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(56) Documents Cited
JP 100206370 A **US 3840439 A**
US 3660249 A

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(54) Abstract Title
Corrosion monitoring system for use in multiple phase solutions

(57) The system applies a polarising potential 13 to a two or three electrode corrosion probe in the solution, and multiple reading of the resulting current 14 are taken at a known read rate. The readings are averaged 15, 17 and used to calculate polarisation resistance and then the average corrosion rate. From this value and the amount of time that the current 14 exceeds a fraction (eg half) 16, 18 of the average current 15, 17, the corrosivity of the phase of the solution with good conductivity is determined. The electrodes are preferably of the same material and area. The polarising potential, which is preferably substantially greater than natural fluctuations, may be a square wave or a wave of different shape which is symmetrical around the couple potential of the electrodes, which can be zero, or an offset value if the electrodes are of different materials. Reading rates can be from one to several thousand readings per second. The multiple phase solution may be oil, gas and saline water.

FIG.2

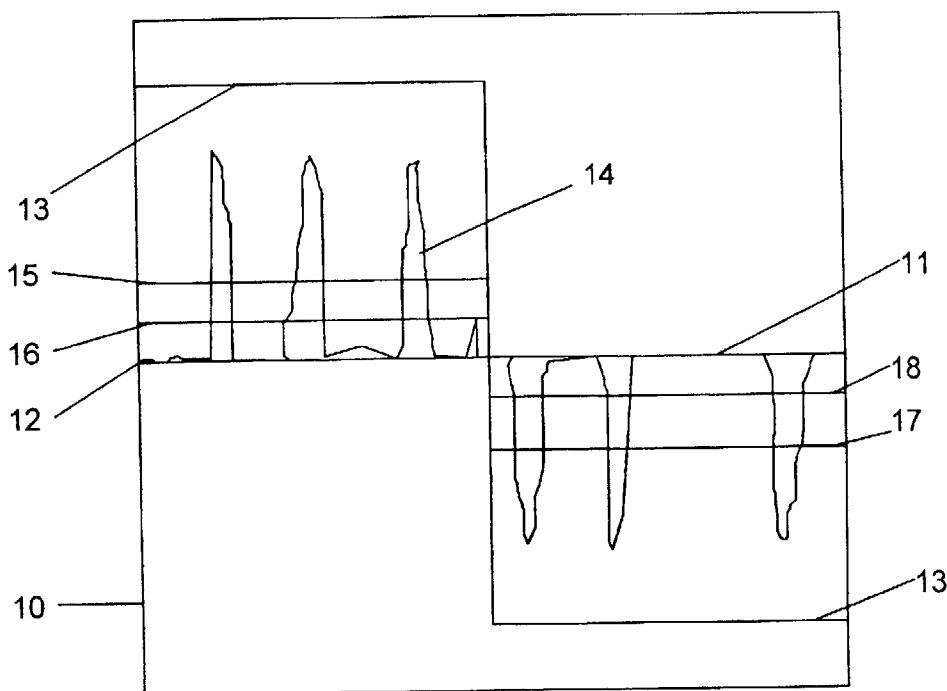


FIG.2

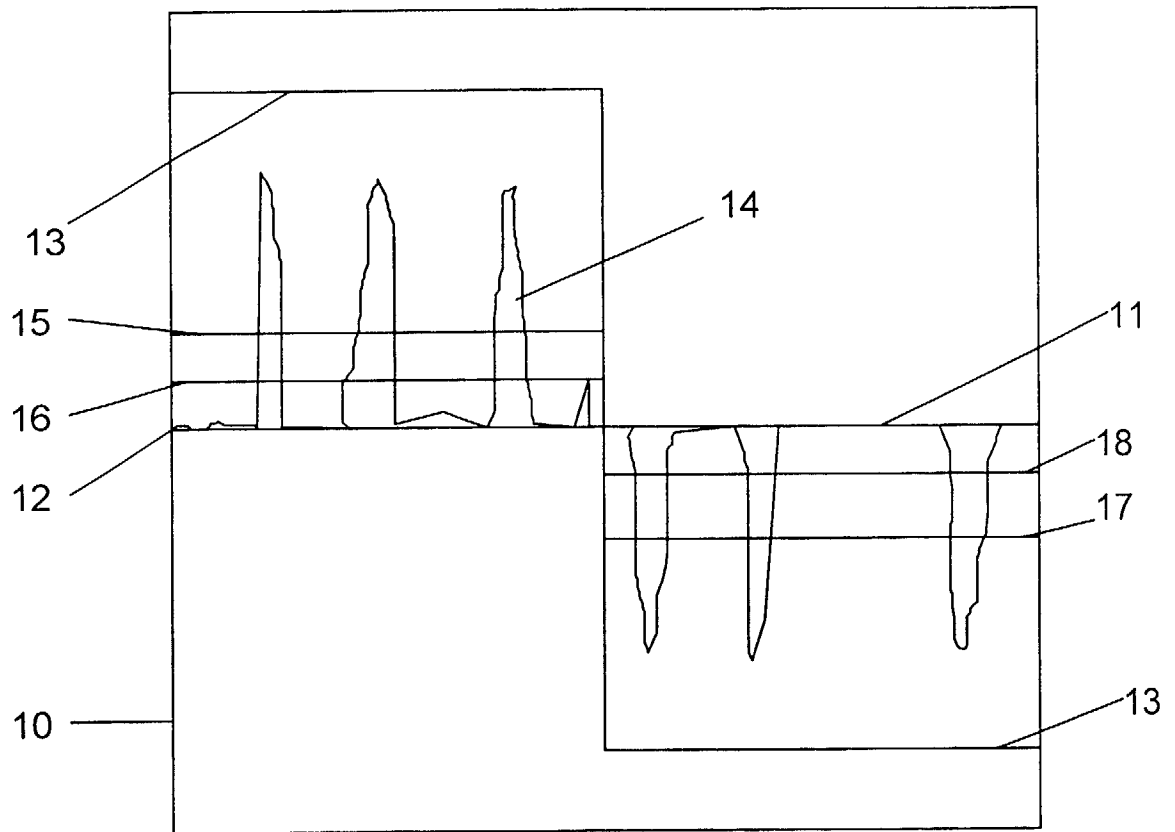
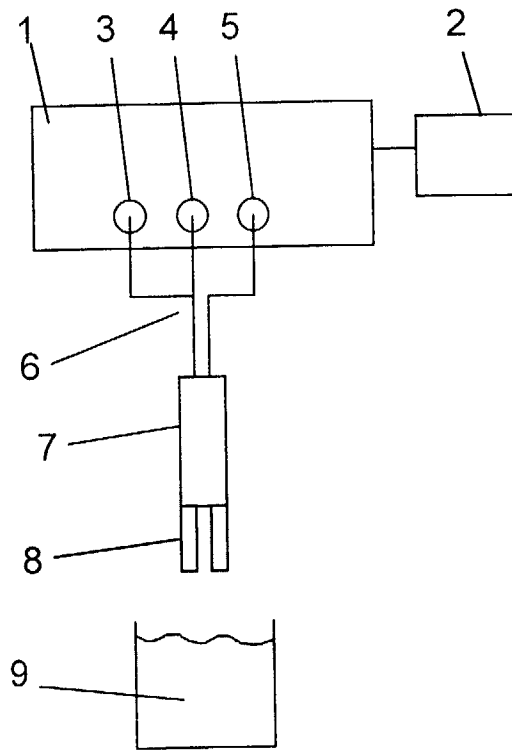


FIG.1



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 = I_a , is calculated as the absolute values of I(15) plus I(17) divided by 2.

$$\text{Thus } I_a = \frac{\text{Absolute } I(15) + \text{Absolute } I(17)}{2}$$

V_s represents the average of the Absolute magnitude of the Square Wave Polarisation (13), where V_1 is the magnitude of the first half and V_2 is the magnitude of the second half. In most cases, V_1 and V_2 will be of the same value but of opposite sign.

$$V_s = \frac{\text{Absolute } V_1 + \text{Absolute } V_2}{2}$$

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

$$R_p = V_s / I_a$$

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)).

$$Rp(S) = \frac{100 * Rp}{\%D}$$

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.

CLAIMS

1. A corrosion monitoring device for multiple phase solutions in which potential polarises a two-electrode corrosion probe to produce a current response monitored at a known read rate and manipulated to give the average corrosion rate and the corrosivity of the conductive phase.
- 2: A corrosion monitoring device as claimed in claim 1, in which the magnitude of the polarisation signal is substantially bigger than the typical natural fluctuations in potential experienced by an otherwise isolated specimen.
- 3: A corrosion monitoring device as claimed in claim 1 and 2, where the resulting absolute mean of the current response is used to calculate the average corrosion rate.
4. A corrosion monitoring device as claimed in claim 1,2 and 3, where the resulting absolute mean of the current response is multiplied by a percentage, typically close or equal to 50%, but otherwise away from 0% or 100%, to give a value known as half the absolute mean corrosion current.
5. A corrosion monitoring device, as claimed in claim 1, 2,3 and 4 where the inverse of the percentage time the absolute monitored current exceeds the absolute half mean corrosion current, is used to multiply the average monitored corrosion rate, to give a value of the corrosivity of the conductive phase.
- 5: A corrosion monitoring device as claimed in claim 1, where the two electrodes are of different material and are first offset to their individual rest potential.
- 6: A corrosion monitoring device as claimed in claim 1, in which a small pause in readings is applied at the start of a change in polarisation potential, in order to allow the electrodes to settle after initial polarisation.
- 7: A corrosion monitoring device substantially as herein described and illustrated in the accompanying drawings.



INVESTOR IN PEOPLE

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Claims searched: 1-7

Examiner: Dave Mobbs
Date of search: 14 December 2001

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Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK Cl (Ed.S): G1N NBMR.
Int Cl (Ed.7): G01N 17/02.
Other: ONLINE: EPODOC, JAPIO, WPI.

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	US 3,840,439 (UNION OIL CO.)	
A	US 3,660,249 (MAGNA CORP)	
A	JP 100206370 A (MITSUBISHI CHEM CORP) - see abstract.	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.