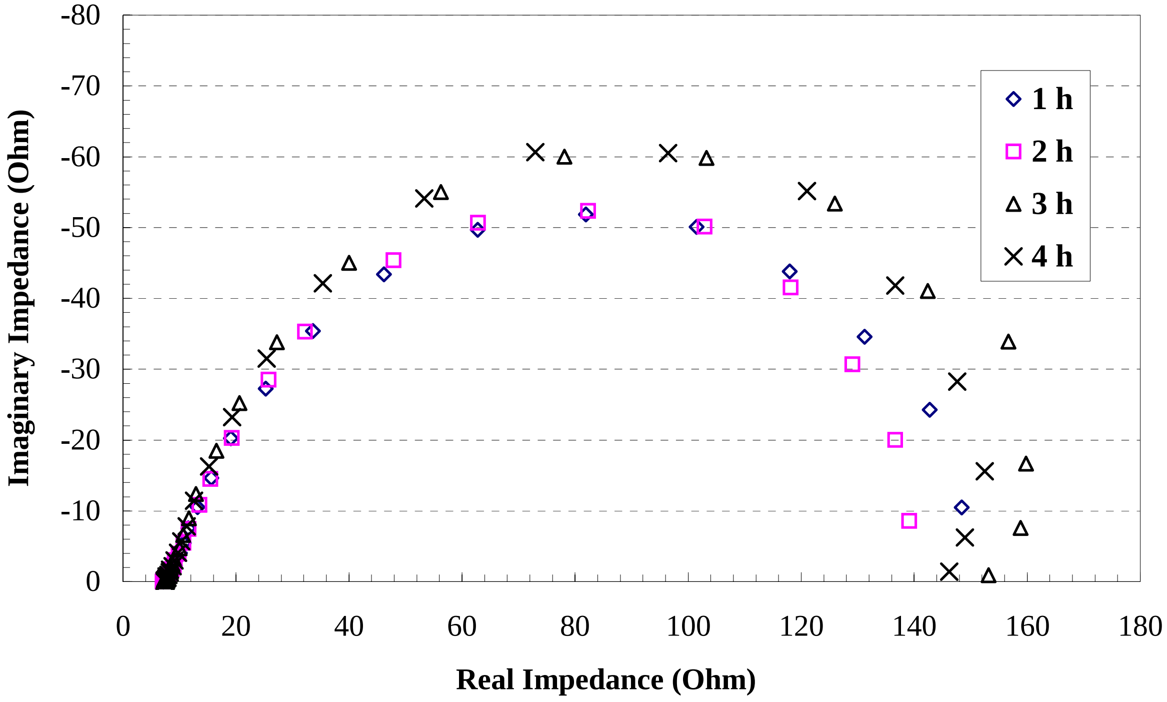


Figure 7. EIS results at different exposure times
Slug Flow, Froude Number=6, 80% water cut, 0 ppm inhibitor

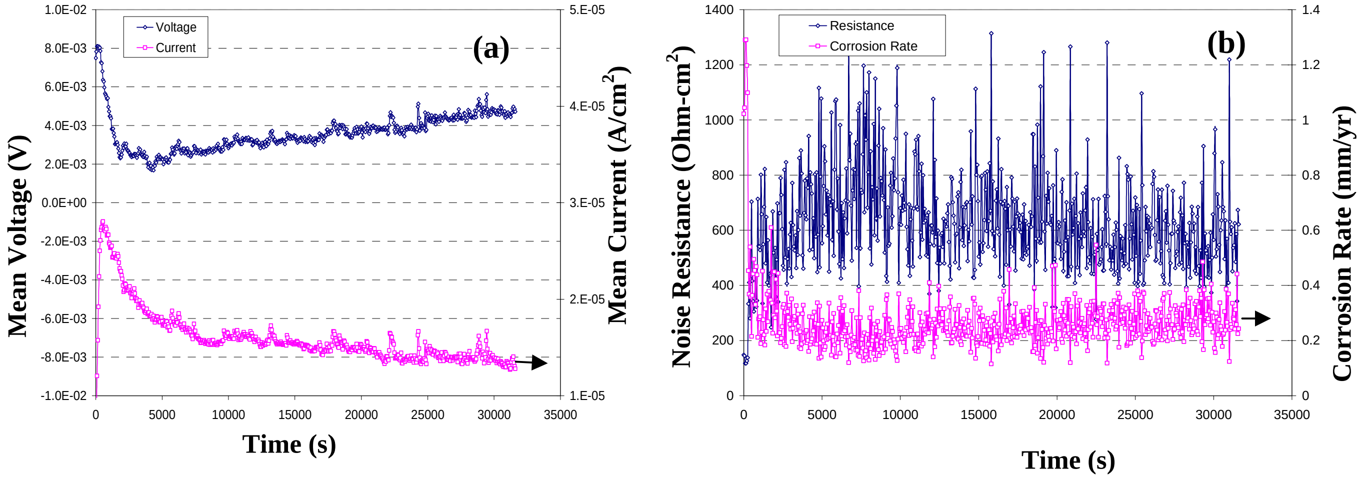


Figure 8. Electrochemical Noise Signals along the exposure time
Slug Flow, Froude Number=6, 80% water cut, 50 ppm inhibitor, 100 Hz sampling rate
Time at 0 s indicates the start of the experiment; the mean voltage and current were calculated using 50s intervals; in corrosion rate calculation, cathode and anode tafel slope were 120 and 40 mV/decade, respectively.

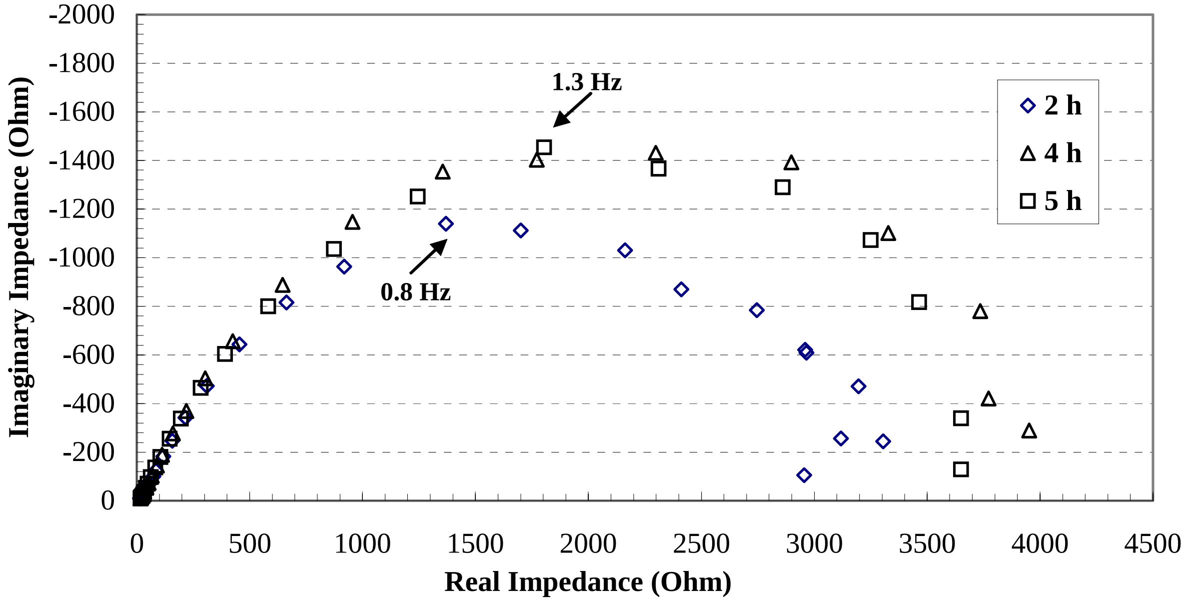


Figure 9. EIS results at different exposure times
Slug Flow, Froude Number=6, 80% water cut, 50 ppm inhibitor

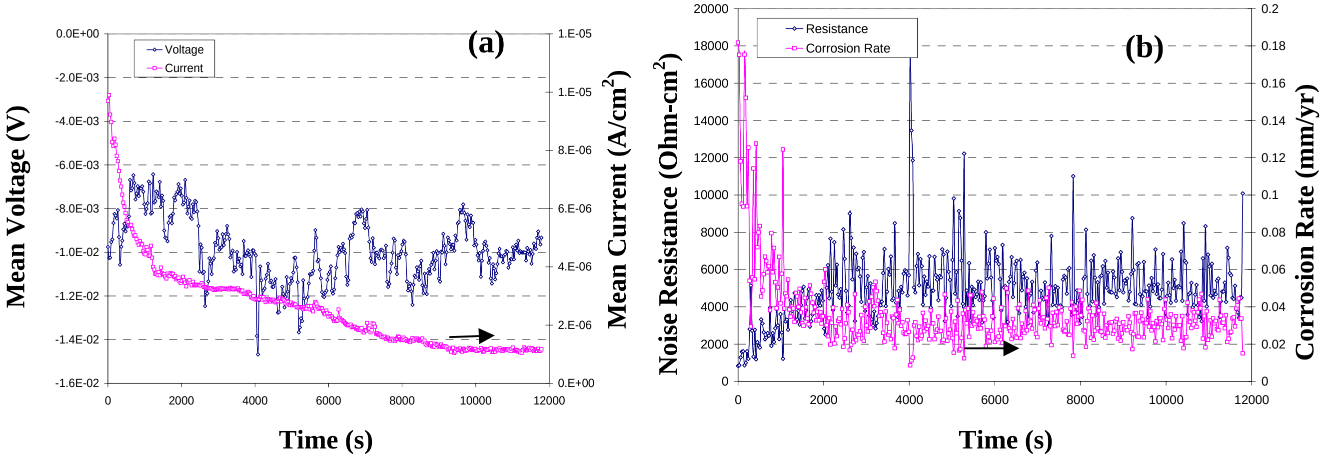


Figure10. Electrochemical Noise Signals along the exposure time
Slug Flow, Froude Number=6, 80% water cut, 100 ppm inhibitor, 100 Hz sampling rate
Time at 0 s indicates the start of the experiment; the mean voltage and current were calculated using 50s intervals; in corrosion rate calculation, cathode and anode tafel slope were 120 and 40 mV/decade, respectively.

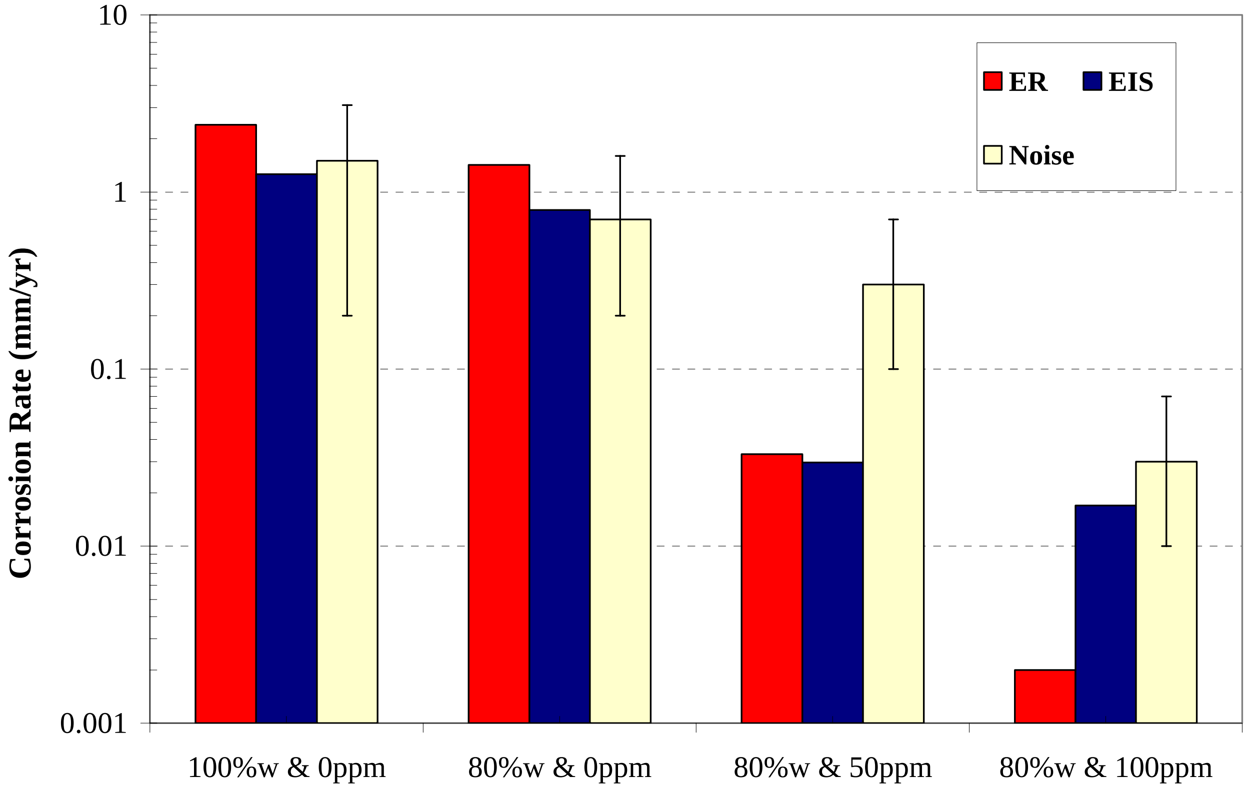


Figure11. Comparison of Corrosion Rates Obtained Using ER, EIS, and EN Techniques (Slug Flow, Froude Number=6, the error bars represent the fluctuations of noise data in previous figures)