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CORROSION 99

ELECTROCHEMICAL METHODS FOR MONITORING PERFORMANCE OF CORROSION INHIBITOR UNDER MULTIPHASE FLOW

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ABSTRACT

This paper presents results of an imidazoline based inhibitor using the Electrochemical Noise (ECN) and Electrochemical Impedance Spectroscopy (EIS) techniques in a multiphase flow pipeline. ECN and EIS measurements were made simultaneously in a 101.6mm I.D., 15m long acrylic pipeline using saltwater and carbon dioxide mixtures. Full pipe flow was studied for liquid velocity of 1.25 m/s and slug flow for Froude numbers 6 and 9. Experiments were carried out at a constant pressure of 136kPa and temperature of 40°C. The ECN signals and EIS spectra of blank and inhibition tests were obtained. The ECN technique is able to monitor the inhibitor film formation continuously. The current noise fluctuation is correlated to the corrosion rate for both blank test and inhibitor test. The higher current fluctuation indicates higher corrosion rates. Different EIS spectra were obtained for blank and inhibitor studies. The simple charge transfer process was seen to occur for blank tests while charge transfer and diffusion processes were taking place under inhibitor effects.

Keywords: Electrochemical Noise (ECN), Electrochemical impedance spectroscopy (EIS), corrosion inhibitor, multiphase flow

INTRODUCTION

The corrosion inhibitor is the main tool used for preventing internal corrosion in carbon steel pipelines, which are used to transport multiphase mixtures from oil production. The successful selection of corrosion inhibitors depends on a clear understanding of the inhibition performance of the inhibitor under multiphase flow conditions. The Electrochemical Impedance Spectroscopy (EIS) technique is seen to be a powerful method for studying the inhibition performance of inhibitor in a multiphase flow system [1]. However, the EIS is unable to monitor inhibitor film performance and corrosion process continuously. Electrochemical noise (ECN) has attracted a lot of research attention for the past twenty years. ECN is able to monitor stochastic processes that might be correlated to the overall kinetic and provide detailed information, which is not available through DC and AC methods. It is recognized that ECN provides scientific answers in corrosion research and solves practical problems in corrosion engineering [2]. The noise resistance, which is calculated by standard deviation of voltage and current noise, might correlate to the polarization resistance for some systems [3-4]. The ECN technique is able to monitor the inhibitor film formation and destruction processes [3].

The ECN is a practical technique in the continuous monitoring of corrosion processes at a fast sampling rate, which is suitable for monitoring corrosion and inhibition processes in multiphase flow systems. A multiphase flow can be classified into many different flow regimes according to the flow rate of gas and liquid for the multiphase flow system. At high production rates, the slug flow regime is prominent. The characteristics of slug flow have been discussed in a previous paper [5]. Froude number is used to describe slug flow[6]. The slug flow is known to significantly enhance internal corrosion in oil/water/gas pipelines. This is due to the high levels of shear and turbulence occurring in the mixing zone of the slug [7-9]. The high turbulence system must be monitored using a technique with a fast sampling rate, which must be at least at a frequency of the order of the perturbing effect, otherwise a significant amount of detail is missed [10]. Hence, the ECN at a higher sampling rate is very helpful for monitoring corrosion process in a turbulent multiphase flow system. The corrosion monitoring by ECN techniques under multiphase flow conditions have been studied extensively at the Corrosion Center of Ohio University. Voltage and current noise signals under full pipe flow and slug flow at different water cuts were obtained [11]. The noise fluctuation shows trends which can be correlated to the type of flow. Agreement of corrosion rates calculated by noise resistance with those obtained by Electrical Resistance (ER) technique was found [5].

This paper studies the validity of the ECN technique to monitor corrosion processes, inhibitor film formation and inhibition performance of the model inhibitor under a multiphase flow system. The EIS technique, which works as the calibration technique, was also carried out.

EXPERIMENTAL PROCEDURE

Experiments were carried out in a 101.6mm I.D., 15m long acrylic pipeline. The schematic layout of the system is shown in Figure 1(a). It is similar to the one designed by Jepson [10]. A prepared ASTM substitute saltwater is placed in the 1.4m^3 stainless steel tank A. The liquid from the tank is pumped into the 76 mm I.D. PVC pipe by a 1.5 kW centrifugal pump. The flow rate of the liquid is controlled by a bypass line B and is measured by a calibrated orifice meter D. Liquid is passed into a 76 mm I.D. PVC pipe and then forced under gate E into the 101.6 mm I.D. plexiglass pipe where it forms a fast moving liquid film. The carbon-dioxide gas is introduced into the system at port F. The gas-liquid mixture passes through the plexiglass pipeline and enters the tank where the liquid is separated using a de-entrainer plate inside the tank. Liquid is recycled and gas is vented to the atmosphere through the exhaust at the top of the tank. The carbon dioxide gas is also used to pressurize the system. The pressure inside the tank is indicated by the gauge I, installed on the top of the tank. All the measurements are taken in the test section G located 8m downstream from the gate. For slug flow, a hydraulic jump is generated and moved to the test section by controlling the gas flow at the inlet F. This is done using a needle valve in conjunction with a flow control system. The liquid inside the tank is heated by two 1.5 kW heater positioned at K. The EIS and ECN probes are inserted into the test section G shown in Figure 1(b), and are flush mounted with the pipe wall. ECN probe has three identical carbon steel C-1018 electrodes. EIS probe consists of three electrodes. The working electrode is made of C-1018 carbon steel. The counter and reference electrodes are made of stainless steel. The surface area of all electrodes for both probes is 0.785 cm^2.

Tests were performed using ASTM substitute saltwater and carbon dioxide gas. Once the deoxygenation process is completed, ECN and EIS probes, which are polished by 600-grid sandpaper and rinsed by acetone and deioned water, are installed into the test section mounted flush with the pipe wall and the corrosion rate measurements are started. For slug flow experiments, the liquid flow rate is adjusted to a value required to obtain the desired Froude number and the liquid is forced under the gate. At this point a hydraulic jump is created. The hydraulic jump is positioned stationary inside the test section by a control system on the gas line. The concentration of the inhibitor is 25 ppm. Full pipe flow was studied for liquid velocity of 1.25 m/s and slug flow for Froude numbers 6 and 9. The system temperature and pressure are maintained constant at 40 °C and 0.136 MPa for all experiments.

ECN and EIS measurements were taken for each set of conditions simultaneously. EIS measurements were carried out at open circuit potentials with amplitude of 10 mV in the frequency range about 20mHz to 5 kHz. Current noise is measured on freely coupling electrodes with zero resistance ammeter while the corrosion potential of coupled electrodes is measured with respect to the reference electrode, which has the same composition as the working electrodes. The sampling rate is 10 points/second.

There are two different experimental procedures, with or without pre-corrosion. For the experiments with pre-corrosion, EIS and ECN probes are set up into system for 2 hours to establish the baseline data, and then the inhibitor of desired concentration (e.g. 25ppm) was then injected into the pipeline. For inhibition tests without pre-corrosion, the probes were set up into the inhibitor containing system directly. ECN and EIS measurements were taken every hour during the inhibition study for both experimental procedures.

RESULTS AND DISCUSSION

Blank Tests

Figure 2 shows the typical voltage and current noise after 3.5 hours of operation for slug flow at Froude number 9. Random fluctuations around a mean value are seen in voltage and current noise response. The magnitude of voltage and current differ for different flow patterns and further studies are continuing to determine the correlation between the magnitude change of voltage and current and different corrosion process. It is well known that the fluctuation of current and voltage is correlated to the corrosion rate. In order to compare the real noise fluctuation under different flow conditions, the DC trends, which cause distortions of the noise data as shown in Figure 2, must be removed from the noise data. Moving Average Removal method (MAR)[3] was used for DC trend removal in this work. At the time t, a series of potential noise data V_t is a combination of the random noise $V_{noise}(t)$ and the DC trend component $V_{DC}(t)$, which are function of time,

$$V_t = V_{noise}(t) + V_{DC}(t) \qquad (1)$$

We assume that an average value of adjacent data points of V_t can be taken as an estimation of $V_{DC}(t)$,

$$V_{DC}(t) = \left\{ \sum_{i-k}^{i+k+1} V_i \right\} / \ (2k+2) \qquad (2)$$

k is equal to 3 in this work. The random fluctuation $V_{noise}(t)$ could be calculated as

$$V_{noise}(t) = V_t - V_{DC}(t) \quad (3)$$

The current signals can be treated by the same method.

Figure 3 show the real voltage and current fluctuations, which are extracted from the their raw data by using MAR method after 3.5 hours of exposure to different flow conditions. In Figure 3, the fluctuations of voltage for slug at Froude number 9 are larger than the others. And real voltage fluctuations of full pipe flow are smaller than slug flow at Froude number 6. The difference of current fluctuations between these three flow conditions is very clear. The current noise fluctuations for the full pipe flow condition are obviously less than those at slug flow conditions. Also the fluctuations for slug flow at Froude number 9 are greater than that for slug flow at Froude number 6. Figure 4 (a) is a Nyquist plot of EIS spectra under the same experimental condition after the probe was exposed to testing solution for 3.5 hours. The shape of Nyquist plot is one semicircle. The circuit as shown in the Figure 4 (b) can be used to fit the experimental data. The diameter of the semicircle represents charge transfer resistance. It can be seen that charge transfer resistance of the full pipe flow is larger than slug flow. And the charge transfer resistance of slug flow at Froude number 9, which represents the higher turbulence, is smaller than Froude number 6. These are caused by the fact that corrosion rate for full pipe flow is lower than slug flow and corrosion rate increases with increase of turbulence. Hence, the noise fluctuations are correlated to the corrosion rate. The more the fluctuations, the greater is the corrosion rate. The current signals are more sensitive than voltage signals to the fluid dynamics and corrosion processes.

The comparison of the noise resistance and charge transfer resistance for the blank test at different flow patterns is listed in Table 1. The results of voltage and current noise by statistic analysis are also listed in Table 1. Since the ECN probe in this work has three identical electrodes in the same test environment, the potential noise from each electrode will be same, and therefore,

$$V_{measured} = (V_1^{\,2} + V_2^{\,2})^{0.5} \quad (4)$$

Given $V_1 = V_2$

$$V = V_{measured} / \sqrt{2} \quad (5)$$

For the potential data after the treatment of MAR in this work

$$\delta V = \delta V_{noise} / \sqrt{2} \quad (6)$$

$$R_n = \delta V / \delta I \quad (7)$$

Where, V_1 and V_2 are the noise signals from the coupled electrodes and reference, respectively. R_n is noise resistance. δV and δI are standard deviation of potential and current noise. In this work, δV and δI are standard deviation of real potential and current noise, which are treated by the MAR method.

The standard deviations of voltage and current for full pipe flow are smaller than slug flows. The standard deviation of voltage and current noise increases with Froude number. The noise resistance for blank test under full pipe flow shows almost the same value as R_t, which is obtained by EIS technique. For slug flow, the trend of noise resistance seems to be the same as charge transfer resistance by EIS.

However the values are different. This could result from the fact that the noise resistance has agreement with resistance obtained by EIS under uniform corrosion condition. It is well known that uniform corrosion occurs under full pipe flow whilst localized corrosion exists under slug flow.

Inhibition Tests

Figure 5 is the typical voltage and current noise signals of C-1018 metal exposed to a 25 ppm inhibitor-containing solution under slug flow at Froude number 9. Compared to Figure 2, which has the same y-axis scale, it is seen that the noise fluctuations for both voltage and current are decreased under the inhibitor effects. The plots in Figure 6 show the comparison of real voltage and current noise for slug flow at Froude number 9 between the blank test and inhibitor test at 25 ppm of the model inhibitor. The voltage fluctuation for inhibitor tests does not show much difference from blank test. The corresponding current noise signals under inhibition effects show smaller fluctuations, which can be confirmed by the standard deviation values of voltage and current shown in Table 1.

In Figure 7 the comparison of real noise for different flow patterns after 3.5 hours exposure time without pre-corrosion experimental procedure is shown. Again, at the same concentration of inhibitor, the noise fluctuation of voltage and current is higher with the higher degree of turbulence. Full pipe flow has the lowest noise fluctuation. Figure 8 is the test results using EIS technique under the same experimental conditions. The shapes of Nyquist plot for all the cases include one semicircle and diffusion tail at low frequency area, which can be simulated using circuit nested in Figure 8(b). Nyquist plot shows that slug flow at Froude number 9 has the lowest charge transfer resistance. The results for full pipe flow and slug flow at Froude number 6 have very similar results. This could result from the fact that slug flow at the higher Froude number (such as Froude number 9) has higher turbulence and the bubbles impact on the pipe wall. The inhibition performance of corrosion inhibitor is degraded and corrosion rate is increased in the turbulent flow condition. The resistance calculated by ECN and EIS and noise fluctuation are listed in Table 1. The table shows that the standard deviations of voltage and current are much higher than full pipe flow and slug flow at Froude number 6. No agreement is found between noise resistance and charge transfer resistance.

Film Formation

Figure 9 shows the electrochemical noise signals during 1800 seconds after addition of the model inhibitor. After 2 hour of pre-corrosion procedure, 25ppm inhibitor was injected into the pipeline system. The injection point is shown in Figure 9. After addition of the inhibitor the potential decreases with time increasing until the value is close to 0mV and then increases. The corresponding current noise decreases with exposure increasing time. For the same experimental set, the comparison of noise response for blank test and inhibition tests at different exposure times shows that the voltage magnitude becomes more positive and current value decreases with increasing time, as shown in Figure 10.

Figure 11 is the voltage noise fluctuation of blank test for 2 hours and inhibition test for 3.5 hours. The noise fluctuations for both voltage and current exposed to the inhibitor containing solution show smaller fluctuation than the blank test. The current signal is much clearer. The same results are found in the Rotating Cylinder Electrode system by other researchers[3]. The relative results are listed in Table 2. As shown in Table 2, the standard deviation values for both voltage and current decreases after addition of inhibitor and decreases with exposure time. No agreement between noise resistance and charge transfer resistance has been found under inhibitor effects in the multiphase flow conditions.

CONCLUSIONS

ECN and EIS were both used to monitor the corrosion processes with/without the model inhibitor effects under a multiphase flow system. Real voltage and current signals were obtained by the Moving Average Removal method to remove the DC treads. The ECN is able to track corrosion and inhibition processes under different flow conditions. The real fluctuations show distinct differences between full pipe flow and slug flow, which might be correlated to the corrosion rate. The higher noise fluctuation indicates higher corrosion rates. The ECN technique is able to monitor the inhibitor film formation continuously. Different circuit models were used to fit the EIS data with/without inhibitor effects. The simple charge transfer process was seen to occur for blank tests while charge transfer and diffusion processes were taking place under inhibitor effects. In multiphase flow system, the agreement between electrochemical noise resistance (R_n) and charge transfer resistance (R_t), which is obtained by EIS technique, was not seen.

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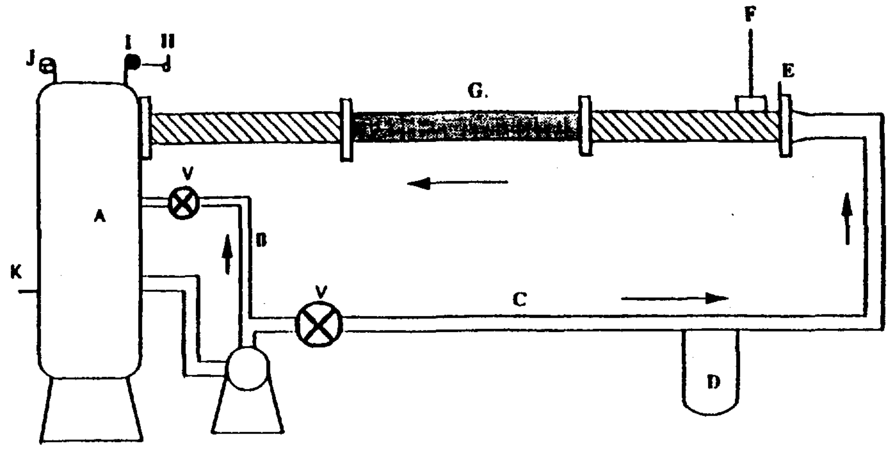
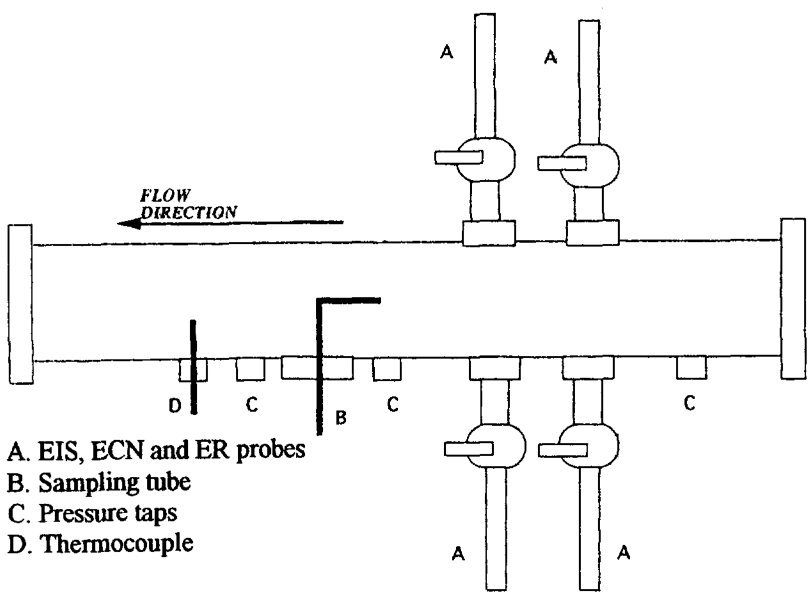


A. Liquid tank
B. Liquid recycle
C. Liquid feed
D. Orifice plate with pressure pipe
E. Flow height control gate
F. Carbon dioxide feed line
G. Test section
H. Gas outlet with filters
I. Pressure gauge with back pressure control
K. Heater
V. Flow control valve

FIGURE 1a – Experimental pipeline system



A. EIS, ECN and ER probes
B. Sampling tube
C. Pressure taps
D. Thermocouple

FIGURE 1b – Test section

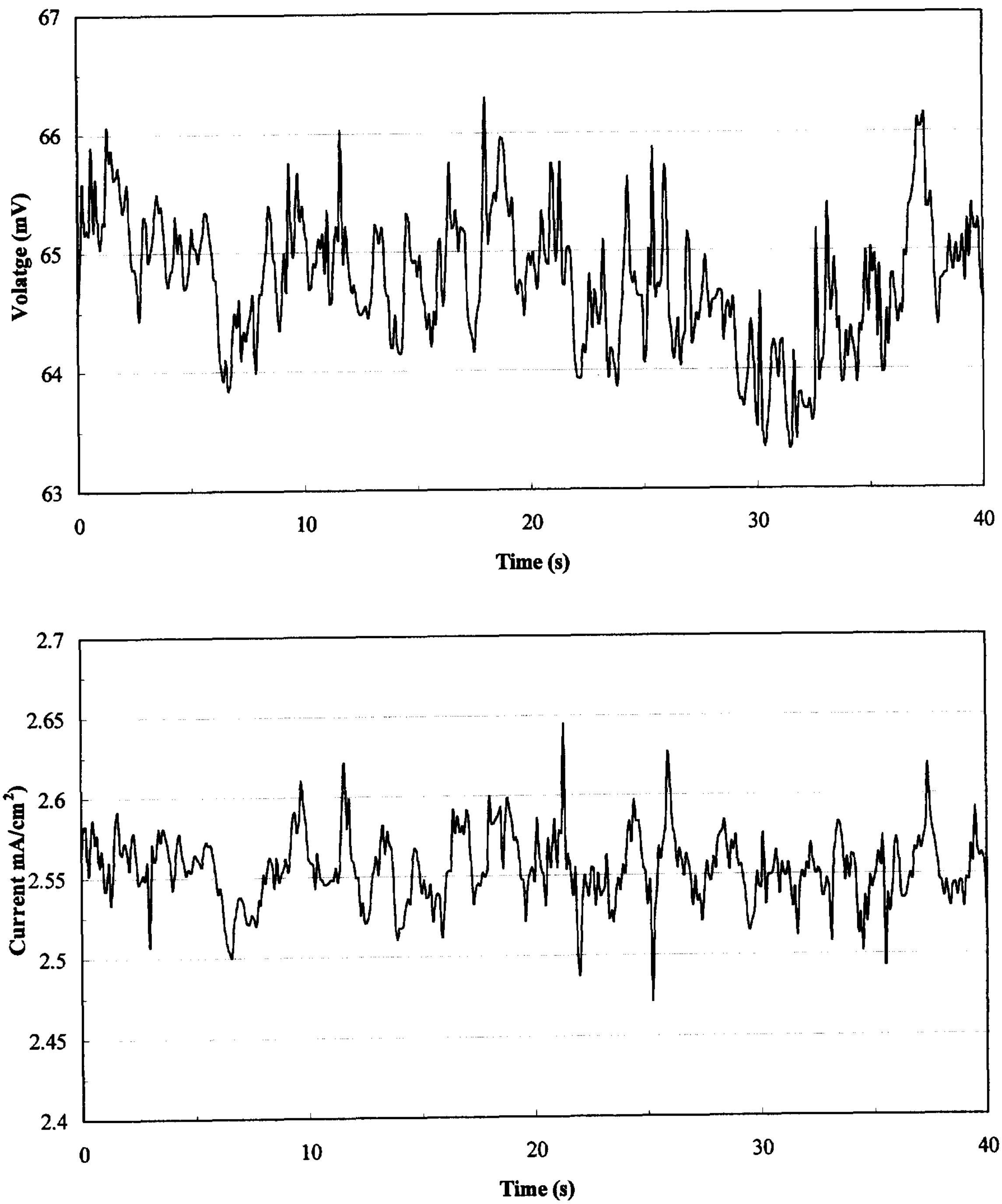


FIGURE 2 – Voltage and current noise response for blank test under slug flow at Froude number 9

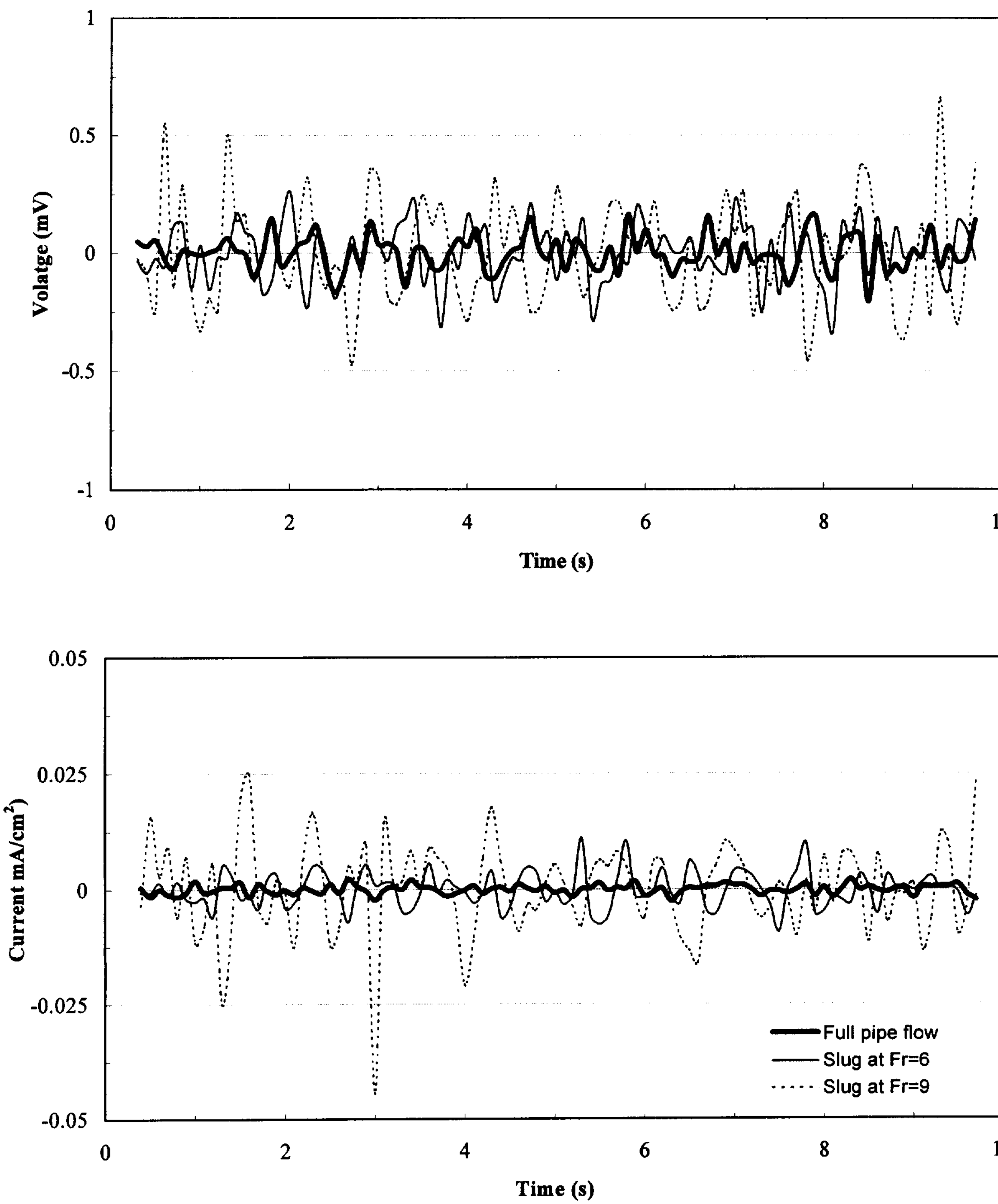


FIGURE 3 – Comparison of noise fluctuations for blank tests under different flow patterns

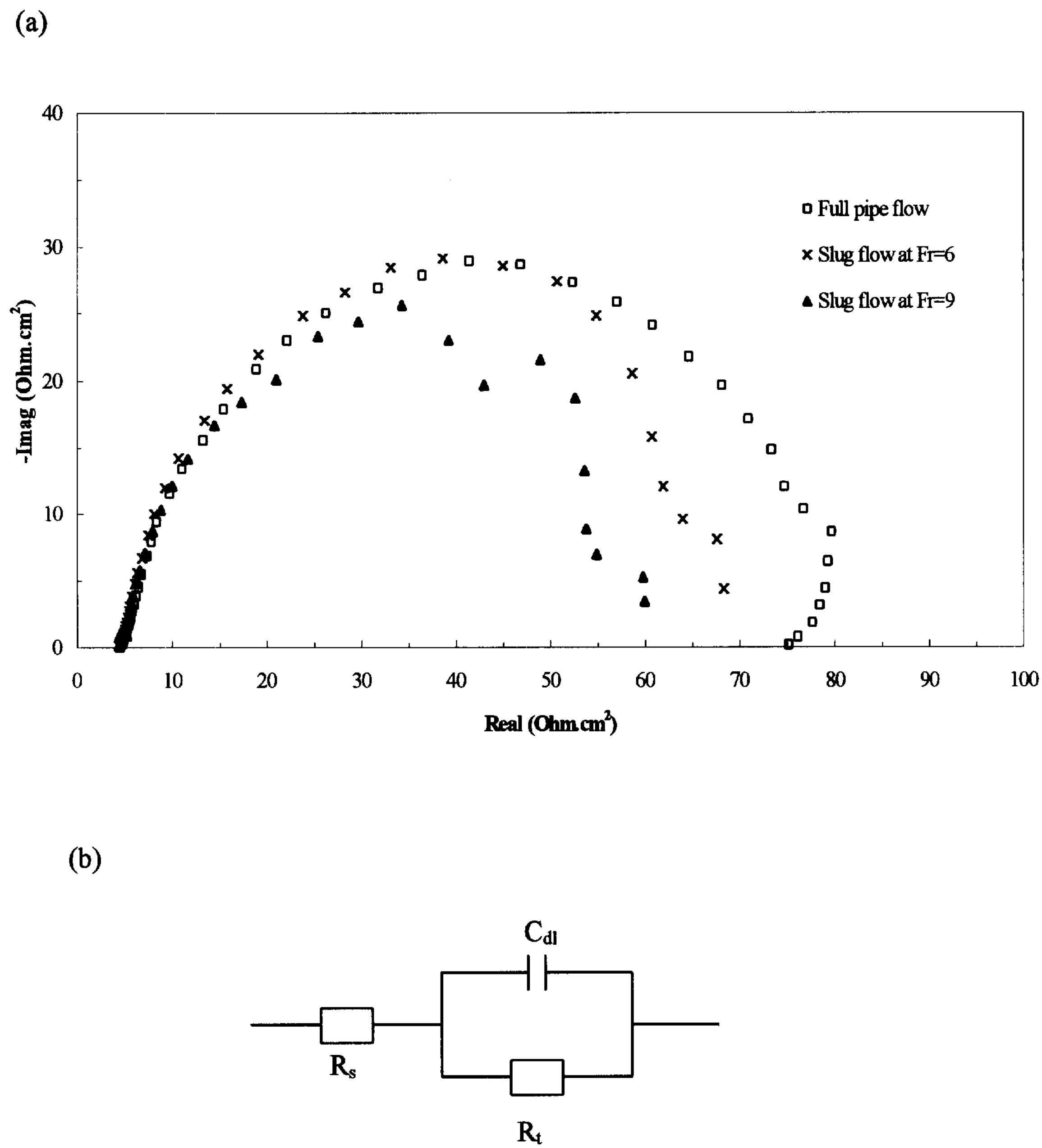


FIGURE 4 – EIS results for blank tests under different flow patterns
(a) Nyquist plots of EIS spectra (b) Circuit model for fitting EIS data

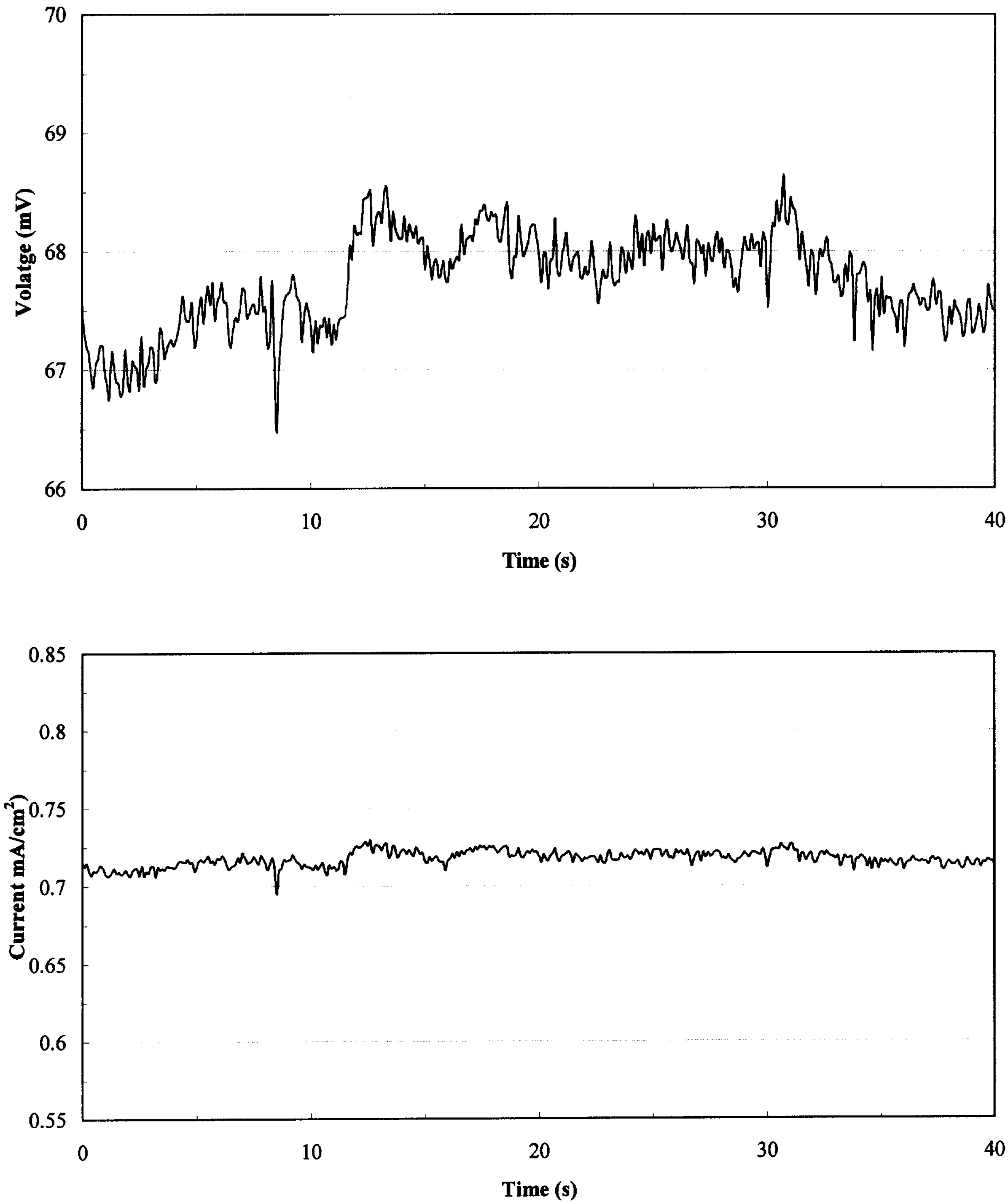
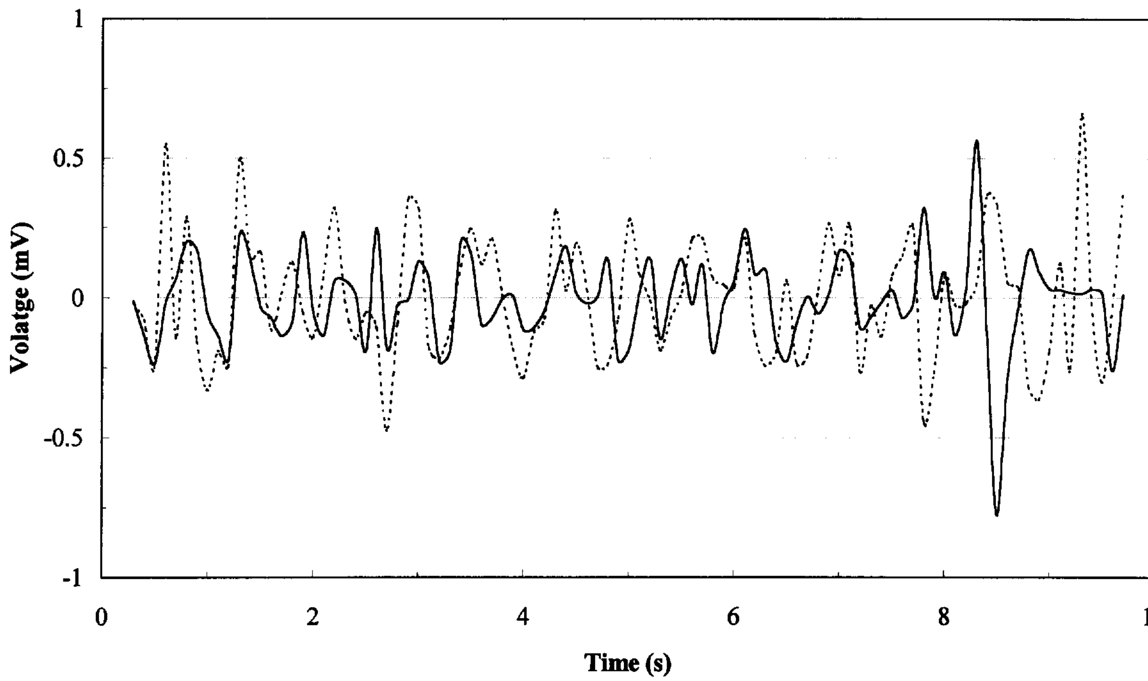


FIGURE 5 – Voltage and current noise response for 25ppm inhibitor test under slug flow at Froude number 9.



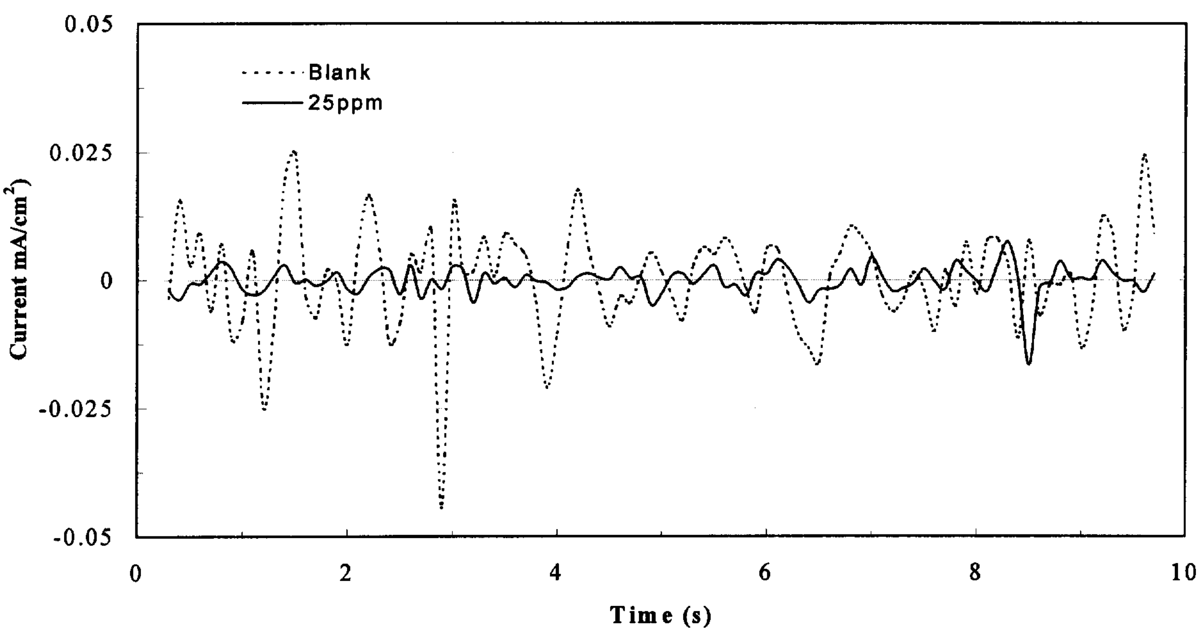


FIGURE 6 – Comparison of noise fluctuation for blank test and 25ppm inhibitor test under slug flow at Froude number 9.

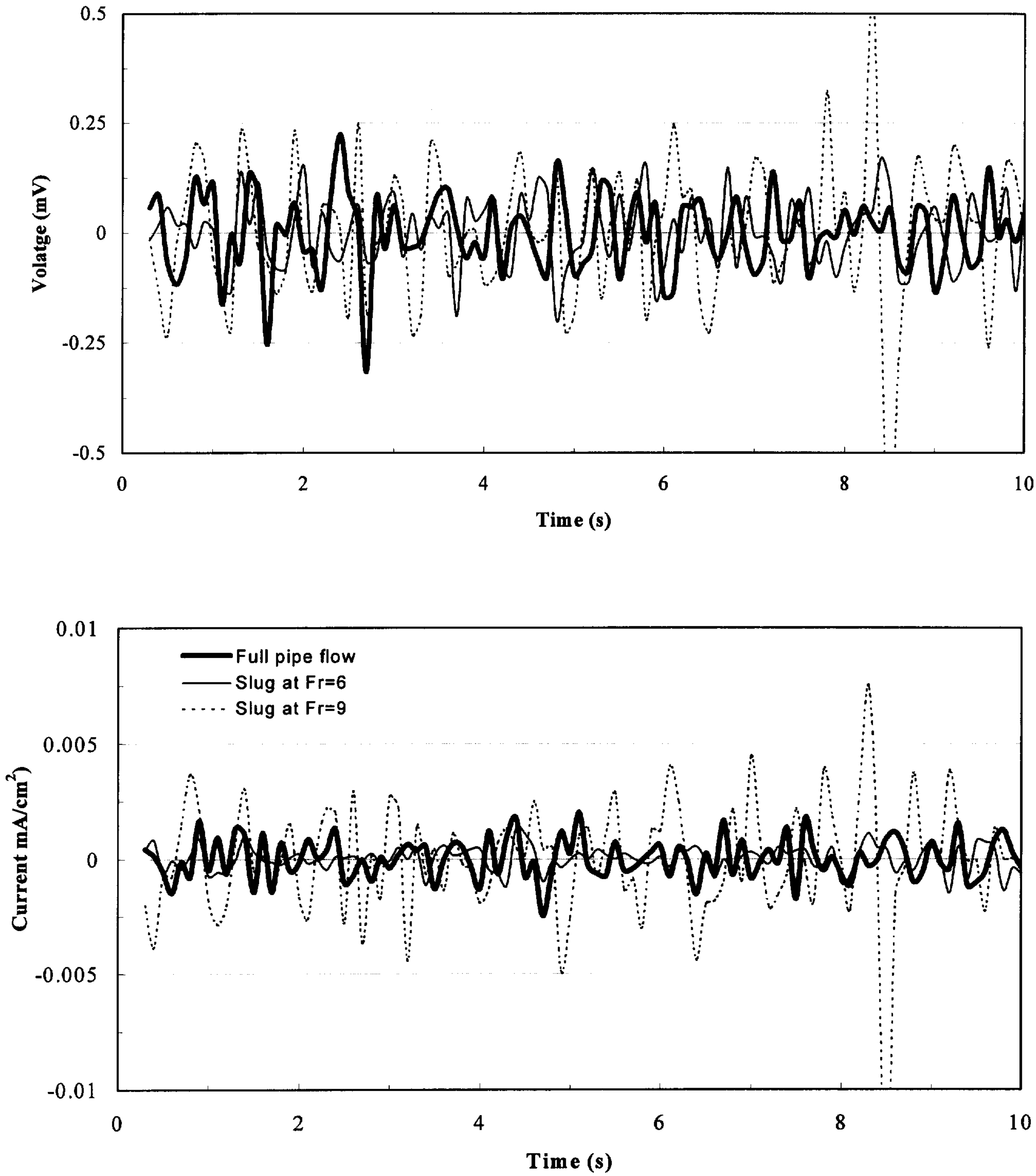
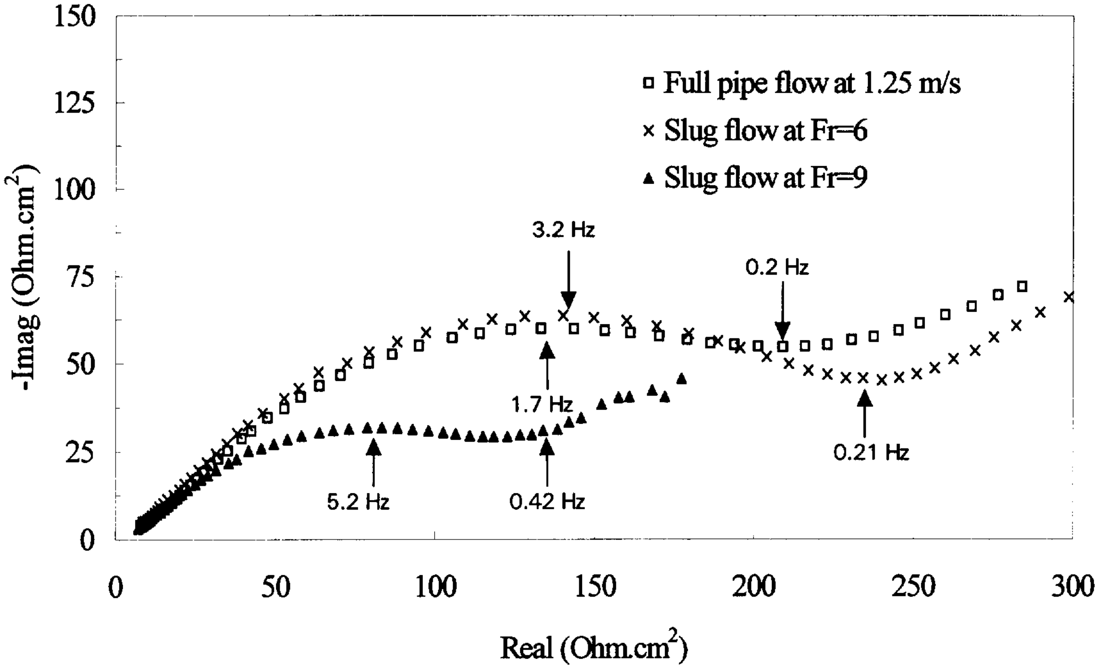


FIGURE 7 – Comparison of noise fluctuation for 25ppm inhibitor tests under different flow conditions

(a)



(b)

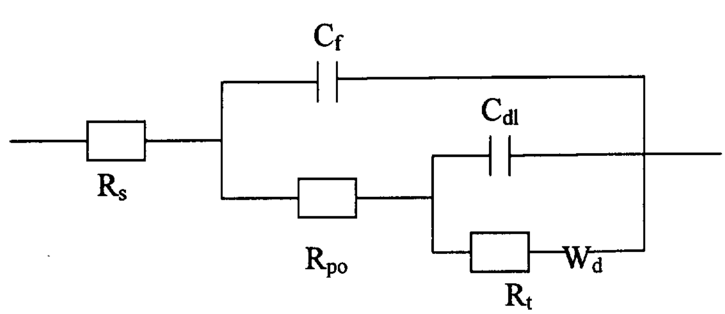


FIGURE 8 – EIS results for 25ppm inhibitor test under different flow pattern (a) Nyquist plot (b) circuit model for fitting EIS data

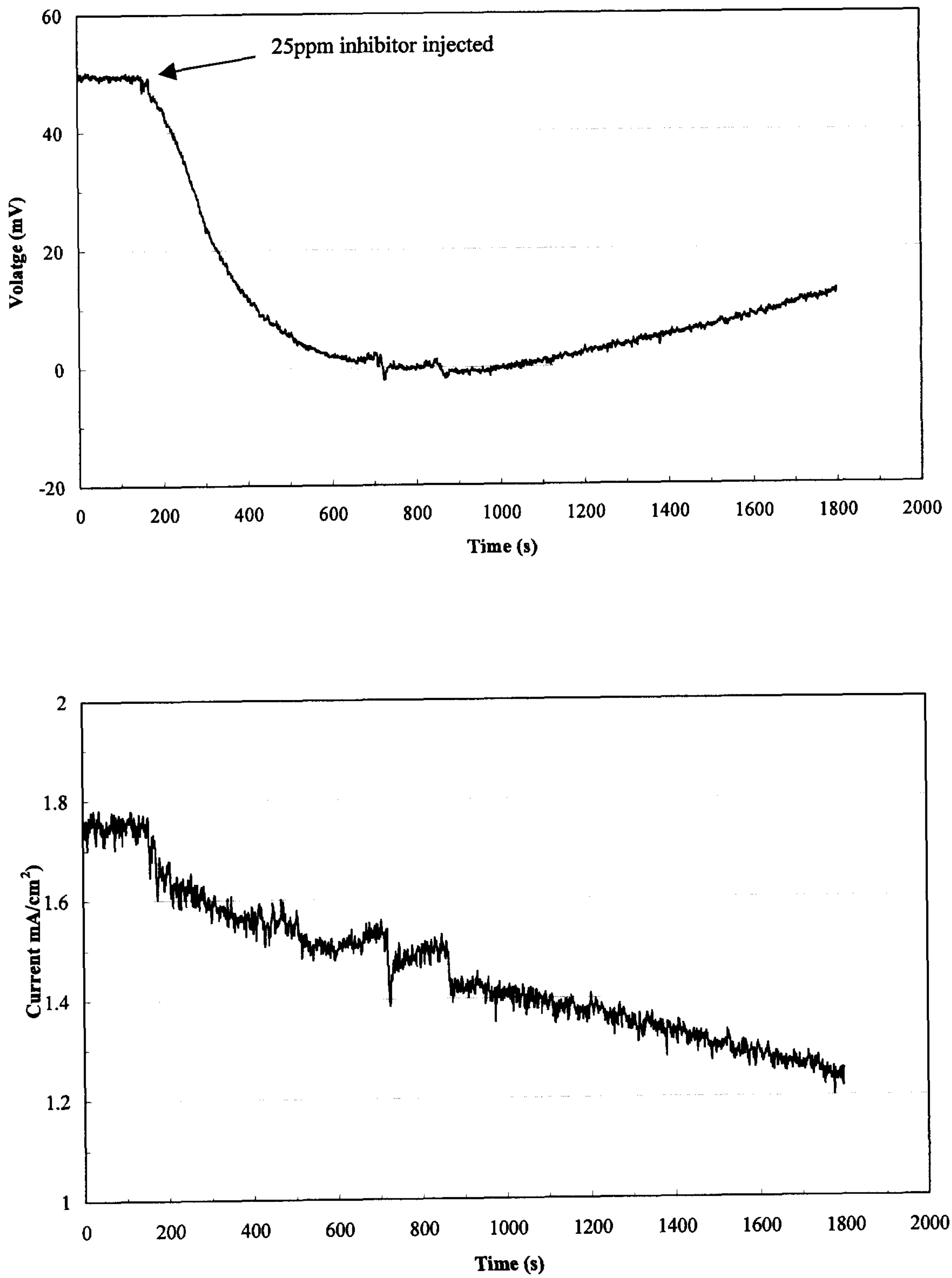


FIGURE 9 – Voltage and current response during addition of 25ppm inhibitor under slug flow at Froude number 9

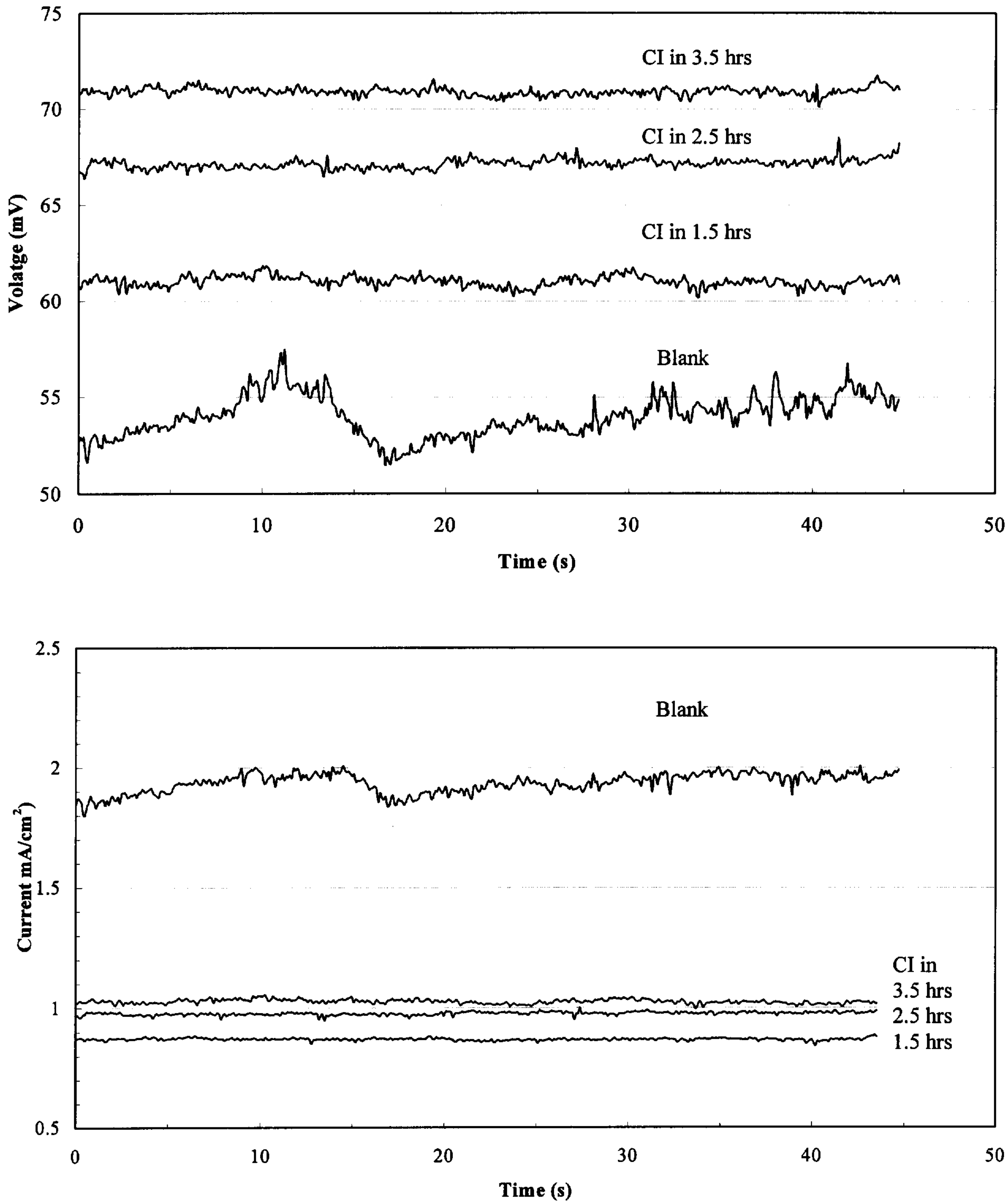


FIGURE 10 – Voltage and current response for blank test and 25ppm inhibitor test with pre-corrosion at different exposure time under slug flow at Froude number 9

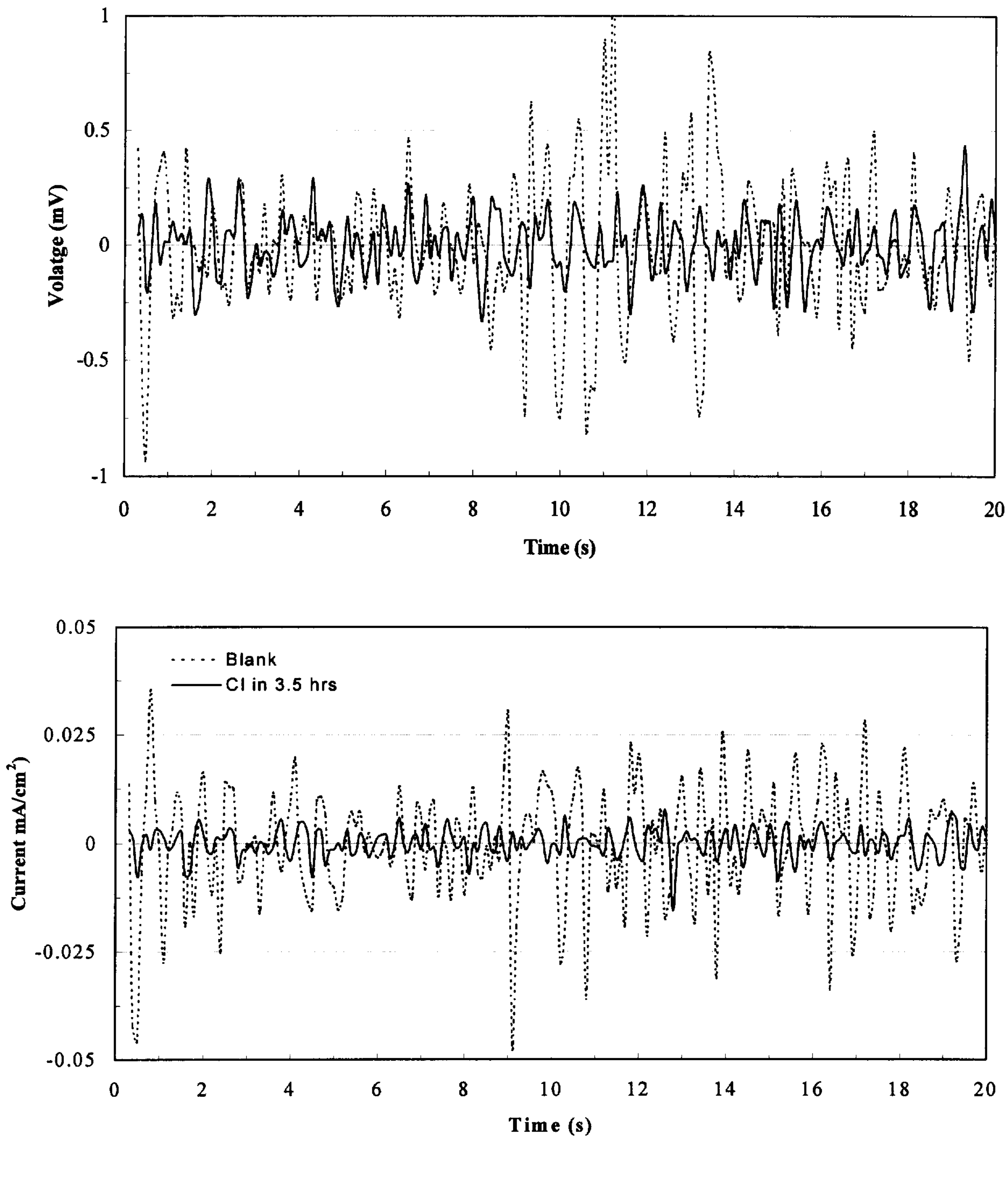


FIGURE 11 – Comparison of noise fluctuation for blank test and 25 ppm inhibitor test at 3.5 hrs with pre-corrosion under slug flow at Froude number 9