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The study of ECN from steel rebars in concrete solution

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Abstract

The potential & current Electro Chemical Noise (ECN) from steel rebar in cement solution were recorded simultaneously. The average Potential, Current noise power and the estimated Charge in the transient were calculated both in the time and frequency domains. The results were compared with ECN of rebar in distilled water, and solution containing chloride. In our future paper, it is proposed to analyse the results with improved Signal to Noise ratio.

Keywords: Electro Chemical Noise (ECN), steel rebar, cement solution

1. Introduction

Instances of damage due to rebar corrosion can be found in most applications of reinforced or prestressed concrete. The corrosion of reinforcement embedded in concrete demonstrates itself by spalling of the concrete. This phenomenon is due to the expansive nature of the corrosion products, which can produce large forces without much loss of surface area. The expansive red rust products are formed by a secondary reaction of $2\text{Fe}(\text{OH})_2$ with oxygen from the air. These can diffuse away from the steel surface. In addition, structural failure may also result due to the reduced cross section of corroded steel bars. Considering the huge cost of damage caused by rebar corrosion, it is necessary to consider the various parameters, internal and external, which lead to corrosion of steel bars in concrete. Electrochemical corrosion is believed to be the cause for essentially all of the corrosion damage to steel in concrete. Electrochemical corrosion in concrete results because of the existence of differences in metals or non-uniformities of the steel or non-uniformities in the chemical or physical environment provided by the surrounding concrete. These non-uniformities can produce significant electrical potential differences and resultant corrosion. A flow of current in the steel from an anodic to a cathodic area, in the presence of moisture and oxygen, results in the production of hydroxyl ions at the cathode. As these migrate to the anode, they react with ferrous iron and form hydrous iron oxides.

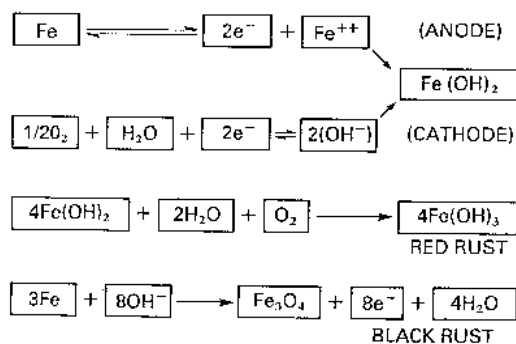


Fig. 1 Electrochemical reactions producing rust.

It is seen from the above equations that a supply of oxygen and water is obviously necessary for corrosion to occur. However, most of the constructional

concretes allow ample access of both water and oxygen. The traditional view is that the corrosion is normally prevented by a passivating iron oxide (γ -Fe₂O₃) film which rapidly forms on the steel surface in the presence of moisture, oxygen and the water soluble alkaline products during the hydration of cement. The principal soluble product is calcium hydroxide, Ca(OH)₂, and the initial alkalinity of the concrete is in excess of 12.5. The protective coating remains intact at high pH values (around 13). The protection afforded to steel by high pH value persists while concrete sets and hardens and remains intact so long as the concrete environment surrounding the steel does not change significantly. Once the hardened concrete has dried to an equilibrium moisture content, the combined protection of steel depends entirely on the ability of the concrete to maintain the appropriate alkaline environment. However, the protective film of γ -Fe₂O₃ on the steel surface is usually disrupted when the pH value is reduced or by the ingress of aggressive ions due to capillary action, cracking and spalling of concrete and poor construction practices or by a combination of both these factors.. The disruption of protective cover leads to corrosive attack on the reinforcement. Once the attack commences, corrosion products start to build up on the steel surface. Loss of alkalinity results from reaction of the hydrating cement matrix with acidic components in the atmosphere, and, to some extent leaching of the hydroxyl ions from the concrete. When the pH of the matrix drops below a value in the range 9.5 to 10 steel can corrode given adequate supplies of moisture (to provide the electrolytic path) and oxygen (to stimulate the cathodic reaction). Likewise passivity can be destroyed by aggressive ions. Chloride is by far the most aggressive ion in relation to steel corrosion and its presence in sufficient quantities in concrete can readily destroy passivity leading to rapid and often serious corrosion. Concrete being a porous medium will allow the ingress of atmospheric gases. These will contain carbon dioxide, which will readily react with the alkalis present so reducing the pH. However, the extent of ingress will be controlled, amongst other factors, by permeability of the concrete matrix and of the aggregate. While carbonation is one important route for the loss of protection to the reinforcement, another is the presence of chloride in the concrete. In the research done by Zhu, Y., & Chen, S. (2019) for the ECN related

to concrete was suggested to use electrodes of biosimilar materials to give signals with acceptable error. It can be introduced in concrete in a number of ways, but in the Middle East if chlorides are present in the concrete they have usually been introduced as contaminants in the aggregate, in the mix water or as a result of exposure to chloride-laden environment. Of these routes that via the aggregate is the most common. As well as with chlorides Middle Eastern aggregates can be contaminated with sulphates and this gives rise to additional problem of containing any potential sulphate attack on concrete.

1.1 General corrosion

General corrosion is the result of general loss of passivity, due either to carbonation or the presence of excessive amounts of chloride. The potential gradients are not great.

1.2 Localised corrosion

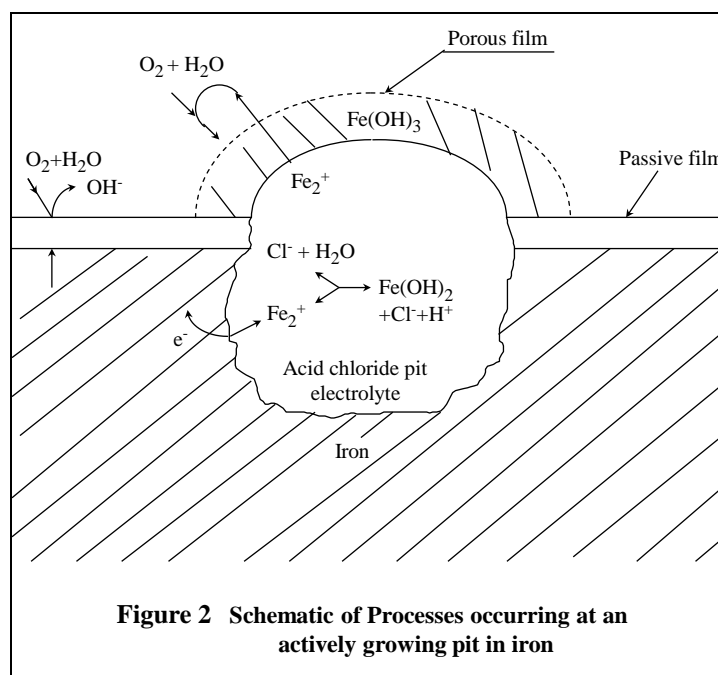
Pitting corrosion is a form of localised attack due to the localised breakdown of the oxide film and chloride is usually present as an essential ingredient to breakdown the film. The passive film remains stable with respect to chemical species and is able to regenerate itself in case of accidental breakdown. However, local areas of passive film can sometimes permanently breakdown electrochemically or mechanically, which allows anions to attack the exposed metal leading to localised corrosion. Pitting is a microscopic phenomenon and not macroscopic in the sense high rates of localised penetration are possible with a very low overall corrosion rate. Crevice corrosion is another form of localised attack occurring at shielded areas on metal surfaces exposed to certain environments. Bertolini, L., Elsener, B., Pedferri, P., & Polder, R. (2013) was concentrating on the methods to avoid localised corrosion. This type of attack is usually associated with small volumes of stagnant solution caused by gasket surfaces, lap joints, holes and crevices under bolts and rivet heads.

1.2.1 The state of Pitting corrosion

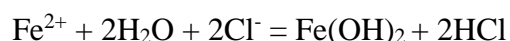
The chloride ions break down the passive film locally in those areas where the concentration is high or the passive film is weak. Then, as soon as the corrosion is initiated a corrosion cell is formed with an adjacent area of passive steel acting as a cathode, where oxygen is reduced and the anodic dissolution of iron taking place only at a small, central anode according to Mills, D.J.; Short, N.R. 2002 and Broomfield, J. P. (2007) and Cheng, Y. F. (2015)

1.2.2 Growth of pits

The following Figure for pitting of iron in a slightly alkaline chloride solution serves as a simplified model.



Copious anodic production of positively charged Fe^{2+} attracts negative anions, eg., Cl^- , to the initiation site. Hydrolysis by



produces local pH reductions at the initiation site. The result is a self-propagating or autocatalytic mechanism of pit growth. The acid chloride solution further accelerates anodic dissolution, which in turn further concentrates

chloride in the pit. An insoluble cap of $\text{Fe}(\text{OH})_3$ corrosion products collect at the pit mouth when Fe^{2+} diffuses out of the acid pit interior to the exterior, where it is oxidised to Fe^{3+} and precipitates in the neutral bulk solution. The cap impedes easy escape of Fe^{2+} but is sufficiently porous to permit migration of Cl^- into the pit, thereby sustaining a high acid chloride concentration in the pit. Anodic polarisation of the pit interior occurs by coupling to the exterior passive cathode surfaces. Cathodic reduction of a dissolved oxidiser such as oxygen consumes the electrons liberated by the anodic pit reaction. The pronounced drop of the corrosion potential brought about by the polarisation of the cathode is one of the factors responsible in preventing formation of new pits in the neighbourhood, at least until much higher chloride concentration are established elsewhere. On the other hand, the potential shift may also start development towards stifling of the attack. The current density at the anode will decrease, both because of the lower driving force and because the area of the anode increases as the low pH liquid at the anode neutralises the concrete at the rim of the anode. Consequently, the electrochemically produced concentration gradients will be flattened by the diffusion of ions in the opposite direction and this could result in the repassivation of the pit. As the corrosion products formed are usually soluble at the conditions of low pH near the anode, considerable amounts of corrosion can occur without spalling of the concrete. The importance of the cathodic reaction to sustain pitting should be understood. Pit growth cannot continue without a cathodic reduction reaction to consume the electrons liberated by (i.e. to polarise anodically) the pit anode reaction Scarfato, P., & Bruno, M. (2018). Thus, pits are widely spaced in aerated salt solutions, because oxygen has limited solubility, and a large surrounding area is needed to provide enough reduction capability to support the central pit anode. Any pit initiating within the cathodic area of a larger pit is suppressed by cathodic protection. A potential-pH diagram can describe the reactions of iron in aqueous solutions. A simplified potential-pH diagram can be divided into regions representing immunity, corrosion and passivity.

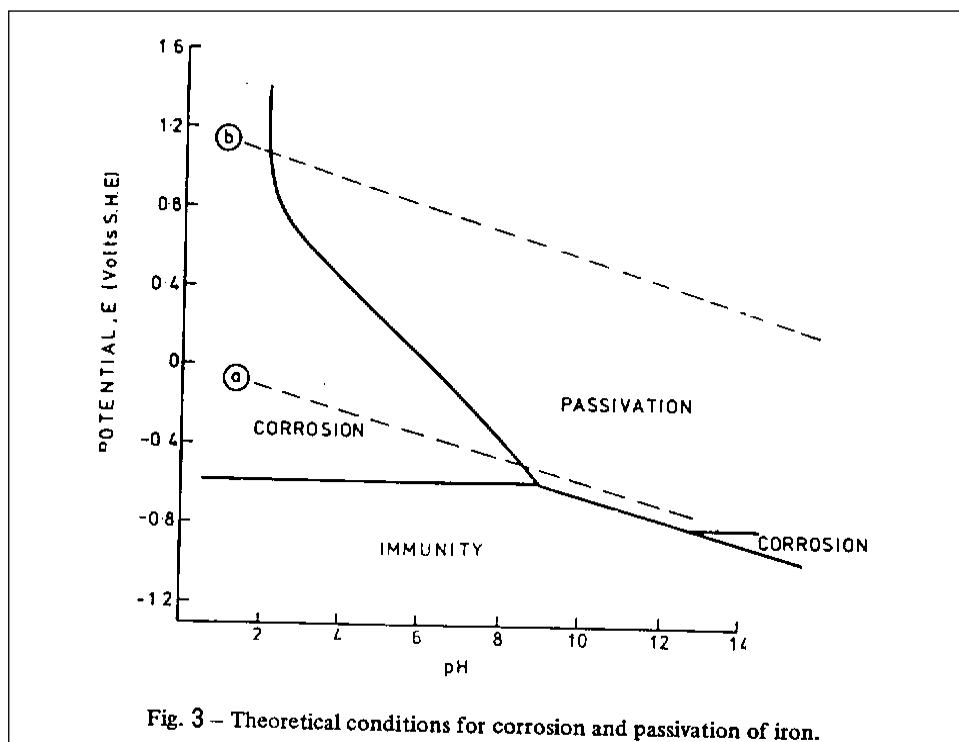


Fig. 3 – Theoretical conditions for corrosion and passivation of iron.

Penetration of chloride to the steel surface does not necessarily destroy passivity. Pourbaix presents a modified potential-pH diagram which indicates that even with very high chloride concentrations, a zone of perfect passivity remains, and it has been shown that corrosion of steel in concrete exposed to a high chloride environment can be prevented by polarising to a potential within this zone.

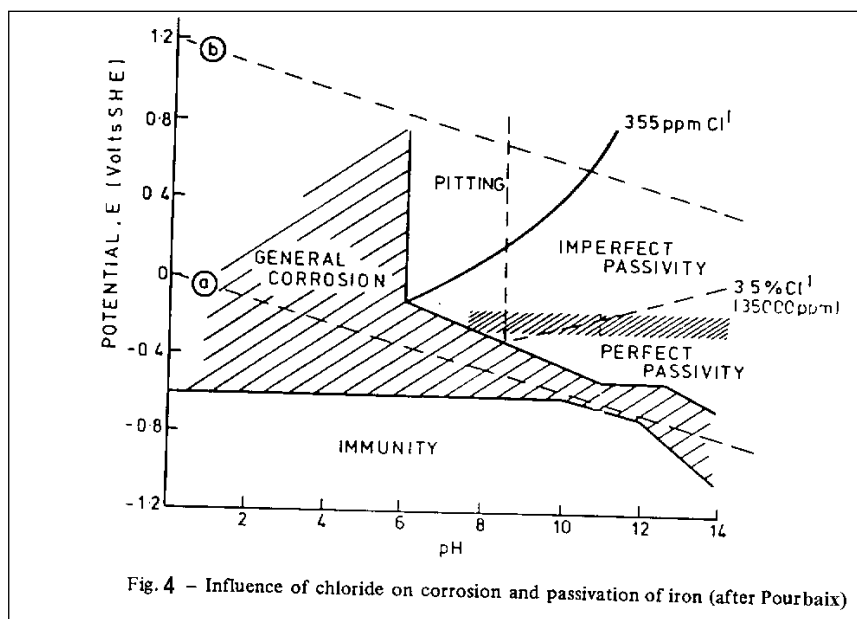
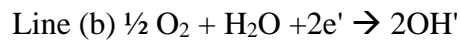
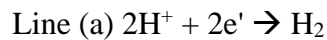


Fig. 4 – Influence of chloride on corrosion and passivation of iron (after Pourbaix)

The two principal cathodic reactions available for the corrosion of steel in concrete are indicated on the potential-pH diagrams:



However, oxygen reduction is recognised as the cathodic reaction in most cases of significant corrosion of steel reinforcement.

2. Corrosion monitoring of steel in concrete

There are various techniques available for the study of corrosion in reinforced concrete. The type of technique to be selected depends upon the aims of the researcher as per Shreir, L. L., Jarman, R. A., & Burstein, G. T. (2010). For example, the requirements of the engineer concerned with a practical on-site examination are somewhat different from the aims of a material scientist interested in laboratory based fundamental studies. For the assessment of corrosion damage to existing structures, the examination would be first used to quantify the extent of corrosion damage and this would be followed by a requirement to predict future performance; a major difficulty is that no one method provides sufficient information, hence there is an element of judgement required in assessing the corrosion hazard. Even though corrosion is an electrochemical process the traditional electrochemical techniques have been surprisingly unsuitable in assisting in the on-site monitoring. Therefore, the inspection of structures has relied on destructive tests to provide the engineering data required for assessing the present condition and predict long-term performance simplified by Schmitt, G., & Baeckmann, W. (2016). The available techniques can be broadly divided into two categories, the first of these being measurements on the actual structural rebar and the second involving measurements on smaller, strategically positioned, embedded rebar probes.

2.1 Potential mapping

Corrosion potential measurements using a reference electrode (calomel preferred) placed on the concrete surface which is connected via a high input impedance voltmeter to the reinforcement cage can provide information on the

state of passivity of the reinforcing steel. This technique is by far the simplest and the measurement procedure is described in the American National Standard ANSI/ASTM C-876, the basis of which is that the corrosion potential of the rebar will shift in the negative direction if the surface changes from the passive to the active state according to Shreir, L. L., Jarman, R. A., & Burstein, G. T. (2010). The advantage of this method is the simplicity and the possibility to automate measurements to cover large concrete surface areas in short time frames. The disadvantages are that the results are only qualitative, without an establishment of an actual rebar corrosion rate. Moreover, very negative rebar potential readings can be misleading and could be due to limiting oxygen diffusion. For example, in submerged concrete, where the corrosion rates are negligible, very negative potential readings are possible due to unavailability of oxygen stifling the cathodic corrosion rate.

2.2 Potentiodynamic sweep or potential step measurements

These well known dc type measurements can be performed using the conventional three electrode system. Typically, the working electrode is a small section of the rebar, while stainless or graphite may be used for counter electrode. Embedded reference electrodes need to be resistant to the highly alkaline pore solution. External reference electrodes can also be used. However, direct adoption for studies in concrete is open to criticism unless allowance is made both for the high resistivity of the environment, i.e. by IR drop compensation, and the very slow kinetics of the electrochemical corrosion reactions on reinforcement steel. The conventional potentiodynamic method would therefore appear to have only a limited application, for example in preliminary investigation, it is unlikely to yield kinetic information or data which can be quantified by Zhu, Y., & Chen, S. (2019).

2.3 AC impedance

Corrosion at the steel/concrete interface is a complex process. It appears that the most appropriate laboratory technique is therefore the impedance method which provides information on the kinetic control mechanisms, either

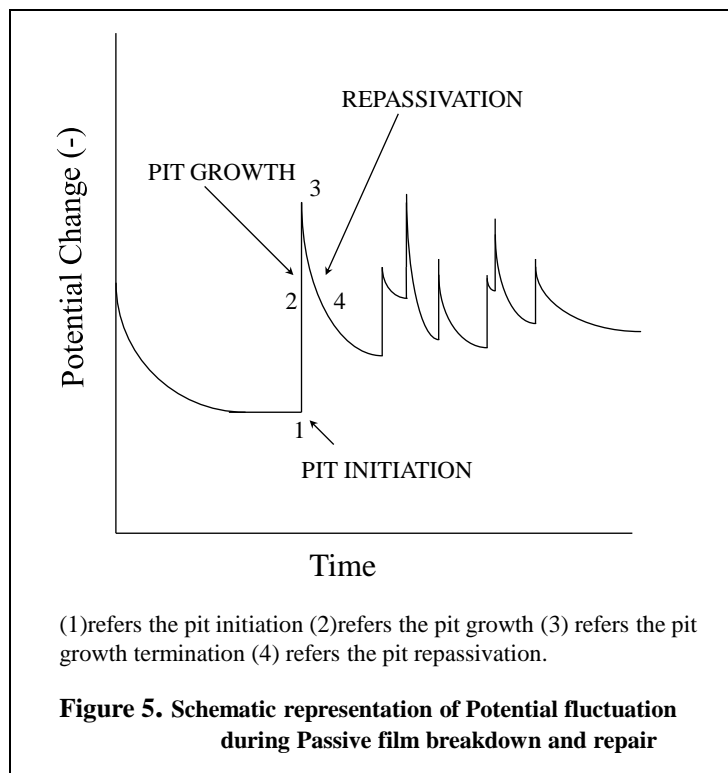
activation or diffusion, and on the film dielectric and electrochemical capacitive elements. The technique is able to measure the pore solution or concrete resistance as well as the electrochemical parameters such as the double layer capacitance, charge transfer resistance and Warburg diffusion. These parameters define the corrosion processes and since each responds to the applied voltage perturbation within specified frequency ranges, it is possible to quantify each component. Electrochemical impedance is essentially a laboratory based technique which may be used for studies on relatively small electrodes or sections of reinforcement bar.

2.4 Electrochemical Noise

Corrosion of rebars in concrete is a major issue regarding the durability and lifespan of reinforced concrete structures. Electrochemical noise (ECN) is an emerging technique to monitor and understand the corrosion processes occurring in rebars embedded in concrete. This report describes the principles of ECN, the application of ECN to detect and analyze rebar corrosion, and the challenges and prospects of this technique. Principles of Electrochemical Noise (ECN) Electrochemical noise refers to spontaneous current and potential fluctuations that occur as a result of corrosion processes at the metal/electrolyte interface. These fluctuations are indicative of the underlying electrochemical reactions and can be used to gain insight into corrosion mechanisms. Current noise: Fluctuations in current due to localized corrosion events such as pitting and crevice corrosion. Potential noise: Potential fluctuations due to changes in the electrochemical environment such as the formation or breakdown of a passive film. ECN measurements are typically performed with a three-electrode setup: a working electrode (steel reinforcement), a reference electrode and a counter electrode. Noise data is recorded over long periods of time and analysed to provide information about the corrosion process. Many localised corrosion phenomena such as pitting, abrasion and gas evolution are random by nature. Hence classical deterministic techniques (I-E plotting) cannot be used. Potential and current fluctuations arising from electrochemical noise represent a random or stochastic process as there is no way to predict an exact value at a future

instant of time. The data collected from this phenomenon are random in character and are hence described in terms of probability statements and statistical averages rather than by explicit equations. The noise intensity arising from surface film deterioration, destruction and recovery is far higher than the thermal intensity, so such noise is much easier to detect and is our area of interest here. If corrosion is regarded as a stochastic process, the corrosion current (potential) at a given potential (current) is a random signal which can be termed electrochemical noise, analogous with the use of the word 'noise' to indicate random, incoherent acoustic or electrical fluctuations. Hence the time and frequency processing techniques, especially devised for random signals can be applied. The phenomenon of electrochemical noise and its analysis, particularly its application as a possible corrosion monitoring method, has received considerable attention during recent years. In some cases the classification of electrochemical noise as random may be debatable as a further knowledge of the mechanism and source of the noise may enable exact mathematical descriptions of the phenomenon which would then become deterministic. The significance of the potential/current fluctuations can be explained in terms of a corrosion system moving from a passive state to that of corrosion. In passive conditions the potential essentially remains constant; any fluctuations are of a slow, long term nature. Any localised initiation of corrosion gives sharp changes in potential/current; typically a sudden fall in potential followed by an exponential recovery. If the conditions become more aggressive these events, 'glitches', become more frequent. The frequency of occurrence of the 'glitches' is related to the electrode area and effectively to the statistical probability of a localised film break down occurring. Since only a fraction of the localised events will cause actual pit formation, the probability of pitting attack is, in this case, still low. The general feature of potential change is a slow decay due to passive film growth over the whole exposed area. Each potential change, quick rise and slow decay, is then superimposed over this background of potential decay. The potential fluctuation can be completely characterised once the stochastic or deterministic nature of the single event 1) film breakdown (pit nucleation) 2) pit growth kinetics 3) pit growth termination and 4)

repassivation kinetics are all known. The situation is schematically illustrated in the Figure below.



Where the elementary current transients (pit nucleation and growth, bubble growth, and departure) are not too numerous to be discernible, a statistical counting can be done on the time series displayed by the current to evaluate a mean appearance rate (e.g. pitting rate). However, in the case closer to the cases of practical interest, where many events occur at the same time so that their current transient overlap, only a spectral analysis of the random signal will allow the characteristic parameters of the processes to be estimated. Further increase in the aggressiveness of the environment, for example an increase in Cl^- concentration, will give rise to an increase in the frequency of the events and the fluctuations apparently become random. Analysis in terms of the frequency spectra should however show that the ensuing output is the result of an overlap of a large number of these events. In this case, the probability of one or more of these localised breaks in the passive film propagating to form a pit is quite high and this type of output tends to indicate eventual pitting attack. Complete loss of

passivity, i.e. a situation where no film formation occurs, gives electrochemical noise output similar to that of a passive system, for example a trace devoid of distinct glitches, and any random noise present is of a low amplitude.

3. Experimental Details

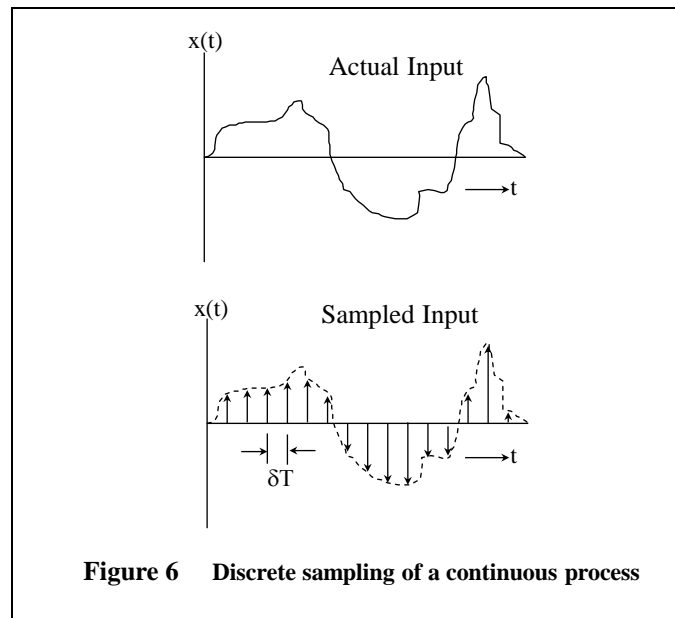
3.1 Electrochemical Potential, Current Noise Measurement

This section summarises the practical methods of implementing the digital data acquisition theory described earlier. The techniques for data acquisition and analysis, used during the practical work in this thesis, were based upon digital procedures controlled by a personal computer. The programs written by the author for data acquisition.

3.1.1 Data collection Procedures

A time record is a history or realisation of any process recorded over a period of time. Recording the corrosion potential fluctuations of a freely corroding electrode can easily be achieved using a suitable reference electrode and chart recorder. Time histories recorded in this way constitute continuous records as they represent the process recorded at every instant of time throughout the measurement time. Data analysis is relatively complex and for transformation of the data into the frequency domain, it is convenient that the data be in digital form. Data could be collected conveniently in digital form, obviating the need for digitisation of a continuous time record such as a chart recorder time trace. Further difficulties in using the chart recorder has already been discussed. Digital data collection requires the transfer of information between the recording device, such as voltmeter, and a processor and the subsequent storage of data for analysis. As a result of finite time required for data transfer, a process can only be sampled at intervals and this sampling interpolated to be an accurate realisation of the particular process. A time record collected in this way is known as a discrete record. The following figure shows the sampling of a continuous process in this manner according to Cui, Jun & Yu,

Dayang & Long, Ziwei & Xi, Beidou & He, Xiaosong & Pei, Yuansheng. (2019).



A sampled representation of a process can be as close to the process by placing the sample points close together, i.e. sampling at a faster rate, although this will obviously be limited by the speed of data transfer of the hardware involved. The number of points sampled, N , must be sufficient to yield the required resolution in the frequency domain after transformation. The Cooley-Tukey FFT algorithm requires the data points to be a power of 2 and $N = 1024$ (2^{10}) is often used for FFT based data analysis.

3.1.2 Sampling rate

Sampling for digital data analysis is usually performed at equally spaced intervals and a suitable sampling interval, Δt , must be determined for the collection of any time record. Sampling at points too close together, i.e. at too fast a rate, yields correlated and highly redundant data. For a time record consisting of a fixed number of points, sampling at too high a rate can result in erroneous data at lower frequencies. Sampling at points too far apart, i.e. too low a rate, can result in high frequency components of interest not resolved in the frequency domain. This phenomenon is called aliasing and is a potential source

of error in all digital processing. The highest measurable frequency which can be resolved in the frequency domain with a sampling interval of Δt is given by: $f_{\max} = 1/2\Delta t$. This frequency is known as the Nyquist, cut-off or folding frequency. Thus for a sampling rate of once every second (1 Hz) the highest frequency which can be resolved in the frequency domain is 0.5 Hz. If the sampling rate is lower than the highest frequency component of a process then this component will not appear at its correct point in the frequency domain, but will be aliased to a lower frequency. One method to reduce the error from aliasing is to filter the input signal at some frequency below the sampling frequency. The low frequency resolution of the spectrum of a discrete time record consisting of N samples is given by: $f_{\min} = 1/N\Delta t$. For example, 1024 points sampled at one second intervals gives a low frequency resolution of $1/1024$ or about 0.001 Hz. For the study of electrochemical phenomenon, such as pitting, a time period of 1024 points sampled at one second interval is considered adequate Cui, Jun & Yu, Dayang & Long, Ziwei & Xi, Beidou & He, Xiaosong & Pei, Yuansheng. (2019).

3.1.3 Time Record Collection

Electrochemical noise describes the spontaneous fluctuations of potential or current which occur at an electrode interface. In contrast to the techniques which apply an external, perturbing signal to the corroding system, non-perturbed electrochemical methods include corrosion potential monitoring and the use of ZRA to measure the galvanic current between two electrodes. The time records collected in this thesis measure the fluctuations in corrosion potential between a working electrode and a reference electrode and the galvanic coupling current flowing between two working electrodes. The coupling current between the working electrodes were converted into a proportional potential using ZRA, and hence we measured effectively two potentials. The controlling software, having set up the voltmeter, then collects data points for a pre selected time period. The controlling program listing is given in Appendix.

3.1.4 Noise measurement at free corrosion potential

Two identical samples were used as working electrodes. These two samples were placed vertically and parallel to each other in the test cell. A SCE reference electrode was placed in between the working electrodes. The difference in potential between the sample (working electrode) and reference electrode (SCE) was measured under freely corroding conditions. To measure the coupling current between two identical samples, a ZRA was connected across the terminals of the samples, and the output voltage of the ZRA, which is proportional to the input current, was measured. The connection schematic for both potential, current noise measurements is shown in the Figure 7 shown later. For both potential and current noise measurements 1 point/sec sampling rate was used and 2048 data were read (data points need to be a power of 2 to facilitate Fast Fourier transformation- 2×2^{10}). The recorded data were studied in the time domain by statistical analysis. The records were subsequently transformed into the frequency domain by Fast Fourier Transformation (FFT) and by Maximum Entropy Method.

For spectral analysis where potential and current fluctuations are correlated in the frequency domain, simultaneous recording of potential and current noise data is necessary.

3.1.5 Instrument Noise Measurement

Although the many unwanted contributions to the noise, which occurs in a system, may at least in principle, be eliminated, the noise due to the fundamental nature of matter cannot be reduced. The outstanding property of man made noise is the fact that it exhibits a certain periodicity and therefore its removal is theoretically possible. However, the second category of noise sources are those which are fundamental to the corpuscular nature of matter and which in any given device under given operating conditions cause a fixed known output. The main sources of such noises are thermal noise, shot noise and flicker noise which are discussed in the Discussions chapter. As they are random in nature, all we can ever say with confidence is the probability of such events occurring and their probable magnitude. As the instrument noise is affected by the source impedance

of the system we are measuring, the instrument noise was measured for source resistance of $100\text{ k}\Omega$ connected across the inputs of ZRA. The noise introduced by the reference electrode and the measurement channel was measured as potential fluctuations between a working electrode (assumed noiseless) and the reference electrode in the solutions used in our tests, and also in distilled water for comparison.

3.2 Electrochemical Cell

The electrochemical cell employed in this work was a 500 ml beaker open to air with the three electrode system described in the following paragraphs.

3.2.1 Working Electrode

Steel rod samples, 4 mm diameter and 100 mm long, were used as working electrodes. The specimens were mechanically polished on silicon carbide paper under flowing water to wash the debris from the surface immediately to avoid surface inclusions and also in order not to raise the temperature. The specimen were polished down to 1000 grade silicon carbide paper, through 600 and 800 grades, washed thoroughly in running water, then with distilled water, degreased in acetone, washed again in distilled water and finally air dried under an airblower.

3.2.2 Reference Electrode:

Unless otherwise mentioned, all potentials reported were measured with respect to a commercial saturated calomel electrode (SCE).

Uncompensated IR drop

When the potential of the working electrode is measured against a reference electrode during the passage of current I , a voltage drop equal to IR_s , where R_s is the solution resistance between the working and reference electrode, will always be included in the measured potential. The effects of the uncompensated IR_s drop on the experiments may be significant or negligible,

depending upon the experimental conditions and the requirements of the experiment. However, in most cases at least three possibilities for the effect of IR drop on the results of the experiment must be considered. First, the measured electrode potentials always involve a IR drop, which leads to an error reading of the true electrode potential and a potential control error. When the current and solution resistance are constant, then this means simply a constant error, which may be subtracted arithmetically, provided the solution resistance is known. Secondly, when linear sweep techniques are used, the current will vary in a non-linear way, making it difficult sometimes to explain the results. Thirdly, in pulse techniques, the existence of a significant voltage drop makes the rise in potential at the working electrode interface exponential, controlled by the time constant of the solution resistance and interface capacitance .

IR drop in experiments can be minimised by three main approaches ⁽³⁾.

1. Cell Design:

- a. Using a Luggin capillary and positioning the Luggin probe in close vicinity to the working electrode.
- b. Using a smaller working electrode.
- c. Using concentrated supporting electrolyte

2. Simple arithmetic correction

If the solution resistance is time-invariant and known by other methods, the real electrode potential for each current can be obtained by subtracting IR_s from the applied potential. This is often used in polarisation experiments.

3. Instrumental Correction:

One of the most common instrumental methods of IR compensation is the positive feedback method. The idea of this method is that a correction voltage proportional to the IR_s drop is added into the input of the potentiostat, so that the total applied electrode potential is compensated for the error. Similarly, the electrode potential measured is exactly E_{true} . In practice, however, there are problems with this scheme because the elements of the cell and the amplifiers in the control circuit introduce phase shifts. Thus, there are significant time lags in

the application of correction signal, the establishment of correction, and the sensing that the correction has been applied. These delays could cause the whole feedback system to overcorrect for changes in the input signal.

3.3 Solutions

To study the effect of chlorides in pour water, noise signals were measured in concrete solution, concrete solution containing 10,000 ppm chloride, 10,000 ppm chloride solution were used. The signals in distilled water also were measured for comparison.

3.4 Equipment

To measure potential and current noise signals, instruments which are highly accurate with a high degree of resolution are required. They must be capable of sensing minute changes in noise of the order of 0.1 μV and at the same time have a fast response time to respond to fast changing transients. With a suitable interface, the measured values could be communicated to a personal computer, providing a continuous time record. The transmitted data could be saved onto storage media such as floppy disk, for later retrieval and analysis. Thus a fully automated data collection system for a period of time, data storage and analysis are possible.

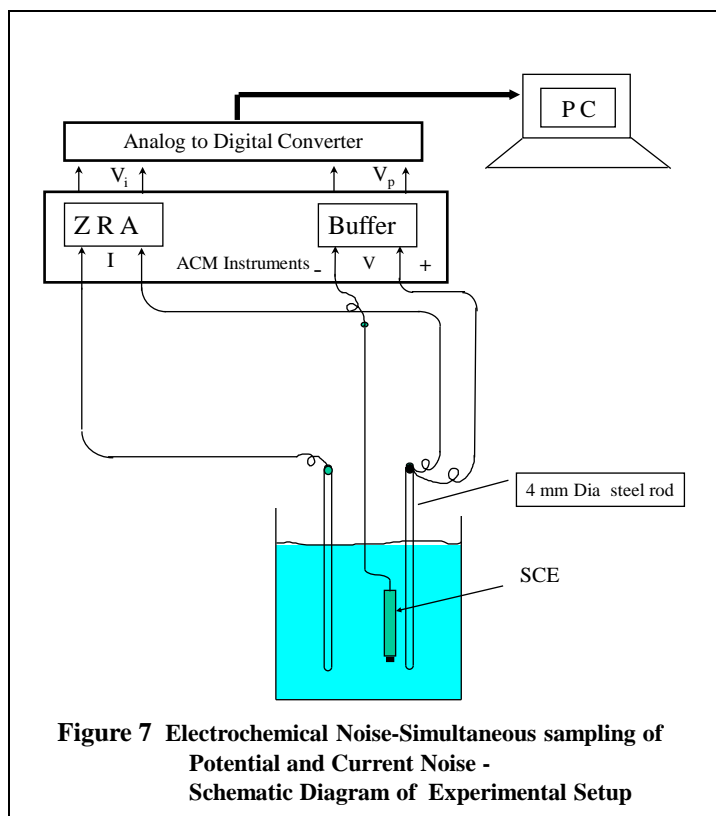
3.4.1 Zero Resistance Ammeter (ZRA)

Electrochemical noise measurements include the measurement of coupling current between two electrodes. It is normally advantageous to use two identical electrodes R.A Cottis, S.Turgoose and J.Mendoza-Flores,1994. A simple ammeter placed between anode and cathode does not measure the coupling current at short circuit conditions, because there is an IR_m drop across the ammeter, where R_m is the meter resistance. Coupling the electrodes together through the ZRA will force their potentials together; hence the difference in rates, together with any fluctuations, are observed as a current flow. This polarisation of electrodes will therefore tend to make one electrode preferably more anodic and one cathodic R.A Cottis and S.Turgoose,1994. The

disadvantage of this technique is that the ZRA current depends not only on the driving force, but also on the resistance of the circuit, for example on the impedance of the two electrodes and the resistivity of the electrolyte. However, if the electrodes are reasonably close, the effects are no different from those obtained between different parts of a single electrode.

3.4.2 ZRA of ACM Instruments

The ACM (Applied Corrosion Monitoring Ltd) Instruments ZRA is a high performance laboratory instrument designed to measure the galvanic current flowing between two electrodes, which act as if they are coupled by a zero resistance wire and to monitor the potential of the galvanic couple. The unit provides buffered current and potential outputs, which were communicated to the computer using an analog-digital converter. The following Figure details the experimental set up. The standards normally allow the method of measurement to match the bench mark of the research work as per ASTM C876-15, 2015 and ASTM G199-09(2020)e1, 2020



4. Analysis methods

Signal analysis techniques developed in communication engineering and related areas can be used in corrosion systems. Analysis could be carried out in the time domain or the frequency domain. A brief introduction to the analysis techniques is given below. For a better understanding of digital signal processing and interpretation a text book on Digital Signal processing may be referred to. One of the most common methods of analysing electrochemical noise data is to transform them into the frequency domain, as separation of the wanted from the unwanted parts can be improved further by applying signal processing techniques. The simplest method to separate out the wanted part of the signal, is that of taking the spectra of the noise of the instrument without the system under study and then subtracting these data from actual measurements. However, since the value of instrumental noise thus obtained is the expected value, rather than the actual noise generated, it could be a serious limitation if the total signal is only slightly larger than the noise to be subtracted. Much better results could be obtained by performing multiple measurements at the same time and separating the contributions of various parts by computing the cross power spectrum. Time and frequency domain analyses are related through the Fourier transforms. The conventional spectrum analyser, whether it be a sophisticated instrument or a software package, gives a breakdown of any complicated waveform into frequency components which can easily be produced and observed. According to Obot, I.B.; Onyeachu, I.B.; Zeino, A.; Umoren, S.A , 2019 that the importance of this decomposition is that the response of a system to the signal can be deduced from these individual components using the superposition principle. These elementary component signals are periodic and complex, so that both the amplitude and phase of the systems can be studied. Given a variable such as electrochemical noise data, expressed as a function of time, Fourier analysis will decompose the variable into a sum of oscillatory functions, each having a specific frequency. These frequencies, with their corresponding amplitudes and phase angles, constitute the frequency contents of the original noise signal from which we could estimate the pit initiation frequency and corrosion behaviour.

The Power Spectral Density (PSD) which is the square of the Fourier Transform is commonly used for analysis. The PSD can be estimated either using Fast Fourier Transforms or the Maximum Entropy Method. Whereas the discrete Fourier transform computes the coefficients of a series of sinewaves that sum to the observed time record, the maximum entropy method effectively computes the coefficients of a particular class of digital filter that would give the observed time record when applied to a white noise input signal. While the MEM technique inherently produces smooth spectra, the FFT can be expected to give a spectrum with a lot of scatter. Consequently some form of smoothing may have to be applied. Electrochemical noise (ECN) is highly valuable for monitoring the corrosion of steel rebars in concrete because it is sensitive to localised corrosion events and can offer real-time data.

Corrosion beginning can be detected by ECN, allowing for early identification of corrosion processes prior to the occurrence of substantial damage. Preventive maintenance and early intervention in reinforced concrete structures are of utmost importance. Corrosion rate assessment: By analysing the noise data, it is feasible to estimate the corrosion rate of steel rebars. This information is crucial for forecasting the remaining operational lifespan of structures. The characterization of corrosion mechanisms involves the identification of the specific type of corrosion taking place, such as uniform corrosion, pitting, or crevice corrosion. ECN is a useful tool in this process. This comprehension assists in choosing suitable measures to reduce or prevent negative consequences. Assessment of Safeguarding Measures: The efficacy of corrosion inhibitors, coatings, and cathodic protection systems can be evaluated using Electrochemical Noise (ECN) analysis. It enables the continuous monitoring of the effectiveness of these preventive measures in real-time. ECN data analysis employs several statistical and mathematical techniques to evaluate noise signals and extract significant insights into corrosion processes. The statistical analysis involves calculating parameters such as the mean, standard deviation, and skewness of the noise data in order to quantify the features of the noise signals. Power Spectral Density (PSD) analysis is a useful tool for determining the frequency components of noise signals. Various corrosion

mechanisms display unique frequency signatures. The Localization Index is a metric that measures the degree of localised corrosion by comparing the variability of current and potential noise signals. The Wavelet Transform is a mathematical technique that allows for the study of noise data by providing a representation of its time-frequency characteristics. This analysis is particularly beneficial for identifying and detecting transient corrosion occurrences. Although ECN is a potent instrument for corrosion monitoring, there are certain obstacles that must be overcome to ensure its successful implementation in practical situations. Signal interpretation is problematic due to the intricate nature of noise signals and the impact of several factors, including ambient conditions and concrete qualities. Standardisation is necessary to establish uniform techniques and rules for ECN measurements and data analysis, in order to guarantee consistency and dependability. The arrangement and positioning of electrodes can have a substantial impact on the accuracy and reliability of ECN data. Ensuring the electrode arrangement is optimised is crucial for obtaining precise results. Data management involves the utilisation of sophisticated tools to analyse and manage substantial amounts of noisy data for analysis purposes. The prospects for ECN in corrosion monitoring appear favourable due to technological developments and improved data analysis techniques. Integration with Smart Sensors: The incorporation of ECN with intelligent sensors and IoT (Internet of Things) devices can provide uninterrupted and remote monitoring of corrosion in concrete structures. Machine Learning and AI: Utilising machine learning techniques allows for the analysis of intricate ECN data and the prediction of corrosion trends with enhanced precision. Hybrid Techniques: The integration of ECN with impedance spectroscopy and acoustic emission, among other non-destructive testing methods, enables a thorough evaluation of corrosion. Practical uses in various fields: Creating durable and easily transportable ECN measurement equipment for on-site use would improve the feasibility and acceptance of this method in the construction sector. Electrochemical noise is an effective method for measuring the corrosion of steel rebars in concrete solutions. Despite the difficulties, its capacity to offer immediate, responsive, and comprehensive data on corrosion processes renders

it an indispensable instrument for guaranteeing the longevity and security of reinforced concrete structures. Further study and development in this field will improve the effectiveness and usefulness of ECN in corrosion monitoring as per Zhu, Y., & Chen, S. (2019).

5. Analysis & Discussion

5.1 Time Domain

Average noise behaviour is typically described by the average noise power, also described as the variance of the potential or current. It is also common to measure the square root of the noise power, $\sqrt{E_n^2}$, also known as the standard deviation of the potential noise. In order to convert the signal that is subject to drift into a better approximation of a stationary process, a straight line was fitted to the original data, and then the deviation of individual points from the straight line was used as the new 'detrended' data set.

5.2 Frequency Domain

Analysis of data in the frequency domain brings out features not readily seen in the time domain. As the individual charge transfer events making up the source of the random fluctuations is mixed with the background noise of the instrumentation used, it is necessary that the analysis be carried out in the frequency domain as well. We have used the unit V^2/Hz to plot PSD, as it relates to the power distribution of the sequence and the 'amplitude-squared' measure has the dimensions of power. The terminology used for current noise is essentially that for potential noise. The current spectral density is reported with units of A^2/Hz . Several techniques are available for the estimation of power spectra, the two most commonly used for electrochemical noise being the Fast Fourier Transform (FFT) and the Maximum Entropy Method (MEM). The MEM has the advantage of producing a smooth spectrum, whereas the FFT necessarily has a large scatter. On the other hand FFT has a more direct relationship with the time record, in the sense that the time record can be

reconstructed by means of inverse transformation. In practice it is reported that both methods give the same information⁽¹⁾ and this is confirmed by our result also. Therefore, we have used MEM to compare the different noise signatures.

6. Experimental Results

The de-trended time records along with their PSD plots calculated using FFT & MEM methods are used and the average potential noise power (variance) of the collected time record, the average potential noise power spectral density at low frequencies upto 0.1 Hz calculated from the MEM results are shown below.

	<i>Potential Noise Power</i>		<i>Current Noise Power</i>	
	<i>Time domain</i>	<i>Freq domain (upto 0.1 Hz)</i>	<i>Time domain</i>	<i>Freq domain (upto 0.1 Hz)</i>
	<i>V²/Hz</i>	<i>V²/Hz</i>	<i>A²/Hz</i>	<i>A²/Hz</i>
<i>Instrument Noise (100 k resistor)</i>	5.966E-10	1.229E-09	1.244E-19	3.168E-19
<i>Distilled Water</i>	8.821E-06	3.382E-05	1.080E-13	5.466E-13
<i>Cement solution-1</i>	9.667E-06	2.654E-05	3.570E-14	1.102E-13
<i>Cement solution-2</i>	2.706E-06	2.167E-05	3.475E-15	1.562E-14
<i>Cement solution + NaCl 10,000 ppm</i>	7.948E-06	8.667E-05	1.129E-13	6.524E-13
<i>Sodium Chloride 10,000 ppm</i>	5.354E-06	3.011E-05	3.507E-12	3.187E-11

7. Discussion

The instrument noise is the minimum noise that is intrinsic to the system due to internal noise sources. Based on a shot noise model⁽²⁾ the average current noise power is related to i_{corr} and q by:

$$\overline{I_n^2} = 2 q_a i_{corr} b$$

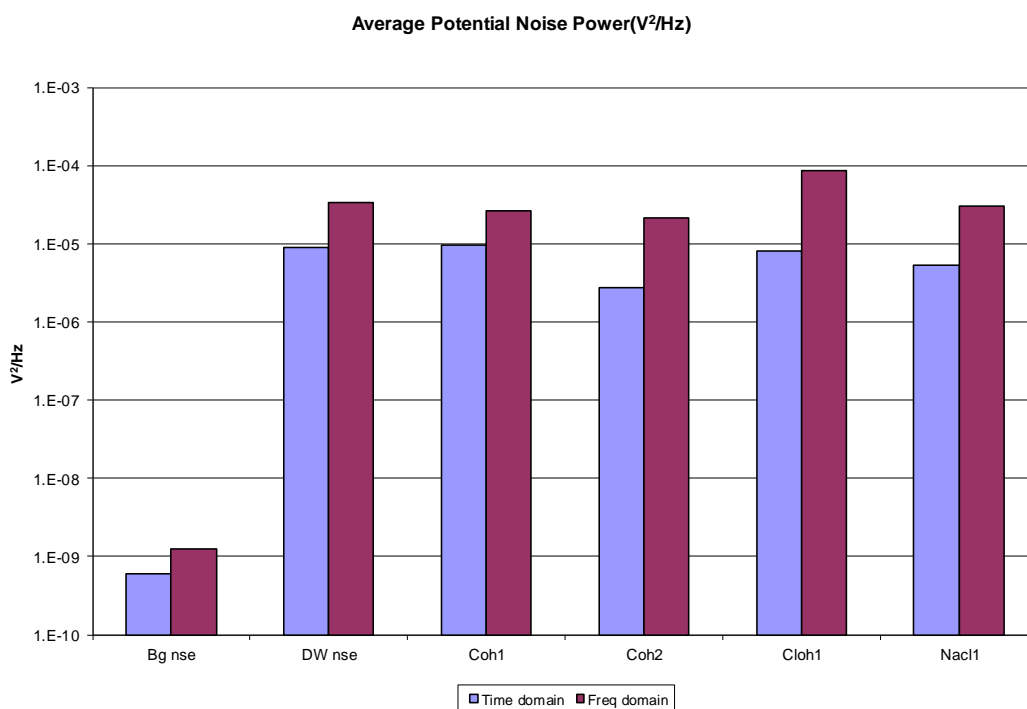
By assuming the potential noise to be the result of the current noise acting on the polarisation resistance, R_p , at the low frequency limit and substituting B/i_{corr} for R_p we get the following equations for potential noise:

$$\overline{E_n^2} = R_p^2 \overline{I_n^2}$$

$$\overline{E_n^2} = 2 B^2 q_a b / i_{corr}$$

From the above equations, it is seen that the current noise power is directly proportional to i_{corr} whereas the potential noise power is inversely proportional to i_{corr} according to M.G. Pujar, T. Anita, H. Shaikh, R.K. Dayal, H.S. Khatak 2007

7.1 Potential Noise

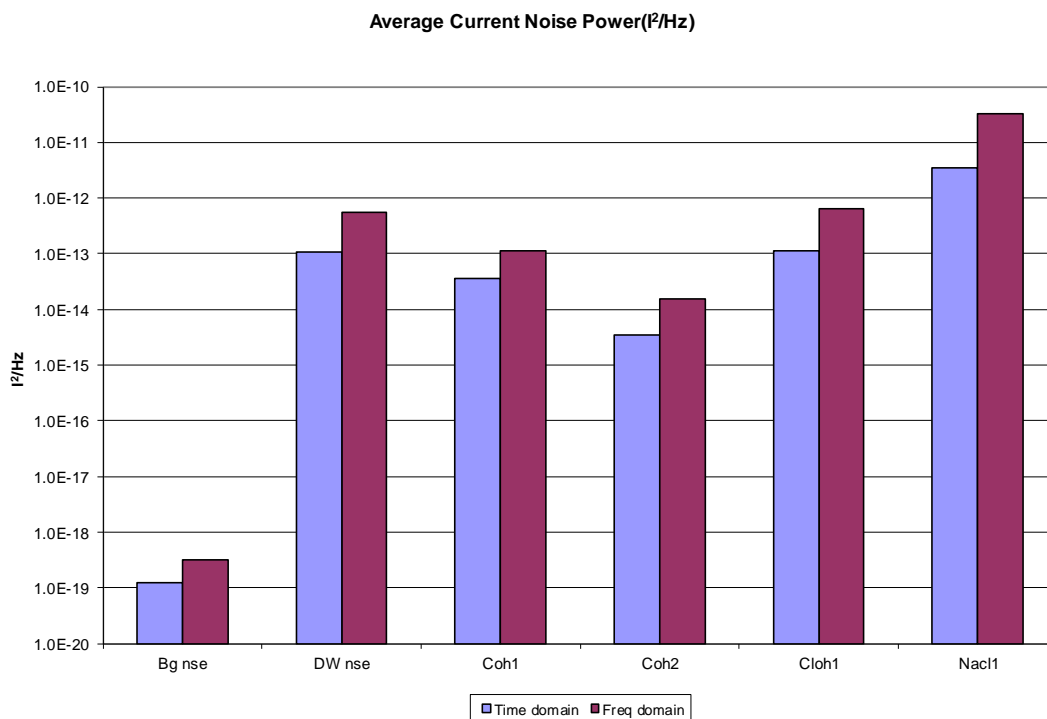


The instrument noise is many orders less than the actual potential noise. Beyond that, it becomes difficult to interpret the results and establish a relationship. However, it is clear from the results that the monitoring of potential

noise alone is not sufficient for making any meaningful predictions about the localised corrosion behaviour.

As pits initiate the increase in the instantaneous pulses of charge causes the potential noise to increase proportionally. However, when pits grow, R_p falls (increase in i_{corr}) and therefore the potential noise either decreases or remains the same depending upon the relative magnitudes of the individual effects. Hence, electrochemical potential noise, by itself, cannot be correlated unambiguously with corrosion rate or even the occurrence of localised corrosion.

7.2 Current Noise



The current noise powers are many orders higher than the background noise. As expected from the shot noise model, the current noise power is higher in solutions containing chloride. The current noise power in cement solution is lower in the cement solution compared to that in distilled water which probably is due to the effect of the passivating iron oxide film which rapidly forms on the steel surface in the presence of moisture, oxygen, and the water soluble alkaline products during the hydration of cement. It appears that the current noise power as well as i_{corr} will decrease progressively as the surface gets coated.

7.3 Estimation of Charge

The dissolution process in an electrochemical reaction can be considered as a series of brief events occurring randomly. For uniform dissolution processes it is expected that the value of charge, q , will correspond to the charge liberated by 10^2 to 10^6 atoms. However, the initiation process of pitting is often found to involve a charge of the order of 10^{-6} C corresponding to about 10^{12} atoms. Therefore, it is expected that the estimation of the charge in the transient will provide a valid parameter for the practical identification of localised corrosion. Conventionally, the calculation of charge exchanged is straightforward and obtained by integrating the current passed over a period of time. If analog chart recorders are used for the noise trace, curve fitting procedures may be used to approximate the growth and decay curves. On the other hand digitised time records do not provide information in the interval between the sampling periods. However, with suitable software one could approximate the growth and decay curves using sophisticated curve fitting techniques. We have not studied the shape of the transients considering the complexity of curve fitting techniques. Moreover, it is difficult to estimate the area under a transient accurately for a sampled time record. Instead, we have attempted to estimate the quantity of the charge in the transient from the statistical properties of the time record. Moreover, an automated analysis capable of coping with many transients is possible using the statistical approach. By considering the parameters at low frequencies only, the effect of the capacitance is minimised and the impedance of the metal-solution interface is just the polarisation resistance at the low frequency limit. If we consider the potential noise to be the effect of current noise acting on the polarisation resistance (at the low frequency limit) then the statistical parameters from potential noise may also be used in the estimation of charge. Armed with the above assumptions, the electrochemical noise may be described using a shot noise model. The charge, q , can be estimated for the assumed shot noise model at the low frequency limit from the relation ^(1,2):

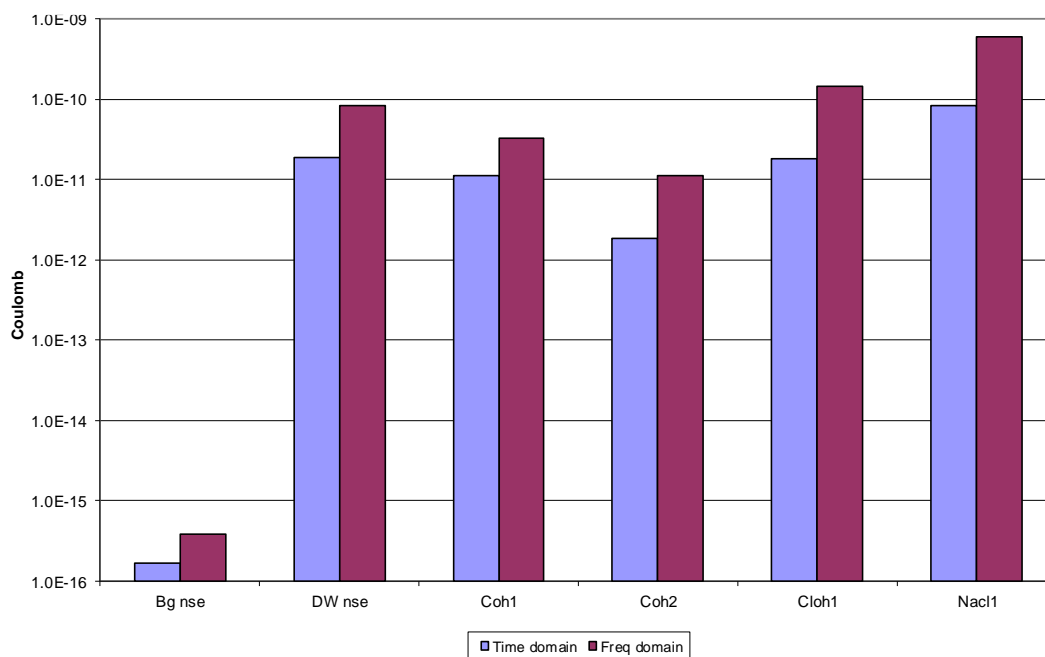
$$q = \frac{\sqrt{E_n^2 \times I_n^2}}{2 B b}$$

The Stern-Geary proportionality constant calculated from the Tafel constants is given as:

$$B = \beta_a \beta_c / 2.303(\beta_a + \beta_c)$$

We have selected Tafel constants, $\beta_a = \beta_c = 118 \text{ mV}$, giving a Stern-Geary coefficient, B , of about 26 mV . The bandwidth, b , is 0.5 Hz in our case. The following Table shows the calculated values of q for the various test conditions.

	Estimated Charge	
	<i>Time domain</i>	<i>Freq domain</i>
	<i>Coulombs</i>	<i>Coulombs</i>
<i>Instrument Noise (100 k resistor)</i>	<i>1.657E-16</i>	<i>3.794E-16</i>
<i>Distilled Water</i>	<i>1.877E-11</i>	<i>8.269E-11</i>
<i>Cement solution-1</i>	<i>1.130E-11</i>	<i>3.290E-11</i>
<i>Cement solution-2</i>	<i>1.865E-12</i>	<i>1.119E-11</i>
<i>Cement solution + NaCl 10,000 ppm</i>	<i>1.821E-11</i>	<i>1.446E-10</i>
<i>Sodium Chloride 10,000 ppm</i>	<i>8.333E-11</i>	<i>5.957E-10</i>



The calculation of charge is based on a shot noise model valid for frequencies that are low enough that individual transients can be regarded as instantaneous pulses. However, our calculations of average potential and current noise power so far are based on time domain data, which includes the power from all the frequencies and not just the low frequencies. The frequency domain analysis enables us to calculate the charge based on average noise power contained in low frequencies only. Based on the shot noise model of electrochemical noise, it has been suggested by Cottis and others ⁽¹⁾ that a large value of q is indicative of localised corrosion. The results shown above appear to conform to the model. The charges estimated in chloride containing solution are higher compared to the other cases. The charge in cement solution is less than that in distilled water due to the formation of a calcium hydroxide passivating film.

7.4 Comparison of q estimated from the Time & Frequency domains:

The quantity of charge in the charge transfer event was calculated from the average noise power by the equation:

$$q = \frac{\sqrt{E_n^2 \times I_n^2}}{2 B b}$$

The calculation of q from the time domain make use of the average potential and current noise powers over the entire time period (variance) in the $\sqrt{E_n^2 \times I_n^2}$ part of the equation. Basically the calculation based on the standard deviation is equivalent to the average PSD over the full frequency range of the spectrum. In contrast the frequency domain calculation is based on the low frequency limit, which normally corresponds to the maximum PSD. Hence, we would expect the frequency domain calculation to give the larger value of q , which is confirmed from our results also.

8. Conclusions

If we consider the fundamental processes underlying the generation of electrochemical noise, a parameter that may be more appropriate is the amount of charge in each transient. Even for uniform dissolution processes occurring as a series of bursts it is expected that the value of q to correspond to the charge liberated by 10^2 to 10^6 atoms. However, the pit initiation process, often found to result in metastable pit nucleation and propagation, gives rise to current transients involving a charge of the order of 10^{-6} C (corresponding to around 10^{12} atoms). Therefore, the electrochemical noise associated with pitting corrosion is much larger than that observed for general corrosion. We have estimated the charge in the transient in the time domain as well as the frequency domain. For the calculations in the frequency domain, the potential and current noise powers contained at low frequencies upto 0.1 Hz only were considered. Various criteria have been developed in the past to assess a material's tendency to localised corrosion based on its electrochemical noise response⁽³⁾. It remains to be seen which of the above parameters is more appropriate for the practical identification of localised corrosion.

9. Future work

The specimen must be inspected using an electron microscope after the test and the topology of the pit studied, and compared with the volume of the pit corresponding to the anodic charge estimated from the potential and current noise powers.

If we assume that the potential noise occurs as a consequence of the current noise, whereby the electrode potential is modified by the action of the current noise on the polarisation resistance, we expect the transients in both current and potential noise to occur at the same instant and therefore to show a strong cross-correlation. Therefore, it would appear reasonable to make use of the correlated potential and current noise powers only, and not the entire spectrum. Such a correlated analysis will be covered in our next paper as it is counted to be the second stage followed by the third stage of translating the simulating phenomenon into the practical using the current cement and concrete mixture.

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