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COMPARISON OF ECN AND EIS MEASUREMENT FOR CORROSION MONITORING UNDER MULTIPHASE FLOW CONDITIONS

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ABSTRACT

Electrochemical Noise(ECN) and Electrochemical Impedance Spectroscope (EIS) measurements were made simultaneously in a 75 mm I.D., 10 m long acrylic pipeline using salt-water/carbon dioxide mixtures. Full pipe flow was studied for liquid velocities of 0.5, 0.75, 1.1, 1.5 m/s and slug flow for Froude numbers 4, 6 and 9. Experiments were carried out at a constant pressure of 136 kPa and temperature of 40°C. ECN data were measured with a fast auto zero resistance ammeter. The ECN technique is able to detect changes in flow regime, showing distinct differences between full pipe flow and slug flow. The choice of sampling rate when using ECN is very important. For slug flows, sampling rates as high as 100 Hz are necessary to include most of the transients in the flow. Distinct differences can be seen in the Fast Fourier Transforms where dominant frequencies exist which correspond to possible bubble action in the slug body. EIS can be used to measure corrosion rate in multiphase flows. It does show an increase in the corrosion rate with liquid flow rates for full pipe flow and Froude numbers for stationary slug flow. A simple statistical analysis of ECN response gives a correlation with corrosion rate. These show ECN could be a very powerful tool for determining corrosion rate and corrosion mechanism in multiphase flow.

KEYWORDS

Electrochemical Noise, Electrochemical Impedance Spectroscope, Corrosion, Multiphase Slug Flow, Bubble Impact

INTRODUCTION

In remote areas, the production from the wells is required to be transported as a multiphase mixture of oil, sea-water, carbon dioxide and nature gas. This results in the formation of a weak corrosion carbonic acid often causing severe corrosion in carbon steel pipelines. It is important that proper design and operation conditions be maintained to minimize corrosion and it is imperative to monitor corrosion carefully.

There are many different flow regions (Lee and Jepson,1993)[1]. At high production rates, the slug flow regime is prominent. Here, highly aerated bodies of liquid called slugs propagate intermittently along the pipe. Slug flow is known to significantly enhance internal corrosion in oil-gas pipelines. This is due to the high levels of shear and turbulence occurring at the slug front. Green et al. (1989)[2] investigated the effects of different flow regime on corrosion rate in field studies. They showed that instantaneous corrosion values for slug flow are at least two orders of magnitude higher than those existing under stratified flow.

Corrosion processes have been studied by various researchers. Many carried out their studies in single phase systems in autoclaves using RCE, using brine saturated with carbon dioxide. Corrosion in Multiphase flow has been studied extensively at the NSF I/UCRC Corrosion Center. Zhou and Jepson (1993)[3] studied flow and corrosion at slug flow condition in the large diameter pipeline. They used Linear Polarization Resistance (LPR) and Electrical Resistance (ER) techniques, and weight loss measurements to quantify overall corrosion rates for full pipe flow and slug flow. Vuppu and Jepson (1994)[4], studied corrosion products on carbon steel coupons at various temperatures and at different flow conditions. They observed uniform corrosion for full pipe flow and pitting type corrosion under slug flow. The measurements were made over long periods of time and instantaneous effects could not be isolated. Slug flow has been characterized by the Froude number, Fr , which is defined as (Jepson, 1987)[16]:

$$Fr = (V_t - V_f) / (g \cdot h_{eff})^{0.5}$$

where: V_t and V_f are the translational velocities of the slug and film velocities, respectively;
g is the acceleration due to gravity ;
h_{eff} is the effective height of the liquid film .

Electrochemical noise (ECN) is defined as the spontaneous fluctuations observed in potential and current at the free corrosion potential. Evaluation of this ECN as a tool of measuring corrosion has increased steadily since 1968 by Iverson[5]. The ability to isolate dynamic events and study them both in the time and frequency domains make ECN a powerful tool for gaining mechanistic information on corrosion in multiphase pipelines. Extensive research has been conducted to develop the ECN technique as an effective analysis tool for corrosion studies. Hladky and Dawson (1981)[6] studied the voltage noise output under uniform or general corroding conditions. They found that pit initiation occurs when the environmental conditions became aggressive. Eden and Rothwell (1992)[7] have shown that during pitting corrosion, the current transient are normally bi-directional with positive and negative excursions. The duration of the transient identifies whether the specimen is undergoing pit propagation or pit initiation. Webster et al. (1994)[8] applied the ECN techniques to monitor corrosion in multiphase flows. They found that the technique can detect change in flow regime and discriminate the performance of inhibitors on a qualitative basis. Deva and Jepson (1995)[9] used ECN to study corrosion mechanism for full pipe flow and slug flow at different water cuts. They demonstrated that electrochemical noise technique is useful for measuring the corrosion mechanisms in slug flow. Sampling rates up to only 20 Hz were available at that time.

The Electrochemical Impedance Spectroscope (EIS) has been successfully applied to the study of corrosion systems for over twenty years because this method yields information about the type of corrosion, the kinetics of the corrosion reaction and also the corrosion rate (Tait) [10]. An important advantage of EIS over other laboratory techniques is the possibility of using very small amplitude signals without disturbing the property being measured. EIS has thus been successful in studying the corrosion of carbon steel in low conductivity media (Chechirlian, et al., 1993) [11]. Both signal magnitude and phase shift are used to characterize the interface impedance. Equivalent electrical circuits can be developed from this and used to provide information regarding the corrosion mechanism. Many workers have tried to use EIS to study the corrosion mechanism and analyze the EIS data for common corrosion processes (Mansfeld, et al.,1993)[12]. The most successful application of EIS is in the coating area and for evaluating corrosion inhibitors (Chen 1994)[13-14].

This paper compares the ECN and the EIS techniques and examines the effect of multiphase flow on corrosion in horizontal pipes.

EXPERIMENTAL PROCEDURE

The flow loop schematic is shown in Figure 1. Liquid is pumped by a 2.3 kW stainless steel centrifugal pump from a 0.6 m^3 stainless steel storage tank through a 50 mm I.D. PVC pipe into a 0.03 m^3 stainless steel mixing tank. The liquid flow rate is controlled by valves and a by-pass line and is monitored by means of an orifice plate.

Carbon dioxide gas, from a pressurized 1.67 m^3 tank, is introduced into the system at an inlet pressure of 900 kpa (100psi). The gas flow rate is controlled by a gate valve and is monitored by means of variable area gas flow meter.

The multiphase mixture flows through a 75 mm I.D., 10 m long acrylic pipeline. The mixture is discharged into the liquid storage tank where it is separated by means of a perforated separation plate. The gas is exhausted to the atmosphere. The system is equipped with a back pressure regulator to maintain a constant system pressure. Slugs are generated in the test section following the same procedure as Zhou and Jepson (1994)[3]. The data in this study was generated using a stationary slug over the probes. This is equivalent to as moving slug flow more than 40 /min frequency.

Measurements are taken in the test section as shown in the Figure 2. At position A, the ECN probe is inserted. At position B and C, flush mounted EIS/LPR and ER probes respectively, can be inserted to measure the corrosion rate at the bottom of the pipe. For all experiments, the iron and oxygen levels are maintained below 10 ppm and 10 ppb, respectively. The levels are monitored with the appropriate test kits from CHEMets.

The ECN probe is shown in Figure 3. It is a three identical carbon steel electrode probe and is inserted through a 3.18 cm inlet. The three electrodes are set in an 3.18 cm O.D. tube. The exposed surface of the electrode is flush mounted on the pipe wall. The working electrode area exposed is 0.7854 cm^2. Current and voltage measurement across the probe are measured with zero resistance ammeter (ZRA) that can sample at rates up to 1000 Hz. The ZRA is connected to a microcomputer. The data is logged and analyzed using software provided with the ZRA.

The design and set-up of EIS/LPR probe are same as that of ECN probe except the material of one electrode is carbon steel as working electrode and other two are stainless steel as counter electrode and reference electrode respectively. The potential and impedance are measured and the data is logged and analyzed using the same microcomputer.

The system temperature and pressure are maintained constant at 40°C and 136 kPa for all experiments. The test are performed using 3% ASTM standard salt-water. The experiment are conducted for full pipe liquid flow and slug flow. Liquid velocities of 0.5, 0.75, 1.1, and 1.5 m/sec are used for full pipe flow whilst slug flow experiments are conducted at Froude numbers of 4, 6 and 9. These correspond to slug velocities of 2, 3 and 4.5 m/s respectively. The gas used is carbon dioxide. ECN and EIS/LPR measurements are taken at each set of conditions.

RESULTS AND DISCUSSION

ECN

Full pipe flow

Figure 4 shows voltage and current fluctuations obtained from the ECN for a liquid velocity of 1.1 m/sec in full pipe flow after 4 hours of operation at a sampling rate of 20 Hz. Random fluctuations around a mean are seen in the voltage and current response and the response is similar to that obtained by Hladky and Dawson(1986)[6] and Deva (1995)[9]. They interpreted the fluctuation around a mean as uniform corrosion.

Slug Flow

To understand the corrosion mechanism and the effect of bubbles within slugs that impact on the pipe wall, noise data is recorded by keeping slugs stationary. Here the intermittent pulses of bubbles within the slug impact on the electrode surface.

Typical ECN response to slug flow is shown in Figure 5 This is for slugs with a Froude number 6 which corresponds to a slug velocity of approximately 3 m/s. Here data is recorded at a rate of 50 Hz. The response is different to that observed in full pipe flow. Characteristic transients are observed in the current fluctuations, but not seen in the voltage fluctuations. These transients represent impacting pulses of bubbles at the front of slug, as shown by Gopal et al . (1995)[15].

The sampling rate for ECN is very important when studying slug flow. Usual instruments can only sample up to a few Hz and much of the transient characteristics of the flow are omitted. This study, which has examined the flow at different sampling rates, shows that the sampling rate should be between 100 and 500 Hz depending on the Froude number (or velocity) of the slugs. This is described in detail later.

Frequency Response

Parameters typically studied in the potential spectrum are the low-frequency cut-off, roll-off slopes and peaks in the potential noise spectrum. There are relations between these parameters and the corrosion type and mechanism. The amplitude is calculated by a Fast Fourier Transform algorithm in $mV/Hz^{1/2}$ or in $dB/Hz^{1/2}$. The reference voltage has been taken as 1V. The slope is calculated in mV/decade or in dB/decade by taking the drop in this amplitude over a decade of frequency.

Figure 6 describes the potential noise spectra of for liquid velocity of a 1.1 m/sec full pipe flow at sampling rate of 20 Hz. The figure shows roll-off values of -31 dB/decade. These correspond to uniform corrosion as shown by Searson and Dawson (1988)[6] and Deva (1995)[9].

Figure 7 shows the potential noise spectra for slug flow Froude number 6 at a sampling rate of 50 Hz. This figure shows roll-off slope of -14.8 dB/decade. Searson and Dawson (1988)[6] and Deva (1995)[9] have shown that shallow slopes less than -20 dB/decade are characteristic of pitting corrosion.

The peaks in the spectrum correspond to characteristic fluctuations in the flow. The peaks between 0.1 Hz to 1 Hz, which are found both in Figure 6 and Figure 7, are interpreted as the characteristic of Fast Fourier Transforms by Deva (1995)[17]. Figure 8 shows that the potential spectra for slug flow at a sampling rate 100Hz. Compared to Figure 7, which is obtained at the completely same experimental condition, a significant number of peaks between 1 to 10 Hz are now observed at the higher sampling rate. Analysis of simultaneous video recordings of flow in the test section has shown that pulses of bubbles impact the electrode every 3-4 per second for Froude number 6 in slug flow. These peaks are probably related to the presence and behavior of the pulses of bubbles and their interaction with the electrode surface. More experiments are being carried out by the authors.

EIS

Figure 9 is the impedance spectrum results from EIS for a liquid velocity of 0.75 m/sec after 4 hours operation. The experimental and fitted impedance spectra are superimposed in the same figure. The spectra have been fitted to a one-time-constant model to obtain the polarization resistance, Rp, capacitance C and the parameter α, which has been used to account for the deviation from ideal capacitive behavior. One time constant impedance spectrum indicates that there was no measurable corrosion products built up on the metal surface.

The impedance spectrum results of EIS for Froude number 6 stationary slug flow after 4 hours operation is shown in Figure 10 . The fitting parameters using one-time-constant model are obtained again . A comparison between full pipe flow and slug flow for the same superficial liquid velocity shows that the Rp for slug flow (163 ohm) is lower than that for full pipe flow (244ohm).

It can be noted that EIS can be used for slug flow and does give averaged values of corrosion rate. However, it does not provide information on the transients present in the flow.

COMPARISON BETWEEN ECN AND EIS METHOD FOR CORROSION RATE

Figures 11 and 12 compare the corrosion rates calculated using EIS, LPR and electrical resistance (ER) for full pipe flow and slug flow. It can be seen that EIS, LPR and ER do follow the same trend with corrosion rate increasing with increase in liquid velocity and/or Froude number. However, the corrosion rate for LPR is not as stable as that for ER and EIS. This probably results from the limitations of this technique. It is known that linear polarization can only measure general corrosion rates but can not be used to determine the corrosion rate for localized corrosion such as pitting or crevice corrosion[10]. So at high corrosion rate, such as for Froude number 9 slug flow, the LPR result is not as stable as other techniques, due to pitting corrosion occurring in this case.

The corrosion rates measured by EIS were consistently approximately 0.75 - 1.0 mm/y higher than those taken from ER probes. For example, The corrosion rates for EIS increase from 1.88 to 2.13 mm/y as the liquid velocity is increased from 0.4 to 1.5 m/s. The corresponding values for LPR and ER are 1.75 to 2.45 and 0.75 to 1.25 mm/y respectively.

For slug flow, the ER corrosion rates increase from 1.2 to 2.5 mm/y as the Froude number of the slug is increased from 4 to 9. The corresponding EIS values increase from 2.25 to 3.38 mm/y respectively. The LPR results seem to present reasonable corrosion rates at low Froude numbers but give very high values at the higher Froude numbers.

Figures 13 and 14 show the comparison of the corrosion rate measured by ECN and ER for full pipe flow and slug flow respectively. The Rn for ECN impedance is defined as the ratio of the RMS of the corrosion potential fluctuation δV to the RMS of the current fluctuation δI. A very good agreement between ECN and ER has been observed. For full pipe flow, the corrosion rates from ECN are slightly larger than the ER at the higher velocities. These are still within the experimental error as shown. It is seen from Figure 14, that the corrosion rate for ER and ECN at Froude number 6 are very close at 1.45 and 1.58 mm/y respectively.

SAMPLING RATE

Figure 15 is the potential amplitude spectra for Froude number 6 stationary slug flow at 500Hz. Compared to Figure 7-8, Figure 15 shows far more detail of flow regime. The effect of data sampling rate on the ECN signal has been demonstrated by Webster and Green (1993)[8]. The data sampling rate must be at least at a frequency an order of magnitude greater than the frequency of the perturbing effect, otherwise a significant amount of details are missed. The group of peaks is found in potential noise spectrum for slug flow in the 1-10Hz frequency domain. Interpreting these peaks by high frequency ECN is the future work of the authors.

CONCLUSIONS

The ECN technique is able to detect changes in flow regime. The ECN signal showed distinct differences between full pipe flow and slug flow. The group of peaks are found in spectrum response for slug flow by high sampling rate in the 1-10Hz frequency domain. These peaks are probably related with pulse behaviors of bubbles.

The effect of data logging rate on the ECN signal has been demonstrated. The sampling frequency for ECN is very important especially for slug flow. The frequency should be between 100 and 500 Hz depending on the slug Froude number. This work used the ZRA with much higher sampling rate (up to 1000 Hz) than most available ECN instruments.

EIS can be used for examining corrosion in slug flows but it cannot provide information on the transients encountered in slug flow. Corrosion rates determined by ECN, LPR, ECN and ER exhibit the same trends and show an increase in the corrosion rate with liquid flow rate for full pipe flow and Froude number for slug flow. LPR was less stable than the others. Corrosion rate for ECN is very close to the ER values but EIS and LPR results are consistently 0.75 - mm/y greater than that of ECN or ER.

These show ECN can be a very powerful tool for corrosion rate and corrosion mechanism in multiphase flow when the proper sampling rate is selected.

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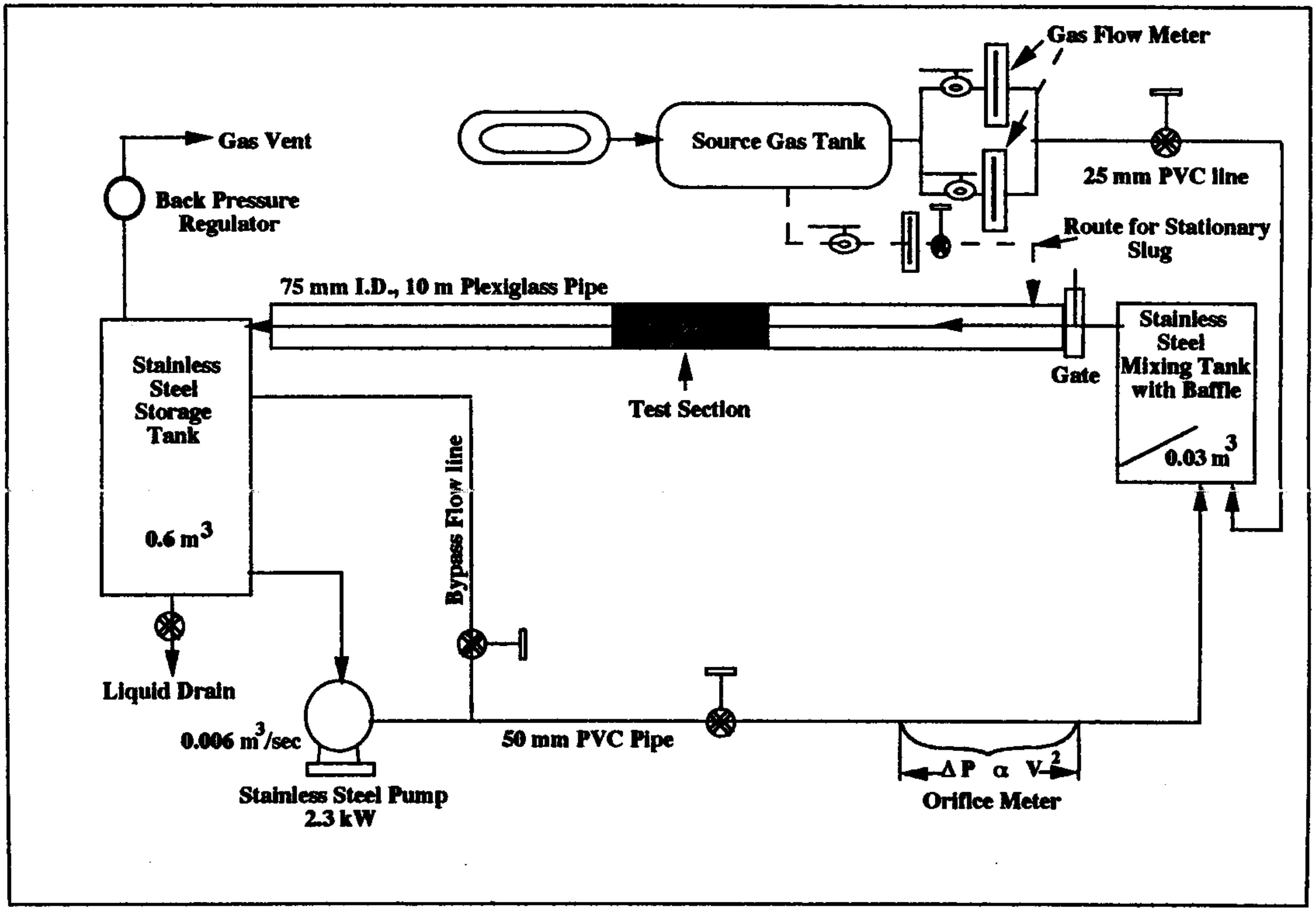
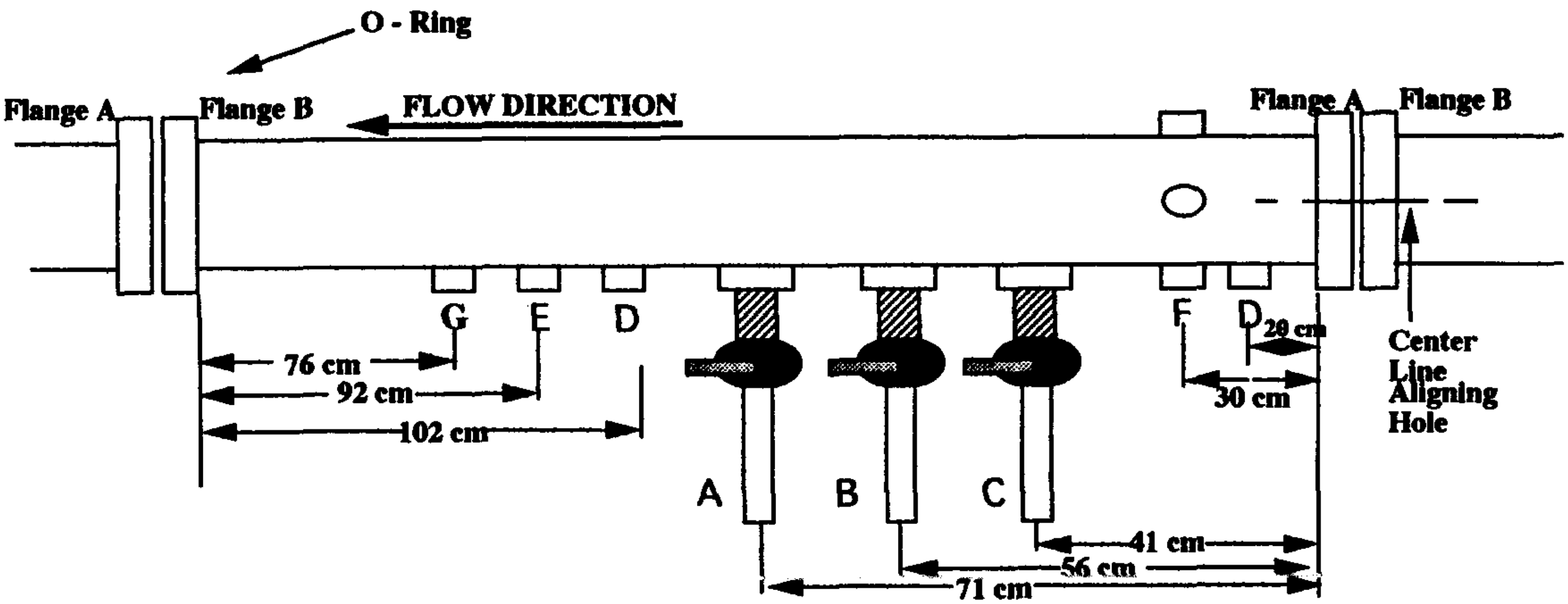
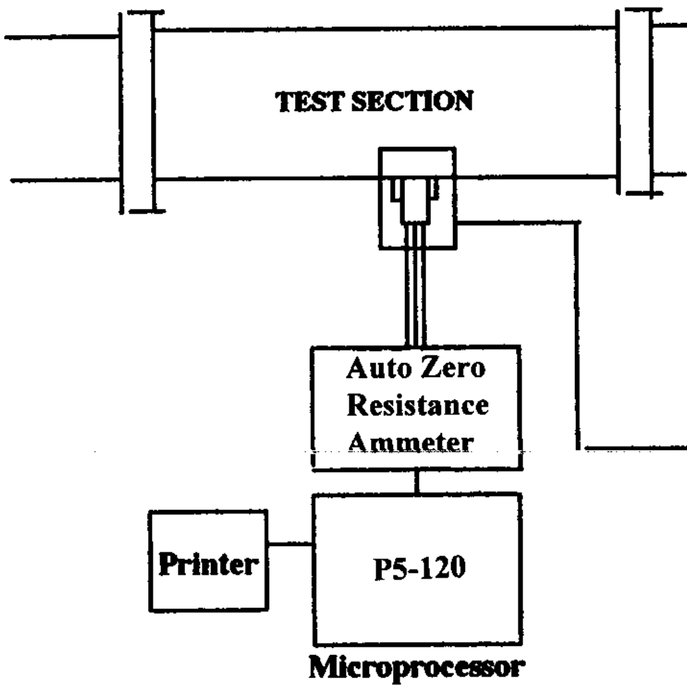


Figure 1. Schematic layout of experimental flow system



A. CORMON PROBE (3 Electrodes of 1cm diameter set into a 3.2 cm tube)
B. ER PROBES (3.2 cm diameter)
C. LPR PROBE (3.2 cm diameter)
D. PRESSURE TAPPINGS (2 cm diameter X 2 cm thickness block with 0.32 cm hole)
E. DIGITAL THERMOMETER PROBE (0.32 cm Probe diameter)
F. SHEAR STRESS PROBES (2 cm diameter X 5 cm thick block with 0.32 cm hole)
G. SAMPLING PROBE (0.8 cm diameter)

Figure 2. Test section



A. Working Electrode 1
B. Working Electrode 2
C. Reference Electrode

Figure 3.1 Data logging section

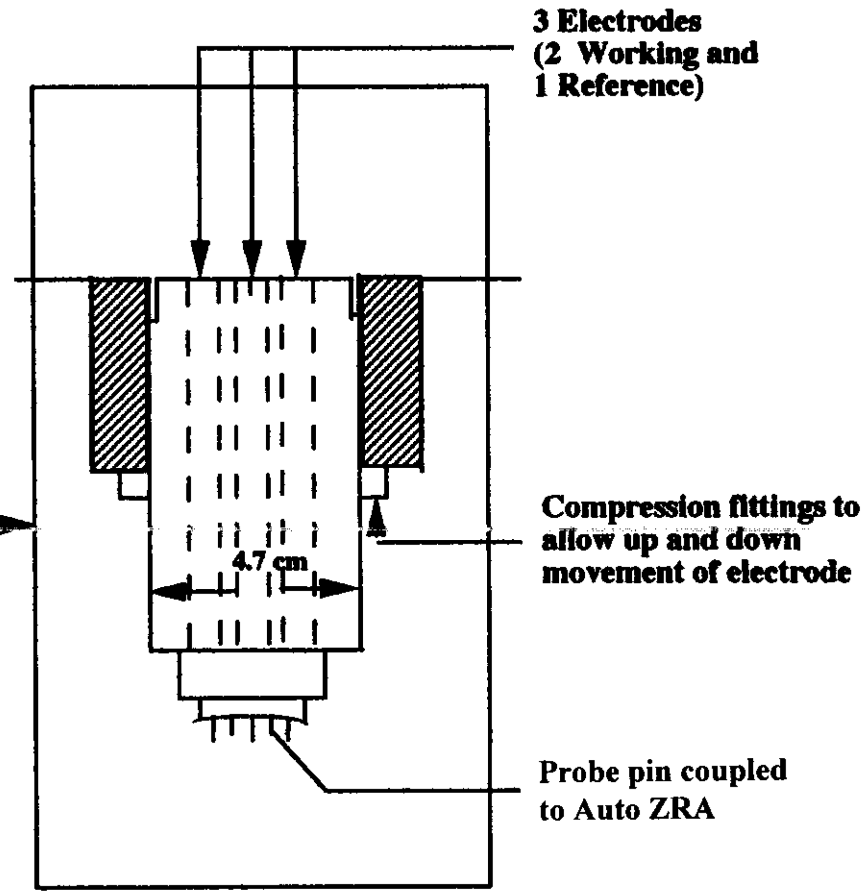
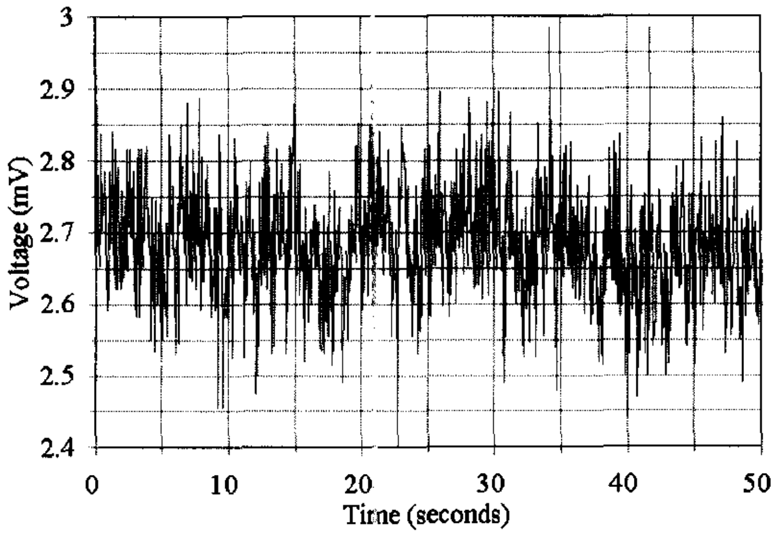


Figure 3. 2. Enlarged view of the noise probe



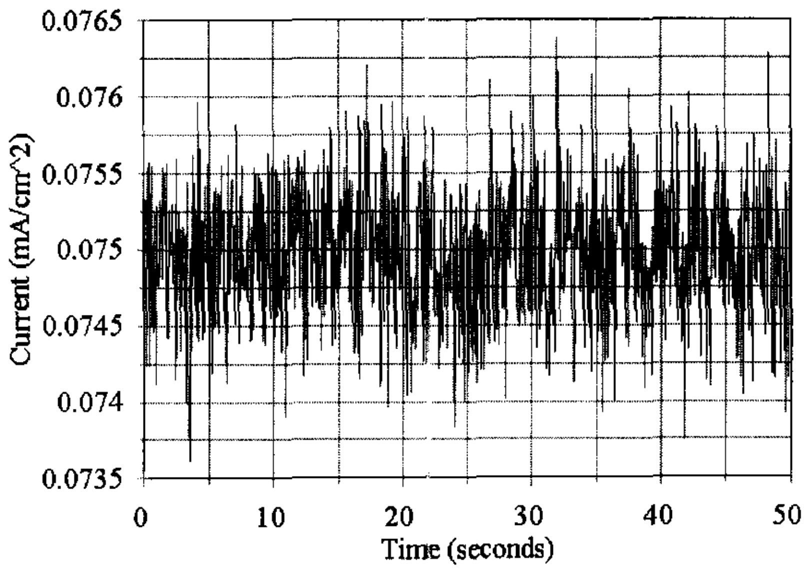


Figure 4. Voltage & current noise response for 1.1 m/s full pipe flow .
Sampling rate = 20 Hz.

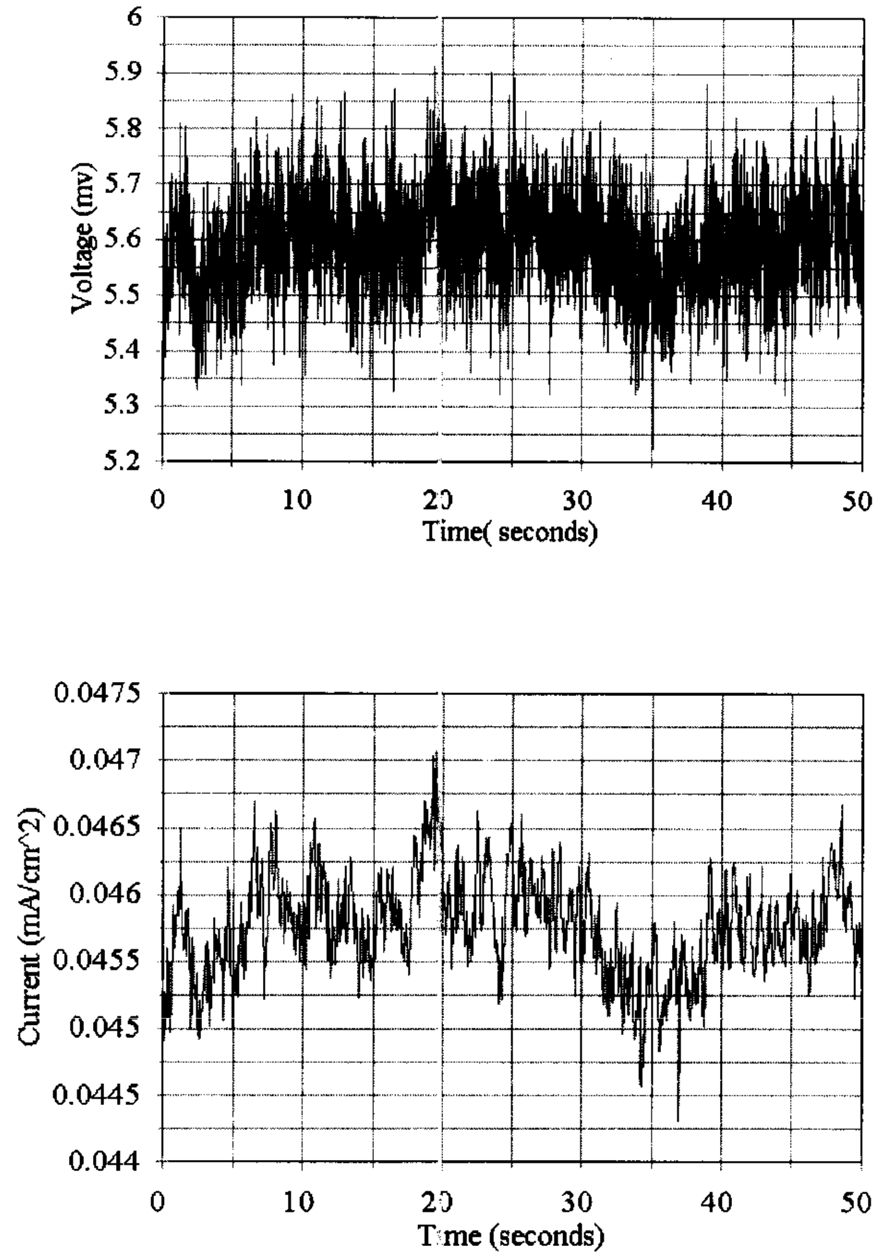


Figure 5. Voltage & current noise response for Froude No. 6 slug flow.
Sampling rate =50 Hz.

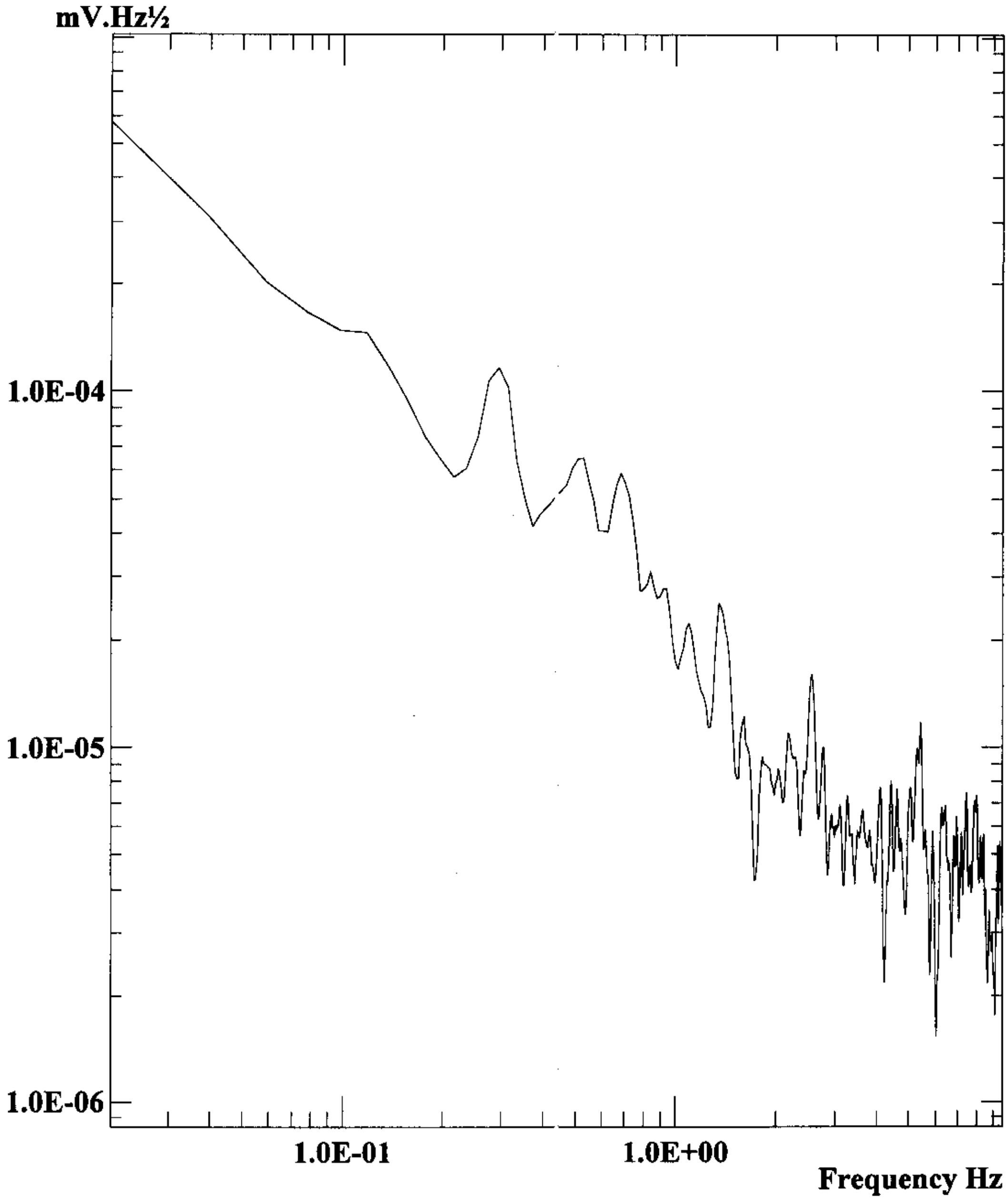


**Figure 6. Potential amplitude spectrum for 1.1 m/s full pipe flow.
Sampling rate =20 Hz.**

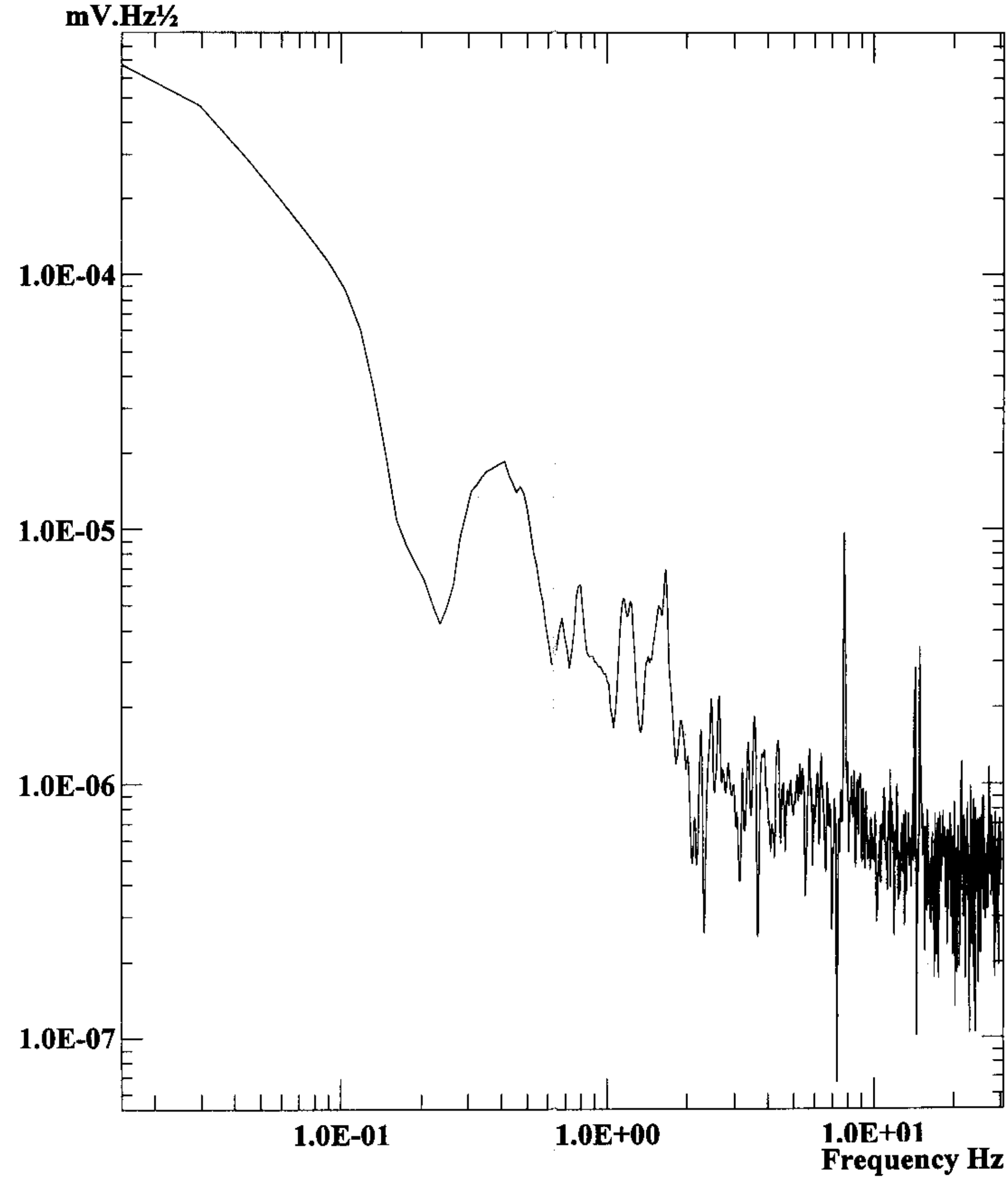


Figure 7. Potential amplitude spectrum for Froude No. 6 stationary slug flow Sampling rate=50Hz.

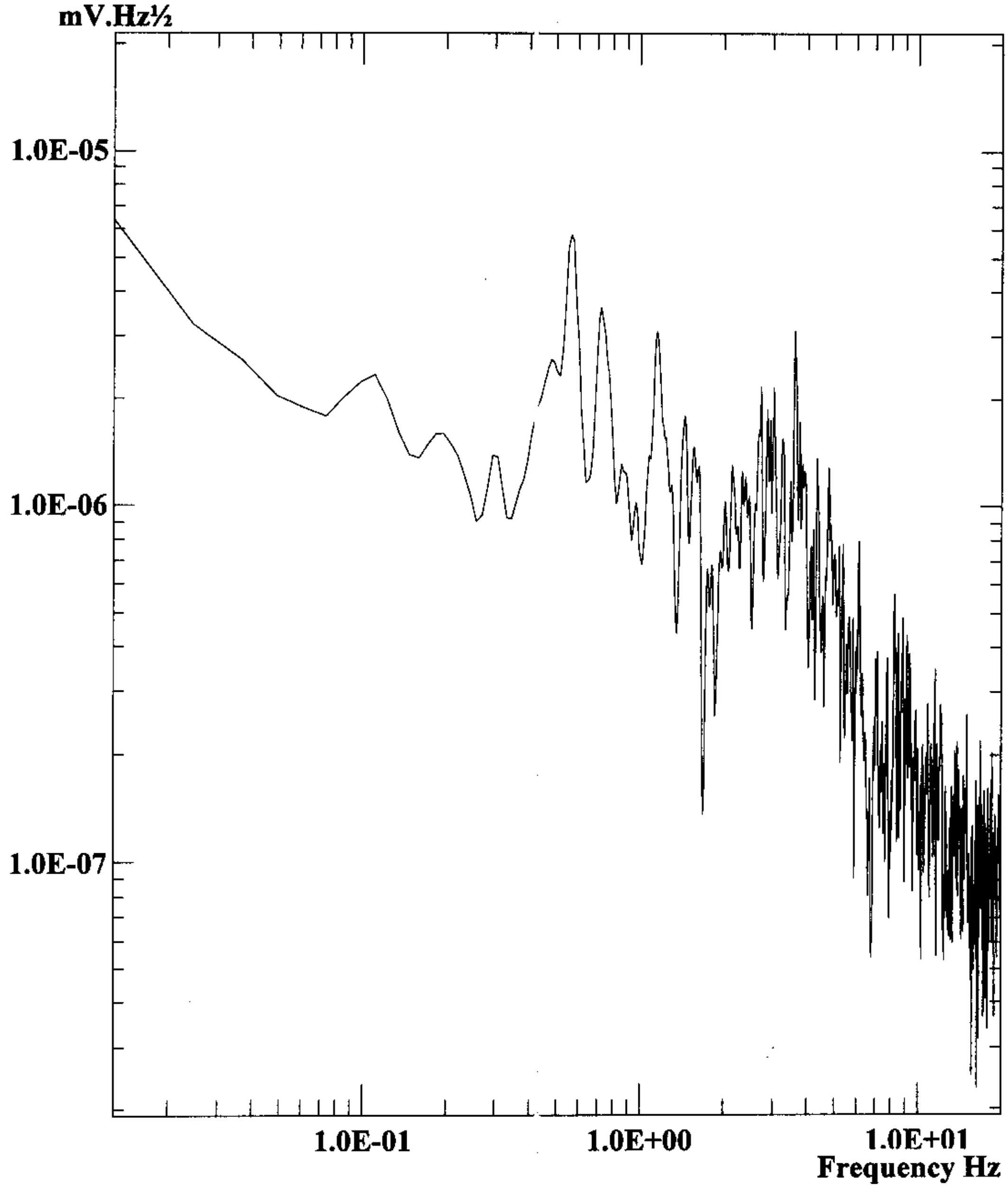
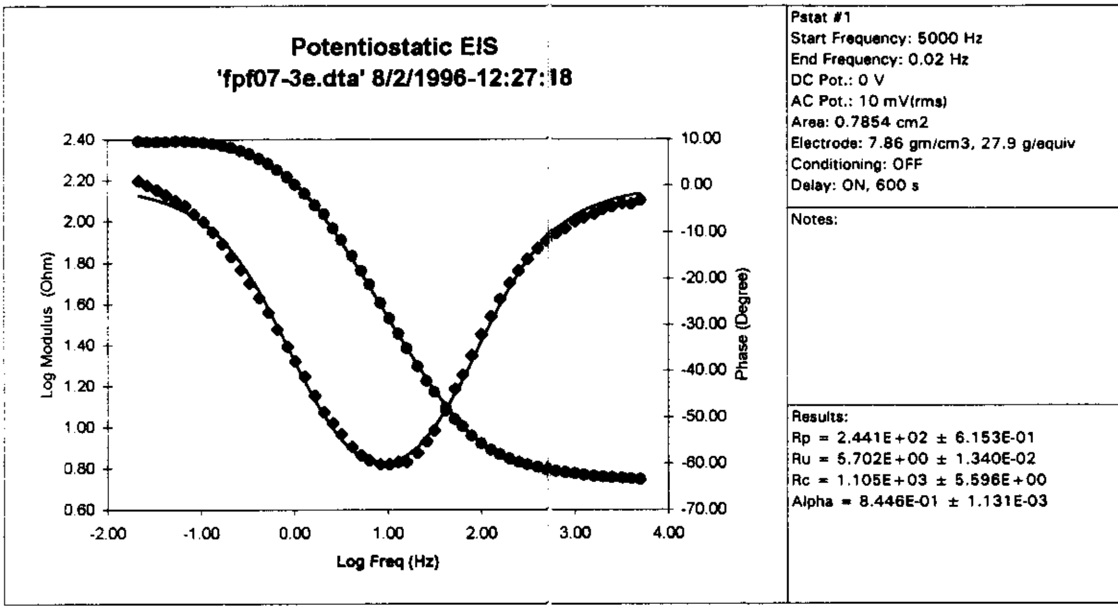


Figure 8. Potential amplitude spectrum for Froude No. 6 stationary slug flow Sampling rate=100Hz.



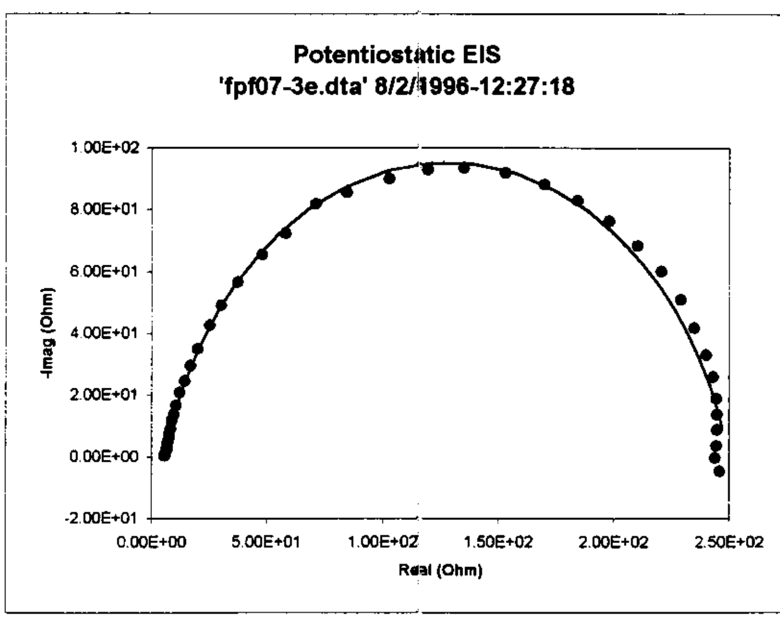
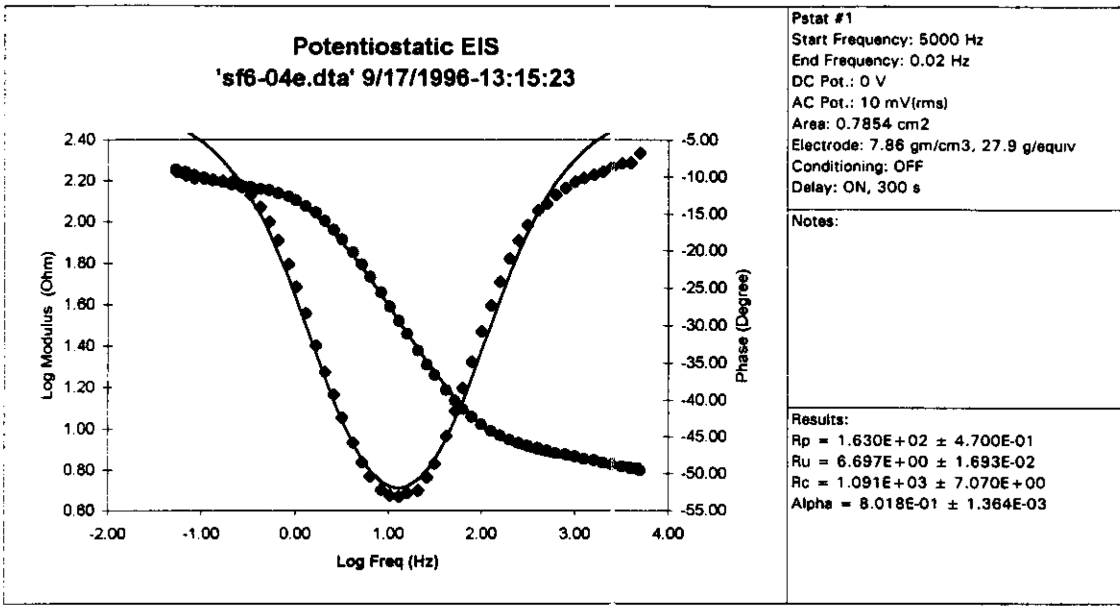


Figure 9. The impedance spectra of EIS for 0.75 m/s full pipe flow



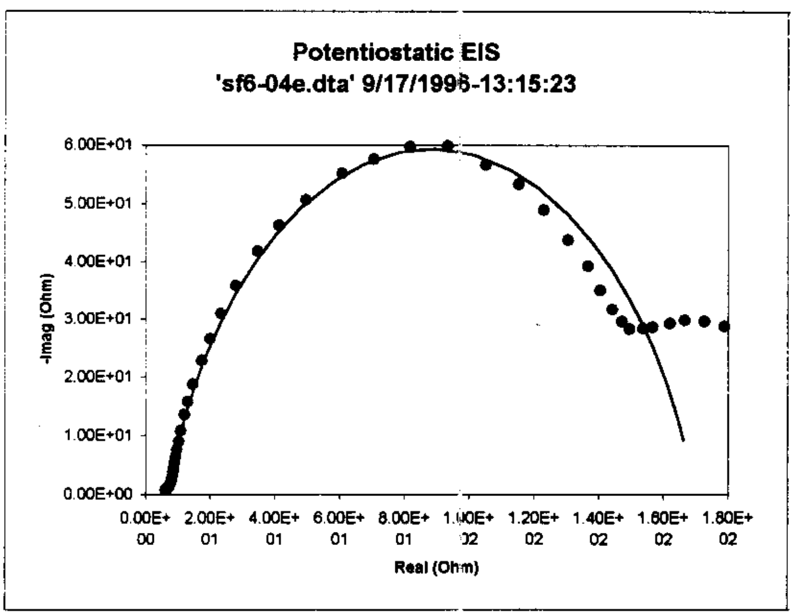


Figure 10. The impedance spectra of EIS for Froude No. 6 stationary slug flow

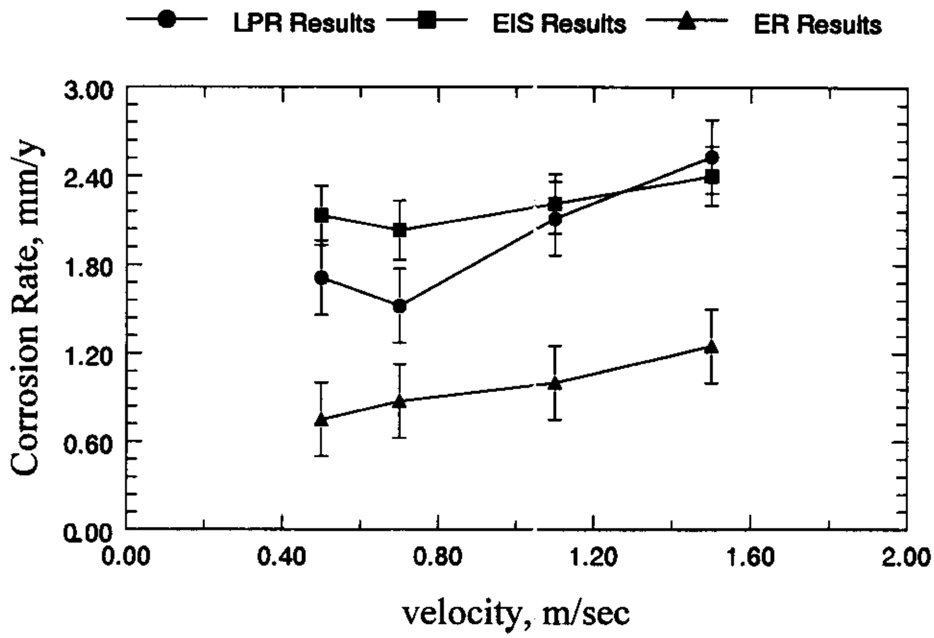


Figure 11. Comparison of corrosion rate among LPR ,EIS, ER for full pipe flow

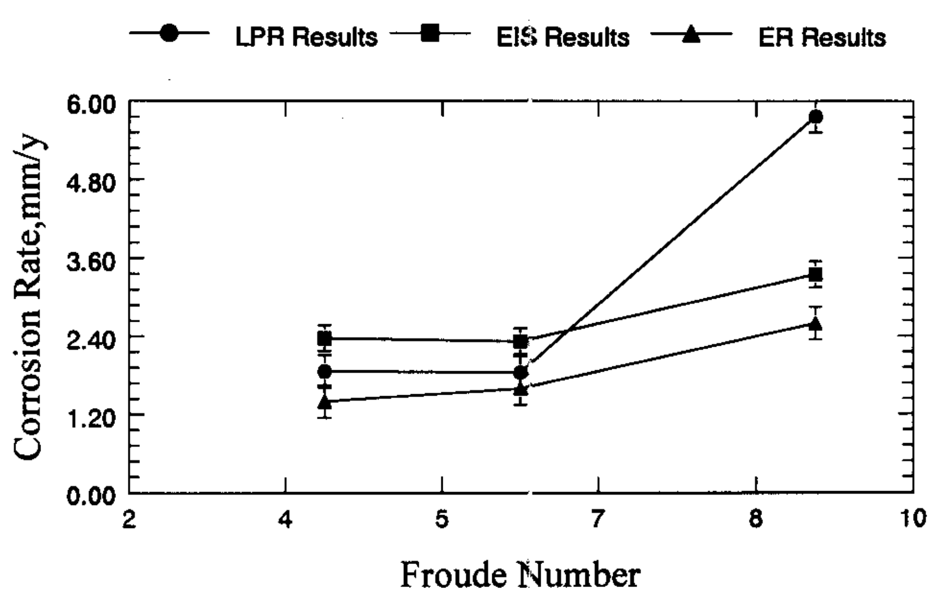


Figure 12. Comparison of corrosion rate among LPR, EIS, ER for slug flow

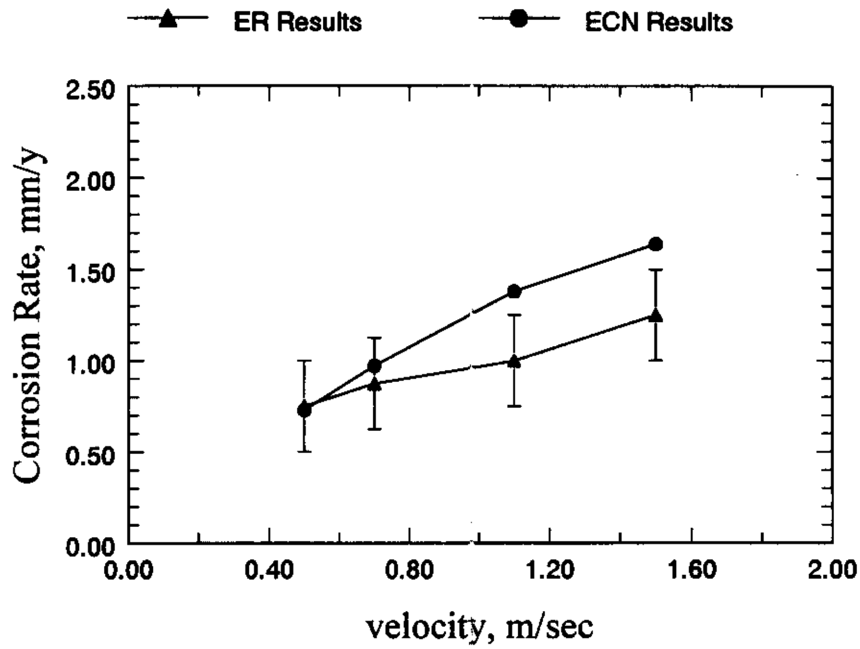


Figure 13. Comparison of corrosion rate between ER and ECN for full pipe flow

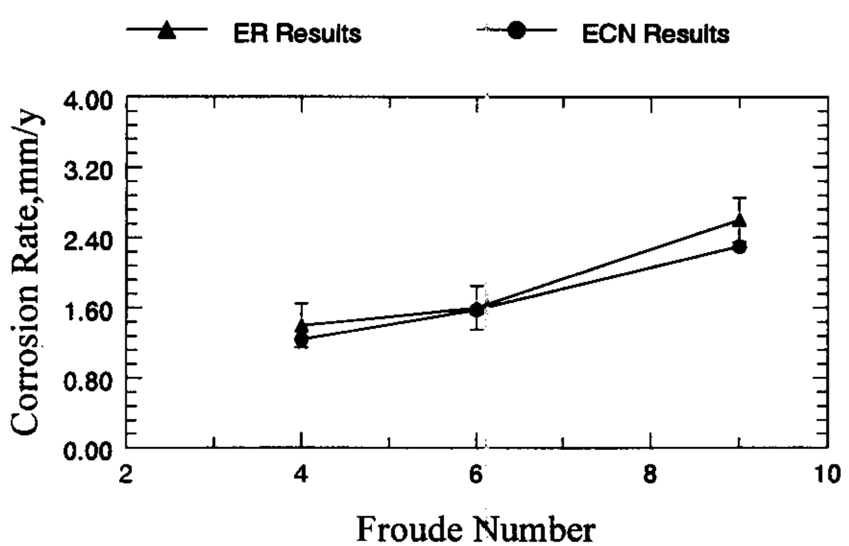


Figure 14. Comparison of corrosion rate between ER and ECN for slug flow

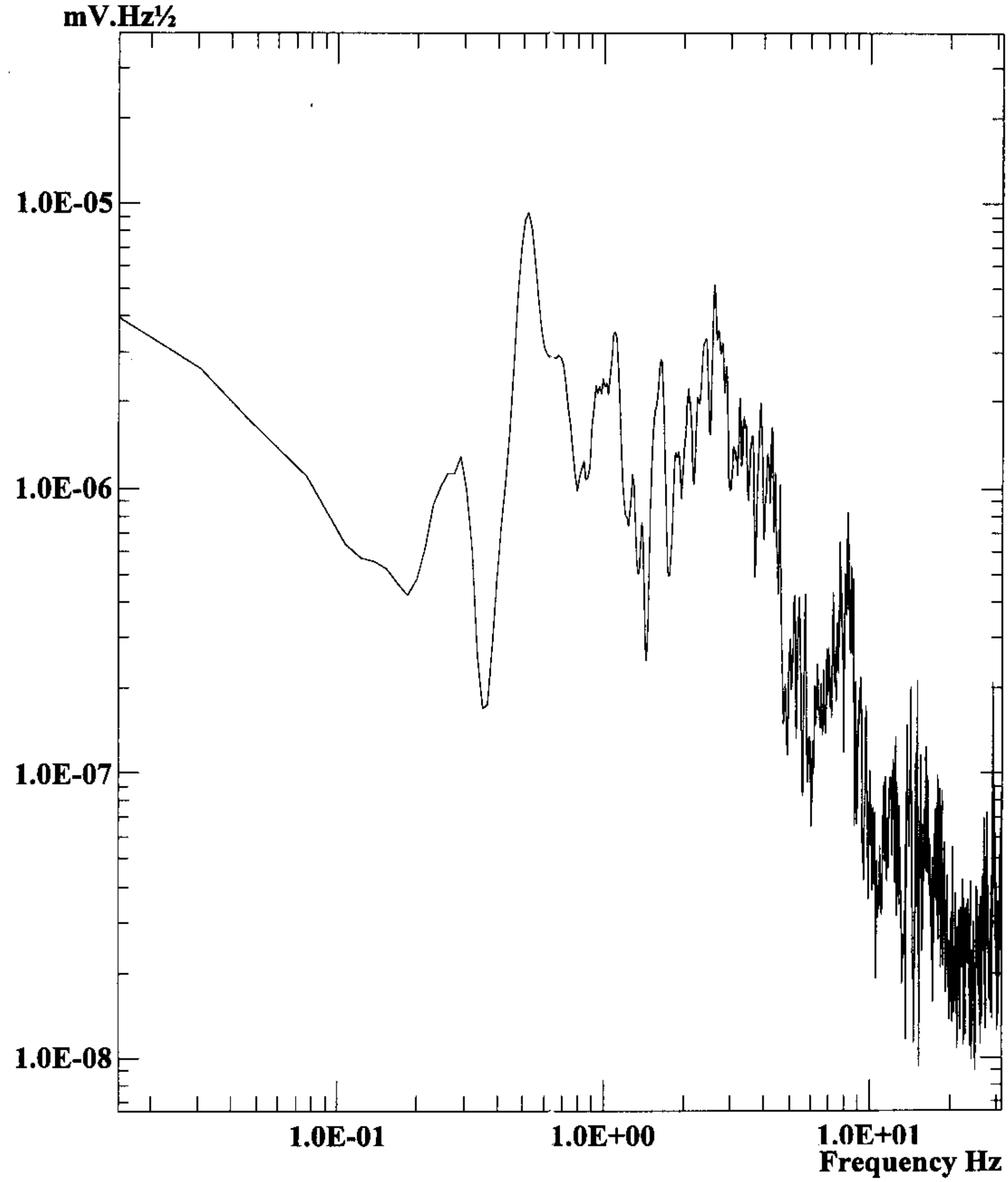


Figure 15. Potential amplitude spectra for Froude number 6 stationary slug flow Sampling rate=500Hz.