ELECTROCHEMICAL NOISE ANALYSIS OF ANAEROBIC (BACTERIAL) CORROSION OF STEEL

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Abstract Corrosion of structural steel in an SRB containing environment for as long as 9 months, is studied using the Electrochemical Noise Analysis technique. The results show that the activity of the system, which was very low initially, started to increase after 6 months exposure to the environment. The power spectral density curves of the Electrochemical Potential Noise of the system, using the maximum entropy method (MEM), indicate the existence of a characteristic pattern in the spectra. The effect of the yeast extract in the culture media, added periodically to support the growth of the bacteria was shown to suppress the signals, which is related to the corrosion inhibition effect of the yeast extract. After feeding, it usually took 3 weeks before the corrosion activities, as manifested by the rms values of electrochemical potential noise of the system, reached the values prior to the addition of the culture media to the system. These preliminary results indicate that analysis of electrochemical noise may offer promise in detection and monitoring of bacterial corrosion.

چکیده خوردگی فولاد ساختمانی در آب دریا حاوی باکتریهای احیا کننده سولفات(SRB) به مدت ۹ ماه با استفاده از روش تحلیل نویزالکتروشیمیایی مورد مطالعه قرار گرفته است. نتایج نشان میدهند که سرعت خوردگی فولاد که ابتدا پائین است، بعداز ۶ ماه شروع به افزایش می نماید. منحنی های دامنهٔ نویز پتانسیل برحسب فرکانس که با استفاده از روش ماکزیموم انتروپی (MEM) محاسبه می گردد، نشاندهندهٔ یک الگوی خاصی در طیف فرکانس است که میتواند نشاندهندهٔ تأثیر باکتریها در پروسس خوردگی باشد. این نتایج بهمراه تغییرات RMS سیگنالها همچنین دلالت بر موضعی بودن خوردگی دارند. محیط کشت که برای ادامهٔ حیات و رشد باکتریها به سیستم اضافه شده، دامنهٔ سیگنالهای نویز را کاهش می دهد. این تأثیر به اثرات بازدارندهٔ خوردگی شیرهٔ مخمر موجود در محیط کشت نسبت داده می شود. بعد از هر بار اضافه کردن محیط کشت به سیستم مدت سه هفته طول می کشد تا سرعت خوردگی مجدداً افزایش یابد و به مقادیر قبل از اضافه کردن برسد. این نتایج اولیه نشان میدهند که روش تحلیل نویز الکتروشیمیایی میتواند در شناخت و کنترل خوردگی بیولوژیکی مورد استفاده قرار گیرد.

INTRODUCTION

Corrosion of iron and steel under anaerobic conditions in the presence of sulphate- reducing bacteria (SRB) is well documented [1]. Based on the electrochemical theory of corrosion, de-aerated soils of near-neutral pH are not expected to be corrosive to iron and steel. However, if the soil contains SRB and a source of sulphates, rapid corrosion has been found to occur [1].

The mechanisms originally proposed for the corrosion involved the removal of atomic hydrogen from the metal surface by the bacteria using the enzyme hydrogenase [2]. The hydrogen was thought to be utilized by the bacteria in the reduction of sulphates to sulphides. It is now recognized that this original mechanism, although it undoubtedly plays an important role, does not represent the entire process. It has been shown that the iron sulphide (FeS) film produced is protective if continuous but that it causes galvanic corrosion of the bare iron underneath if defective. Other corrosive substances, such as H_2S, can also be produced. The SRB have also been identified as contributors to corrosion of

stainless steel, copper and aluminium alloys, but the details of the mechanism are still being debated [3, 4].

Pipelines and other metal objects buried in the ground and structures erected in estuaries frequently show anaerobic sulphide attack. Booth [5] estimated in 1964, that at least 50% of corrosion failures of underground pipes in the UK are caused by bacterial corrosion. Pipeline corrosion is most severe in wet clay or clay loam of about neutral pH value. Progressive pitting corrosion is common: cast iron pipes with wall thicknesses of 6.3 mm have occasionally become perforated within a year of installation under these conditions and perforation within 4 years is quite common [6].

Local anaerobic conditions favoring growth of SRB can arise under heavy mixed microbial growth in industrial situations such as open recirculating cooling water systems [7] the paper making industry [8] or heat exchangers cooled by river water [9]. Catastrophic corrosion of condensers by marine sulphate- reducers in a once-through system has also been observed [10]. Ships berthed in estuaries in which they rest on bottom mud at low tide have also been reported to suffer from this type of corrosion [11]. The oil and gas industry is known to have extensive SRB induced corrosion problems [12].

Electochemical noise is simply flucuations in cell current and electrode potential of an electrochemical cell, and is related to changes that are occurring at the metal solution interface. The analysis of electrochemical noise can provide information concerning the nature of the reactions that are occurring at the interface [13-15]. Noise analysis is very well developed in various fields (electronics, chemistry, biology, and electrochemistry). In particular, it seems that this method can give information which cannot be reached by normal impedance measurements. Therefore, there is an increasing interest to apply electrochemical noise analysis to Corrosion Science and Engineering [16-25].

The study of electrochemical noise which started in early 1970, has been carried out in a wide spectrum, ranging from interfaces generating small amplitude fluctuation (of the order of μV) often related to the microscopic nature of the process involved at the interface, to other interfaces with larger amplitude fluctuations (of the order of mV) related to semimicroscopic events (gas evolution, nucleation and growths, pitting corrosion, etc.) which involve many particles.

In principal, detecting electrochemical noise consists of recording the variations with time of cell voltage and cell currents. Special low noise equipment such as amplifiers and potentiostats, battery operated for mains interferences and extensive shielding may be necessary in some cases where the amplitude of fluctuations is very small. The resultant "time records" can then be analyzed by various mathematical techniques. The magnitude of the rms or standard deviation of the recorded signals indicates the stability of the interface. The more unstable the interface, the greater will be these values. The most common way to analyze noise data is to transform the time records data into the frequency domain, that is, obtain the power spectral density (PSD) or its square root, power spectral amplitude (PSA). The advantage of frequency domain analysis is mainly that deconvolution of unwanted signals becomes much easier, so that a better picture of the main reactions is obtainable.

The main uses of electrochemical noise analysis (ENA) in corrosion have been the study of pitting and localized corrosion and in looking for characteristic signatures in the noise specter, as an indication of specific kinds of corrosion attack [16-21].

The aim of the present study was originally to explore the possibility of differentiating between biological and nonbiological corrosion. In fact, at the present time, there are no available electrochemical techniques which can accurately determine the location on the steel structures where SRB are actively causing corrosion. Electrochemical noise has been discussed by some as a promising technique for

the detection of bacterial corrosion [26-27], however there are no published data on this subject.

In this work, only low frequency (1 to 1000 mHz) potential noise of SRB influenced corrosion of steel has been studied. In the frequency range studied, conventional equipment with no shielding could be used. Our preliminary results indicate the possibility of detection of microbial corrosion using ENA technique exists. However,there is need to extend the frequency range of the analysis and to evaluate more closely the changes that occur during microbial and other localized corrosion processes.

EXPERIMENTAL PROCEDURE

Specimen Preparation

Samples with the dimensions 23 × 23mm^2 were cut from low C structural steel sheet with 3 mm thickness. Some samples were prepared and immersed in the cell for measuring the corrosion rate by the weight loss method and for electron microscopy and X-ray diffraction of the surfaces. For electrochemical studies, a copper wire was soldered on one side of the samples and then mounted in epoxy resin. The surface of all the samples was polished up to 1000 grit size emery paper, washed with distilled water and acetone and kept in a dessicator before exposing to the corrosion cell.

Table 1. Chemical Composition of Modified Post Gates Double Strength Mekium

	g/l
Resazurin	0.01
D_2HPO_4	1.0
NH_4Cl	2.0
Na_2SO_4	2.0
$MgSO_4 7H_2O$	4.0
Na lactate	10.0
Yeast extract	2.0
Na_2SO_3	1.0
Sea water (aged 4° C)	1000

PH adjusted to 7.4 with 1 molar Na OH, bottled and autoclaved at 121°C for 20 minutes, stored 4°C.

Anaerobic Environment

The steel samples were exposed to 2 litres of sea-water containing modified Postgate B Culture medium to support the growth of the bacteria. The chemical composition of the modified Postgate B medium is shown in Table 1. The top of the cell was covered with about 1 cm thick layer of liquid paraffin to prevent oxygen diffusion from the air into the cell.The cells were initially contaminated with SRB strains. SRB were isolated from 3 separate oil and gas rigs located in the northwest of Western Australia. All of these strains were *Desulfovibrio salixigiens.* The number of bacteria in the cells was of the order of 10^9 per ml. 500 ml of the test solution were replaced with fresh Postgate B medium every 30 days during each test. The cells were in duplicate and also a sterile cell of the same composition was used for comparison. In constructing the anaerobic corrosion cells, the recommendations of Stott, Skerry and King [6] regarding the ratio of metal surface to the volume of the cell and semi-continuous and long term exposure in excess of 6 months were followed to obtain reliable results as regards to SRB corrosion. The temperature of the bath was held constant at 22± 0.5°C, and all the results presented here are at that temperature.

Table 2. Procedure for the Fixation and Dehydration of the Biofilm for SEM.

1. Fix for 4 hrs in 5% Glutaraldehyde in O.1 M Sodium Cacodylate (buffer) pH 7.
2. Wash with buffer 3 times, soaking time 10 minutes.
3. Post-fix in 1% Osmium tetraoxide in buffer for 45 minutes.
4. Wash with buffer 3 times, soaking time 10 minutes.
5. Dehydrate in the following mixtures of Ethanol + buffer (50%, 75%, 95%, 100%, 100%), soaking time 10 minutes.
6. Dehydrate in the following mixtures of Amyle Acetate + Ethanol (50%, 75%, 95%, 100%) soaking time 10 minutes.
7. Flush with CO_2 at 1000 psi and 25°C in Critical Drying Unit to replace Amyl Acetate.
8. Increase temperature to 30-35°C to reach the triple point of CO_2.
9. Devacuum chamber and store the specimen in an oven at 60°C.
10. Sputter coat with gold and deliver to SEM laboratory.

Microscopic Observation

The motility of the SRB'S was checked periodically using "phase microscopy" to ensure the viability of these microorganisms. The preweighted coupons exposed to the corrosion cell were also taken out periodically for scanning electron microscopy of biofilm, corroded surface, X-ray diffraction of corrosion product and weight loss determination.

The procedure for the fixation and dehydration of the biofilm for SEM is shown in Table 2. The corrosion product on the coupons were removed by immersion in 10% HCl solution for 5 minutes in a sonic bath for the determination of the weight loss and SEM of corroded surfaces.

Electrochemical Noise Measurement

The open circuit potential between two identical electrodes in the cell was measured using a high impedance voltmeter. The voltmeter output was connected to an IBM-PC compatible computer and a Metrabyte (28) DAS-8PGA analog to digital converter board (12 bit resolution, 4μs acquisition time and ±10 mV to ±10V input ranges). Time records consisted of up to 16,200 data points taken at sampling frequencies in the range 1 to 10 Hz.

Data Analysis

The time domain records were transformed to the frequency domain to give both power density and amplitude spectra, using the maximum entropy method (MEM) developed by Burg [29]. The MEM technique was preferred to the alternative Fourier Transform technique as it inherently produces smoother spectra, without apparent loss of information [30], and is simpler to use when the number of data points is not a power of 2.

All calculations were carried out with double precision floating point arithmetic, to minimize rounding off errors, and the data were corrected for linear drift prior to calculation of RMS noise levels and transformation to the frequency domain. As the frequencies beyond the limits of the experiment cannot realistically be computed, the frequency domain was restricted to a lower limit of 1/t where t is the length of the time record in seconds, and an upper limit of the Nyquist frequency 1/2f, where f is the sampling frequency. Six coefficients (poles) were used to calculate the power density and amplitude spectra as it was found that a greater number of coefficients did not alter the spectra significantly, other than producing less smooth results.

RESULTS AND DISCUSSION

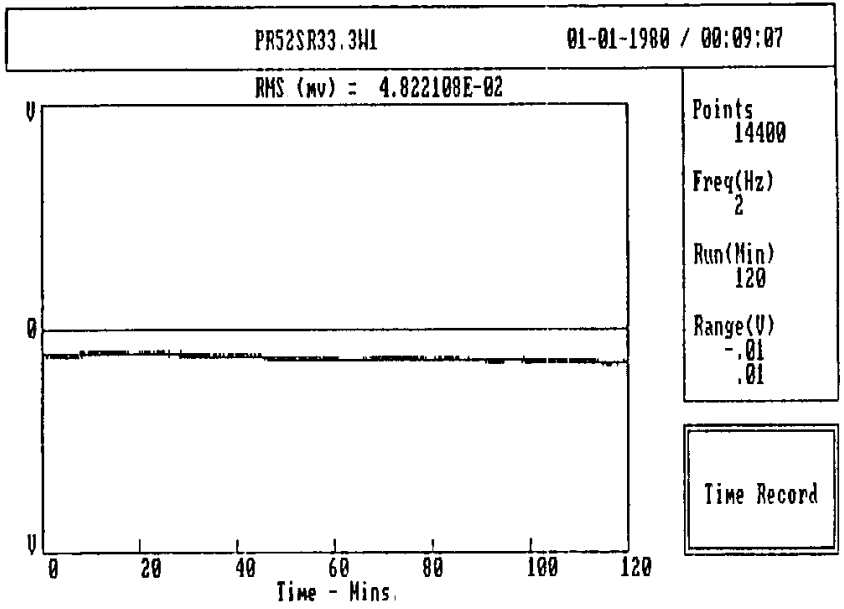
Potential-time Records

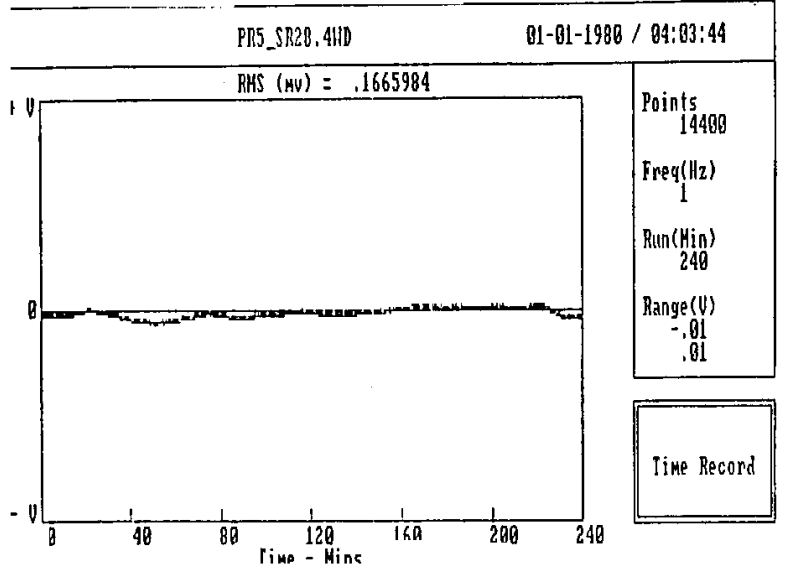
Figure 1 shows the typical examples of potential-time records of the identical pair of steel electrodes immersed in seawater containing SRB under anaerobic condition. The time records can be classified in the following categories:

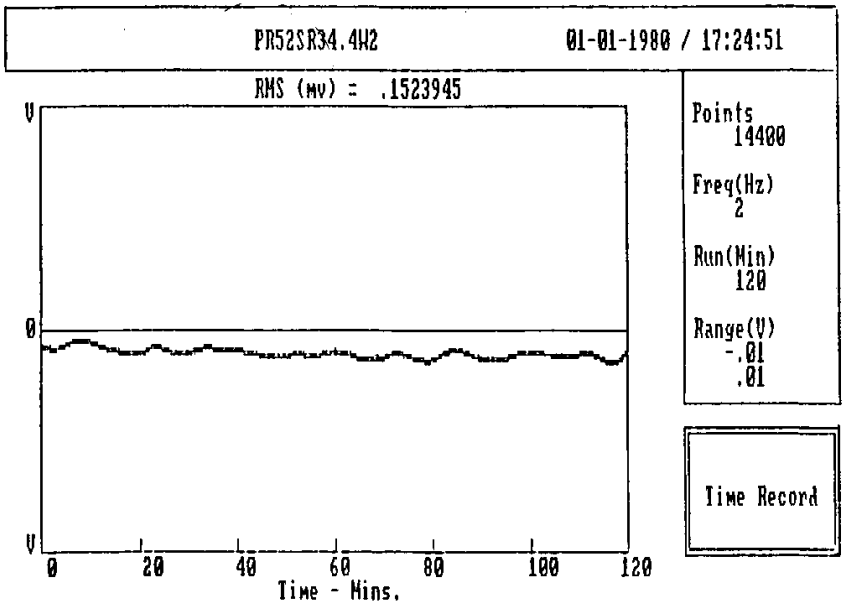
1. Almost steady, such as Figure 1(a), where potential difference drifts at a few microvolt per minute.
2. Unstable and irregular, such as Figure 1(b).
3. Unstable and regular, such as Figure 1(c).
4. Very unstable, such as Figure 1(d) where there is an abrupt shift in the potential difference, greater than a few volts.

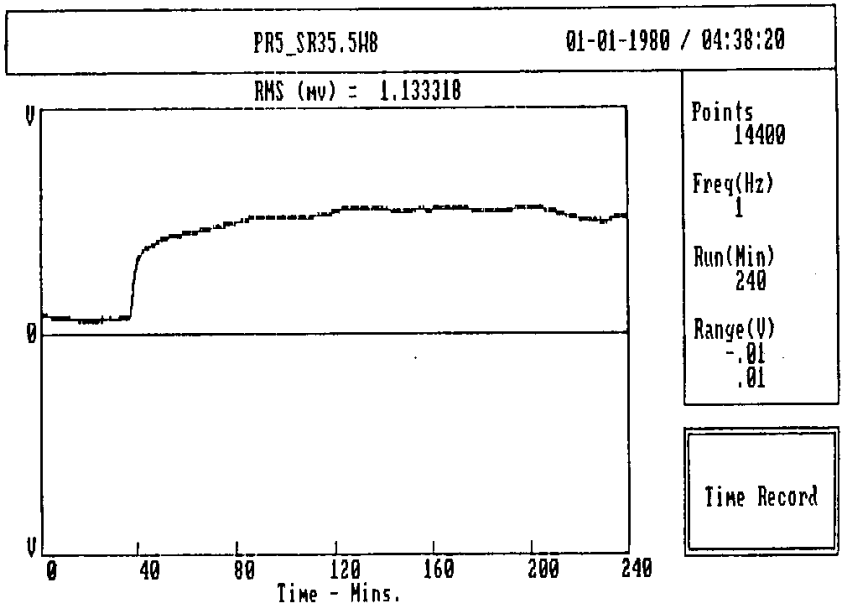
As seen from Figure 1, the potential variation is in the range of ±5 mV, with the exception of the first few days after the addition of the culture media to the cell to support the growth of bacteria every 4-6 weeks. In these cases, the potential difference variations were in the ±20 mV range for the first few days before it drifted back to the smaller range prior to the addition of the culture media. Whereas all the time records showed a very small high frequency potential fluctuation of <0.1 mV, during the 9 months monitoring of the potential of the cell, there was only two instances with high frequency potential in the range of a few mV for short times, about 90 minutes. One of these instances is shown in Figure 2.

Based on experience with potential fluctuations of steel in a non-biological









general clas

(c) unstabl

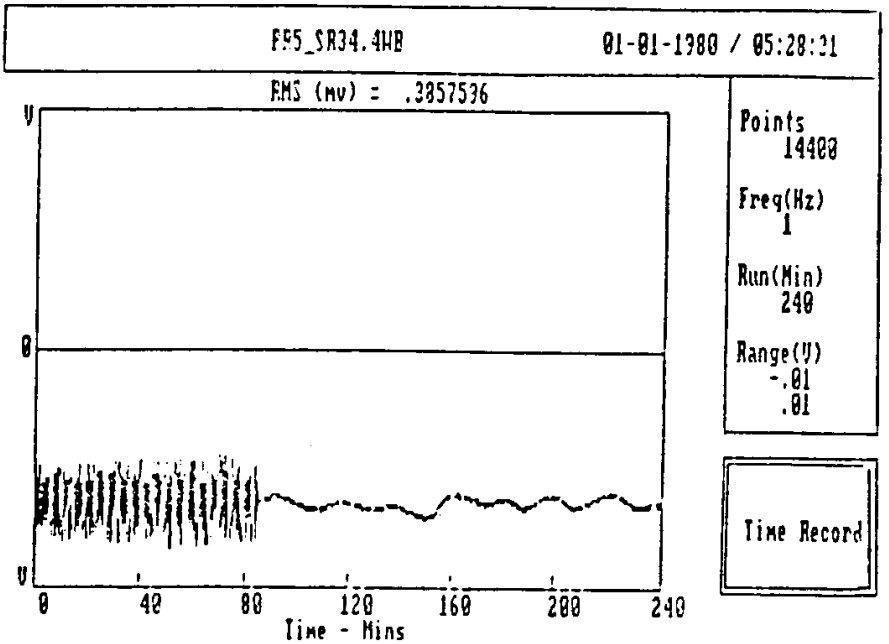


Figure 2. One of the two instances of time records showing high frequency fluctuation in the range of a few mV. Notice that it is temporary, about 90 minutes in this case.

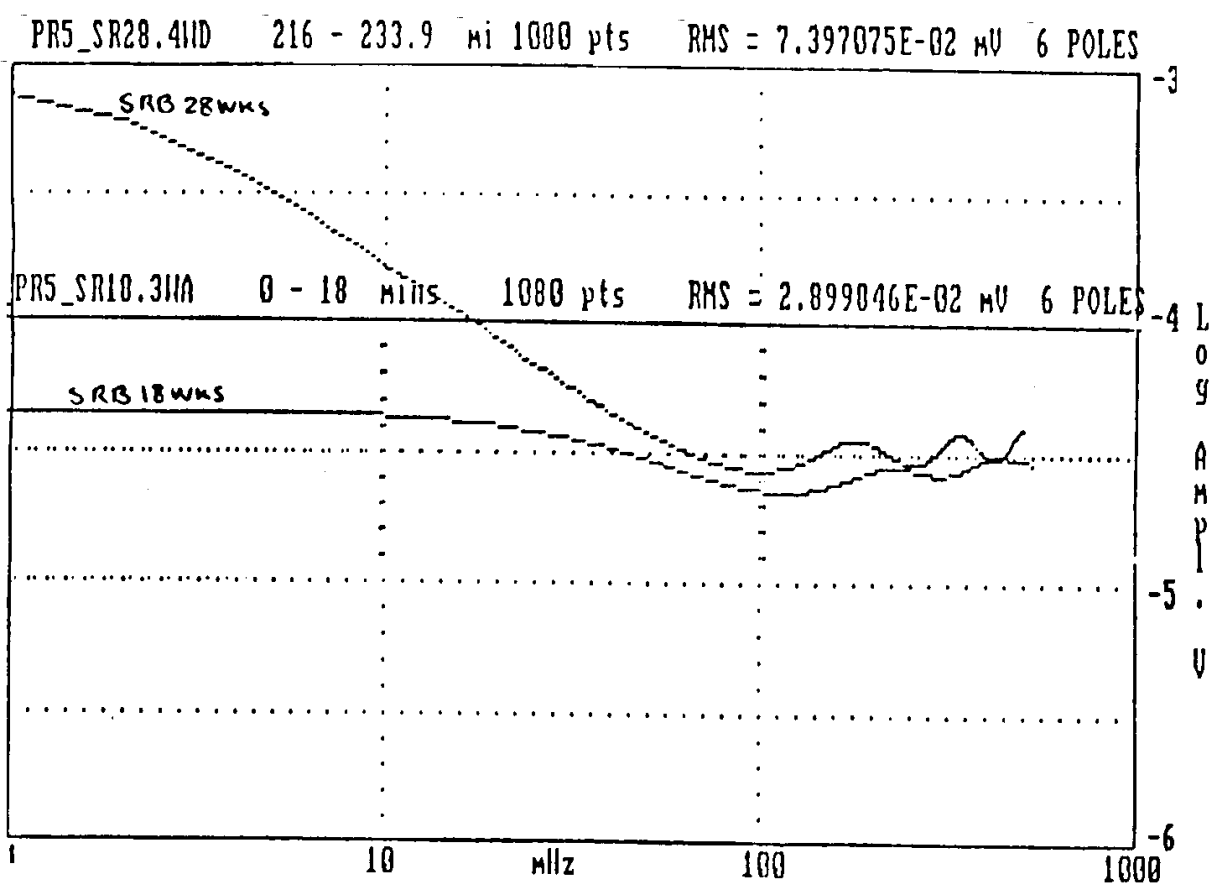


Figure 3. Spectral density curve of steel electrodes after 18 and 28 weeks of exposure to SRB, showing the start of SRB attack after about 6 months.

environment undergoing localized corrosion and based on the prevailing theories about SRB corrosion, the above behavior can be pictured as a passivated steel (Figure 1(a) behavior) situation which eventually undergoes localized corrosion (Figure 1(b) and (c) behavior) by the process of passive layer break down and repassivation. The typical behavior corresponding to Figure (1b), where there is an abrupt shift in the potential, could be associated with either a sudden change in passive film stability, when the magnitude of the shift is a few mV, or else the start of a new localized corrosion system, when the magnitude of the shift is more than 10 mV. The latter case was only observed once after 8 months although there could have been such cases in the whole 9 month long tests because the potential was not recorded continuously. The addition of the culture media to the cell every four to six weeks seems to have caused a depolarization effect by introducing various chemicals in the cell such as ferrous ions and yeast extract, thus increasing the potential momentarily. Obviously, the new culture media leads to further growth of SRB and hydrogen sulphide production which causes the system to drift back to a passive state in the following days.

Spectral Density Curves And RMS Values

Figure 3 shows the spectral density curve of the electrochemical potential fluctuations of the steel electrodes after 18 and 28 weeks exposure to the cell. Each curve shows the frequency composition of a portion of the time records comprising the total 1080 points which corresponds to 18 minute time records, recorded at the rate of 1 point per second. Figure 3 shows that the spectral density curves consist of 3 different sections:

1. A plateau in the 1-10 mHz frequency range, indicating the amplitude of the low frequency fluctuations of the potential.
2. A roll off in the intermediate frequency range of 100-500 mHz which, in conjunction with the plateau, is related to corrosion activity of the system.
3. A peak structure in the frequency range >100 mHz, which does not change very often and seems to be the characteristic pattern of a particular process at the interface.

In Figure 3, the RMS values for each curve are also shown. The RMS value is equivalent to the area under the spectral density curve, and is an overall measure of the activity of the system. In fact, since the higher frequency peak structure always occurs at a fixed position, then, the RMS value is proportional to the amplitude of the plateau and the slope of the roll off. The higher the RMS value, the higher the amplitude of the plateau and therefore the steeper the slope of roll off and vice versa. It is therefore useful to look at the variations in RMS values during the total length of the test life and its various stages, before discussing the spectral density further.

Figure 4 shows the typical variations in the RMS values in the 4th and 6th months of cell life. As was the case for spectral density calculations, the RMS values also correspond to 1080 points of time record readings. Figure 4(a) shows the typical variations in the RMS values of the system for the periods less than 6 months and Figure 4(b) represents the typical variations of the RMS values for the periods greater than 6 months. The RMS values in the former were very low and almost constant at about 0.025 mV.

From 6 months and onwards, and usually after 3 weeks of feeding time, the RMS values started to fluctuate around 0.03 mV. This was an indication of an increase in the corrosion rate of the system. More importantly, this change in corrosion activities was accompanied by a well defined and reproducible peak structure in the high frequency range (>100 mHz) of spectral density curves, which was different for periods less than 6 months where the corrosion rate was also very low (Figure 3). These findings are in agreement with previous results by others [6] that in anaerobic corrosion by SRB, between 4-6 months are necessary to allow a stable crystallographic form of iron-sulphide, which is non-protective to the metal, to form when the corrosion rate is increased several fold.

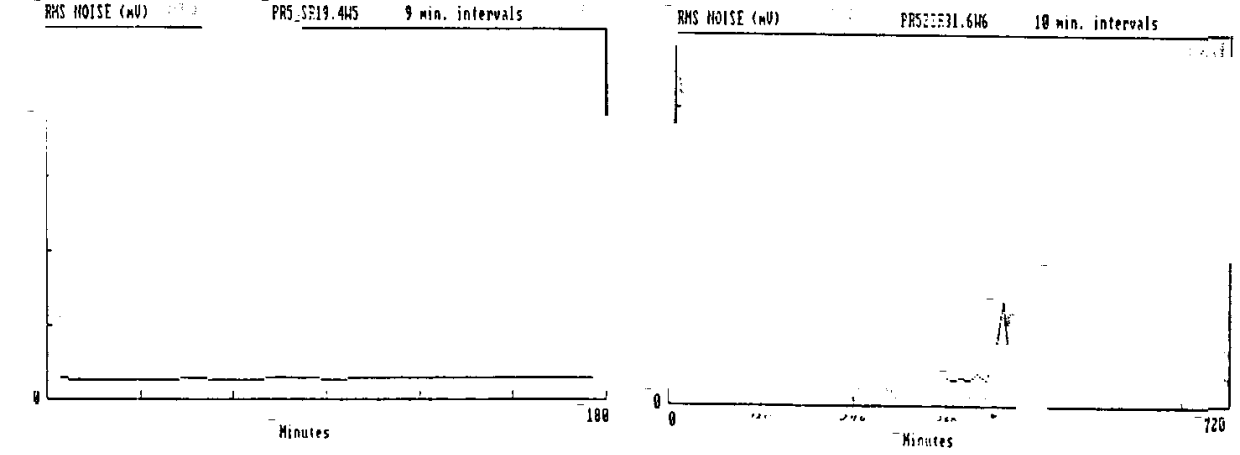


Figure 4. RMS values of the data shown in Figure 3.

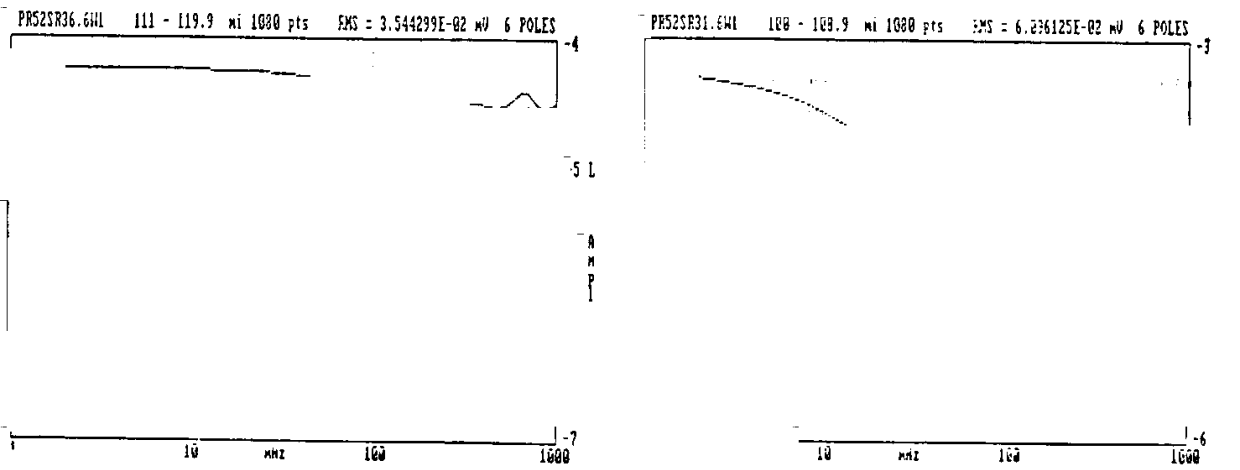


Figure 5. Spectral density curve of potential noise of steel electrodes recorded at the rate of 2 readings per second, thus enabling spectral density estimation to extend to 1000 mHz.

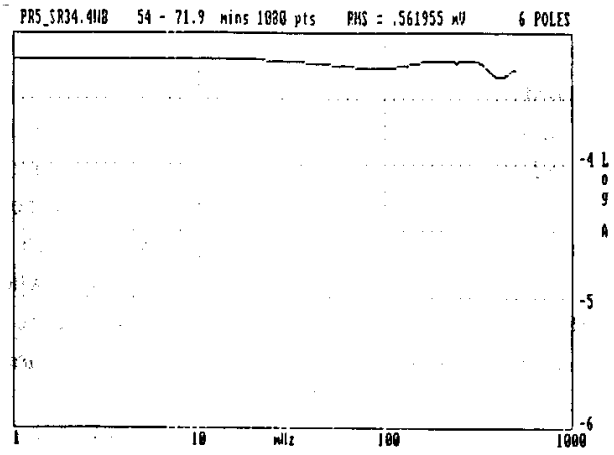


Figure 6. Spectral density curve corresponding to the portion of time record of Figure 2, which contains high amplitude high frequency signals.

In order to expand the range of frequency in spectral density calculations, a second set of data was recorded at two points per second, thus enabling the spectral density estimations to extend to 1000 mHz, (Figure 5). These results confirmed the existence of a consistent peak structure in the frequency range 100–1000 mHz, for test periods longer than 6 months. The notable exception to this behavior was in instances when there was a dramatic change in potential (time records such as Figure 1(d)) and therefore a dramatic change in corrosion activities. In these instances, the peak structure in spectral density curves showed a different peak structure for a while before it returned back to the usual shape. Another exception was for the cases where the time records showed temporary high frequency fluctuations in the order of a few mV (Figure 2), in which case the peak structure failed to match the usual shapes. Figure 6 shows the spectral density curves corresponding to this case, showing the peak structure and also the existence of the high frequency higher amplitude fluctuations as was depicted simply from the time records before. These exceptional cases indicate a sudden change in the interface reactions. The origin of these changes remains to be investigated and studied by other techniques.

Renewing the nutrients in the system, by replacing 25% of the total volume of the cell with fresh culture media, reduced the RMS values to the low and almost constant value of 0.025 mV. This became evident after the 6 month periods where the signals became stronger so that the effect of culture media addition could be noticed.

It usually took about 20 days before the RMS values started to increase again. This is thought to be due to the presence of yeast extract at the level of 2 mg/l (2000 ppm) in the culture media. It has been shown [6] that yeast extract, even at a level of 1 mg^{-1}, is an effective corrosion inhibitor. Therefore, when this substance is consumed by bacteria, then the corrosion activities and therefore RMS values, start to increase again and reach the values prior to the addition of culture media to the cell.

In the final tests, a culture media 'without yeast extract was added to the cell. This special culture media did not have the effect to suppress the signals, but in the meantime, the signals could not increase to the previous values either. Yeast extract, which acts as a corrosive inhibitor, is also a source of nitrogenous nutrient and, therefore, its elimination from the culture medium may have affected the bacteria and thus reduced the corrosion activities of the system.

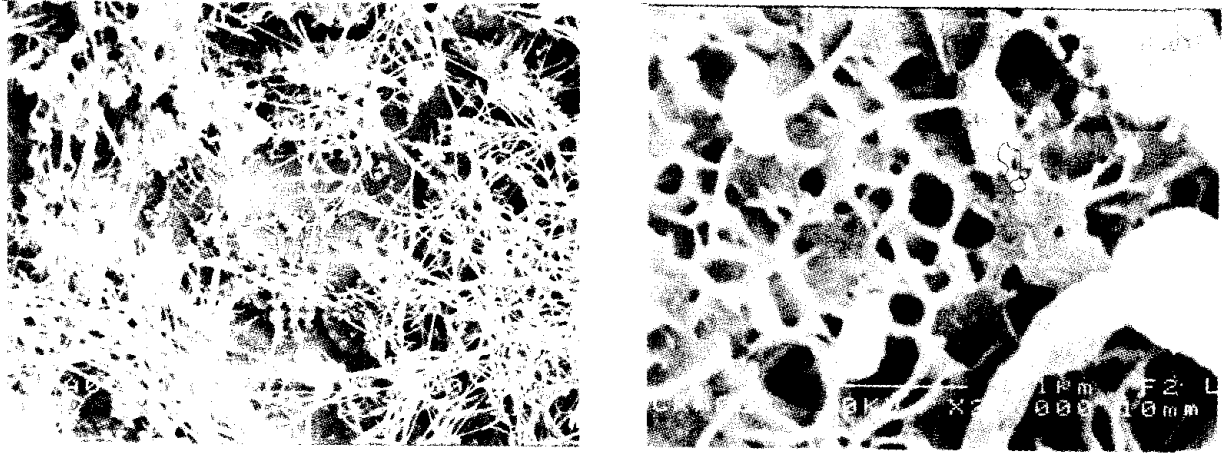
X-ray Diffraction

X-ray diffraction data obtained from the corrosion product on a steel coupon which had been exposed to the corrosion cell for 300 days, are presented in Table 3. These data indicate that the corrosion products formed were comprised mainly of iron sulphide (FeS) and iron carbonate ($FeCo_3$), iron phosphide (Fe_3P) and hydrated magnesium sulphate ($MgSO_4$, $3H_2O$). These structures being assigned on the basis of standard powder diffraction file data. These results are generally in accordance with literature suggested corrosion product formation in a natural SRB containing environment [6, 27].

Scanning Electron Microscopy

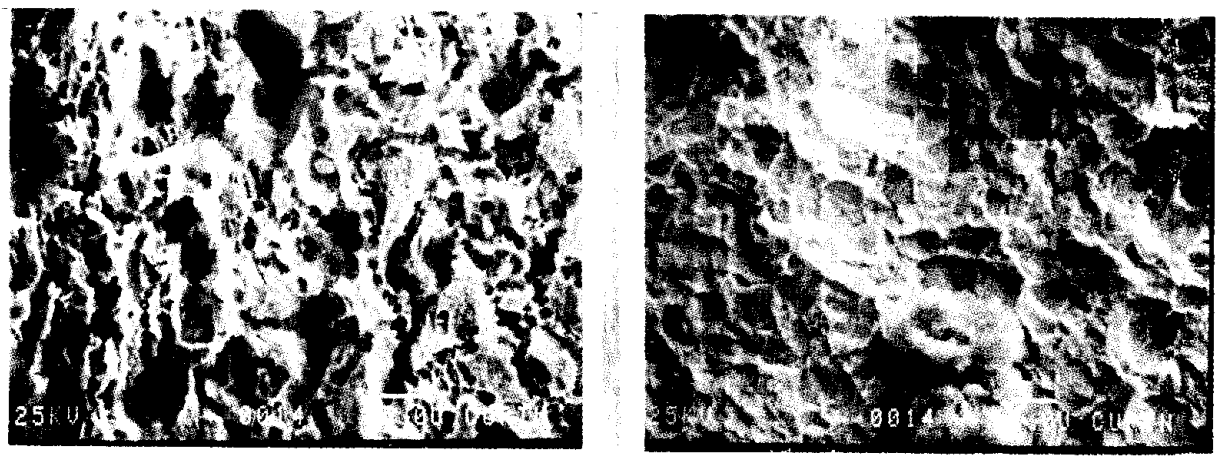
Figure 7 shows the SEM photomicrograph of a biofilm on steel coupon exposed to the corrosion cell for 4 months. Figure 7(a) shows that the slime structure on the sample consists of exopolymer fibres. Figure 7(b) shows at higher magnification, comma shaped SRB embedded on a sludge on the surface. Comma shaped impressions of the SRB's on the sludge prove the high population of them, many of which have been washed away due to numerous washing/decanting operations during the preparation stage (Table 2).

Figure 8 shows the corroded surface of a steel coupon exposed to the corrosion cell for 10 months, indicating the extensive pitting. This clearly demonstrates the existence of a microbiologically induced corrosion, which is localized in nature.



(a) (b)

Figure 7. SEM photomicrograph of a biofilm on a steel coupon exposed for 4 months to anaerobic seawater containing SRB. (a) the slime structure consisting of exoplolymer fibres, (b) comma shaped SRB embedded on the sludge in the biofilm.



(a) (b)

Figure 8. SEM photomicrograph of corroded surface of a steel coupon exposed for 10 months to anaerobic seawater containing SRB. (a) the general pitted surface, (b) one of the pitted region at a higher magnification.

Weight Loss Measurements

Weight loss data obtained for the steel coupons are presented in Table 4. It is shown that the corrosion rate of the coupon, which has been in the corrosion cell for 10 months, is twice as much as the one which has been there for four months. Although the calculated corrosion rates from weight loss data provide a useful assessment of the corrosion condition, they represent an integrated uniform corrosion rate for the total test period, thus the instantaneous corrosion rate has been increasing with time. This is in agreement with the rms values of the electrochemical potential noise, as discussed before. Moreover, based on SEM photomicrograph (Figure 8), the type of attack is localized. Therefore the weight loss data do not truly reflect the pitting corrosion rate. No attempt was made to measure the pitting rate, but it can be estimated to be in the range of 4 mpy from the SEM photomicrographs of the 10 month old coupon.

Table3. X-ray Diffraction Data for Corrosion Products Formed on Steel Coupons Exposed for 300 Days to Anaerobic Sea Water Containing SRB.

X-Ray Peak No.	Brag Angle	Accuracy AD 20	Lnter-planer	Relative Intensity D	Matched structure 1/1
1	20.33	0.04	4.386	317	Not identified
2	20.61	0.04	4.306	34	$MgSO_4\ 3H_20$
3	27.66	0.02	3.223	123	Not identified
4	28.02	0.02	3.181	137	$MgSO_4\ 3H_20$
5	28.82	0.02	3.096	738	$FeS/MgSO_4\ 3H_20$
6	31.34	0.02	2.852	288	$MgS0_4\ 3H_20$
7	31.60	0.02	2.829	175	$FeCO_3$
8	35.71	0.01	2.512	140	$MgSO_4\ 3H_20$
9	37.59	0.01	2.391	130	$FeCO_3/FeS$
10	40.30	0.01	2.236	30	$MGS0_4\ 3H_20/Fe3P$
11	41.43	0.01	2.178	195	$FeCO_3/MgSO_4\ 3H_20/Fe3P$
12	42.43	0.10	2.129	164	Fe3P

.Cu Ka_1 has been used at 40 Kv and 30 mA

Table4. Weight-loss Data and Calculated Uniform Corrosion Rate of Steel Coupons Exposed to Anaerobic Seawater Containing SRB.

Test Duration days	Weight Loss mg	Calculated Corrosion Rate, mpy
20	10	0.5
50	25	0.4
90	54	0.6
300	310	2.0

CONCLUSION

Electrochemical potential noise analysis of steel corrosion in an anaerobic environment containing SRB indicated the generally accepted behavior of this type of corrosion, as summarized below.

1. Corrosivity of the environment containing SRB is variable, depending upon the test conditions. In general, the corrosivity

increases after an incubation time, presumably for the establishment of biofilm and development of stable crystallographic forms of iron sulphide.

2. The rms values of the potential noise indicate the localized nature of the process.
3. Corrosivity decreased after fresh nutrient addition, due to the corrosion inhibition effect of yeast extract in the culture media, and it usually takes sometime before this substance is consumed by the bacteria and the corrosion process proceeds further.
4. The spectral density curves using MEM method began to show a fixed pattern in the high frequency end of the spectrum after the initial incubation time when the corrosion activities started to increase.
5. This pattern in the high frequency range of spectral density curves changed temporarily whenever there was a sudden change in potential time records indicating substantial changes occurring on the corroding interface. The importance of these instances has yet to be further investigated.

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REFERENCES

1. S.C. Dexter, in «Metals Handbook», Vol 31, 9th Ed. p. 11 4, ASM, (1988).
2. C.A.H. Von Wolzogen Kuhr, and L.S. Van der Vlugt, Water, *Den Haag*, 18, 147 (1934).
3. Microbial Corrosion, Proceedings of the Conference, National Physical Laboratory, The Metals Society, (1983).
4. S.C. Dexter ed, "Biologically Induced Corrosion", Proceedings of the Conference, National Association of Corrosion Engineers, (1986).
5. G.H. Booth, *Journal of Applied Bacteriology.* 27, 174, (1964).
6. J. F. D, Stott, B.S. Skerry, and R.A. King in "the Use of Synthetic Environments for Corrosion Testing, "ASTM STP970, P. E Francis and T. S. Lee. eds, American Society for Testing and Materials, Philadelphia, p.98-111, (1988).
7. B.E. Purkiss.in "Microbial Aspects of Metallugy", 1st Ed, J. D. A. Miller, ed, Medical and Technical Publishing Company, Aylesbury, England, P. 107, (1971).
8. J. Soimajarvi M. Pursiainen, and J. Korhonen, *European Journal of Applied Microbiology and Biotechnology*. 5, 87, (1978).
9. G. Kobrin, *Materials Performance*, 15, 38, (1976).
10. T.G. Temperley, *Corrosion Science,* 5. 581, (1965).
11. W.S. Patterson, *Transactions of the North East Coast Institution of Engineers and Shipbuilders* 68, 93, (1951).
12. NACE Manual of the Role of Bacteria in the Corrosion of Oil Field Equipment, Book Item Number 52106, National Association of Corrosion Engineers, Houston, Tx.
13. G.C. Barker *J Electroanal, Chem,* 21, 127 (1969).
14. G, Blanc, Epelborin, I, Gabrielle, G, and Keddam, M. J. *Electronal Chem* 75, 97 (1977).
15. D. E. Williams, C. Westcott, and M. Fleischmann, "Passivity of Metals and Semiconductors". Amsterdam Elsevier, pp. 217-28 (1983).
16. K. Hladky, and J. L. Dawson, *Corros. Sci*, 21, 317 (1981).
17. K. Hladky, and J.L. Dawson, *Corros. Sci* , 22, 237 (1982).
18. M. Kendig, S. Jeanaquet, and M. Mahoney, Paper No. 383, *Corrosion,* 88, National Association of Corrosion Engineers, Houston, (1988).
19. A. M. P. Simoes, M. G. S., Ferreira, Br. *Corros, J., 22*, 21 (1987).
20. C.A. Loto, and R.A. Cottis, *Corrosion* 43, 499 (1987).
21. C.A. Loto. and R.A. Cottis. *Corrosion* 45, 136 (1989).
22. D.E. . Williams., L. Westcott, and F. Fleischman, *J. Electroanal. Chem*. 180, 549 (1984).
23. U. Bertocci, M. Koike, S. Leigh, F. Qiu ., *J Electrochem. Soc* 133, 101, (1984). 1782 (1986).
24. U. Bertocci. and Y.X. Ye *J Electrochem Soc* 131,101(1984).
25. G. Gabrielli F. Huet M. Keddam. and R. Oltra,Proceedings of the Localised Corrosion Conferece, Orlando, Florida, (1987).
26. W.P. Iverson, and L.F. Heverly, Corrosion Monitoring in Industrial Plants using NDT and Electrochemical Methods. ASTM STP 908, G.C. Morgan Ed ASTM Philadelphia pp. 459-471 (1986).
27. W. P Iverson and L.F. Heverly Biologically Induced Corrosion. NACE-8, C, Dexter . Ed. National Association of Corrosion Engineers (1986).
28. Metrabyte Corp, Taunton, MA.
29. J.P. Burg.,"Modern Spectrum Analysis", D.G. Childers ed., New York, N. T. IEEE, pp. 42-48 (1978).
30. R.A. Cottis, and C.A. Loto *Corrosion*, 46, 12 (1990).