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CORROSION MONITORING OF TOP FLOW IN WET GAS ENVIRONMENT USING ELECTROCHEMICAL NOISE MEASUREMENT (ECN)

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ABSTRACT

The corrosion of the top flow in wet gas environment was studied in this work by using Electrochemical Noise Measurement (ECN). All the tests were carried out in a 3-inch I. D., 28-ft long acrylic pipeline. A CO_2 or N_2 wet gas environment was generated by using high-velocity gas to entrain low-velocity seawater, which formed a annular-mist flow in the pipeline. The ECN results show less current and voltage noise fluctuation in a wet gas environment, which suggests a low corrosion activity. The slope of voltage and current amplitude during low frequency domain in Fast Fourier Transform (FFT) plots indicates the corrosion type as uniform. The spectral noise impedance, Rsn, obtained from FFT plots is high because the liquid film is very thin, therefore the corrosion activity of top flow in wet gas environment is relatively low. The results obtained from N_2 and CO_2 wet gas environment give a further proof that ECN can be used to monitor the corrosion rates since the difference of the current and voltage between N_2 and CO_2 wet gas environment is evident. The increase of current and voltage noise fluctuation with increase in gas velocity shows that the corrosion activity increases with increase in gas velocity.

Keywords: wet gas environment, electrochemical noise, top flow, corrosion activity

INTRODUCTION

With the increasing demand of natural gas motivated by its clean-burning characteristics, deep offshore reserves will play a key role in the future natural gas supply scenario. This means that produced natural gas, which may be wet and often times accompanied by liquid water, will be transported over substantial distances in pipelines. Prior to processing, a typical natural gas is composed of several hydrocarbon compounds, water, carbon dioxide, nitrogen and sometime other compounds such as hydrogen sulfide. Much of the flow in the wet gas transportation pipeline takes place in the annular and annular-mist flow. The presence of seawater and CO_2 in a wet gas environment will cause corrosion problems due to the extensive use of carbon steel as pipeline material in the oil and gas industry. The previous studies[1, 2] show that the corrosion rate in the top of the line increases with CO_2 partial pressure, gas flow rate and condensation rate, and is significantly reduced when inhibitor is added to the gas. However, the corrosion problem under wet gas environments is still not well investigated and understood especially at the top of the pipes.

Electrochemical Impedance Spectroscopy (EIS) cannot be used as a reliable corrosion monitoring technique in a wet gas environment because a liquid phase/ liquid film may not be present at all times. Thus, Electrochemical Noise Measurement (ECN) is used in this work. Fluctuation of the electrical quantities (electrode potential and current) in electrochemical systems is commonly referred to as electrochemical noise.[3] It originates, in part, from natural variations in electrochemical rate kinetics during a corrosion process. So electrochemical noise is often regarded as a random (stochastic) phenomenon coupled to deterministic kinetics. The most important data are the current and potential transients which are related to metal dissolution or cathodic processes (or both) that constitute a corrosion process. Noise data are typically acquired by monitoring the evolution of a corrosion process on two coupled electrodes without the application of an external signal.

The present article is aimed at determining whether or not electrochemical noise measurement can be used to monitor corrosion rates in a wet gas environment and studying the corrosion activity in a CO_2 wet gas environment. The corrosion activity in a N_2 wet gas environment is carried out for the purpose of comparison. The influence of gas velocity on the corrosion activity in a CO_2 wet gas environment is also studied.

EXPERIMENTAL SETUP AND PROCEDURE

All the experiments were carried out in a 3-inch (7.62 cm) I.D., 28-ft (8.53 m) long acrylic pipeline. The overall flow loop schematic is shown in Figure 1. Electrochemical noise measurements were taken in the test section shown in Figure 2.

By using high-velocity CO_2 or N_2 gas to entrain low-velocity seawater, a CO_2 or N_2 wet gas environment was simulated. An annular-mist flow in the pipeline was obtained. Test solution was prepared from de-ionized water dissolved with ASTM synthetic sea-salt. The liquid velocity used was 0.08 m/s for all the different gas velocities. Before the tests, the solution was deoxygenated with CO_2 for 5 hours in order to reduce the concentration of dissolved oxygen to less than 20 ppb.

At the beginning of each experiment, the noise probe was polished with Grit 600 and 1500 sandpaper, and then washed with acetone. The probe was then flush mounted on the top of the pipe. In each experiment, the probe was held for 30 minutes in the pipe for surface stability before collecting current and voltage noise data. Noise data under various deferent gas velocities were measured using different sampling rates successively.

Three nominally identical C-1018 carbon steel electrodes were used as working electrodes and reference electrode in this work. The surface area of each working electrodes is 0.07 cm^2. The current and voltage measurements across the noise probe were measured with an ACM Instrument Fast AutoAC® and analyzed by an in-built software. Zero resistance ammeter (ZRA) mode, which maintains a negligible potential difference between two working electrodes, was selected to measure the current between these two working electrodes.

In present study, the following tests as shown in Table 1 were carried out in order to determine the validity and comparability of using ECN as method to study corrosion rates in a CO_2 wet gas environment.

DATA ANALYSIS

The data analysis is the key of ECN application. Both statistical analysis in time domain and spectral analysis in frequency domain were used in present work. In order to get a direct view of real current and voltage noise fluctuation, the MAR (Moving Average Removal) method [4] was used in this work. The main idea behind this method is to remove the DC trend from raw noise data, and get the transient noise components. The extraction of real noise fluctuation ($M_{i,noise}$, M represents voltage or current) from the raw noise-time record (M_i) is the key step of noise analysis as shown in the Equation (1) and (2).

$$M_{i,noise} = M_i - M_{i,DC} \tag{1}$$

$$M_{i,DC} = \left\{ \sum_{i-p}^{i-p+1} Mi \right\} \Big/ (2p+2) \tag{2}$$

where p=3 in this work which means that 8 data points were used to get the DC limit.

The noise data obtained by simultaneous collection of potential and current noise were also analyzed in the frequency domain using Fast Fourier Transform (FFT).[5] To evaluate the frequency dependence of the electrochemical noise data, the spectral noise response (noise impedance) $R_{sn}(f)$ [6] was calculated at each frequency f as:

$$Rsn(f) = |V_{FFT}(f)| / |I_{FFT}(f)| \tag{3}$$

where $V_{FFT}(f)$ and $I_{FFT}(f)$ are complex numbers obtained from FFT by using the ACM software. Extrapolation to the DC limit (f→0) allows the determination of the spectral noise impedance R^{o}_{sn}, which was suggest to be compared to polarization resistance. [7, 8]

EXPERIMENTAL RESULTS AND DISCUSSION

Validity of ECN in a Carbon Dioxide Wet Gas Environment

The results obtained with successive collection of potential and current noise for the corrosion in a CO_2 wet gas environment at a gas velocity of 10 m/s are displayed in Figure 3 and Figure 4 for sampling rates of 10 Hz, 60 Hz and 100 Hz. The comparison of voltage or current curve in Figures 3 or 4 shows that the level of voltage or current activity is almost the same with a voltage range of 145 mV to 155 mV for 10 Hz and 60 Hz sampling rates, and a current range of 0.06-0.09 mA/cm^2 for 10, 60 and 100 Hz. However, the voltage range with 100 Hz sampling rate is slightly lower than that of 10 Hz and 60 Hz. This is probably due to small differences on the metal surface.

It is noticed that, for a wet gas environment, the fluctuations in both current and voltage are random about a mean value, similar to those in full pipe flow at steady state. This may be caused by the small amount of liquid in contact with the probe at wet gas conditions. Lower fluctuation suggests that there is less activity on the probe surface.

When the MAR method of analysis is used, i.e., when the DC has been removed, the magnitude of the noise fluctuations can be more clearly seen. This is illustrated in Figures 5 and 6. The current noise fluctuations are given in Figure 5 and show that the magnitude of the fluctuation is almost the same for each sampling frequency. However, much more detail is noted at 60 and 100 Hz. For these two sampling rates similar results are found. This would suggest that a frequency of 60 Hz or greater would capture more of the detail of the corrosion processes. For the voltage fluctuations, Figure 6 shows similar results except that at the 10 Hz frequency, slightly larger fluctuations are noticed at some isolated locations. The spontaneous current and voltage noise fluctuations are shown in Figures 7. In this Figure, electropositive potential transitions were always accompanied by equivalent electropositive shifts in the current at the same instant. This is an indication of uniform corrosion.

Figures 8 and 9 show the noise amplitudes of electrochemical current and voltage data obtained from FFT at sampling rate 10 Hz and 60 Hz respectively. The noise amplitudes of current can be related to the general corrosion rate, whereas the slopes of the noise amplitudes may indicate the different types of corrosion in the low frequency domain.[9] In both plots, there are no obvious differences or changes in the shape and slope in the low frequency domain between 0.1 Hz and 10 Hz. The slope in low frequency domain is around –40 dB/decade for voltage or a little higher than –40 dB/decade for current, which may indicate the corrosion type as uniform corrosion.[10] For 10 Hz and 60 Hz sampling rate, similar slopes for current or voltage are obtained during data collection procedure.

Figure 10 shows the spectral noise responses (R_{sn}) calculated from Equation (3) as a function of frequency for two experiments at a sample rate of 10 Hz. As we have seen, the noise resistance R^{o}_{sn}, obtained by extrapolating the trend line of R_{sn} to a frequency equal to zero, is high in a wet gas environment. This high impedance suggests a very low corrosion activity since there is only a thin liquid film at the top of the pipe. Along the low frequency domain, the noise resistance trend lines do not shift much in log scale. These frequency-independent Rsn values at low frequency in these plots indicate that the corrosion type in a wet gas environment is mostly a uniform corrosion process.

ECN in a Nitrogen Wet Gas Environment

In order to get a direct view of the magnitude of the corrosion activity in a CO_2 wet gas environment, experiments were carried out in a neutral solution environment of N_2 wet gas for the purpose of comparison. Figures 11 and 12 show the current and voltage noise fluctuation obtained by MAR method in a N_2 wet gas environment at sampling rate of 1 Hz. This sampling rate is chosen because of the very low corrosion activity here. Again, less random fluctuations are seen. In a N_2 wet gas environment, the lack of hydrogen ions can significantly suppress the cathodic reaction. Hence, little corrosion is expected. This can be verified by the current and voltage noise fluctuation in the time domain as shown in Figures 11 and 12. The voltage noise fluctuation range is less than ±0.15 mV and the current fluctuation range is less than ±0.0001 mA/cm^2. The noise fluctuation values in Figures 11 and 12 indicate that the level of both voltage and current noise activity is relatively very small as compared to that in a CO_2 wet gas environment, where the range of fluctuations is ±1.0 mV and ±0.002 mA/cm^2 at 1 Hz sampling rate.

Influence of Gas Velocity in a Carbon Dioxide Wet Gas Environment

Table 2 shows the current and voltage noise fluctuation for different gas velocity for 1 Hz sampling rate. It is shown that both voltage and current noise fluctuation obtained by using MAR method increased when the gas velocity is increased from 10 m/s to 17 m/s. This suggests an increase in corrosion activities. Compared to the corrosion activity in a N_2 wet gas environment, current noise activity at 17 m/s gas velocity is almost 100 times higher. This is further exemplified in Figures 13 and 14. Figure 13 shows the current noise fluctuation at a gas velocity of 10 m/s, 15 m/s and17 m/s respectively using 1 Hz sampling rate. Figure 14 shows the equivalent voltage noise fluctuation. These behaviors can be considered as follows: at the lower gas velocity, there would be a thin liquid film at the top of the pipe may be thin. With the increase of gas velocity, more liquid is presented and liquid film will be completely spread around the pipe, resulting in increases in corrosion activity.

CONCLUSIONS

The above results of electrochemical noise experiments and analysis indicate the following conclusions:

1. Current and voltage noise fluctuations in a wet gas environment suggest a low corrosion activity. Both the frequency-independent spectral noise resistance Rsn and the slope of voltage and current amplitude during low frequency domain in FFT plots indicate the corrosion type as uniform. The noise resistance R^osn is high because the liquid film is very thin, so the corrosion activity is relatively slow.
2. The results obtained from a N_2 and CO_2 wet gas environment shows that ECN can be used to monitor the corrosion rates since the difference of the current and voltage noise fluctuation between N_2 and CO_2 wet gas environment is evident.

3. The increase of current and voltage noise fluctuation with the increase in gas velocity indicated that the corrosion activity increases with the increase in gas velocity.

   In a summary, ECN is a practical technique for continuously monitoring the corrosion activity of carbon steel pipelines in present work. The quantitative analysis still requires further investigation.

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TABLE 1
TEST MATRIX

Parameter	Condition
CO_2 partial pressure, MPa	0.136
Temperature, °C	40
Water cut, %	100
Test gas	CO_2 & N_2
Superficial liquid velocity, m/s	0.08
Superficial gas velocity, m/s	10, 15, 17
Sampling rates, Hz	1, 10, 60, 100

TABLE 2
COMPARISON OF NOISE FLUCTUATION UNDER DIFFERENT GAS VELOCITIES

	10 m/s	15 m/s	17 m/s
Voltage noise fluctuation (mV)	±1.0	±5.0	±15
Current noise fluctuation (mA/cm^2)	±0.002	±0.005	±0.01

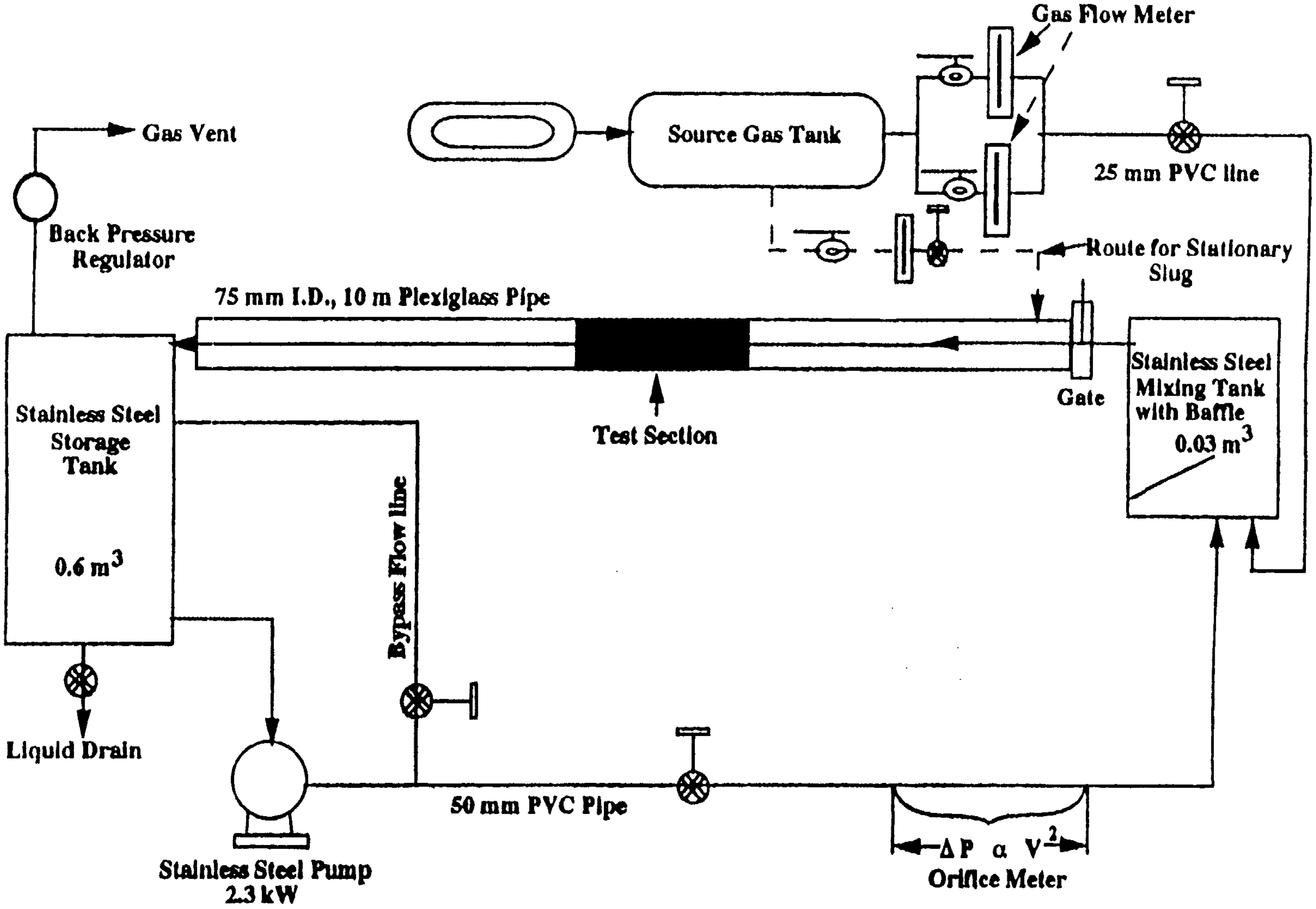
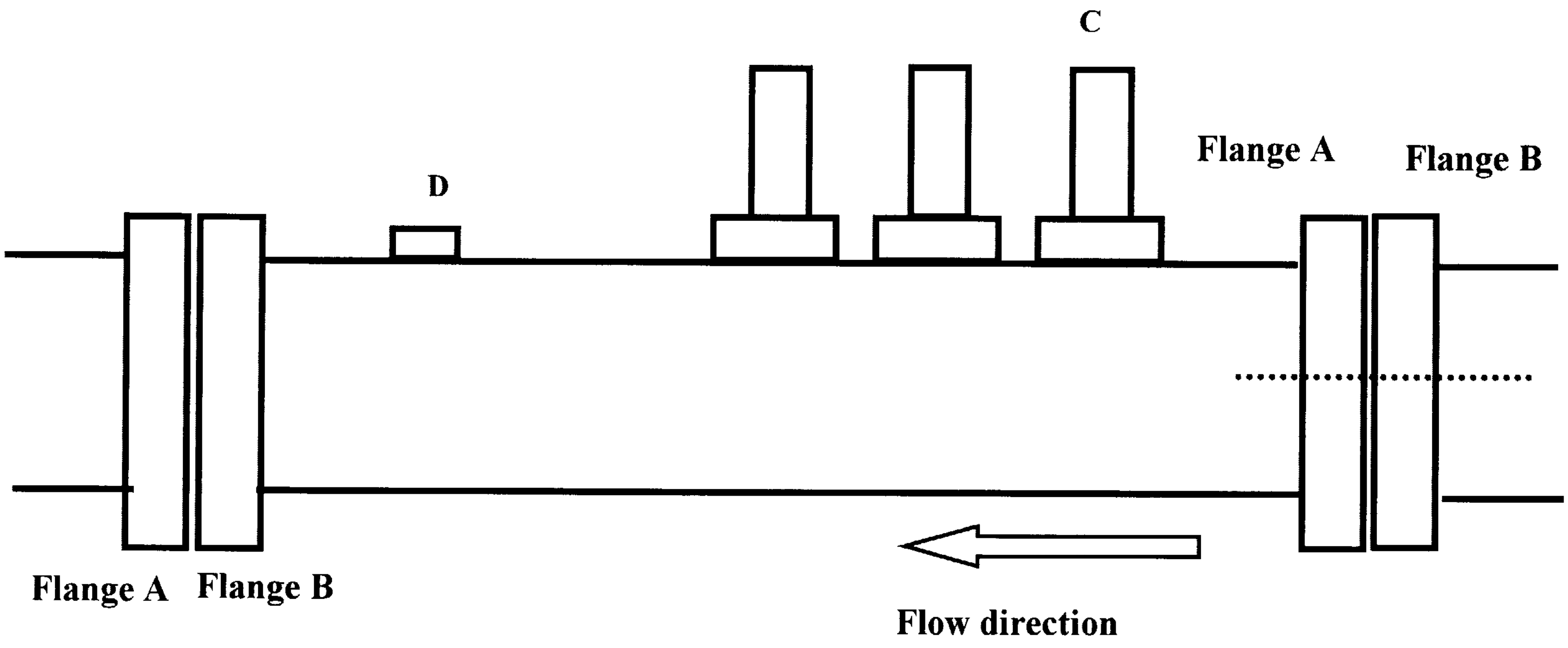


Figure 1. Schematic layout of 7.5 cm I. D. experimental flow system



C: ECN probe (3.2 cm diameter)
D: Digital thermometer probe

Figure 2. Schematic of test section

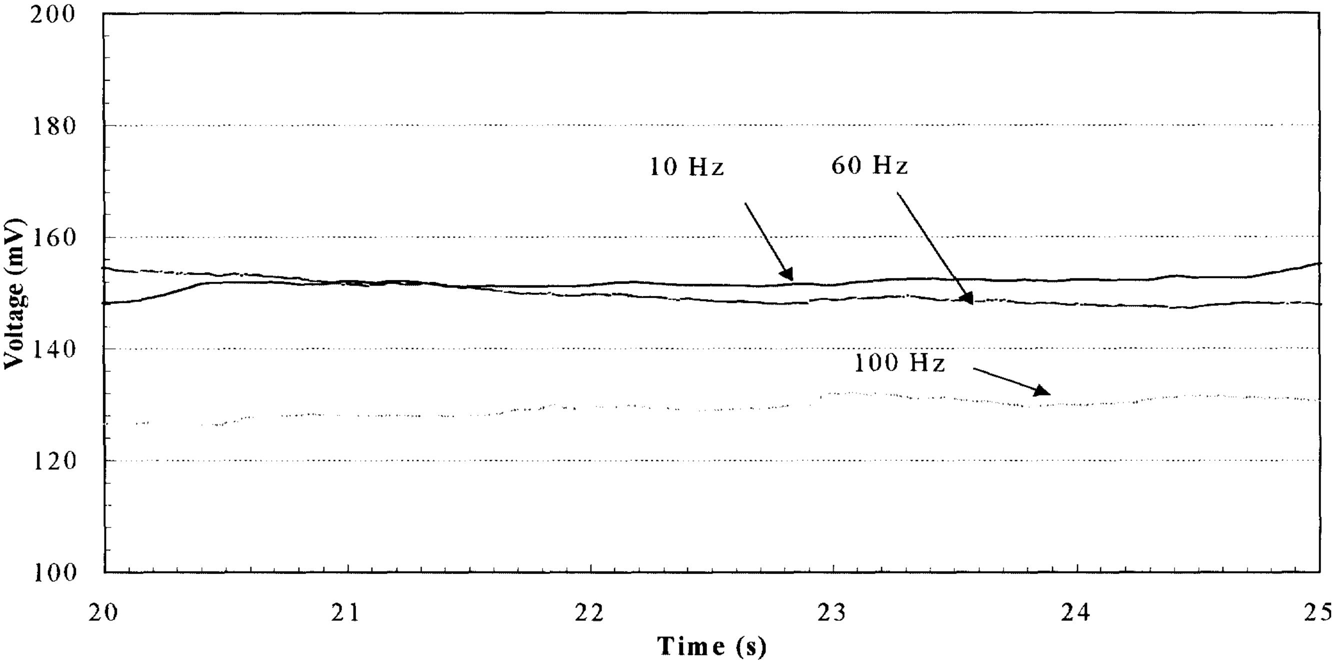


Figure 3. Noise response of wet gas for 10 m/s CO_2 flow rate
Sampling rate=10, 60, 100 Hz

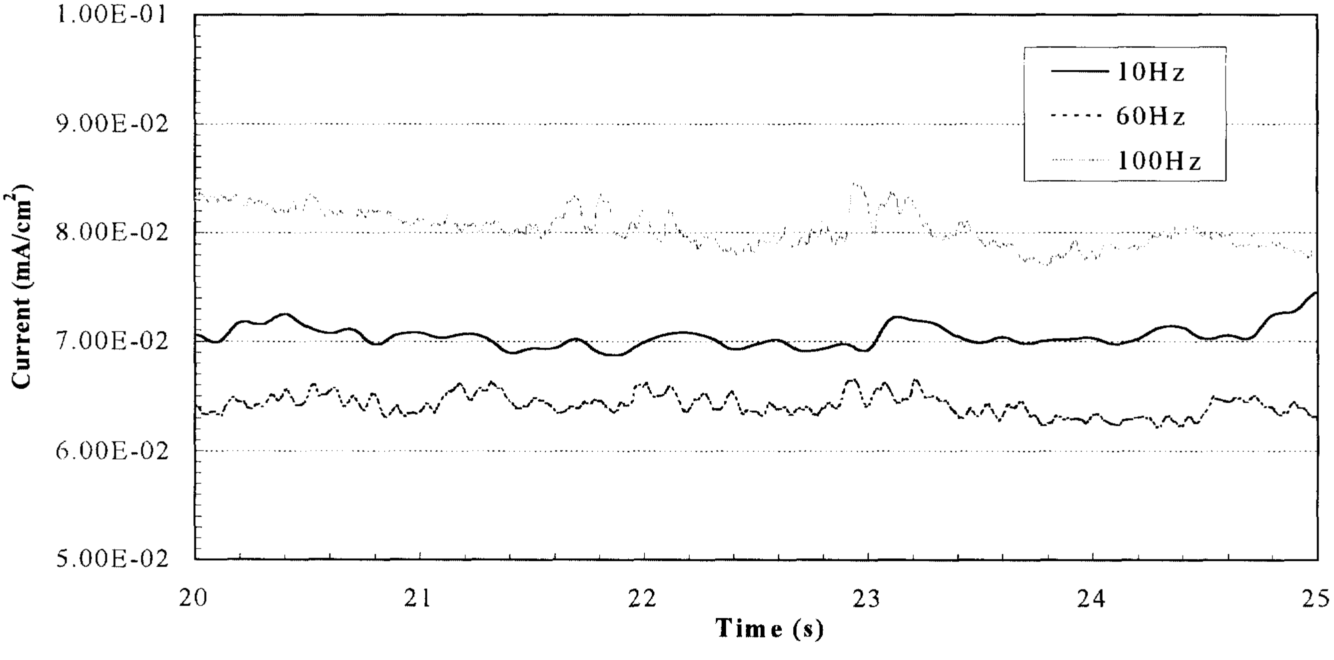


Figure 4. Noise response of wet gas for 10 m/s CO_2 flow rate
Sampling rate=10, 60, 100 Hz

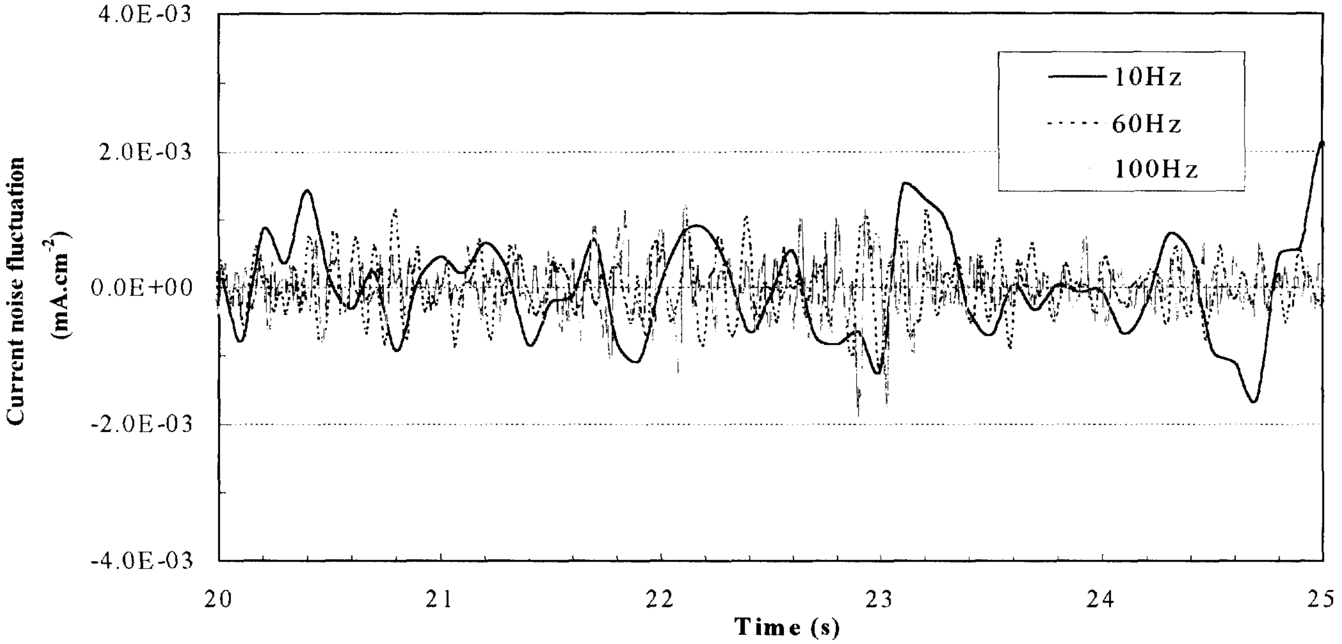


Figure 5. Noise response of wet gas for 10 m/s CO_2 flow rate
Sampling rate=10, 60, 100 Hz

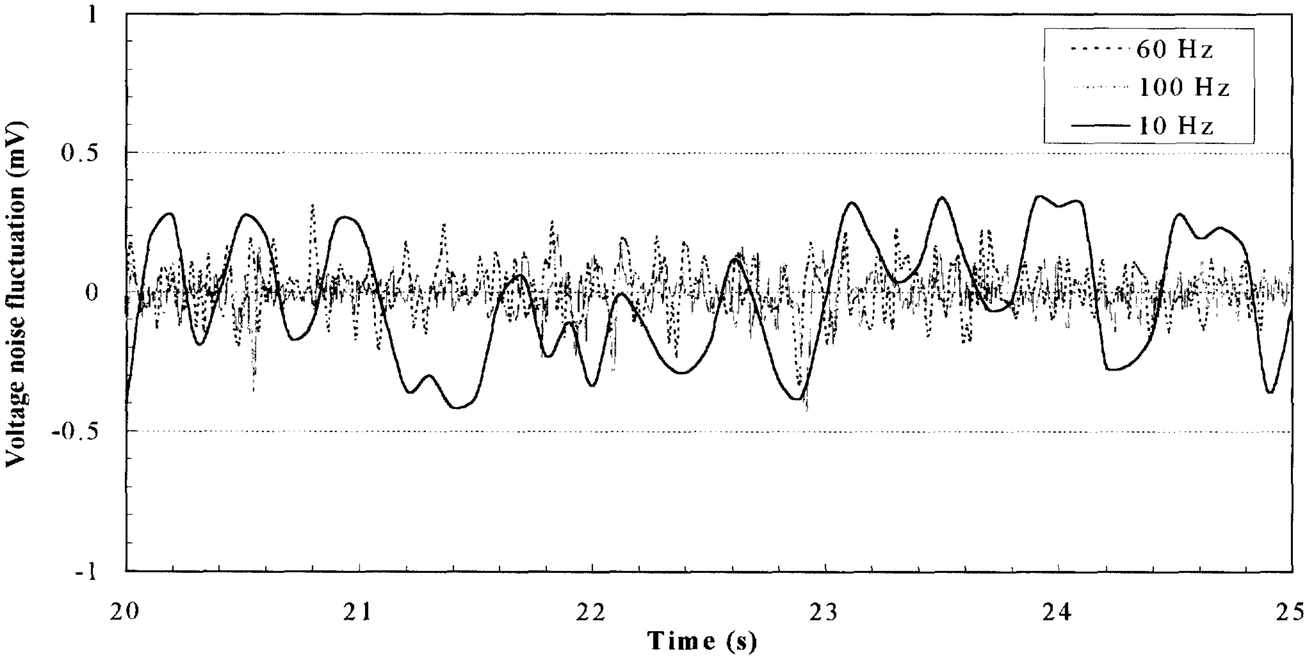


Figure 6. Noise response of wet gas for 10 m/s CO_2 flow rate
Sampling rate=10, 60, 100 Hz

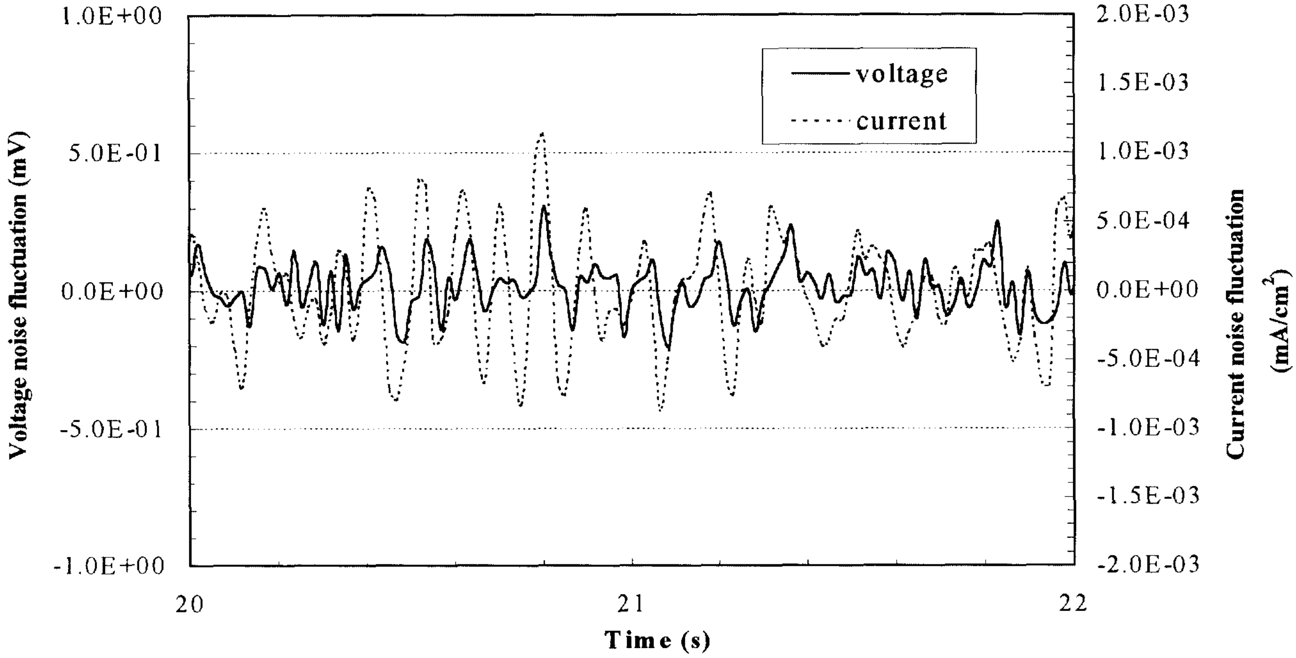


Figure 7. Noise response of wet gas for 10 m/s CO_2 flow rate Sampling rate= 60 Hz

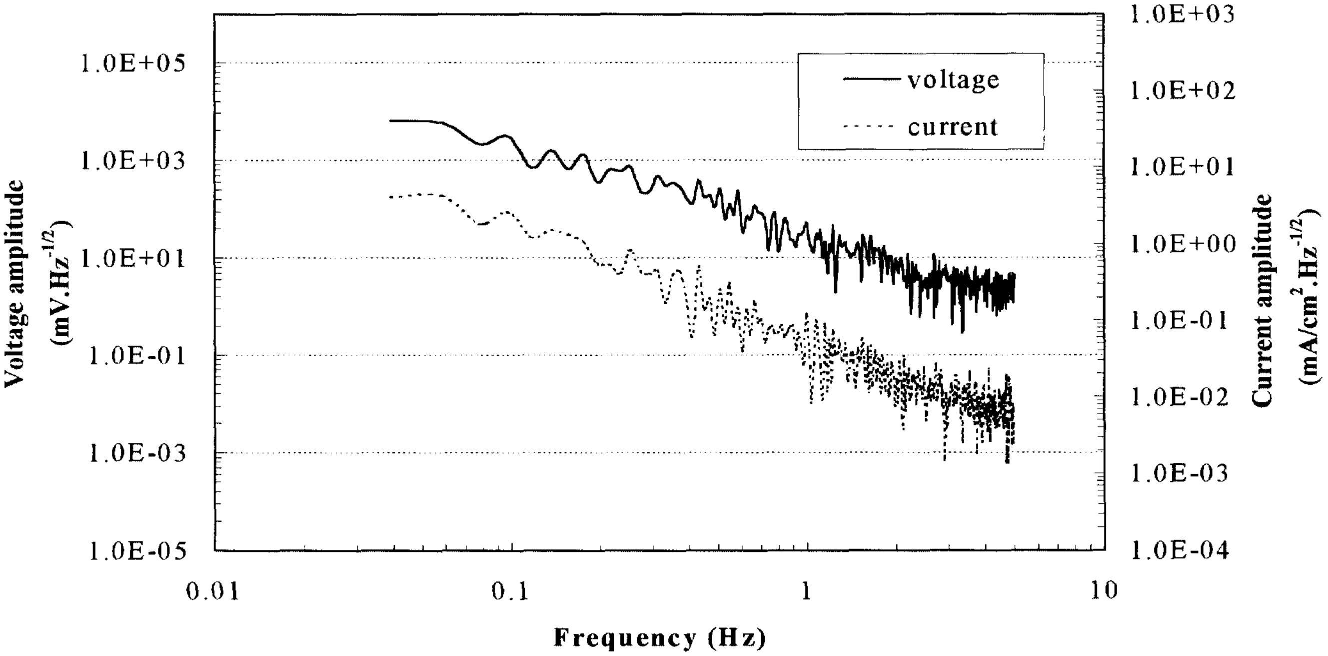


Figure 8. Noise response from FFT for CO_2 wet gas (gas velocity=10 m/s, sampling rate=10 Hz)

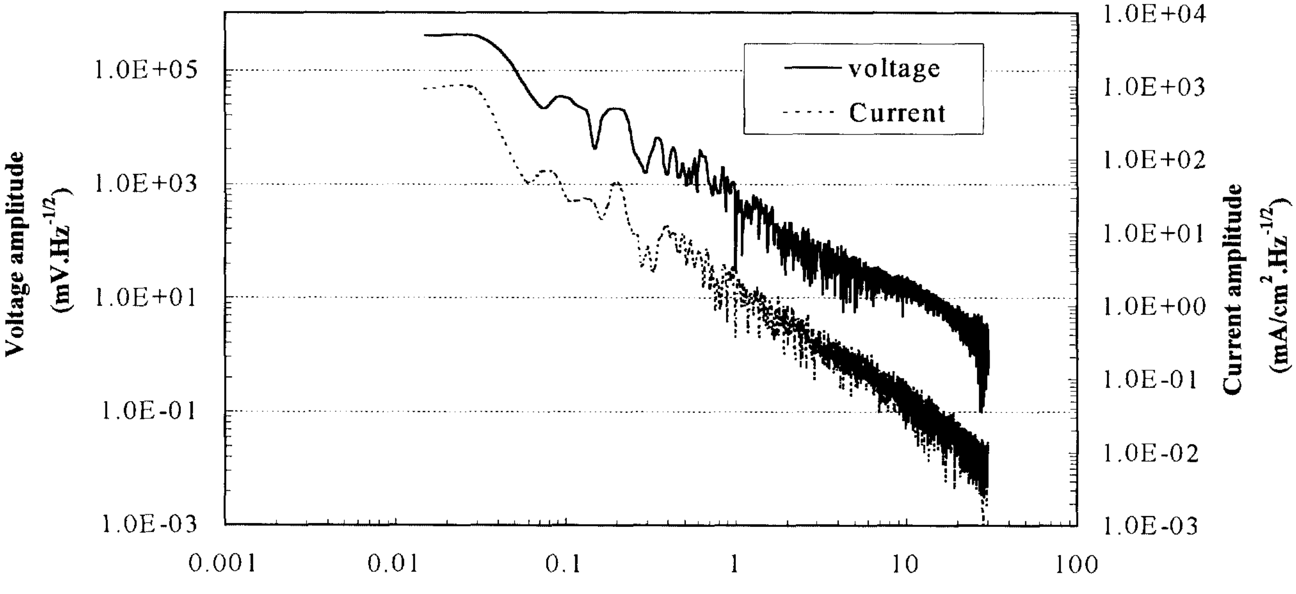


Figure 9. Noise response from FFT for CO_2 wet gas (gas velocity=10 m/s, sampling rate=60 Hz)

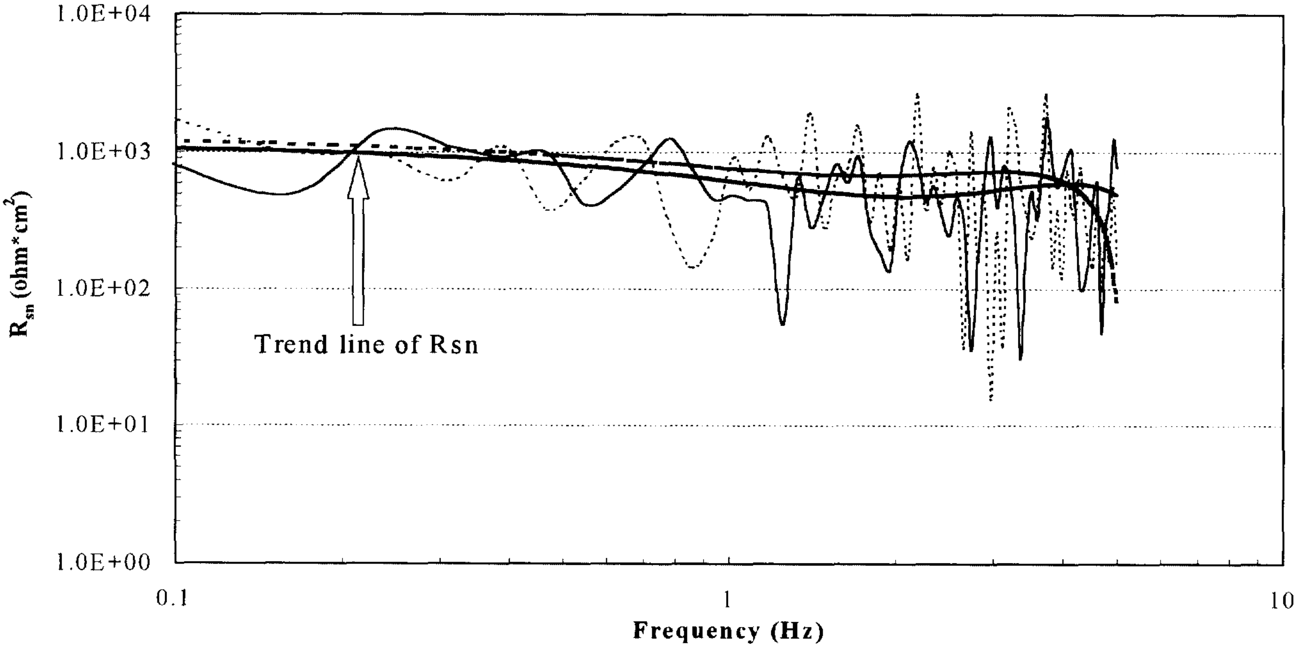


Figure 10. Noise resistance R_{sn} for wet gas (gas velocity=10 m/s, sampling rate=10 Hz)

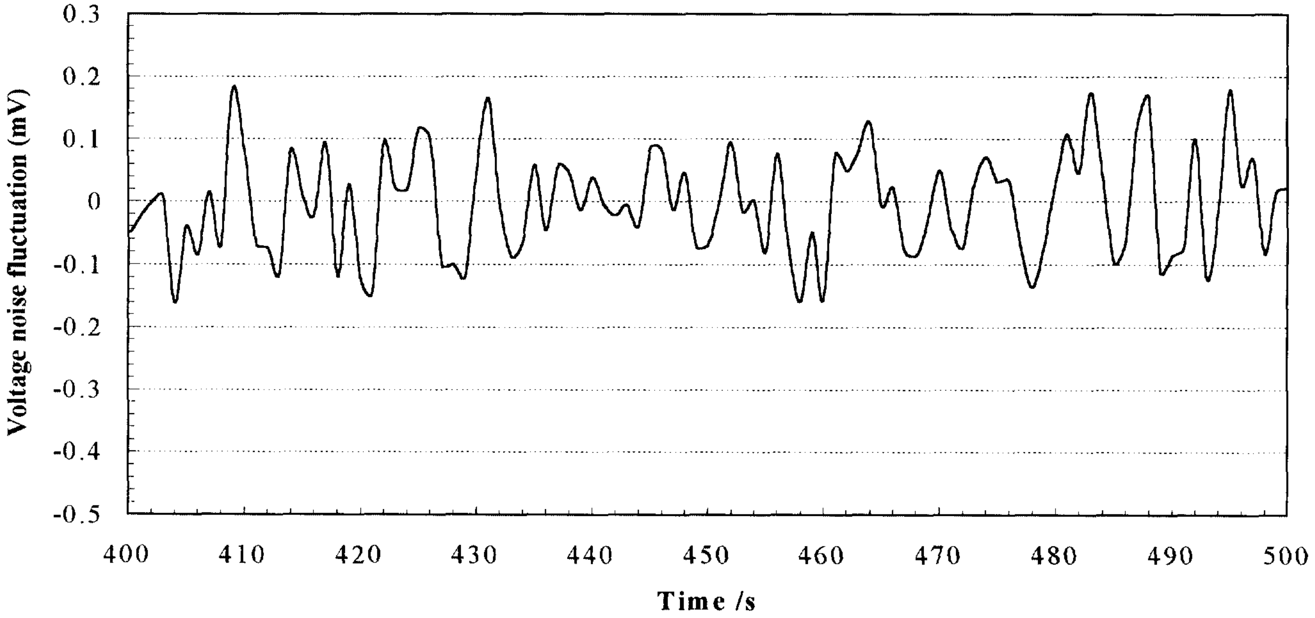


Figure 11. Noise response of wet gas for 10 m/s N_2 flow rate
Sampling rate=1 Hz

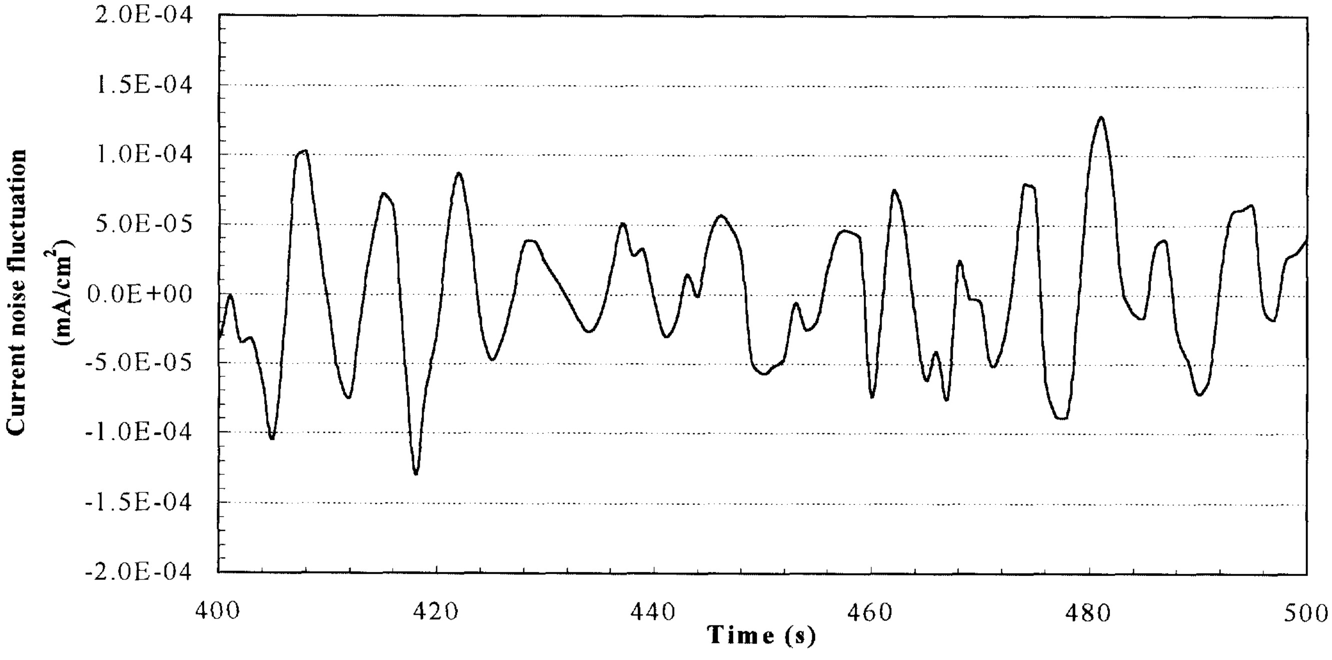


Figure 12. Noise response of wet gas for 10 m/s N_2 flow rate
Sampling rate=1 Hz

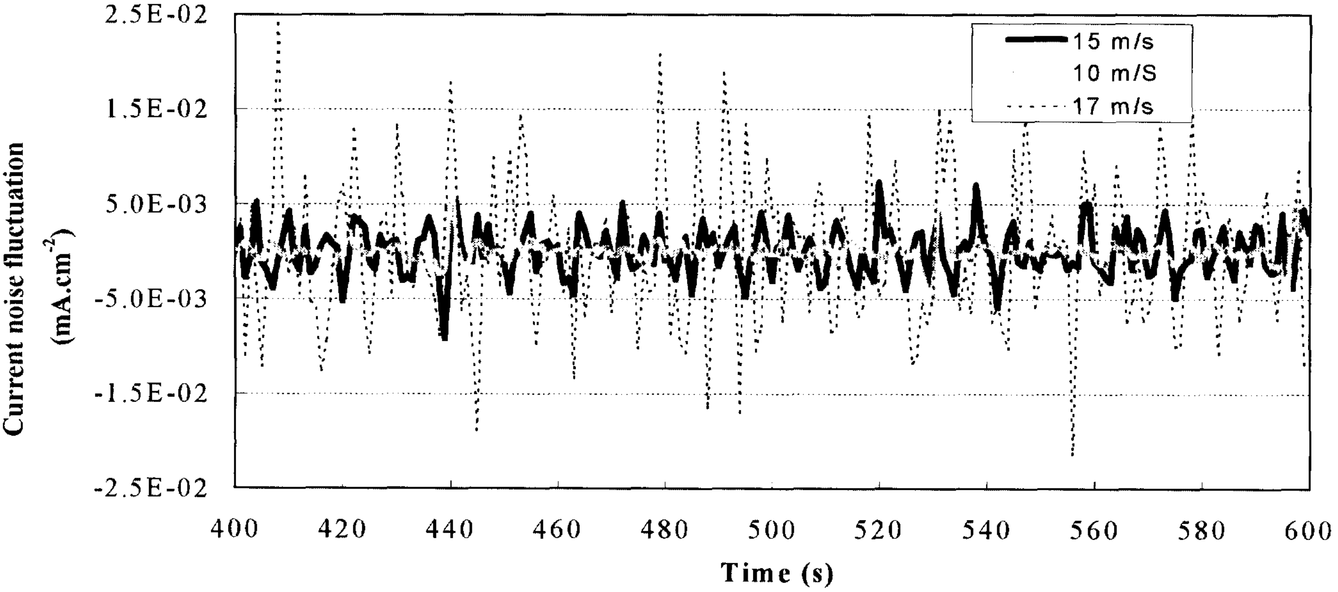


Figure 13. Noise response of CO_2 wet gas
(10, 15, 17 m/s CO_2 flow rate, Sampling rate=1 Hz)

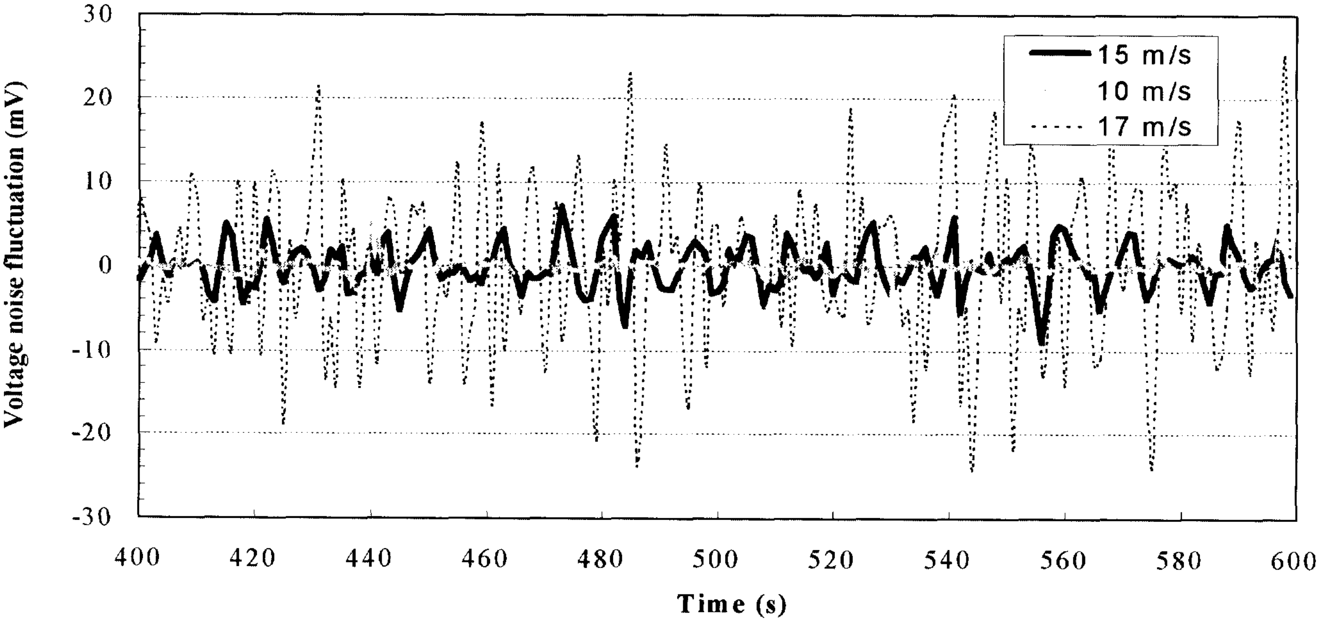


Figure 14. Noise response of CO_2 wet gas
(10, 15, 17 m/s CO_2 flow rate, Sampling rate=1 Hz)