CORROSION MONITORING USING LOW FREQUENCY ELECTROCHEMICAL NOISE.

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Introduction.

Electrochemical noise is a generic term describing the phenomenon of spontaneous fluctuations of electrochemical systems. It manifests itself in two guises, as potential noise or as current noise, depending on the mode of measurement. The work described in this paper relates to the measurement and analysis of fluctuations of potential of freely corroding electrodes, i.e. potential noise, but the techniques and procedures described below apply equally well to the case of current fluctuations.

The sources of electrochemical noise may be classified in three categories. Charge carrier effects contribute noise whose spectral density, the amount of noise present in a given bandwidth, is essentially constant over a wide range of frequencies and is of a low amplitude. This category covers noise originating from thermal agitation of charge carriers, noise caused by charge being transferred in discrete amounts and by other such phenomena.

A second source of noise relates to surface processes occurring on the electrodes and specifically to their inhomogeneities. These give rise to fluctuations at frequencies of approximately 1 Hz and below. The observed spectral density of these fluctuations in general varies with frequency and the amplitude can be much higher than that caused by charge carrier effects.

At very low frequencies environmental changes, such as variations of the physical and chemical parameters of the observed system, result in slow fluctuations of the electrode potential or current. These often have the

appearance of drift of the electrode potential and can sometimes be accounted for by existing theories of electrode thermodynamics and kinetics.

Measurement Procedure.

The measurement and analysis of electrochemical noise may be accomplished using either analog or digital equipment and techniques. The digital method employed in the present work offers a number of advantages and can be easily implemented on a desk-top microcomputer.

The basic steps in the procedure adopted for the present work were:

1. Data collection
2. Time record storage
3. Pre-processing
4. Time record analysis
5. Output and classification

Data Collection.

Data collection involves sampling of the measured parameter, potential or current, at predetermined intervals for a required number of samples. The sampling rate should be sufficiently high to cover the frequency range of interest and must be, in order to prevent aliasing, at least twice the highest frequency present in the input signal.

Spectral Density Estimates.

Traditional methods of spectral density estimation use some form of Fourier transform (FFT), either via the autocorrelation function (2) or directly (3). An alternative procedure known as the Maximum Entropy Method (MEM) exists (4) and is in many respects preferable when the time data is only weakly stationary.

The traditional approach assumes that data outside the time record is either zero or that the time record repeats periodically in time. In order to satisfy these requirements and to improve the resolution of the spectral estimates by reducing 'leakage' it is common to apply a 'window' function to the time record. This involves a multiplication of the original time

record by a function which is zero at the extremes of the time record and rises smoothly to unity in its centre. A large number of such functions exists, each having its own merits. A l/l0th raised cosine window (1) was used in the present work.

These procedures are a direct violation of Jayne's First Principle of Data Reduction (5). The MEM technique avoids these problems by acknowledging our ignorance of the data outside the time record and computes a spectrum most consistent with the available data and at the same time most non-committal in respect of the unknown values. In information theory terms this means that the entropy (ignorance) of the unavailable data is maximised.

The computational procedures of the MEM have been developed by Burg (6) and the underlying ideas have been summarised by Ables (7). A useful algorithm for the computation has been published by Andersen (8). All of these papers appear in an anthology published by the IEEE (9), a more recent anthology is also available (10).

The number of samples taken, i.e. the length of the time record, determines the lowest frequency that may be reliably measured in the collected data and is largely determined by the storage capacity and speed of the computer used. It is wise to choose an integer power of two number of samples in order to take a full advantage of some of the Fourier transform algorithms available.

The hardware used for the measurement can be an accurate analog to digital converter (ADC) or, since the frequencies involved are relatively low, a digital voltmeter.

Our measurement system comprised a Solartron 7055 voltmeter controlled over the IEEE 488 bus from a Hewlett-Packard 85A computer, also used for the data processing. A Hewlett-Packard 7225A plotter was used for the final graphics output.

Potential fluctuations were measured, whenever possible, as potential differences between two 'identical' electrodes placed near each other in a test cell. This arrangement minimises the de potential difference between the electrodes, enabling the voltmeter to operate on its optimally sensitive range. Environmental changes tend to affect both electrodes equally, reducing the amplitude of the resultant drifts. The similarity of the electrodes also guarantees that any observed fluctuations originate from the test electrodes.

In some situations, such as in our cavitation tests and plant measurements, this arrangement is not practicable. In such instances measurements are best made using a suitable 'inert' (noise free) reference electrode.

External electromagnetic interference was not found to be a problem in any of the measurements.

Time Record Storage.

The acquired time record can be stored in a digital format on a suitable storage medium such as a floppy disk or a magnetic tape cartridge.

Pre-processing.

Before analysis it is desirable to carry out certain pre-processing operations on the collected time records. The first of these involves the isolation and removal of outliers, data points corrupted during acquisition and far removed from the data mean. These may be isolated using first or second difference procedures and replaced by values equal to the mean of their neighbouring data points. It is also useful to compute and remove the mean and trend of the data, i.e. the de value and any slow drift present in the time record. Finally the number of data points may be reduced by the application of digital filtering techniques. All these operations are standard data processing procedures and have been described in detail elsewhere (1).

Time Record Analysis.

The pre-processed time record may be analysed in terms of its simple statistics and in terms of its spectral composition. The simple statistical procedures can be the computation of the standard deviation of the data, probability density distribution computations and tests for statistical stationarity. Conventional spectral analysis procedures are designed to operate on stationary data, electrochemical noise is usually only weakly stationary and this fact must be taken into account when considering parameters such as confidence limits of the results.

The MEM method is ideally applicable to the analysis of weakly stationary data, such as the electrochemical noise, and the computed

spectra have the useful properties of optimal flatness and minimum phase (10).

Output and Classification.

The final stage of the procedure consists of plotting and classification of the results. The most informative plots are those of a logarithm of amplitude spectral density against logarithm of frequency and of logarithm of standard deviation versus time. In the former case the required logarithmic spacing of the plotted frequencies can present problems with data obtained via a FFT algorithm, this procedure usually computes spectral values at linearly spaced frequency points. The variance of the FFT spectral estimates is usually high, resulting in 'peaky' spectral plots. This effect, which can hinder interpretation, can be alleviated by the use of spectral smoothing or rms averaging. These procedures either average spectral estimates at adjacent frequencies or rms average spectra of consecutive time records. None of these problems arise when the MEM technique is used.

Comparisons of the spectra and of the variations of the standard deviation with known parameters, such as weight loss data or visual observations of the features of the corrosion attack, then make it possible to establish correlations between these parameters and features.

Results.

The application of the technique may be illustrated by the following examples. We have published some of our early results previously (11) and hope to present more detailed data in the future.

Mild Steel in Sulphuric Acid.

The possibility of corrosion monitoring using analysis of the statistics of the potential fluctuations was tested on the ubiquitous mild steel - 1N H_2SO_4 system. A pair of mild steel electrodes of 1 cm^2 area each was immersed in 1N H_2SO_4. The potential difference between the electrodes was sampled at 1 second intervals over a period of 100 samples using the instruments described above.

The standard deviation of each of these time records was then computed and its values are shown in Fig. 1, plotted against immersion time. The behaviour of the standard deviation follows that of the corrosion rate as determined by weight loss tests, impedance measurements and harmonic analysis (12), suggesting a possible linear relationship between the rate of attack and the magnitude of the potential fluctuations.

Chemical Plant Measurements.

Potential noise measurements were made on a chemical plant operated by I.C.I. during the plant start-up period, in order to assess the feasibility of such measurements and to identify any potential problem areas. A Pd reference electrode was used, inserted in a stainless steel transfer line with the monitoring equipment situated at some distance from the probe. The potential of the plant against the reference electrode was sampled every 1.5 seconds over a time record of 1024 points.

Fig. 2 shows the results of initial analysis of the data obtained, presented as a plot of standard deviation versus time. The plot reflects the large fluctuations observed during the initial stages of the start-up, standard deviations of data obtained during normal operating of the plant were nearly an order of magnitude lower than those observed towards the end of the period shown.

Cavitation Tests.

Electrochemical noise measurements were made on a large scale sea water cavitation rig at the Admiralty Marine Technology Establishment. The test cell comprised a cylindrical specimen inserted in a rectangular flow channel forming a part of a large flow loop. A section of pipe upstream of the test electrode was used as a reference electrode.

Fig. 3a shows a typical time record obtained on a Al specimen. The potential fluctuations exhibit a distinctly asymmetrical probability density distribution and non-stationarity. Fig. 3b shows a FFT spectrum of this data, while Fig. 3c presents an equivalent MEM spectrum plot. The spectral densities computed by the two methods are similar, the MEM spectrum is considerably easier to interpret.

Selective Dissolution Experiments.

Electrochemical noise measurements seem to be ideally suited to the monitoring of localised corrosion attack. Fig. 4 shows two MEM spectra obtained on nickel aluminium bronze (NAB) specimens in sea water of pH 7.5 and 5.0. Previous results have shown that a shallow roll-off slope and a high frequency position of the break point of the spectral density plot is indicative of localised corrosion attack (11). The NAB alloy is susceptible to selective dissolution attack (13) and electrochemical noise measurements could provide a means of monitoring of this type of corrosion.

Conclusions.

Potential noise measurements provide a non-perturbative means of investigation of corrosion processes. Even simple measurements, such as standard deviation determination, can give an indication of the rate of the corrosion attack. Spectral analysis of these fluctuations provides data relating to the morphology of the attack (11). The MEM technique of spectral analysis was found preferable to the more conventional methods, such as the FFT.

At present we find it difficult to suggest satisfactory theoretical explanations of the observed empirical correlations and we hope that this situation will be remedied in the future.

Acknowledgements

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Figures.

Fig. 1 Time variation of standard deviation (σ) of potential fluctuations between two mild steel electrodes immersed in 1N H_2SO_4

Fig. 2 Time variation of standard deviation (σ) of potential fluctuations of I.C.I. chemical plant.

Fig. 3a Time record of potential fluctuations (E) of an aluminium specimen undergoing cavitation.

Fig. 3b FFT spectrum of Fig. 3a.

Fig. 3c MEM spectrum of Fig. 3a.

Fig. 4 MEM spectra of potential fluctuations between two NAB electrodes immersed in sea water of pH 7.5 and pH 5.0.

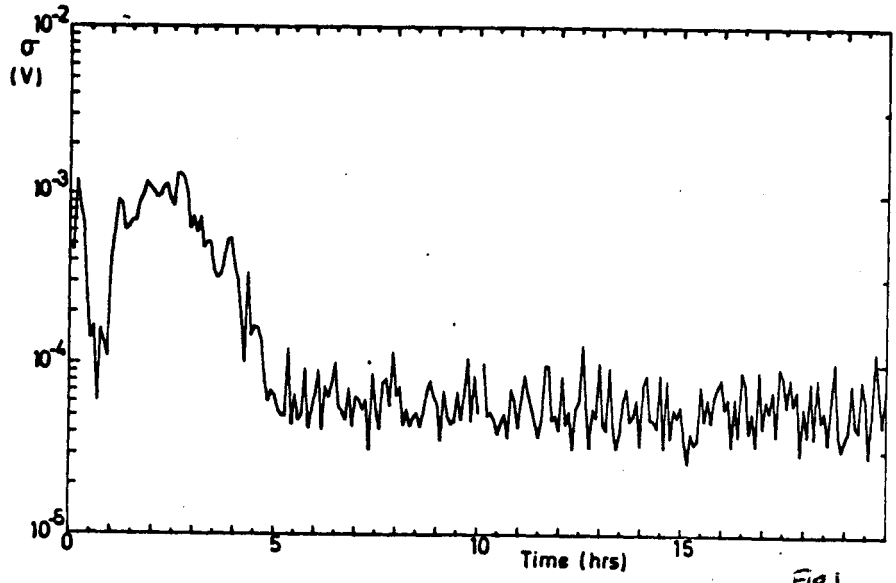

Fig 1

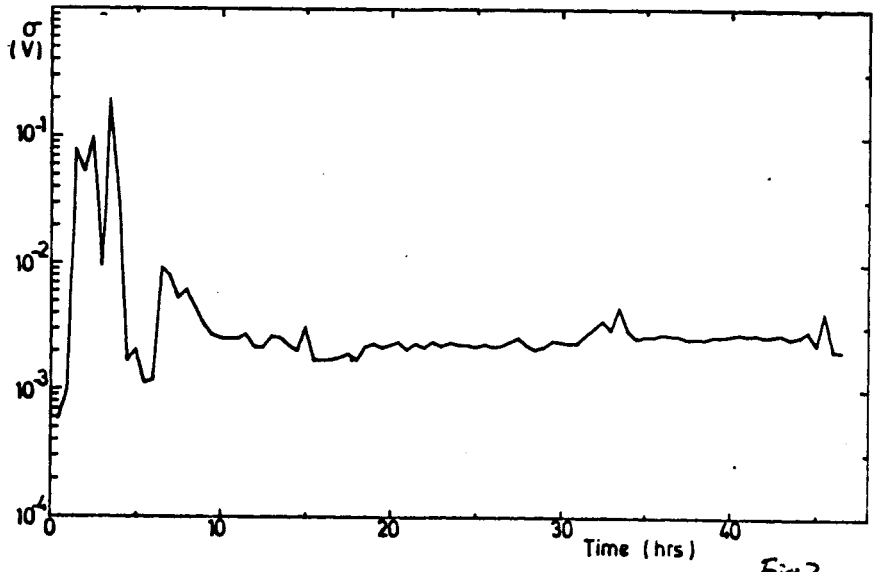

Fig 2

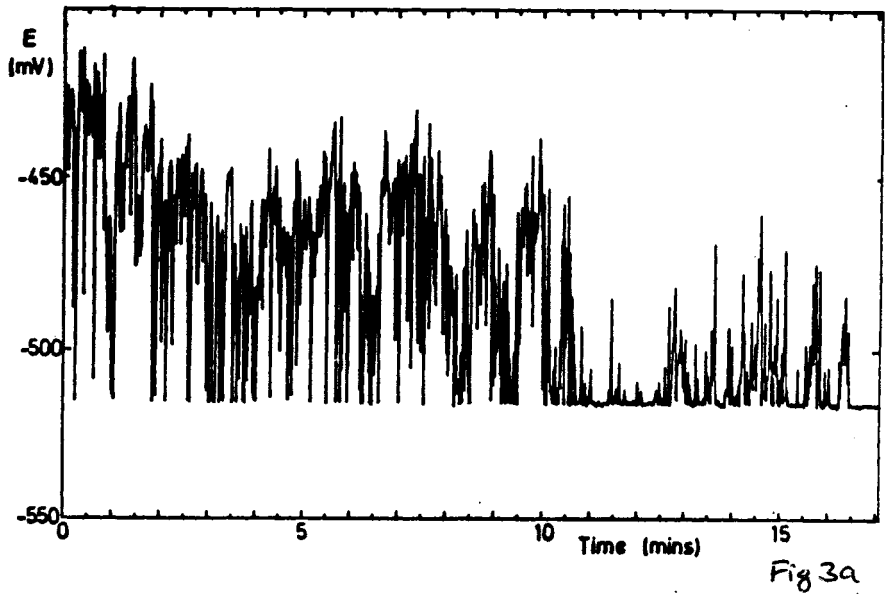

Fig 3a

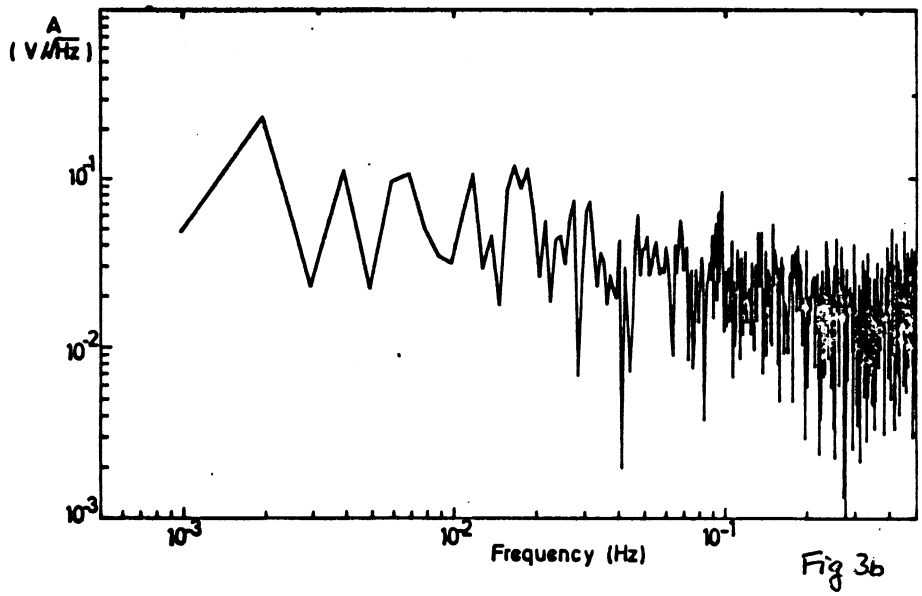

Fig 3b

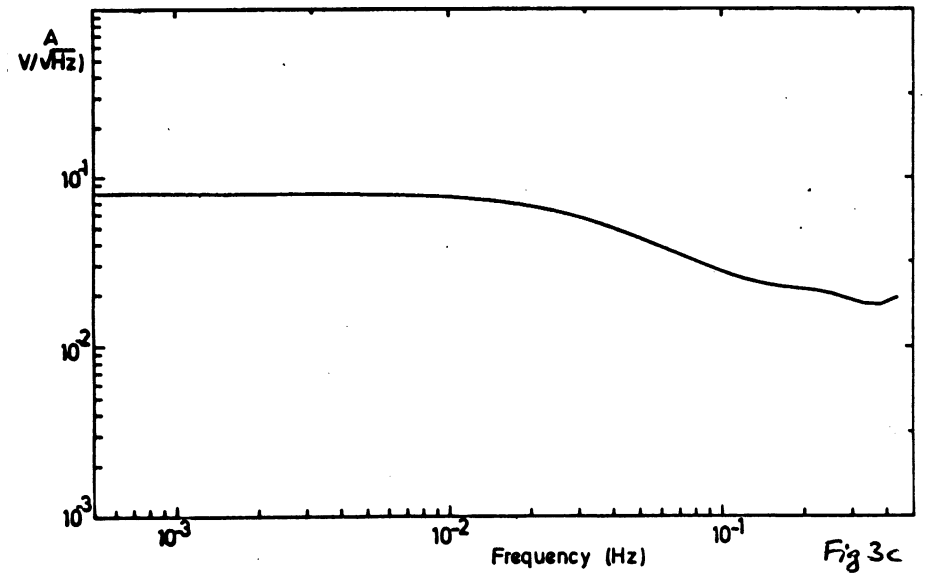

Fig 3c

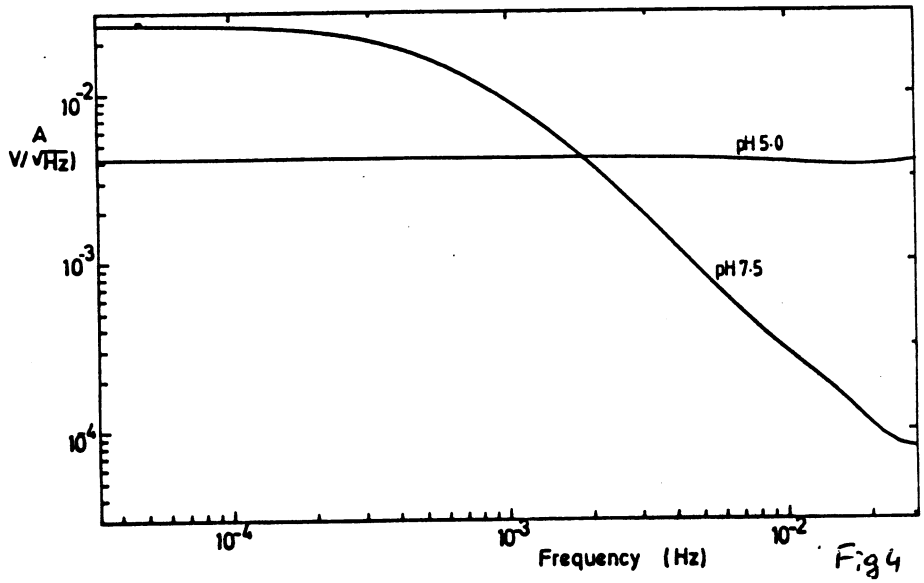

Fig 4