ACM Instruments

Linear Polarisation Noise for Corrosion Monitoring in Multiple Phase Environments.
(Patent Pending)

Linear Polarisation Resistance Noise gives two results: the average monitored corrosion rate and the corrosivity of the conductive fluid. It works in situations where other more established techniques have technical difficulties and especially in every location where Current & Voltage Noise is used to calculate corrosion rate.

In many cases the Corrosivity of the Conductive Fluid is the most valuable result. For instance in a pipeline where there is a possibility of separation and localised pooling the corrosivity of the conductive fluid can be of greater value when calculating the injection rate for inhibitors.

Multiple Phase Systems are typically any which interrupt the conductivity between the test electrodes used to obtain the measurement. Examples are electrodes situated in a splash zone or multiple phase flow involving mixtures of saline water gas and oil. Traditional techniques such as Current and Voltage Noise Linear Polarisation Resistance and Electrical Resistance all have limitations when operating in these environments. These are briefly noted below. Linear Polarisation Resistance is generally upset in multiple phase environments leading to erratic spiky results if the conductivity between the electrodes changes significantly throughout a test. The situation is worse in three electrode systems where a feedback loop through the cell is used to control the Cell Potential.

Current & Voltage Noise.
Often thought of as the solution to all monitoring problems the technique simply employs a two electrode Potentiostat that polarises the electrodes at 0mV with respect to each other. A third electrode is then used to monitor Potential fluctuations. Unfortunately during periods of low conductivity large Potential Perturbations do not correspond to significant current activity due to high solution resistance. This is a fundamental error in the technique which leads to corrosion rates that are lower than expected.

Electrical Resistance.
This gives a reading of the metal loss on the metals surface. Trends in the data can then be used to calculate the historic corrosion rate. The technique is limited however in that it only gives the average historic corrosion rate at the probe and does not attempt to give the corrosivity of the conductive elements in the multiple phase medium.

Linear Polarisation Noise.
This combines the practical nature of Linear Polarisation Resistance with the subtlety of Noise. The technique works with two electrode probes of a standard design and is resistant to any changes in the medium surrounding the electrodes as like Current Noise no feedback mechanism operates through the test fluid. Two results are obtained from the technique the Average Monitored Corrosion Rate and the Corrosivity of the Conductive Fluid. Data trends are presented in real time in mpy or mmpy.

As with Current and Voltage Noise the technique has further possibilities with regards to monitoring of localised corrosion as well. Knowledge of the system under test is paramount.

The technique is available as an option for operation with the portable Field Machine or desk top models such as our Gill AC. Models suitable for in-situ monitoring on site can also be supplied on request.

Copy of Patent Application

Description

Short Title: Corrosion Monitoring Device for Multiple Phase Solutions

Corrosion rate measurements are frequently taken by techniques such as Linear Polarisation Resistance using two or three electrode probes in single phase solutions such as sea water. If the conductivity between the electrodes or the rate of fluid flow passing past the electrodes changes significantly and at a rate which is typically faster than the time taken to perform the Linear Polarisation Resistance test for instance the probe is dipped in and out of the sea water then this typically interferes with the measurement process and leads to erratic unreliable results.

In recent times Current & Voltage Noise has been used for measurement in such Multi Phase systems often involving Gas Oil and Saline Water. Simultaneous measurements of Current and Voltage are typically taken from between 1 to 60 readings per second. Calculation of the Resistance Noise from the Standard Deviation of the Potential divided by the Standard Deviation of the Current is used to calculate the corrosion rate. The Corrosion Rate being inversely proportional to the Resistance Noise. The problem with this technique is that

when there is a high resistance between the two electrodes caused by a non conducting phase such as oil or gas it is possible to get large perturbations in the Potential Noise signal without any significant Current perturbation. This in turn will lead to a higher standard deviation for the Potential Noise a corresponding increase in the Resistance Noise and a lower Corrosion Rate.

Electrical Resistance techniques are often thought of as being the only technique to use in multi phase environments such as those experienced in pipe lines carrying oil saline water and gas. Electrical Resistance can give the average of the corrosion rate experience over the past few hours or days generally depending on the sensitivity of the probe and stability of the temperature at the probes surface. This technique is limited however in that it typically can not give a quick indication of the corrosion rate only gives the average corrosion rate and does not indicate the corrosivity of the conductive solution which may be pooling at another part of the system and causing a high localised level of corrosion.

This invention solves the problem of erratic measurements when the Linear Polarisation Resistance technique is used and significantly reduces such as to make insignificant the problem of Potential perturbations when there is little conductivity between the electrodes. The technique enables both the average monitored corrosion rate to be calculated and the corrosivity of the conductive fluid. In many cases where the electrodes are still wet and corroding when there is little conductivity between them it is the corrosivity of the conductive fluid that is most important as this more realistically represents the actual corrosion rate of the Electrodes.

The essential features of the instrumentation are:

A Polarisation around the couple potential of a two electrode system is used which is significantly larger than the Potential perturbations that are typically found in the monitored system.
The Polarisation Current response is measured at a set rate typically from approximately one reading per second to several thousand readings per second. Each point is stored for further analysis. Fifty readings per second have been used here.
The average of the Current Measurements taking both sides of the polarisation is then used to calculate the Polarisation Resistance and hence the average corrosion rate.
The inverse of the percentage of time the current exceeds half the average level of the current for both sides of the polarisation is calculated. This number is then multiplied with the average corrosion rate to give the corrosivity of the solution with the good conductivity.

The important but not essential features are:

The system should be used with a two electrode system rather than a three electrode system.
It is easier to use a Square Wave Polarisation which is symmetrical around the couple potential however waves of a different shape could also be conceived such as a Potentiostatic polarisation.
The test Electrodes are preferably made of the same material and of the same area.
The polarisation should be performed around the couple Potential. However an offset can be applied if the electrodes are of different materials the Polarisation is then taken around the offset potential.
A small measurement delay can be used at the start of the positive and negative polarisation's to allow the electrodes to settle.
The duration of the polarisation can be lengthened for less sensitivity or shortened for greater sensitivity.
In calculating the percentage of time the polarisation current is higher than half the average of the polarisation current for each side of the square wave polarisation a value other than half can be used to obtain similar results. In some cases it will be possible to have more than one level such as a system with three distinct phases one highly conductive and corrosive one conductive but only moderately corrosive and one not conductive or corrosive.

Introduction to the Drawings

Key.

FIG 1: Shows a typical laboratory apparatus with a corrosion probe 7 attached to a Potentiostat (1) which is controlled by a computer (2).

1. A Potentiostat.
2. A computer or data manipulation unit.
3. Auxiliary electrode connection.
4. Reference electrode connection.
5. Test or working electrode connection.
6. Connection between auxiliary and reference electrodes.
7. Two electrode corrosion probe.
8. Two test electrodes connected to terminals (3 and 4) and 5 respectively. Normally made of the same material.
9. A cell containing water with a small percentage of salt added.

Figure 2: Shows in a graphical format the Polarisation signal the current response lines showing the average current response and half the average current response.

10. x axis of a graph showing either Voltage or Current.

11. y axis displaying time.
12. Mid point of the x axis showing 0mV or 0mA.
13. Symmetrical square wave polarisation in this case the x axis is showing mV's.
14. Erratic current response x axis shows current.
15. Average of the Current Response for the first half or Anodic part of the square wave.
16. Half the average of the current noted in 15.
17 and 18 the corresponding opposite of 15 and 16.

Particular Example

FIG 1. Shows a typical laboratory apparatus in which a two electrode probe (7) is wired to a Potentiostat (1). In this case one of the electrodes (8) is wired to both the Auxiliary (3) and Reference Electrode (4) terminals whilst the other electrode (8) is wired to the test or working electrode connection (5). Assuming the test electrodes (8) are of the same material such as Mild Steel the Potentiostat is initially configured to couple the two test electrodes (8) as if by wire with a 0 mV polarisation. The Computer (2) controls the Potentiostat (1) to Polarise the cell using a square wave polarisation (13) around the couple potential and record the Current response at a set read rate. Typical square wave duration would be from about ten seconds to several minutes. Each point is stored for later use with preferably no averaging of points. Typical levels of polarisation would be from +/- 10mV to 50mV. This data is then passed back to the computer (2) for analysis. During a test to simulate multi phase conditions the electrodes (8) are repeatedly dipped in and out of the test solution 9 by hand.

Fig 2. shows the Polarisation signal (13) and resultant current response (14). The spikes on the current response (14) indicate relatively high levels of corrosion and high conductivity between the electrodes (8). These spikes of current response (14) correspond to when the electrodes (8) were immersed in the test solution (9). The more horizontal parts of trace (14) which are close to the change of sign on the x axis (12) show levels of low conductivity between the electrodes (8). This corresponds to periods of time when the electrodes (8) were not immersed in the test solution (9).

The current magnitude of Line 15 represents the average of all the current values recorded in the first half of the square wave polarisation (13). That is the sum of all the individual currents divided by the number of data points in the first half of the square wave polarisation (13). The Current value of Line 17 represents the average of all the current values recorded in the second half of the square wave polarisation (13).
For mathematical purposes I have termed the current value of line (15) to be I(15) and the Current value of line (17) to be I(17).

The average current = Ia is calculated as the absolute values of I(15) plus I(17) divided by 2.

Thus   Ia = Absolute I(15) + Absolute I(17)
                         2

Vs represents the average of the Absolute magnitude of the Square Wave Polarisation (13) where V1 is the magnitude of the first half and V2 is the magnitude of the second half. In most cases V1 and V2 will be of the same value but of opposite sign.

Vs = Absolute V1 + Absolute V2
                    2

Polarisation Resistance (Rp) is calculated by the following equation.

Rp = Vs / Ia

This value of Polarisation Resistance is then used to make a calculation of the average monitored corrosion rate in the same manner as if the polarisation resistance was obtained using a typical Linear Polarisation Resistance test on a typical two electrode system.

Line 16 is set at half the level of line 15. Another value other than half or 50% can be used provided it is not close to 0% or 100% of the value of line (15). The number of data points which have a current magnitude that is greater in magnitude than the value set by line 16 namely the tops of the peaks in the current trace (14) are counted automatically. The number of these points can be represented as a percentage of the total number of points measured in the first half of the square wave polarisation (13). We will call this value %A. The same process is done for the negative part of the Square Wave polarisation (13) this time the mean of the current is represented by line (17) and half the mean is represented by line (18). The percentage of points with a current magnitude greater than the half mean value set by line (18) is calculated in the same way to produce %C. %D represents the average of %A and %C.

The following equation is then used to calculate the corrosivity of the conductive solution polarisation resistance (Rp(S)).

Rp(S) = 100 * Rp
             %D

This value of Polarisation Resistance is then used to make a calculation of the solution corrosivity in the same manner as if the polarisation resistance was obtained using a typical Linear Polarisation Resistance test on a two electrode system.

In a system as shown in Figure 1 where the electrodes (8) are cyclically dipped in and out of the test solution 9 the value of the conductive solution corrosivity is closer to the actual corrosion rate of the electrodes than the average monitored corrosion rate. This is due to the fact that the electrodes remain wet whilst they are not immersed in the test solution 9 and corrode of their own accord even though there is a non conductive gas between the electrodes.

In other systems such as those involving an oil and conductive / corrosive saline solution phase. In this case the average of the monitored corrosion rate may be the most appropriate value of corrosion rate to use as the assumption can be made that when the electrodes are coated with oil the corrosion rate is low. The Corrosivity of the Conductive Solution is useful for setting the rate of inhibitor injection as some parts of the system experiencing the multi phase flow may be exposed to the corrosive conductive solution only with possible corresponding higher average corrosion rates.
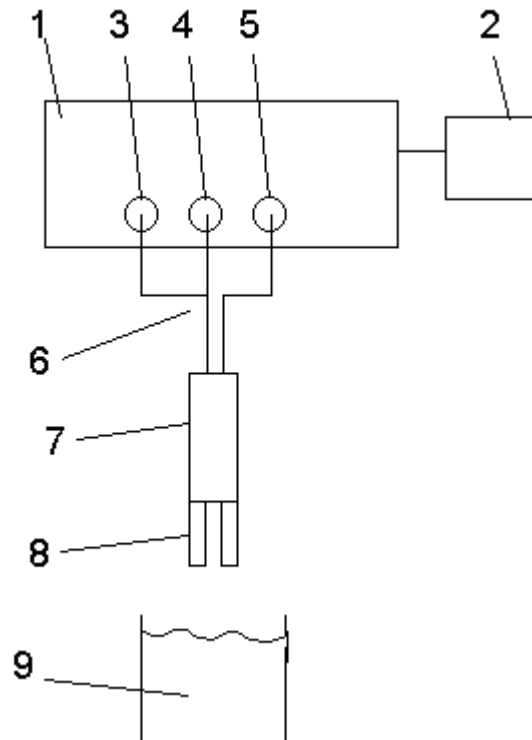
Fig 1.

Fig 2.