

# **KH Design and Development**

Electrochemical Corrosion Measurement and Control Consultancy

9 Victoria Grove, Fallowfield, Manchester M14 6BF, UK

Tel./Fax: +44 161 225 9712

e-mail: [khladky@khdesign.co.uk](mailto:khladky@khdesign.co.uk)

www: <http://www.khdesign.co.uk>

## **OVERVIEW OF ELECTROCHEMICAL CORROSION MONITORING TECHNOLOGY**

**July 2005**

Prepared for:

Pepperl+Fuchs, Inc.  
1600 Enterprise Parkway  
Twinsburg,  
Ohio 44087  
USA

## Overview of Corrosion Monitoring Technology

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### 1. INTRODUCTION

This report presents an overview of electrochemical corrosion monitoring technology and intellectual property relating to the Pepperl+Fuchs CorrTran device and was compiled at the request of Pepperl+Fuchs Inc.

### 2. BACKGROUND OF THE MEASUREMENT TECHNIQUES

#### 2.1. Electrochemistry of mixed potential electrodes.

Corrosion of metals usually occurs as an electrochemical dissolution process.

At the anode, metal atoms oxidise to metal ions. The metal anions then either react further with the surrounding electrolyte to form soluble or insoluble corrosion products or simply diffuse away from the metal surface. Electrons are produced by the anodic process.

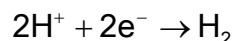
In general:  $M \rightarrow M^{n+} + ne^{-}$

At the cathode, a corresponding reduction reaction takes place, consuming the generated electrons. The rates of the anodic and cathodic process, the anodic and cathodic currents (not current densities) must match, as there can be no net build-up of electrons in the metal.

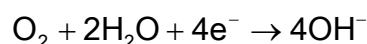
The anodic and cathodic reactions cannot occur at the same point on the electrode surface. In the case of uniform corrosion, they will normally occur at microscopically adjacent points on the metal surface, the anodic and cathodic areas will move in time across the electrode surface. In the case of pitting corrosion, the pit will form the anodic area whereas the surrounding surface will be predominantly cathodic.

The relative sizes of the anodic and cathodic areas are important as the rate of penetration is determined by the current density (current per unit area). In the case of pitting corrosion a large cathodic area of a relatively small cathodic current density may support a high anodic current density (and hence penetration rate) in a small anodic area of the active pit.

In acid aqueous environments, the cathodic reaction is usually that of hydrogen evolution.



In neutral and alkaline aqueous environments, the cathodic reaction can be that of oxygen reduction.



There are two aspects to electrochemistry: thermodynamics and kinetics. Thermodynamical considerations determine whether a reaction can occur at particular pH and overpotential levels, kinetic considerations then determine the rate of that reaction. For example, at a particular pH and overpotential, the oxygen reduction

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reaction may be thermodynamically possible but due to a very low concentration of oxygen in the solution, its rate could be very low. Overpotentials are measured with respect to a reference electrode (a half-cell).

Each of the anodic and cathodic reactions will have a reversible potential – at some potential the rate of the forward process (e.g. metal oxidation and dissolution) will equal that of the reverse process (e.g. metal ion reduction and re-deposition onto the metal surface).

Hence, even in the simple situation where the anodic process is metal dissolution and the cathodic process is hydrogen evolution there will in fact be four processes possible. In practice, the anodic and cathodic reactions will be polarised away from their reversible potentials to some common potential – the mixed or ‘free corrosion’ potential,  $E_{\text{corr}}$ . This causes the metal dissolution direction of the anodic reaction to be preferred and similarly the hydrogen evolution direction of the cathodic reaction will predominate.

Assuming that both the anodic and cathodic corrosion processes can be described by the Butler-Volmer equation and that the free corrosion potential is sufficiently far from the reversible potentials of the two partial reactions, then the potential-current response of a corroding electrode is given by:

$$I = I_{\text{corr}} \left( \exp\left(\frac{\Delta E}{b_a}\right) - \exp\left(-\frac{\Delta E}{b_c}\right) \right)$$

where  $\Delta E$  is the applied overpotential from  $E_{\text{corr}}$  and  $b_a$  and  $b_c$  are the anodic and cathodic Tafel constants (related to the Tafel slopes  $\beta_a$  and  $\beta_c$  by  $b = \beta/\ln 10$ ).

The Tafel slopes are relate to temperature etc. by:

$$\beta_a = \frac{RT}{\alpha_a z_a F} \qquad \beta_c = -\frac{RT}{(1-\alpha_c) z_c F},$$

where R is the universal gas constant, T absolute temperature, F the Faraday constant,  $z_a$  and  $z_c$  the number of electrons transferred in the anodic and cathodic reactions, and  $\alpha_a$ ,  $\alpha_c$  the reaction symmetry factors. In practical terms,  $\beta$  is about 120 mV at room temperature for a single electron transfer, 60 mV for a two electron process etc.

Expansion of the exponentials as series, neglecting higher power terms and rearranging gives:

$$I_{\text{corr}} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \times \frac{1}{R_p}, \quad \text{where the polarisation resistance } R_p = \frac{\Delta E}{\Delta I}$$

This is the Stern-Geary equation, which forms the basis for the linear polarisation resistance method of corrosion rate measurement. It simply states that the corrosion current may be calculated from the slope of the potential-current curve at the free corrosion potential (polarisation resistance); the proportionality constant being related to the Tafel slopes.

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In practice, pure activation control assumed in these calculations may not exist – the rates of the anodic, cathodic or both processes may be limited by for example the rate of diffusion of reacting species to and from the electrode surface. The above equations may be modified to take diffusion (also termed concentration) control of one of the reactions into account - the Tafel constant of the diffusion limited process will tend to infinity.

For example, if the cathodic process is diffusion limited then:

$$I_{\text{corr}} = \frac{\beta_a}{2.3} \times \frac{1}{R_p}$$

It is important to note that these forms of the Stern-Geary equation also assume that the areas of the anodic and cathodic processes are equal – this will rarely be the case in practice.

In practice the Stern-Geary constant is often determined by comparison to weight loss data, it usually lies somewhere in a relatively narrow range of between about 10 and 50 mV.

The potential-current response of an electrode corroding under activation control is the difference between two exponential curves, that describing the anodic process and that describing the corresponding cathodic process. The response is near linear at the corrosion potential; the amount of curvature depends on the values of the Tafel constant parameters.

In such a situation it is possible to use a measurement of the curvature of the curve to calculate the values of the Tafel constants and hence the corrosion current and the rate of metal loss. The harmonic distortion and harmonic intermodulation techniques do just that.

### 2.2. Corrosion Potential Measurements

Perhaps the simplest measurement that can be carried out on a corroding test electrode is that of the free corrosion potential measurement,  $E_{\text{corr}}$ . As explained above,  $E_{\text{corr}}$  is a potential at which the currents of the anodic and cathodic processes occurring on the test electrode equal. It will lie somewhere between the reversible potentials of the anodic and cathodic reactions. Its precise value depends on the rates of the anodic and cathodic processes, on the nature of the control of these processes (e.g. activation, diffusion etc.) and on the relative sizes of the anodic and cathodic areas.

Measurement of  $E_{\text{corr}}$  does not give any information as to the rate of the dissolution process.

Measurement of the fluctuations (short term changes) of  $E_{\text{corr}}$  forms the basis of electrochemical potential noise (EPN) measurement. The principle is that localised dissolution events, such as pit initiation, result in a short term increase in the anodic current at the active locations on the electrode surface and hence in a corresponding change in  $E_{\text{corr}}$ .

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$E_{\text{corr}}$  and EPN may be measured against a true reference electrode (an electrode which has a well defined and stable potential, e.g. a calomel or Ag/AgCl electrode), or against a second electrode, 'identical' to the test electrode. In the latter case, the observed fluctuations may originate from either of the two electrodes. Measurement must be carried out using a high input impedance voltmeter as not to perturb the test and reference electrode potentials by the measurement current.

### 2.3. Zero Resistance Ammetry

Zero resistance ammetry (ZRA) uses a current to voltage converter to measure the current flowing between two electrodes. The ZRA circuit minimises the voltage drop across the current measuring device by the gain of the ZRA amplifier.

As outlined above, the anodic and cathodic reactions on a corroding electrode cannot occur at the same points on the electrode surface. In practice, at any point in time, parts of the electrode surface will form an anode and the remainder of the surface will be the cathode. With time, the anodic and cathodic regions will move and change. This is especially true in situations of low corrosion rate or when concentration or diffusion effects, such as oxygen diffusion or passive film formation, limit the corrosion rate.

The ZRA technique is normally used to measure galvanic currents between dissimilar electrodes. When applied to a pair of nominally 'identical' electrodes, no current should flow between the electrodes. In practice, due to the separation and constant movement of the anodic and cathodic areas on each of the electrodes, a measurable current will flow and its polarity and magnitude will change in time.

Perhaps the best way to visualise the effect is to consider a single electrode with separate anodic and cathodic areas. A current will normally flow through the metal between these two regions. The ZRA technique then effectively physically divides this electrode into two and measures the current flowing between the two halves. Most of the current will flow between adjacent anodic and cathodic sites on each of the electrodes, but a proportion will flow between say an anodic site on one of the electrodes and a cathodic area on the other electrode.

The effect is more pronounced if localised corrosion, such as a pit initiation, occurs on one of the electrodes. The small anode of the pit will draw current not only from the adjacent cathodic area on the same electrode but also from the cathodic areas of the other electrode, resulting in current flow through the ZRA.

This is the basis of the electrochemical current noise measurement (ECN).

The ECN technique uses measurement of both the fluctuations (noise) of the ZRA current and the ZRA current mean (dc) to estimate the degree of localisation of the corrosion attack. The localisation 'factor' is usually defined as some ratio of the standard deviation of the current fluctuations to the mean (dc) ZRA current. As can be seen from the above considerations, neither of these values accounts for all of the anode-cathode current flow at either of the electrodes and hence any such calculated parameter will be only qualitative.

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### 2.4. Electrochemical Resistance Noise

It is possible to measure both EPN and ECN at the same time. This involves a measurement of the ZRA current, as described above, together with a simultaneous measurement of the potential of the ZRA coupled electrodes against a reference electrode.

An additional, often employed, step is an attempt to relate the potential and current fluctuations, usually by computing the ratio of the standard deviations of the potential fluctuations to that of the current fluctuations – electrochemical resistance noise (ERN).

This only makes sense if the two are causally related, i.e. if any change in the potential and current is caused by the same localised corrosion event occurring on one or other of the ZRA coupled electrodes. In order to ensure that this is true, the potential noise must be measured using a 'noise-free' reference electrode, otherwise localised corrosion events could occur on the 'reference' electrode, giving rise to potential fluctuations, which would have no corresponding related current changes.

Also, since as outlined above, not all of the current between an anodic site and the corresponding cathodic area is intercepted by the ZRA, it is difficult to see how the computed ERN values can be anything more than quantitative estimates and how the ERN value could be used in place of the polarisation resistance parameter to compute the corrosion current and penetration rate.

### 2.5. Potential-Current Response Measurement

The third possible electrochemical measurement is that of a determination of the voltage-current response of the corroding electrode.

Either a current or potential perturbation is applied from an external source to the test electrode and the resulting change in the potential or the resulting current flow is measured.

The potential-current response of a corroding electrode is in principle described by the mixed potential Butler Volmer equation. This indicates that the E-I response should be the difference between two exponential curves (anodic and cathodic reactions). It can be shown that at a potential ( $E_{\text{corr}}$ ) where the anodic and cathodic currents are equal (and equal to  $I_{\text{corr}}$ ) and at potentials nearby the total E-I response will be approximately linear, the slope being  $R_p$ , the polarisation resistance.

It is crucial to be aware of the assumptions made in the usual mathematical derivation of the Stern-Geary equation. The following are three of the most important:

Firstly, it is normally assumed that both the anodic and cathodic processes are activation (charge transfer) controlled. The derivation may be extended to cover concentration (diffusion) control of the rates of either the anodic or the cathodic processes – essentially the appropriate Tafel constant tends to infinity in that case.

Secondly, the derivation assumes that the corrosion potential is far removed from the reversible potential of either the anodic or the cathodic reaction. This implies that the rates of the back half reactions of these processes (e.g. metal deposition etc.) are so low as to be negligible. This will be true in many practical situations and the derivation

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can be expanded to include situations where  $E_{\text{corr}}$  lies near one of the reversible potential. However, the activities of the reacting species must then be considered – these are in general difficult to determine exactly in practice.

Thirdly, the simple derivation assumes that the corroding electrode is both an anode and a cathode at the same time or that the anodic and cathodic areas are exactly equal. This is nearly true in cases of uniform corrosion at a high rate, but not true for localised corrosion attack.

In its basic form the measurement of linear polarisation, resistance simply involves the application of a small overpotential (10-20 mV) and a measurement of the resulting current. If the applied overpotential does not polarise the electrode outside the 'linear' region then the slope of the potential-current curve (polarisation resistance) may be determined and the corrosion current estimated.

In order to convert the estimated corrosion current to penetration rate it is then usually assumed that all of the electrode area undergoes corrosion attack (conversion to current density) and that the electrode material is homogeneous and a given number of electrons are transferred in the dissolution reaction (conversion to mass loss using Faraday law).

A further measurement complication arises due to the existence of the electrochemical double layer and the time dependence of any diffusion processes. The double layer capacitance (usually of the order of  $30 \mu\text{F}\cdot\text{cm}^2$  for aqueous systems) appears in parallel to the polarisation resistance, any diffusion related time dependent terms appear in series with the polarisation (or more accurately, charge transfer) resistance. This means that it is the electrode impedance, which is actually being measured - electrochemical impedance spectroscopy is a field of electrochemistry devoted to the study of the variations of the electrode impedance at different frequencies.

The response of the test electrode current (or potential) to a voltage (or current) perturbation will hence depend not only on the shape of the dc E-I curve but also on the impedance of the test electrode at the measurement frequency (or range of frequencies if the perturbation is for example a voltage step or a voltage ramp).

### 2.6. Harmonic analysis

The techniques of harmonic distortion or intermodulation analysis (HAD or HIA) attempt to measure the curvature or shape of the E-I response and hence to calculate the constants controlling the equations describing the anodic and cathodic processes.

It can be shown that in cases where both the anodic and cathodic processes are activation controlled the values of the Tafel slope constants and the corrosion current may be calculated either from the amounts of harmonics generated when the perturbation is a low amplitude sine waveform, or from the magnitudes of intermodulation products, when the perturbation is the sum of two sine waveforms of differing frequencies.

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For example:

$$I_{\text{corr}} = \frac{I_1^2}{\sqrt{48(2I_1I_3 - I_2^2)}}$$
$$\beta_a, \beta_c = \frac{I_2 \pm \sqrt{(48I_1I_3 - I_2^2)}}{I_1}$$

where  $I_1$ ,  $I_2$  and  $I_3$  are the amplitudes of the fundamental, second and third harmonics of the cell current.

Detailed derivation of the theory of the intermodulation measurement procedure, including considerations of cases where either the anodic or cathodic process is diffusion limited, are presented in Corrosion, 57, 1, pp 60-70.

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### 3. INTELLECTUAL PROPERTY HISTORY

#### 3.1. Electrochemical Noise

The first publication noting fluctuations of the natural corrosion potential (electrochemical potential noise, EPN) was by Warren P. Iverson (Iverson W.P., J. Electrochem. Soc. Electrochemical Science, pp 617-618, June 1968). Iverson noted that fluctuations of the free corrosion occurred on metals, which were susceptible to localised corrosion attack (e.g. aluminium) and did not occur on inert materials such as platinum. Fluctuations of a lesser amplitude were observed on metals undergoing general corrosion attack, such as steel.

The subject was independently re-visited by Hladky, Callow and Dawson in the late 70's and early 80's. Hladky and Callow were engaged as post-doctoral workers in the Corrosion and Protection Centre at the University of Manchester Institute of Science and Technology (UMIST) on two research contracts sponsored by the UK Ministry of Defence and I.C.I., looking at novel corrosion monitoring techniques in a research group lead by Dawson. In the course of their investigations using electrochemical impedance spectroscopy, Hladky and Callow noted that measurements were often degraded by fluctuations of the test cell potential and current. The fluctuations appeared to occur mainly at low frequencies (< 1Hz) and could not be removed by time domain averaging of the measurement signals.

Hladky and Callow decided to investigate the origin of these fluctuations in detail and to determine whether analysis of the fluctuations could provide information relating to the corrosion processes occurring on the test electrodes. At this stage Hladky, Callow and Dawson were unaware of the prior Iverson publication.

Tests and measurements were carried out on a variety of corroding systems of interest to the sponsors of the projects and the results were reported in internal progress reports. It soon became apparent that the fluctuations originated from localised corrosion attack events, such as pit or crevice initiation. Hladky and Dawson (Hladky K. and Dawson J.L., Corrosion Science 21, pp 317 to 322, (1981)) published the results of the initial investigations. This paper describes an analog qualitative method of measurement of the corrosion potential fluctuations relating to pitting corrosion initiation.

Further work was then carried out in order to quantify the measurements. This was published by Hladky and Dawson in a second paper (Hladky K. and Dawson J.L., Corrosion Science 22, 3, pp 231 to 237, (1982)). This paper describes a digital method of measurement of the corrosion potential fluctuations and their analysis in terms of frequency spectra. The authors note that different types of localised corrosion attack generate potential fluctuations of differing frequency content. They also note that the standard deviation of the fluctuations seems to be directly related to the intensity of the attack.

At this stage (late 1981), the sponsors of the project and UMIST decided, despite objections from Hladky, that the technique should be patented. A provisional patent application was submitted on 5<sup>th</sup> January 1982, just prior to a publication of further results at a research conference held at UMIST in January 1982. Further work by Hladky covered measurements in a variety of other corroding systems, including I.C.I.

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chemical plant and MoD cavitation rigs. Hladky also improved the data analysis technique by the use of the maximum entropy method of spectral analysis.

The electrochemical noise technique was also adopted by a second research group at the Corrosion and Protection Centre, UMIST, lead by Scantlebury and including Callow, Eden, Gill and others.

In September 1982, Hladky left the Dawson research group and joined the Corrosion and Protection Centre Industrial Services (CAPCIS), a consultancy organisation owned by UMIST and working closely with the Corrosion and Protection Centre academic department.

Work on electrochemical noise continued in both the research groups (Dawson and Scantlebury) and in CAPCIS. In the Scantlebury group, Eden further developed measurement of electrochemical current noise (ECN) and Gill developed and applied the harmonic distortion analysis (HDA) technique. Cox, Mok, John and others in the Dawson research group applied the electrochemical noise technique to a variety of corroding systems, including high temperature corrosion.

Between 1983 and 1986 other workers from the Corrosion and Protection Centre joined CAPCIS (Eden, Cox, Aylott etc.) and electrochemical noise measurements were made on a number of projects for external clients. Computer software was developed to capture and analyse electrochemical noise data, both in terms of its statistical parameters (means, standard deviations, skewness, kurtosis etc.) and in terms of frequency spectra.

At the time the data analysis was severely limited by the power and storage capacity of the then available computers and much of the analysis was carried out by visual inspection of the plotted electrochemical noise traces (either as EPN or ECN plots with time or as some of the statistical parameters plotted against time).

The electrochemical noise technique formed a part of the CAPCIS Multi-technique corrosion monitoring system (MUSYC), together with two frequency ac impedance measurement, ZRA coupling current measurement and others, using circuitry developed by Hladky for CAPCIS.

At about 1986, a decision was made to commercialise the corrosion monitoring work in CAPCIS and a separate company, CAPCIS-March Ltd., was set up for that purpose. Eden, Cox and others joined CAPCIS-March Ltd. whereas Hladky remained in employment of UMIST and on secondment to CAPCIS Ltd.

A second patent was applied for in 1986 by Eden, John and Dawson to cover ECN measurements. This patent covered the simultaneous measurement of EPN and ECN using a three electrode arrangement and a zero resistance ammeter (ZRA). It also included the computation of electrochemical resistance noise.

In 1994, Hladky left CAPCIS to set up his own consultancy, KH Design and Development. Eden, Cox and others continued working for CAPCIS-March Ltd. and RTCML. Gill and Gill set up an instrumentation company of Applied Corrosion Monitoring Ltd. (ACM).

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CAPCIS-March Ltd. run into financial difficulties in 1993 and was purchased by MacKenzie Investments, a Scottish venture capital partnership. The company was then re-formed as Real Time Corrosion Management Ltd. (RTCML). RTCML went into liquidation in 1997, owing substantial amounts to its creditors, and was recreated by MacKenzie and his other technology company, Diagnostics and Measuring Systems Ltd. (DMS), with a further injection of venture capital, as Integriti Systems Ltd. In 2003 Integriti purchased US based Intecorr Inc. with more venture capital, became Intecorr International Ltd. and relocated to the US. At present (2005), Intecorr are being purchased by Honeywell Inc.

Eden and others have applied for and have been granted a number of other patents in course of their employment with CAPCIS-March Ltd. and its later incarnations. Clients of CAPCIS and CAPCIS-March/Integriti/Intecorr have also been granted several patents, mainly relating to specific applications of the technique. After 1991 further patents were granted to companies such as Mitsubishi in Japan (connected through Cox to the original research group), Baker Hughes (possible connection through Gill and ACM) and Gamry (a competitor to ACM). Academic work also continued in the Corrosion and Protection Centre UMIST under Cottis.

### **3.2. Harmonic Distortion Analysis**

This technique is largely in the public domain. Following the initial publication by Meszaros, a number of workers have used the technique. Workers in the Corrosion and Protection Centre UMIST (Gill, Scantlebury, Callow and others) have published a number of papers describing its use.

Two patents have been granted to McKubre and Syrett (1987 and 1991).

Currently the technique is commercially used in the Intecorr and P+F on-line corrosion monitoring devices and is supported by laboratory equipment manufacturers such as Gamry, Solartron and ACM in their hardware and software for laboratory corrosion measurements.

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### 4. PATENTS

#### 4.1. Electrochemical Noise

The tables below list electrochemical noise related patents and patent applications currently in existence. The following is a summary of the key features of the important patents.

##### **US 4,575,678 Hladky**

This is the original patent on the electrochemical potential noise (EPN) measurement technique. It describes the measurement of low level fluctuations of the free corrosion potential of a single corroding electrode measured with respect to a second electrode. The second electrode can be a similar corroding electrode, an inert electrode or a reference electrode. The patent then claims that the standard deviation (or root mean square) of the amplitude of these fluctuations may be used to provide a measure of the rate of dissolution of the corroding electrode. Additionally, the patent claims that localised corrosion such as crevice attack or pitting corrosion may be detected by examination of the form of the fluctuations (e.g. sharp peaks etc.), after filtering the signal with a bandpass filter. The output of the filter may be monitored and used to control inhibitor injection or gas bubble injection (in case of cavitation corrosion).

In the body of the patent, the text describes the measurement and analysis of the electrochemical potential noise signal using either analog filtering or digital frequency spectrum analysis techniques. It is suggested that different forms of localised corrosion attack give rise to frequency spectra of differing slopes and shapes and that the rate of localised corrosion attack is directly proportional to the standard deviation of the noise signal.

The patent priority date was 5<sup>th</sup> January 1982 and hence it had now expired.

##### **US 5,139,627 Eden, John and Dawson**

This is the original patent on the electrochemical current noise (ECN) measurement technique. It describes measurement of both the fluctuations and the mean value of the coupling current between two electrodes made of the same material and exposed to the same environment using a zero resistance ammeter (ZRA) circuit. Additionally, the electrochemical potential noise (EPN) of the two coupled electrodes and a third electrode may also be measured. Several parameters may be calculated, these being the ratio of the EPN/ECN magnitudes (resistance noise), the ratio of the ECN magnitude and the magnitude of the dc component of the coupling current (pitting index). Corrosion rate is also calculated from the foregoing.

The claims do not specify the method of determining the current noise magnitude; this is implied in the body of the patent as being the standard deviation of the current fluctuations.

The body of the patent includes a table of values of the ratio of ECN to the dc coupling current value and a description of the ranges of these values relating to localised corrosion and pitting. Some convoluted simple algebra is used in an attempt to show how the corrosion rate can be calculated from the three measured parameters.

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Note that this patent does not describe a situation where the electrodes are in under potentiostatic control – i.e. where the potential between one electrode (test) and a second electrode (reference) is forced to zero by the application of external current through a third electrode (auxiliary).

This patent had expired on 18<sup>th</sup> August 2004 due to non-payment of fees.

### **US 5,425,867 Dawson, Eden and Carr**

This patent covers what was at the time prior art, namely the computation of EPN and ECN spectra from data obtained using a three electrode ZRA arrangement. The body of the patent describes a situation where one electrode of the ZRA connected couple is a coated sample, the second electrode is then made of an inert metal and is placed in the electrolyte outside the coating. A third (reference) electrode is also placed in the electrolyte outside the coating. A procedure is described whereby the impedance spectrum of the coated sample is determined from the EPN and ECN spectra, these spectra being computed using the maximum entropy method. The specific application described is that of coatings evaluation. There is some doubt as to whether the described frequency and impedance spectra actually relate to those of the tested specimen or whether they are an artefact of the spectral analysis method.

This patent had expired on 20<sup>th</sup> June 2003 due to non-payment of fees.

### **US 5,151,163 Miller**

This patent describes the measurement of electrochemical noise between a pitting sample and an inert electrode. It is not clear whether EPN or ECN is measured (the patent terms electrochemical noise as ECN). The patent claims that by plotting the frequency spectra of the measured noise signal and computing their range (max – min) the pit initiation rate may be estimated.

### **US 6,015,484 Martinchek and Yaffe**

This patent describes a three electrode arrangement with a ZRA between two of the electrodes to be used to measure EPN and ECN. A dc current bias is applied in order to promote pitting corrosion on the test electrode. Of the three electrodes, two are made of the test material; the third may be an inert reference electrode. Alternatively, the test electrode may be the plant item itself. Either statistical processing or transform into the frequency domain are used to relate the EPN and ECN signals to localised corrosion propensity.

### **US 6,264,824 Reid and Eden**

This 70+ page patent relates to the analysis of EPN and ECN signals using neural networks with a view to recognise signal patterns corresponding to the various forms of localised corrosion attack.

Measurement of ECN is carried out using a pair of similar electrodes connected through a ZRA, EPN is measured using a third (reference) electrode. The resulting noise time variations are digitised and their statistical properties (mean, standard deviation, skewness and kurtosis) are computed.

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The body of the patent describes in some detail the process of training a neural network for the recognition of the signal patterns, which is a standard procedure used in neural network design. The process of computing the higher statistical parameters (skewness and kurtosis) is also a standard practice and had in fact been used by Hladky and other workers in CAPCIS since approximately 1983.

The originality of the patent only appears in Claims 22, 24 and 27, which claim the means of computation of the higher statistical parameters to be a neural network. This is somewhat misleading, since in practice a neural network would not be used for the computation as such, but rather for the differentiation between sets of parameters.

### **WO0034759 Eden**

This patent is a precursor of the approach used in the SmartCET and CorrTran devices. The patent describes the use of a two electrode system where one electrode is formed by the surface of the plant item itself and the other if an electrically insulated probe element made of the plant material.

The measurement procedure uses a cycle of three techniques. Firstly, ECN measurement is carried out either with or without added dc bias. The ECN response is analysed in terms of its statistical parameters or by frequency domain analysis and localised corrosion rate is calculated from the mean dc current and ECN. After a period of time, a low frequency sine waveform is applied to the two electrodes and harmonic distortion analysis is used to determine corrosion current density and the Tafel slope constants. Finally, a high frequency (2 kHz) waveform is used to measure the conductivity of the environment.

The patent does not include any details of the measurement circuitry.

### **US 6,280,603 Jovancicevic**

This patent was assigned to Baker Hughes Inc (Petrolite). Petrolite has a long history of supply of corrosion monitoring equipment.

This is the first patent, which uses a three electrode potentiostat arrangement to measure ECN. The method used is that of a three stage cycle. The free corrosion potential of a test electrode is measured with respect to a reference electrode for a period of time to obtain an EPN response. The corrosion potential at the end of the EPN period is stored, the cell is brought under potentiostatic control and the potential is held at the stored value while the resulting cell current is recorded as ECN. In the third period of the cycle, the potentiostatic control is removed and the test electrode is allowed to recover. The cycle is repeated as necessary. Corrosion rate is computed from the changes in the dc values of the potential and current at various points in the test cycle.

It should be noted that the patent text and figure numbering are somewhat unclear in parts and that the claims are poorly formulated.

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### **US Patent Application 2004/0149594 Eden**

This is a patent application for the technology used in the SmartCET and CorrTran devices, namely the measurement of corrosion rate using harmonic distortion analysis and electrochemical noise measurement using a three electrode potentiostatic circuit.

The sequencing of the measurement, i.e. the measurement of the harmonic distortion, followed by a measurement of electrochemical noise and a measurement of the electrolyte conductivity, is described in the body of the patent but is not included in the claims.

Close examination of the 42 claims of the patent reveals nearly all of them to be prior art.

Claim 1 is a combined description of electrochemical noise measurement (ECNM) and harmonic distortion analysis measurement (HDAM), both being prior art at the time of submission of the application. Claims 2 and 3 expand the scope of Claim 1.

Claim 4 is possibly innovative in that it describes a comparison of the results of the ECNM and HDAM techniques. However, the comparison of results obtained by different measurement techniques is normal practice in scientific investigations.

Claims 5 and 6 define the probe electrode arrangement and are self-evident.

Claim 7 defines that potential difference between two of the three electrodes shall be maintained at zero volts during the measurement. This is what a ZRA measurement does and hence this is prior art.

Claims 8 and 9 and 12 describe measurement of EPN and ECN by periodic sampling of the signals. This is a standard practice in analog to digital conversion and prior art.

Claims 10 and 11 describe the computation of statistical descriptors of the current noise signal. This is a standard practice in the statistical analysis of experimental data and not an innovative step.

Claims 13 and 14 describe the same process relating to the EPN measurements.

Claims 15 and 16 describe the application of a low frequency sinusoid to the test electrode. This is a standard practice in electrochemical impedance spectroscopy and not an innovative step.

Claim 17 covers a situation where the perturbing signal is applied during the noise data acquisition. It would not make sense to do this in practice.

Claim 18 describes the measurement of a current response by measuring the current flowing. This is a standard and a self-evident method of current measurement.

Claims 19 and 20 describe the computation of the standard deviations of the EPN and ECN signals. This was already described in foregoing claims and is prior art.

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Claim 21 describes the analysis of the harmonic content by periodic sampling of the signal. Periodic sampling of a signal is a standard practice in digital measurement and alone cannot provide harmonic content information.

Claim 22 describes analysis of the current response signal in terms of its harmonic components. This is the principle of harmonic analysis and is prior art.

Claim 23 describes the Discrete Fourier Transform (DFT) method, a well established prior art.

Claim 24 is possibly innovative as it describes a comparison of the measured ECN standard deviation to the current response of the test electrode at the fundamental frequency of the applied sine waveform.

Claim 25 is as Claim 23 prior art, here applied to the second harmonic frequency.

Claim 26 is as Claim 24, again possibly innovative and concerning the second harmonic of the applied sine waveform.

Claim 27 is as Claims 23 and 25, here concerning the third harmonic.

Claim 28 involves the computation of the corrosion current from the harmonic data. This is well established prior art.

Claim 29 involves a comparison of the calculated corrosion current and the standard deviation of the ECN signal. In some aspects, this could be considered innovative.

Claims 30, 31 and 32 describe the calculation of Tafel and Stern-Geary constants from the harmonic data. This is well established prior art.

Claim 33 describes a comparison of the Stern-Geary constant to the standard deviation of the EPN signal. This could be considered a novel step, although in practice it equates to comparing two physically unrelated quantities.

Claim 34 describes the standard method of corrosion rate calculation using the linear polarisation resistance technique.

Claims 35 to 41 describe additional mathematical manipulations of the measured data, being an attempt to patent a set of mathematical formulas.

### **WO3106976 Cottis**

This patent describes an innovative electrochemical noise measurement technique, which may however be difficult to implement in practice.

The described technique involves a simultaneous measurement of the test electrode EPN or ECN together with a measurement of the test electrode impedance. A single test electrode is used made of the plant item material together with a reference electrode and an inert auxiliary electrode. The circuit arrangement is that of a potentiostat or galvanostat. When under potentiostatic control the ECN signal is measured and the EPN signal is calculated using the measured test electrode

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impedance. In the case of galvanostatic control the situation is reversed, i.e. EPN is measured and ECN calculated.

In the potentiostat arrangement, the potential of the test electrode is held at some level (which could be equal to the free corrosion potential) and a small perturbation is applied around this potential. The current response of the test electrode is filtered as to recover the response at the perturbation frequency and the test electrode impedance is computed using standard techniques. The remaining current signal is analysed using ECN analysis techniques. EPN is calculated from the ECN data and the test electrode impedance (which will vary with frequency).

### Other Patents

The remaining patents tend to deal mainly with specific applications of the electrochemical noise technique and range from interesting to completely bizarre (US6524466 and US6551491). The Mitsubishi patents are only available in Japanese.

## 4.2. Harmonic Distortion Analysis

There are two relevant patents in existence, both by Syrett and McKubre.

### US 4,658,365 Syrett and McKubre

This patent relates to the measurement of harmonic distortion on cathodically polarised electrodes. A sinusoidal voltage is superimposed onto the cathodic protection voltage. The resulting current is analysed in terms of the rectified dc value and the amplitudes of the harmonic components (0 to 5). An iterative computation method is then used to calculate the anodic dissolution current at the cathodic protection voltage and hence the metal dissolution rate.

### US 5,006,786 McKubre and Syrett

This follow-up patent extends the applicability to general corrosion rate measurement at any overpotential, including freely corroding electrodes.

The body of the patent presents a derivation of the harmonic distortion analysis equation arriving at the Meszaros formula. A similar equation is derived for the case of overpotentials other than zero. The body of the patent carefully notes the scope of applicability of the technique – i.e. only to systems under activation (Faradaic) control. In as far as it is possible to patent a mathematical formula this patent covers the measurement of corrosion rate using harmonic distortion analysis.

Similar European and Japanese patents have also been granted to the authors.

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Patent Number	Issue Date	Priority	Expired	Inventor	Assignee	Title	Summary
US4575678	11 Mar 1986	05 Jan 1982	05 Jan 2002	Hladky	UMIST	Corrosion monitoring	Original EPN patent. Measures EPN from a test electrode and a reference electrode. Uses FFT to analyse noise spectra. Suggests standard deviation related to amount of localised activity.
US5139627	18 Aug 1992	12 May 1986	18 Aug 2004	Eden, John, Dawson	CAPCIS Ltd	Corrosion monitoring	Original EPN and resistance noise patent. Measurement of ECN from two electrodes with a ZRA and EPN with a reference electrode. Calculates resistance noise and pitting index.
US5425867	20 Jun 1995	23 Mar 1991	20 Jun 2003	Dawson, Eden, Carr	Capcis March Ltd	Method and apparatus for producing electrochemical impedance spectra	Measurement of ECN from two electrodes and a ZRA and EPN with a reference electrode. Does MEM spectral analysis on noise and derives noise impedance. Effectively measures artefacts of the MEM technique.
US5151163	29 Sep 1992	26 May 1991		Miller	US Navy	Electrochemical noise measurement technique for the determination of aluminium alloy pit initiation rates	EPN measurement using a reference electrode and a test electrode. Uses FFT to plot noise spectra and determine pit initiation.
US5286357	15 Feb 1994	04 Aug 1992		Smart, Cox	BAe Ltd	Corrosion sensors	Thin film stick-on electrodes. Could be used for electrochemical noise. Probe patent.
WO9412862	09 Jul 1994	20 Nov 1992		Withlow, Lee, Gallagher, Cox, Mok	Westinghouse Electric Co	Apparatus and method for real time corrosion monitoring in high temperature systems	Measurement of ECN from two electrodes and a ZRA and EPN with a reference electrode. Also ac measurement. Mainly a probe patent for high temperature systems.
US5323429	21 Jun 1994	15 Jan 1993		Roarty, Eden	Westinghouse Electric Co	Electrochemical monitoring of vessel penetrations	Measures EPN and ECN using a probe measuring against actual vessel. Detects stress cracking. Probe patent.
US6010889	04 Jan 2000	30 Sep 1994		Gearey, Wooley, Eden	UMIST	Electrochemical noise measurement to assess cellular behaviour and metabolic activity	EPN, ECN and noise resistance measurement using three electrodes, two coupled by a ZRA, third as a reference. Electrodes immersed in culture medium. Detects cancer cells.
US5858204	12 Jan 1999	14 Mar 1996		Jambo, Gomez	PetroBras	Electrochemical sensor and process for assessing hydrogen permeation	Hydrogen permeation sensor. Uses ECN and a ZRA on the hydrogen sensing side. Not sure why.
JP10019826	23 Jan 1998	30 Apr 1996		Yutaka, Shigeo, Masazumi, Kenji	Mitsubishi Chem Corp	Apparatus for measuring corrosion of metallic material	Measurement of ECN from two electrodes and a ZRA and EPN with a reference electrode. In Japanese.
DE19617906	28 Aug 1997	03 May 1996		Schiller		Corrosion measurement method	Measurement of EPN and ECN from two electrodes by switching these rapidly between a voltmeter and a ZRA, then using synchronous rectification to extract the original dc levels. In German.

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Patent Number	Issue Date	Priority	Expired	Inventor	Assignee	Title	Summary
JP10170482	26 Jun 1998	09 Dec 1996		Shigeo, Yutaka	Mitsubishi Chem Corp	Corrosion measuring device of metallic material	Appears to switch between a number of electrodes to measure EPN. In Japanese.
US5888374	30 Mar 1999	08 Mar 1997		Pope, Lin, St Martin, Frank	Uni of Chicago	In-situ process for the monitoring of localised pitting corrosion	Measurement of ECN from two electrodes and a ZRA and EPN with a reference electrode. Does spectral analysis on noise. Not sure how this could have got patented.
US6015484	18 Jan 2000	26 Nov 1997		Martinchek, Yaffe	Gamry Instruments Inc	Detection of pitting corrosion	Measurement of ECN from two electrodes and a ZRA and EPN with a reference electrode. ZRA is dc biased to some level.
US6264824	24 Jul 2001	20 Feb 1998		Reid, Eden	Integriti Investments Ltd	Assessment of corrosion	Measurement of ECN from two electrodes and a ZRA and EPN with a reference electrode. Uses neural network to detect signatures of localised activity.
US6132593	17 Oct 2000	08 Jun 1998		Tun		Method and apparatus for measuring localised corrosion and other electrochemical processes	Array of microelectrodes, each connected to a ZRA. Not sure where electrochemical noise is used.
WO0034759	15 Jun 2000	07 Dec 1998		Eden	Integriti Investments Ltd	Corrosion monitoring	Early version of the harmonic analysis ECN patent. Measurement of LPR using harmonic analysis and ECN with a three electrode arrangement and a potentiostat.
US6280603	28 Aug 2001	10 Dec 1998		Jovancicevic	Baker Hughes Inc	Electrochemical noise technique for corrosion	Measures potential and EPN of test electrode against a reference electrode, then connects a ZRA or potentiostat between test electrode and a third electrode and measures current and ECN. Repeats. Claims to be able to calculate corrosion rate directly.
WO0045148	03 Aug 2000	26 Jan 1999		Quirk	Integriti Investments Ltd	Corrosion sensors contained within the thermally insulating member of a metal pipe	Under-lagging corrosion probe. Could be used for electrochemical noise. Probe patent.
JP200128713	03 Aug 2001	26 Jan 2000		Masazumi, Takao	Mitsubishi Chem Corp	Method and apparatus for measuring corrosion in non-aqueous organic fluid	Measurement of ECN from two electrodes and a ZRA and EPN with a reference electrode. For use in non-conductive media. In Japanese.
US6294074	25 Sep 2001	18 May 2000		Lin, St Martin, Frank, Pope	Uni of Chicago	Electrode design for corrosion monitoring using electrochemical noise measurements	Measurement of ECN from two electrodes and a ZRA and EPN with a reference electrode. The two electrodes have a different surface finish.
US6355157	12 Mar 2002	22 Jun 2000		Martin	US Filter Co	Process for real-time detection and inhibition of localized corrosion	Combination of LPR and ECN to detect localised corrosion and inject water treatment. Computes 'activation factor'.

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Patent Number	Issue Date	Priority	Expired	Inventor	Assignee	Title	Summary
US6419817	16 Jul 2002	22 Jun 2000		Marin	US Filter Co	Dynamic optimization of chemical additives in a water treatment system	Combination of LPR and ECN to detect localised corrosion and inject water treatment. Not clear what circuitry is used.
US6524466	25 Feb 2003	18 Jul 2000		Bonaventura, Ignarro, Dowling, Spivack	Applied Semiconductor Inc	Method and system of preventing fouling and corrosion of biomedical devices and structures	A screwy patent where filtering out of electrochemical noise prevents the corrosion of just about anything.
GB2365977	27 Feb 2002	19 Jul 2000		Gill	ACM Instruments Ltd	Corrosion monitoring system for use in multiphase solutions	Not really a noise patent. Uses switched LPR to measure corrosion in non-aqueous phase.
US6611151	26 Aug 2003	21 Sep 2000		Ruedisuelli, Bowles, Layer	US Navy	Coating assessment system based on electrochemical noise	Measurement of EPN and ECN using a single test electrode, a reference electrode and an inert auxiliary electrode. Electrodes contained in a clamp-on cell. Used for testing of coatings in-situ. Partially a probe patent.
US6478948	12 Nov 2002	26 Feb 2001		Breen, Tobias, Eden, Gabrielson, McConnell	ESA Corrosion Solutions Ltd	Method of monitoring and controlling corrosion of furnace boiler tubes	Application of EPN/ECN to boiler tube corrosion monitoring. Probe patent.
US2004/0149594	05 Aug 2004	08 Mar 2001		Eden		Estimation of localised corrosion penetration	Measurement of LPR using harmonic analysis and ECN with a three electrode arrangement and a potentiostat. Essentially SmartCet/CorrTran device.
US6683463	27 Jan 2004	27 Mar 2001		Yang, Sridhar	Southwest Research Institute	Sensor array for electrochemical corrosion monitoring	Three electrode potentiostatic arrangement but the auxiliary electrode comprises an array of microelectrodes. Measures ECN on these to detect localised corrosion. Probe patent.
US6776889	17 Aug 2004	08 Jul 2001		Atherton		Corrosion monitoring	Uses three electrodes. Filters EPN signal to remove dc. Filters current path to maintain dc current at zero. Measures ECN.
JP2002286622	03 Oct 2002	23 Oct 2001		Masazumi	Mitsubishi Chem Corp	Device for measuring corrosion of metallic material	Measurement of ECN from two electrodes and a ZRA and EPN with a reference electrode. Calculates resistance noise. In Japanese.
JP2002286623	03 Oct 2002	23 Oct 2001		Masazumi	Mitsubishi Chem Corp	Corrosion measuring device	Measurement of ECN from two electrodes and a ZRA and EPN with a reference electrode. Calculates resistance noise and corrosion rate. In Japanese.
JP2002286678	03 Oct 2002	23 Oct 2001		Masazumi	Mitsubishi Chem Corp	Corrosion control-supporting apparatus for metal material	Measurement of ECN from two electrodes and a ZRA and EPN with a reference electrode. Feedback to plant control. In Japanese.
US6551491	22 Apr 2003	09 Nov 2001		Dowling, Spivack	Applied Semiconductor Inc	Method and system of preventing corrosion of conductive structures	A screwy patent where filtering out electrochemical noise stops corrosion of a metal structure.

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Patent Number	Issue Date	Priority	Expired	Inventor	Assignee	Title	Summary
US2003/0183537	02 Oct 2003	02 Apr 2002		Eden, Breen, Gabrielson, Schrecengost, Valvano		Method of spatial monitoring and controlling corrosion of superheater and reheater tubes	Measurement of EPN/ECN at high temperatures. Probe patent.
US6797149	28 Sep 2004	02 Apr 2002		Eden	Intercorr Holdings Ltd	Apparatus and method for electrochemical detection and control of inorganic scale	Measurement of LPR using harmonic analysis and ECN with a three electrode arrangement and a potentiostat. Used to detect scale formation in a flow-through heated cell. Partially a probe patent.
WO03106976	24 Dec 2003	17 Jun 2002		Cottis	UMIST	Method and apparatus for monitoring corrosion	Uses ac voltage superimposed on dc. Filters response to get ac back. Uses this and EPN/ECN to measure corrosion and detect localised activity.
US2003/0184329	02 Oct 2003	02 Apr 2003		Breen, Gabrielson, Eden		Detection, measurement and control of ammonia in flue gas	Control of ammonia injection by monitoring EPN/ECN. Probe patent.

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### 5. SMARTCET – CORRTRAN APPROACH ANALYSIS

The SmartCET and CorrTran devices appear to operate on similar principles.

Both use a test probe comprising three nominally identical electrodes. The circuitry cycles through a measurement cycle comprising corrosion rate measurement, electrolyte conductivity measurement and electrochemical noise measurement.

Depending on the configuration of the devices, the corrosion rate of the test electrode and the localised corrosion propensity are computed from the measured parameters and transmitted to the host device (via RS-485 in the case of SmartCET and 4-20ma loop / Hart protocol in the case of CorrTran).

A circuit diagram of the SmartCET device was not made available for the purpose of this report and hence the following discussion applies only to the CorrTran implementation. It is understood that the SmartCET circuit configuration, operation and measurement sequencing are similar to that of the CorrTran device, albeit using different semiconductor devices and a slightly different circuitry.

#### 5.1. Conductivity Measurement

The CorrTran device attempts to measure the conductivity of the electrolyte using a 1 kHz, 50% duty cycle square waveform, switched between 0 and 30 mV levels. The test electrode is potentiostatically polarised to the potential of the reference electrode and the polarisation current is applied using a third, auxiliary, electrode. All three electrodes are made from the same material and are of identical shapes and surface areas.

The polarisation current is measured as a voltage drop across a 1k $\Omega$  resistor in the auxiliary electrode path. This measurement is carried out asynchronously to the applied waveform, at 1 second intervals, and the result is averaged over a 30 second period.

This measurement approach is somewhat unusual. Normally, electrolyte conductivity would be measured using say a sinusoid voltage waveform of a sufficiently high frequency (>1 kHz) as to minimise the effects of electrode processes, taking care as not to apply a mean dc voltage to the measurement electrodes. The resulting current response would then be rectified and averaged to give a dc value proportional to the electrolyte conductivity.

The CorrTran approach polarises the test electrode by the mean of the applied waveform (15 mV) for the duration of the measurement. This in itself would be of little consequence, as long as an appropriate length of time was allowed at the end of the measurement for the test electrode to depolarise. Of more concern is the measurement method, which will be affected by any distortion of the perturbation signal by the test cell impedance, by the dc current, resulting from the test electrode polarisation and by the position of the analog to digital converter sampling window in time relative to the applied waveform. The approach adopted is hence unlikely to result in a measurement related to any degree of accuracy to the electrolyte conductivity.

The measured electrolyte conductivity does not always appear to be used in the corrosion rate calculations.

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### 5.2. Harmonic Distortion Measurement

The CorrTran device uses a 0.01 Hz sine waveform to measure the real part of the test electrode impedance. Additionally, a measurement of the second and third harmonic content of the cell current is used to determine the Stern-Geary constant and the corrosion current using the harmonic distortion analysis (HDA) method.

The HDA method is not always used in practice and the device employs a 'fallback' user programmable or default value for the Stern-Geary constant.

The 0.01 Hz sine perturbation of 25 mV peak amplitude is generated using an accurate digital to analog converter as a series of 100 voltage steps and is symmetrical about zero. It is applied to the test electrode using a potentiostat circuit, as for the conductivity measurement. The period of measurement is one cycle of the applied waveform, i.e. 100 seconds.

Prior to each successive step of the applied waveform, the cell current is measured using a 20 bit sigma delta analog to digital converter. A discrete Fourier transform (DFT) method is used in real time to compute the amplitude of the fundamental, second and third harmonic components of the current response by multiplication of the individual current data samples by the respective  $\sin(\omega t)$ ,  $\sin(2\omega t)$  and  $\sin(3\omega t)$  values.

Although theoretically correct, there are obvious practical difficulties to this measurement approach.

The harmonic measurement is started immediately following the conductivity measurement. At that point, in the measurement cycle, the test electrode would have been polarised to +15 mV by the conductivity measurement waveform and hence a dc offset will be present in the sampled cell current measurement data, which will decay over the 100 second measurement period. Additionally, any changes in the reactions occurring on the test electrode surface will result in a slow drift of the measured current – electrochemical current noise of  $1/f$  spectral density. As no trend removal or windowing are used prior to the DFT computation and the measurement is carried out over only one cycle of the perturbation waveform, this will lead to severe errors in the estimates of the magnitudes of the frequency components of the current response. In particular, any discontinuity in the data (last – first data point difference) can give rise to a considerable error in the estimate of the third harmonic.

It should be remembered that the harmonic distortion analysis formulae used for the calculation of the corrosion current, Tafel slopes and Stern-Geary constant are applicable only to activation controlled processes, a situation unlikely to exist in a practical application. A simple simulation can also be used to show that the approximations used in their derivation only hold true for a limited range of Tafel slope values.

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### 5.3. Electrochemical Noise Measurement

The circuit arrangement for the measurement of electrochemical potential and current noise is also somewhat unconventional and seems to show a basic lack of understanding of the operation of a potentiostat circuit.

Electrochemical current noise measurement is carried out by polarising the test electrode to the potential of the reference electrode (zero applied overpotential) and measuring the resulting current between the test and auxiliary electrodes. Any fluctuations of the reference electrode potential will result in fluctuations of the cell current as the potentiostat circuit attempts to maintain the difference between the test and reference electrodes at zero by injecting a current via the auxiliary electrode.

This is not the same as measuring the ZRA coupling current between two 'identical' electrodes in the conventional implementation. In the present case, there is no measurable current flowing between the two electrodes (test and reference) being held at the same potential, due to the high input impedance of the reference electrode connection. The auxiliary electrode will be polarised to some indeterminate potential dependent on ratio of its and the test electrode electrochemical impedances, electrolyte conductivity and the magnitude of the cell current. This is a basic effect of the operation of the potentiostat circuit and is usually of no consequence as the potential of the auxiliary electrode is usually of no interest. The auxiliary electrode is normally made of an inert material and is simply used to inject a current into the cell electrolyte and to the test electrode.

Electrochemical potential noise is measured as the potential difference between the auxiliary and the test electrodes. However, as the potential of the auxiliary electrode is being altered to some indeterminate value by its inclusion in current path of the potentiostat circuit this measurement is largely meaningless.

The EPN measurement result is not used in any of the computations and is not output.

The ECN and dc current measurements are then used for the calculation of a 'localisation factor'. The firmware employs a convoluted set of rules, presumably added to account for situations where the noise and harmonic measurements do not give 'acceptable' results, and several 'fiddle factors' to compute this value and to place it between the bounds of 0.001 and 1.

### 5.4. Conclusion

The present circuit arrangement and operation of the SmartCET and CorrTran devices are unlikely to give reliable measurements of the corrosion rate of the test electrode. Although the 'localisation factor' parameter, as output, will probably be related in some way to the degree of localised attack propensity on the test electrode, the method of its measurement and computation have little, if any, sound theoretical basis.

The actual corrosion rate measurement aims at a high degree of accuracy. It is doubtful whether this is achievable using any electrochemical technique. In practice, it is measurement reproducibility that matters – the user is often primarily interested in a reliable detection of trends and changes of the corrosion rate. The present CorrTran device gives an unacceptable amount of scatter in the corrosion rate output.

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### 6. COMPETING MANUFACTURERS AND TECHNOLOGIES

There are several manufacturers of on-line corrosion monitoring equipment for plant use.

The 'industry standard' technique is that of electrical resistance measurement, since advances in both probe construction and measurement circuitry have improved its sensitivity and responsiveness. Electrical resistance (ER) probes and instruments are sold by Caproco, Baker Petrolite, Metal Samples and Corrmon.

Instruments and probes based on electrochemical techniques are usually sold by the same manufacturers as ER devices. The LPR technique used is normally that of a simple dc polarisation measurement using either two or three electrode probes. Although a localised corrosion detection capability is often claimed, this is usually at a very unsophisticated level.

Portable instruments predominate in the market – the choice of devices capable of permanent installation and an easy integration into existing plant automation systems is very limited.

Electrochemical corrosion rate measurements continue to be viewed as a 'specialty' technique and are perceived as being harder to interpret and being less reliable than ER measurements. The corrosion monitoring market tends to be very conservative and it can be difficult for new techniques to gain acceptance in the mainstream oil, gas and chemical process industries.

Caproco supply a portable LPR instrument. It uses a very simple measurement technique and operates on 2 and 3 electrode probes.

Baker Petrolite supply equipment made by ACM, a portable instrument with a laboratory use origin. This is capable of diverse electrochemical measurements but is not intended for on-line monitoring in a permanent installation. The company also supplies simple LPR instruments.

Metal Samples supply hand held instruments and devices for permanent on-line installation. The technique used is that simple dc LPR measurement.

Rohrback Cosasco supply a range of portable and field mountable instruments. Although the company claims to measure electrochemical noise, in practice the instrument simply measures the dc voltage between the two test electrodes.

Corrmon specialise in electrical resistance based instruments and supply some LPR based equipment.

Corrosion Instruments supply LPR devices developed by the Southwest Research institute, mainly intended to operate with their range of multi-element probes.

ACM supply a range of instruments, mainly intended for laboratory use.

Intecorr supply the SmartCET device.

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### 7. CONCLUSIONS

Although the individual measurement techniques used by the SmartCET and CorrTran devices appear to be covered by a number of patents, close examination shows that nearly all of the technology could now be considered to exist in the public domain.

The two key electrochemical noise patents have now expired and the harmonic analysis technology had always been based on open scientific publications.

The innovative step is the use of the combination and sequencing of the various electrochemical techniques for measurements on a single corrosion probe.

The implementation of the electrochemical noise and harmonic distortion measurement and analysis in the SmartCET and CorrTran devices has a number of flaws and it is unlikely that the present measurement circuitry and firmware can give reliable and reproducible corrosion rate measurements. Further hardware and firmware changes may be needed in order to make the device operate correctly.

The P+F CorrTran device concept is well suited to the corrosion monitoring market in regard of its ease of installation, operation and interface to existing control systems. If operating as intended, it would be technologically superior to any existing competing products.