

Laboratory Evaluation of an Electrochemical Noise System for Detection of Localized and General Corrosion of Natural Gas Transmission Pipelines

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ABSTRACT

Gas transmission pipelines are susceptible to both internal (gas side) and external (soil side) corrosion attack. Internal corrosion is caused by the presence of salt laden moisture, CO₂, H₂S, and perhaps O₂ in the natural gas. Internal corrosion usually manifests itself as general corrosion. However, the presence of chlorides in entrained water also can lead to pitting corrosion damage. The electrochemical noise technique can differentiate general from localized corrosion and provide estimates of corrosion rates without external perturbation of the corroding system. It is increasingly being applied to field and industrial installations for *in situ* corrosion monitoring. It has been used here to determine its suitability for monitoring internal and external corrosion damage on gas transmission pipelines. Corrosion measurements were made in three types of environments: 1) aqueous solutions typical of those found within gas pipelines in equilibrium with the corrosive components of natural gas; 2) biologically-active soils typical of wetlands; and 3) a simulated, unpressurized, internal gas/liquid gas pipeline environment. Multiple sensor designs were evaluated in the simulated pipe environment. Gravimetric measurements were conducted in parallel with the electrochemical noise measurements to validate the results.

Keywords: Corrosion, pitting, electrochemical noise, gas pipeline, soil

INTRODUCTION

A study¹ conducted in the US from 1970 to 1984 reported that 54% of the service failures of gas pipelines were attributable to outside forces. Of those failures, 17% were attributable to corrosion, and 17% to material failures. A later study² in Canada from 1980 to 1997 concluded that 63% of pipeline failures were caused by corrosion with 50% due to internal corrosion and 13% due to external corrosion. Corrosion failures represent a significant proportion of the number of total failures. Sensors that can detect internal and external corrosion in real time before failure occurs will enhance gas transmission pipeline reliability.

Gas transmission pipelines are susceptible to internal (gas side) and external (soil side) corrosion attack. Internal corrosion is caused by the presence of H_2O , $NaCl$, CO_2 , O_2 , CH_4 , and H_2S in the natural gas. There are certain areas of the US that are more prone to this type of corrosion than others. This is due to the production of moist sour gas in areas such as Louisiana and Texas, for example. This type of attack usually manifests itself as general corrosion, forming either non-protective carbonate scales or semi-protective sulfide scales. The presence of chlorides (salt) in entrained water also can lead to pitting corrosion that can result in leaks or rupture of the pipe.

External corrosion of gas transmission pipelines is usually controlled by the application of various polymeric coatings augmented with cathodic protection (CP). When corrosion does occur on the outside of the pipeline, the combination of general and localized corrosion with the high stresses in the pressurized pipelines can sometimes lead to stress corrosion cracking (SCC). In cases where CP is inadequate or non-existent, pipelines exposed to ground waters can experience transgranular SCC due to low pH (6.5) carbon dioxide containing water.³ Even when CP is adequate, gas pipelines may be susceptible to intergranular SCC due to the higher pH external environment generated by CP.³

There are a variety of electrochemical techniques that can be used to measure the corrosion rates of metals in almost any process environment. Of all of the electrochemical techniques, electrochemical noise (EN) has the most potential for being used successfully to measure general and localized corrosion rates of equipment. EN is increasingly being applied to field and industrial installations for *in situ* corrosion monitoring.

The field instrument selected for measuring the corrosion rates consists of a three-electrode sensor with hardware that couples electrochemical noise with linear polarization resistance (LPR) and harmonic distortion analysis (HDA), and software that can provide continuous data analysis. The electrochemical noise technique can differentiate general from localized corrosion and provide estimates of corrosion rates without external perturbation of the corroding system. EN measurements are based on fluctuations in electrochemical potential and corrosion current that occur naturally during corrosion. Electrochemical potential is related to the driving force (thermodynamics) of the reaction, while corrosion current is related to the rate (kinetics) of the reaction. Electrochemical events on the surface of a corroding metal will generate fluctuations (noise) in the overall potential and current signals. Each type of corrosion (for example general corrosion, pitting corrosion, crevice corrosion, cavitation attack, and stress corrosion cracking) will have a characteristic “fingerprint” or “signature” in the signal noise. This “fingerprint” can be used to predict the type and severity of corrosion that is occurring.⁴

Electrochemical noise measurements refer to the fluctuations in current and/or potential that occurs between two coupled identical electrodes at the open circuit corrosion potential. The fluctuations in the corrosion current and potential occur because of changes in anodic and cathodic areas.

When pits begin to form on the metal surface, occasional sharp increases and decreases in the amplitude of both the potential and current noise data occur. The amplitude can change from a few millivolts to hundreds of millivolts, depending on the metal or alloy being studied. When the existing pits continue to grow or propagate the amplitude of both the potential and current noise continues to increase.

In the present investigation, EN is being evaluated to determine its suitability for monitoring internal and external corrosion damage on gas transmission pipelines. The objective of this research is to demonstrate the use of EN/LPR/HDA sensors for measuring the internal and external corrosion of natural gas transmission pipelines.

EXPERIMENTAL DESIGN

Data evaluation

Electrochemical Noise For general corrosion it is possible to relate the electrochemical potential noise (V_n) and electrochemical current noise (i_n) mathematically and calculate the electrochemical noise resistance (the polarization resistance derived from EN) for the system⁴. The electrochemical noise resistance, R_n is defined as the ratio of the standard deviation of the electrochemical noise potential signals to the standard deviation of the electrochemical noise current signals. These signals are generated spontaneously by corroding electrodes in the probe.

$$R_n = \sigma_{V_n} / \sigma_{i_n} \quad (1)$$

σ_{V_n} = the standard deviation of the electrochemical potential noise.

σ_{i_n} = the standard deviation of the electrochemical current noise.

The corrosion current density (i_{corr}) is obtained from Stern-Geary approximation,

$$i_{corr} = B / R_n \quad (2)$$

where B is the Stern-Geary constant. The Tafel coefficients are calculated from Harmonic Distortion Analysis and B is calculated using the Tafel coefficients. The general corrosion rate is calculated from the corrosion current density by means of Faraday's law.

For localized corrosion, the risk of pitting on the metal surface is derived from the electrochemical noise and the harmonic data. This value is termed the Pitting Factor (PF)⁴ and is always examined together with corrosion rate. The Pitting Factor has a value between 0 and 1. As the value approaches 1, the system will be in a pitting regime rather than a regime of general corrosion. The calculation for PF is as follows:

$$PF = (ECN) / (A * i_{corrHDA}) \quad (3)$$

ECN = EN current noise (standard deviations)

A = Electrode surface area, cm^2

$i_{corrHDA}$ = Corrosion current from Harmonic Distortion Analysis, A/cm^2

When the pitting factor is between 0 and 0.1, pitting does not occur. If the pitting factor is between 0.1 and 0.2, then pitting may occur on the metal surface. If the pitting factor is greater than 0.2, then pitting is occurring on the metal surface⁴.

Linear Polarization LPR measurements involve the in-phase measurement of the current response to a small amplitude ($\pm 25\text{mV}$) sinusoidal polarization of the electrodes under potentiostatic control. The polarization resistance, R_p , is then calculated from 100 pairs of data points using Fourier transform techniques.

Harmonic Distortion Analysis Harmonic distortion is a measure of the non-linear current distortion arising during the LPR measurement. The data is analyzed (using Fast Fourier Transform analysis) to provide a measurement of the corrosion current, and to provide an on-line calculation of the Tafel and Stern-Geary constants. Harmonic distortion analysis measurements become unstable under pitting corrosion conditions (or other localized attack). However, this phenomenon, together with an increase in the PF can be used to alert the operator to pitting of the metal surface.

Corrosion tests

All the electrochemical corrosion tests were performed using three electrode electrochemical sensors identical in surface area and made of the same material. The first electrode was used as the working electrode, the second as the counter electrode, and the third as the reference electrode. Electrochemical corrosion measurements were made in three types of environments: 1) aqueous solutions typical of those found within gas pipelines in equilibrium with the corrosive components of natural gas (H_2O , NaCl , CO_2 , and O_2), 2) biologically-active soils typical of wetlands (soil, H_2O , and NaCl); and 3) a simulated, unpressurized, internal gas/liquid (H_2O , CO_2 , O_2 and NaCl) gas pipeline environment. Gravimetric measurements in aqueous and soil environments were conducted in parallel with the electrochemical measurements.

For the aqueous and soil tests, cylindrical electrodes were made from X42 transmission pipe. The chemical composition of the cylindrical electrodes is shown in Table 1. The electrodes were 5 cm in length and 0.79 cm in diameter. The exposed area was 12.5 cm^2 . The cylindrical electrodes were finished to 600 grit with SiC paper. Prior to the test the cylindrical electrodes were cleaned and degreased in methanol.

The electrochemical tests for measuring the corrosion of gas transmission pipeline metal in aqueous solutions typical of those found within gas pipelines were performed in the corrosion cell shown in Figure 1. Two lexan containers sealed with silicone were used; one for the corrosion cell (Figure 1) and one for a trap to minimize carry-over of liquid in the off-gas stream. In a previous study⁶, where the internal corrosion behavior of gas transmission pipeline material was measured in solutions representative of those found in the field, analyses showed that these solutions contained chloride in the form of calcium, potassium, magnesium and sodium chlorides. The Cl^- concentration ranged from approximately 0.006 wt % to 0.13 wt %. For the aqueous electrochemical tests, the solution used was 3.5 wt % NaCl solution (a standard laboratory solution) with 1000 mL/min N_2 , 0-2 mL/min O_2 and 0-10 mL/min CO_2 . The test was performed at room temperature.

For measuring the external corrosion of gas transmission pipelines, electrochemical noise tests were performed in soil. The test cell (Figure 2) was a typical soil box as specified in ASTM G57, "Field Measurement of Soil Resistivity Using the Wenner Four-Electrode Method." Three cylindrical electrodes of X42 gas transmission pipeline steel were inserted into the soil box as the corrosion sensors

and four stainless steel electrodes were inserted for measuring soil resistivity. The soil resistivity was measured on a daily basis and the pH measured before and after each test.

The soil used was Dayton type soil, which is defined as fine, montmorillonitic, mesic Typic Albaqualf, and is poorly drained soil. It was taken from the well-characterized Lake Creek site in the southern Willamette Valley in Western Oregon near an oil pipeline. The soil was air dried and crushed prior to placing it in the test cell. Table 2 shows that the air dried soil contained 12.6 wt % water, 0.129 wt % Cl^- and a pH of 6.00.

Two electrochemical tests were performed using. In the first experiment, 2488 mL (16 wt %) of additional water was added to the “as received” soil over a period of time in increments of 340 mL. In the second experiment, 3000 mL (20 wt %) of additional water in increments was added to soil containing 1 wt % of NaCl. Table 2 shows that after NaCl was added, the soil contained 7.6 % water, 0.655 wt % Cl^- and a pH of 5.72. The test was performed at room temperature, with no gases added, and left open to the atmosphere.

For measuring the internal corrosion of gas transmission pipelines in simulated internal gas/liquid pipeline environments, electrochemical measurements were performed in a pipeline cell. The apparatus for this phase of the research consisted of a section of X42 gas transmission pipe that contained two different sensor configurations (Figure 3). The first sensor configuration consisted of three insulated carbon steel flanges in series with the pipe. The chemical composition of the flange electrodes is shown in Table 1. The flange electrodes were cleaned and degreased and the surface area left as received. The total exposed area was 60.76 cm^2 . The second sensor configuration consisted of three solid disc electrodes (Figure 3 inset) inserted at the bottom of the pipe in a tee adapter. The material used to make these electrodes was No. 12, Grade A615 rebar. The exposed area was 6.48 cm^2 . The disc electrodes were finished to 600 grit with SiC paper. Prior to the test the disc electrodes were cleaned and degreased in methanol. The electrochemical noise experiment was performed in an environment that consisted of water saturated 1000 mL/min $\text{N}_2/0, 5$, and 10 mL/min $\text{CO}_2/0, 2$, and 4 mL/min O_2 gas phase and 800 mL of 3.5 wt % NaCl added over time.

Weight loss measurements

Weight loss measurements were made only on the cylindrical X42 electrodes. The areas were measured and the electrodes degreased in methanol, and weighed. After the corrosion tests, the electrodes were chemically cleaned of the corrosion product in a 12 volume % H_2SO_4 solution containing 2.5 mL of Rodine 95 per liter of solution. After cleaning and drying, the electrodes were weighed and the mass loss corrosion rates in millimeters per year (mmpy) were calculated.

RESULTS AND DISCUSSION

The instrument used in this research has multi-technique capabilities for combined electrochemical monitoring. The comparison of the corrosion rates determined from harmonic distortion analysis, electrochemical noise, and linear polarization measurements of the cylindrical electrodes in soil is shown in Figure 4. There was good agreement between the three techniques.

The X42 gas transmission pipe cylindrical electrodes were exposed to a 3.5 wt % NaCl solution for 6 weeks. Figure 5 shows the EN corrosion rate as a function of time. The EN corrosion rate stayed at 0.1 mmpy for a month, rose briefly to 0.4 mmpy, then dropped back to 0.1 mmpy. During this 6 weeks period, O_2 and CO_2 levels were varied and responsible for these changes in corrosion rate. Figure 6

shows the same EN corrosion rates plotted as a function of O₂ and CO₂ concentration. The results showed that O₂ concentrations increased the corrosion rates as did increasing the CO₂ concentration.

The corrosion rate of the X42 gas transmission pipeline steel cylindrical electrodes in “as received” soil, mL of water added, and the resistivity of the soil as a function of time is shown in Figure 7. For soil to be corrosive there must be: oxygen, moisture, and soluble salts⁶. Table 2 shows the moisture and salt contents before and after the tests. In the “as received” soil experiment, as 2488 mL (16 wt %) of additional water was added to the soil over a period of 2.5 months, the resistivity decreased from relatively less corrosive⁶ ($> 60,000$ ohms-cm) to moderately corrosive⁶ (8000 ohms-cm). Figure 7 shows that beginning at 1028 mL (8 wt %) added water and a resistivity of 10,000 ohms-cm, the corrosion rate increased to 0.15 mm/yr. At 2488 mL (16 wt %) additional water and a resistivity of 8000 ohm-cm, the corrosion rate decreased to <0.01 mm/yr, possibly due to the lack of availability of oxygen in the water-saturated soil.

Figure 8 shows the corrosion rate of the X42 gas transmission pipe cylindrical electrodes in soil +1 wt % NaCl, and the mL of water added, and the resistivity of the soil as a function of time. In this environment, after the addition of only 300 mL (2 wt %) additional water, the resistivity dropped from 35,000 to 10,000 ohms-cm and the corrosion rates began increasing. At approximately 2400 mL (~16 wt %) of added water, the resistivity dropped to 1000 ohms-cm and the corrosion rates became constant possibly due to the lack of availability of oxygen in the water-saturated soil.

The effect of NaCl on the corrosion rate of the X42 gas transmission pipe cylindrical electrodes in soil is shown in Figure 9. It showed that NaCl increased the corrosion rate 35 fold in soil. The response of these soil corrosion rates to increased room temperature and moisture is shown in Figure 10. In the soil experiments, when the water and air temperatures increased, the corrosion rates increased.

Figure 11 shows the effect of NaCl on the pitting factor of the X42 transmission pipe electrodes in soil. The electrodes in the as received soil showed pitting factors between 0.0001 and 0.0008 indicating that there was no pitting. The electrodes in the soil with 1 wt % NaCl showed an initial spike between 0.1 and 0.2 indicating that pitting may have initiated on the metal surface, then decreased, possibly due to pit repassivation or to a transition to general corrosion. After 20 days the pitting factor remained at approximately 0.02 until the end of the experiment. Examination of these electrodes after removal from the soil showed a rough general corrosion of the majority of the surface and some pitting of the ends.

The cylindrical X42 transmission pipe electrodes for the aqueous and soil tests were measured and weighed before each test and cleaned and weighed after the test. A mass-loss corrosion rate in mm/yr was calculated for each electrode. Table 3 shows the comparison between the electrochemical noise and gravimetric corrosion rates. The corrosion rates measured by two different techniques, show good agreement.

For the corrosion tests in simulated internal gas/liquid pipeline environments, one sensor configuration consisted of three insulated steel flanges in series with the pipe. The flange electrodes were exposed to both the liquid and gas phases. To evaluate the corrosion rates and pitting factors for the flange electrode, the test exposure area was taken to be only that area that was submerged in the liquid phase. The second sensor configuration that consisted of three solid disc electrodes inserted at the bottom of the pipe remained submerged in the liquid phase throughout the experiment. Figure 12 shows the corrosion rates of the flange and disc electrodes as a function of time. The corrosion rates of the disc electrodes were approximately 0.01 mm/yr throughout the test. The corrosion rates of the flange electrodes increased from 0.005 to 0.08 after three weeks and increased to 0.35 after two months. The

higher corrosion rate of the flange electrodes compared to the disc electrode could be due to the different surface finish, commercial finish (usually 120 to 180 grit) for the flange electrodes and 600 grit for the disc electrodes and possibly corrosion at the interface between the liquid and gas phases for the flange electrodes as opposed to corrosion in the liquid phase only for the disc electrodes. The flange and disc electrodes were also made from different materials (Table 2). Figure 13 shows the pitting factors of the flange and disc electrodes as function of time. Initially the Pitting Factor for the flange electrode was in above 0.2 (in the pitting regime). The Pitting Factor for the flange electrode dropped to 0.001 possibly due to pitting repassivation and remained at 0.001 throughout the remainder of the test. The Pitting Factor for the disc electrodes remained below 0.1 throughout the test, indicating no pitting. Visual examination of the flange and disc electrodes showed no pits.

CONCLUSIONS

- The corrosion rates from electrochemical noise, linear polarization, and harmonic distortion analysis measurements show good agreement.
- Corrosion rates are sensitive to changes in oxygen and carbon dioxide contents in the aqueous phase.
- Corrosion rates and pitting factors are sensitive to moisture and salt in the soil and ambient temperature changes.
- EN corrosion rate shows good agreement with the gravimetric weight loss.
- Corrosion rates and pitting factors can be measured in a pipeline using different configurations.
- Using the sensor configurations described here, EN with LPR and HDA techniques are excellent for monitoring the occurrence of corrosion in gas transmission pipelines.

REFERENCES

1. R. I. Eiter et al., "Outside Force Causes Natural Gas Pipeline Failures," *Oil and Gas Journal*, 85(11), 16 Mar 1987, pp 52-57.
2. Alberta Energy and Utilities Board, "Pipeline Performance in Alberta 1980-1997," Report 98-G, Calgary, Alberta, Canada, December 1998.
3. R.N. Parkins, "A Review of Stress Corrosion Cracking of High Pressure Gas Pipelines," *Corrosion/2000*, paper No. 00363, March 2000.
4. "SmartCETTM Technology Overview 8-6-1," InterCorr International Ltd., Houston, TX.
5. N. Sridhar, D. S. Dunn, A. M. Anderko, M. M. Lencka, and H. U. Schutt, "Effects of Water and Gas Compositions on the Internal Corrosion of Gas Pipelines: Modeling and Experimental Studies, *Corrosion*, Vol 57, No. 3, 2001, pp. 221-235.
6. W. C. Robinson, "Testing Soil for Corrosiveness," *Materials Performance*, Vol 32, No. 4, April 1993, pp 56-58

Table 1
Chemical composition of the electrodes

Electrodes	Standard	Chemical composition, wt %					
		C	Mn	P	S	Si	Fe
Cylindrical	API Grade X42	0.27	1.25	0.03	0.03	NA	Bal
Flange	ASTM A105	0.35	0.60	0.04	0.05	0.35	Bal
Disc	No. 12, Grade A615 rebar*	0.31	1.36	0.013	NA	0.25	Bal

NA – not applicable

* also Cu, 0.41; Ni, 0.14; Cr, 0.081; Mo, 0.27

Table 2
Soil analyses

Soil	pH	Cl ⁻ , wt %	H ₂ O, wt %
“As received”	6.00	0.129	12.6
+ 1 wt % NaCl	5.72	0.655	7.6

Table 3
Corrosion rate comparison

Test	EN CR, mmpy	Gravimetric CR, mmpy
3.5 %NaCl sol'n	0.095	0.039
Soil	0.005	0.004
Soil +1 wt % NaCl	0.349	0.364



Figure 1- Test cell for aqueous solutions with three electrodes.



Figure 2- Soil test cell with three electrochemical electrodes and four electrodes for soil resistivity.



Figure 3 – Pipeline test cell with three flange electrodes and three disc electrodes (inset) in the side arm.

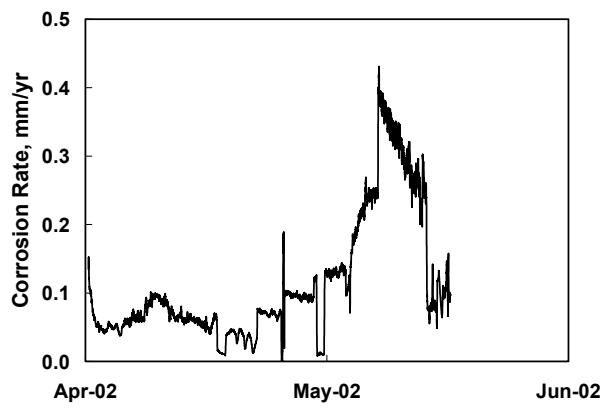


Figure 5- EN Corrosion rate of X42 transmission pipeline electrode in 3.5 wt % NaCl aqueous solution.

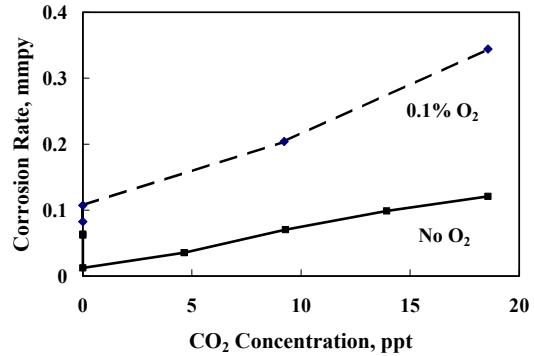


Figure 6 – The effect of O₂ and CO₂ on the corrosion rate of X42 transmission pipeline electrode in 3.5 wt % NaCl aqueous solution.

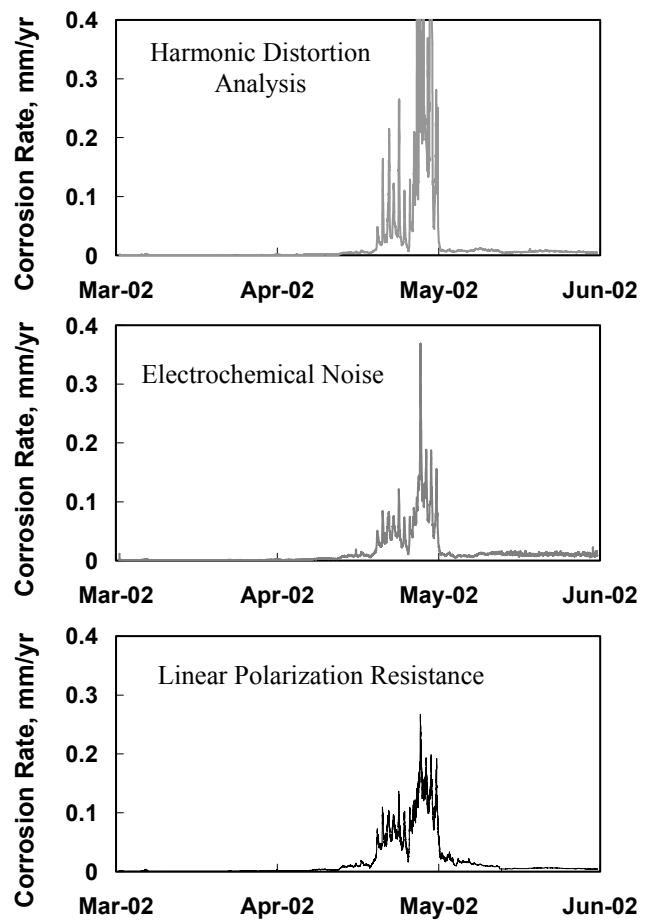


Figure 4 – Comparison of corrosion rates from harmonic distortion analysis, electrochemical noise, and linear polarization resistance measurements.

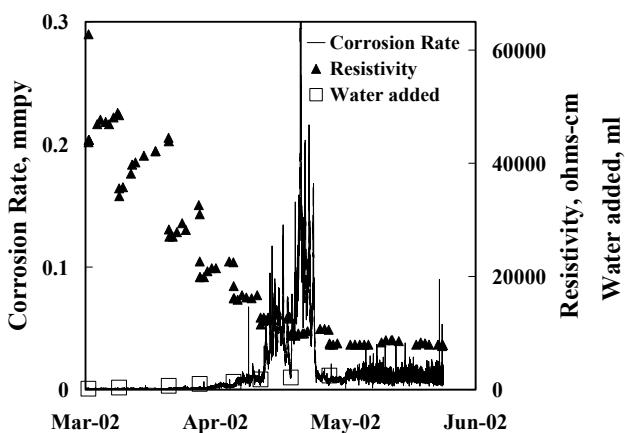


Figure 7 – Effect of resistivity and water on the corrosion rate of X42 transmission pipeline electrodes in "as received" soil. The squares represent mL of water added. The triangles represent the resistivity of the soil.

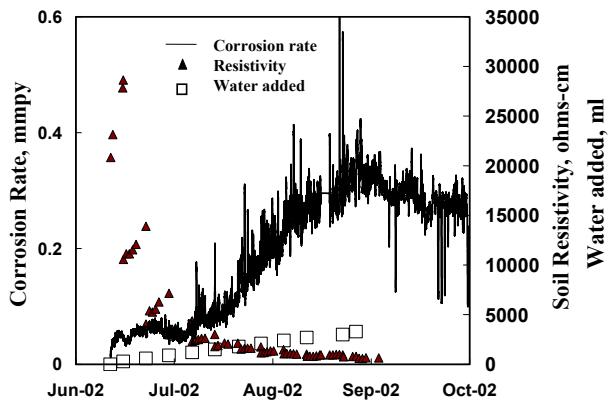


Figure 8 – Effect of resistivity and water on the corrosion rate of X42 transmission pipeline electrodes in soil + 1 wt % NaCl. The squares represent the mL of water added. The triangles represent the resistivity of the soil.

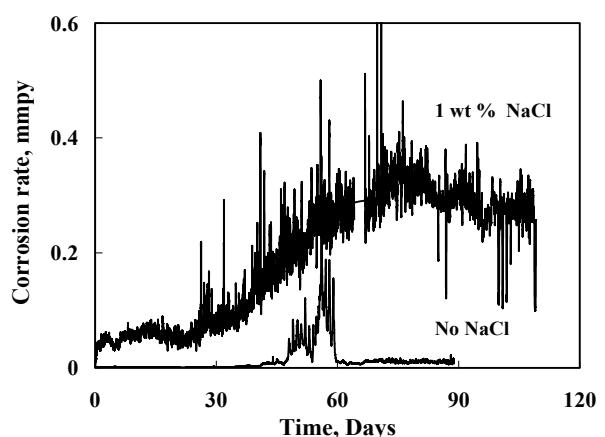


Figure 9 – Effect of NaCl on the corrosion rate of X42 transmission pipe cylindrical electrodes in soil.

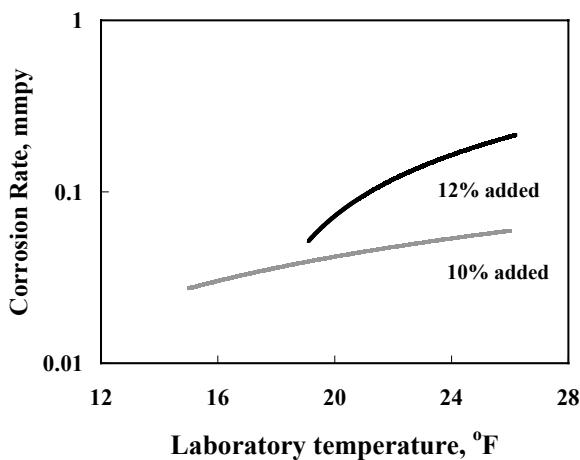


Figure 10 – Effect of water and temperature on the corrosion rate of X42 transmission pipeline electrodes in soil.

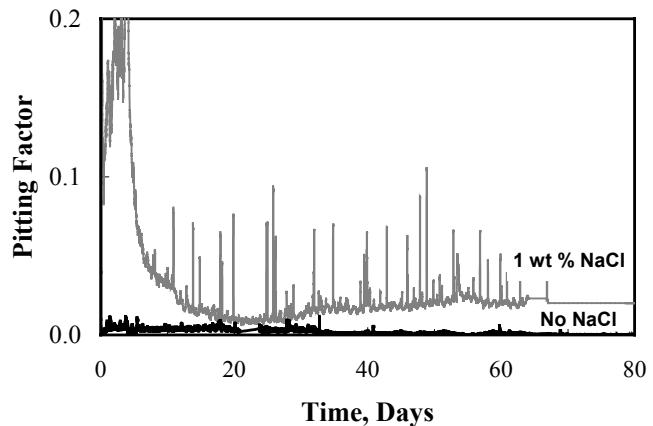


Figure 11 – Effect of NaCl on the Pitting Factor of X42 transmission pipe electrodes in soil.

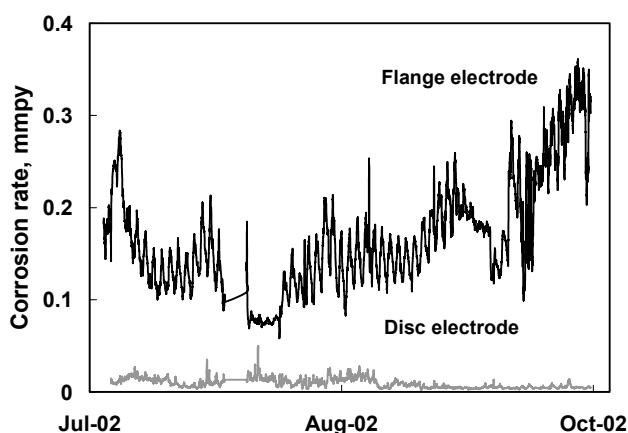


Figure 12 – Comparison of the corrosion rates of flange electrodes to the disc electrodes.

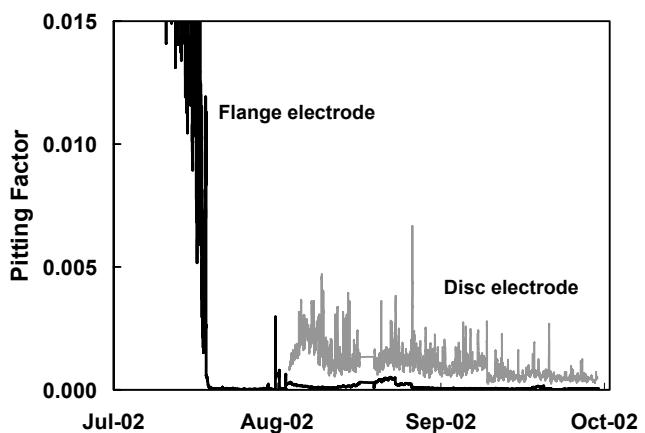


Figure 13 – Comparison of the Pitting Factors of flange electrodes to the disc electrodes