MONITORING IRON CORROSION BY DIRECT CURRENT TECHNIQUES

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ABSTRACT: *Corrosion is an inevitable process, results in degradation of materials' properties due to its interactions with its environment. Considering, electrochemical nature of corrosion, a broad range of electrochemical techniques being employed for its measurements. In our current work, we utilized direct current corrosion monitoring techniques to evaluate Tafel constants and corrosion rates of mild steel and stainless steel specimens in simulated environment (tap water and saline water).*

INTRODUCTION

Iron and steel are the most important structural materials used in our domestic life. These materials are highly susceptible to corrosion and can cause dangerous and expensive damage to everything from automobiles, home appliances, and drinking water systems to pipelines, bridges, and public buildings. Corrosion rate provide an estimate about the shelf life of the material, enabling to take remedial actions. Corrosion is an inherently very slow process; a typical corrosion rate is 10 milli-inches per year (mpy) or 0.254 millimeters per year (mmpy) or 254 microns per year. A large number of corrosion monitoring techniques exist. Among them weight loss coupon for corrosion measurements are considered the best and simplest of all corrosion monitoring techniques. However, due to very slow evaluation nature (require months or years) electrochemical techniques are preferred. Electrochemical techniques are fast and sensitive and can make corrosion measurements in minutes or hours [1].

Different electrochemical methods were used to determine corrosion rate. Among them are polarization curves, polarization resistance transient and electrochemical impedance techniques were utilized. In addition, few semi quantitative methods like measurement of corrosion potential, concrete resistivity or galvanic current were also described. On-site corrosion rates measurement of concrete-specimen using electrochemical technique was explored and accordingly loss of material and its related risk were visualized [1].

Corrosion monitoring of metal specimen is of great value in order to monitor industrial processes and for research and development. A comparison of the conventional polarization resistance method with that of theoretical model developed from electrochemical noise data and frequency of anodic and cathodic transient for corrosion monitoring. Main advantage of this method, in comparison with others is of short time records normally less than a minute [3].

The coulostatic method was successfully applied to a rapid evaluation of metal corrosion rate in solution, where a known amount of small charge was supplied to the test piece, and the potential decay curve recorded was analyzed to obtain the corrosion rate. According to the theory developed, polarization resistances of mild steels in sulfuric acid and in distilled water were obtained, which agreed fairly well with resistances measured by usual methods. The coulostatic method developed in this study can be useful without ohmic drop correction, even in a high impedance solution. The time needed for measurement is considerably shorter, compared to the well known linear polarization method [4].

The various methods of evaluating corrosion rate and charge transfer resistance were critically reviewed on the basis of the recent developments on the measurement and interpretation of faradaic impedances. It is demonstrated that the entity, which is most accurately correlated with corrosion rate, is the transfer resistance, the limit of the faradaic impedance at infinite frequency. In the case of iron, with and without inhibitor (propargylic alcohol), it was ascertained, under various experimental conditions, that the measurement of this resistance constitutes nowadays the best electrochemical test for corrosion [5].

Evaluation of corrosion rates from polarization measurements in the vicinity of the corrosion potential (the linear polarization method) depends on acknowledge of the Tafel slopes for the anodic dissolution reaction and for the corresponding cathodic process. A method is presented for derivation of these parameters from the polarization data. One calculation, based on the extent to which the polarization curve is symmetrical about the corrosion potential, yields a reliable value for the difference between the inverses of the two Tafel slopes. A second calculation computes the separate values of the parameters from this difference and measurements of the degree of nonlinearity in either the anodic or cathodic direction. This approach is presented in the form of a simple algorithm, which gives Tafel constants of sufficient accuracy to make possible reliable calculation of the corrosion current from the polarization data [6].

The use of the exponential form for monitoring the corrosion rate of a metal or the kinetics of an electrochemical reaction in real time and with a good degree of reliability is examined. In this case the exponential form is associated with a computerized system driven by suitable software, which permits the choice of the experimental technique. The mathematical bases that justify the use of this technique are discussed and it is demonstrated that the determination of the polarization resistance using the limit for $(\alpha + \beta) \to 0$ of the function $[(\alpha + \beta)Ic]-1$, provides the same evaluation obtained by the best-fitting of the experimental points (ηk, ik) with the monomial $i = Rp-1\eta$. The numerical examples of the calculation of the polarization resistance over potential difference intervals of the type $[-X, X]$, $[0, X]$ and $[-X, 0]$, examining an ideal case described by the law $i = 0.1 [\exp(\eta/26.06) - \exp(-\eta/39.09)]$ mA, have shown the validity of this approach and confirmed that the width of the interval selected must be such as to ensure a determination very near the value of the first derivative of the previous function at the point $\eta = 0$. It has also been demonstrated that the true value of the polarization resistance can be obtained through an accurate selection of the distance R. The experimental applications for evaluating the behaviour of ARMCO iron in the two solutions of H_2SO_4 (1 N) + KCl (x N) and HCl 1 M + n-butylamine (x M) at 25°C, which were very satisfactory from the standpoint of the corrosion rate monitoring in real time, have shown that the determinations of the corrosion current density inside the over voltage interval (−10, 10) mV by linear approximation and exponential form are coincidental when the values of α and β are obtained by numerical analysis of the experimental polarization curves [7].

The electrochemical behavior of AISI 316 stainless steel in natural seawater collected from Canary Archipelago was investigated. A comparative study on a large number of samples immersed during three weeks in this environment with and without sulfate-reducing bacteria was made. Open circuit potential measurements, cyclic polarization, Scanning Electron Microscopy and Electrochemical Impedance Spectroscopy were used. The obtained results permitted an interpretation of the contribution of biofilms to corrosion of stainless steel and a mechanism of the process is checked [8].

A new numerical method has been developed for the determination of the values of the corrosion current density and polarization resistance. Though requiring, in principle, preliminary knowledge of the values of the Tafel slopes, the method differs substantially from the technique of the linear response because its formulation is of a global type and is independent of the geometrical shape of the polarization curve near the corrosion potential. After illustrating the mathematical concepts on which the method is based, the author examines the behavior of the characteristic function R(ΔE), which plays the same role of the quantity (α + β) in the theory of the linear response, in order to demonstrate that, under appropriate conditions, it can be considered independent of the Tafel slopes so that it is no longer imperative to use their exact values. Some applications are then presented which refer to two systems, ARMCO iron + sulfuric acid at different pH and ARMCO iron + 1 N sulfuric acid + Borg P16, both at 25°C. All the polarization curves examined were interpolated with the INTER program, while the integrals were calculated numerically by the Simpson method. The results obtained were quite satisfactory and show the validity of this formulation for corrosion monitoring [9].

The three-point method (TPM) as introduced by Barnartt, is shown to have some advantages over the linear polarization method in measuring corrosion rates. Experimental results on iron, theoretical limitations, and various potential sequences were discussed [10].

A direct method for monitoring the corrosion rate of metals or alloys, based on the use of computerized systems, is described. Polarization measurements were performed using a suitable system driven by a specific program, which permits, also to process experimental data with the NOLI method after the completion of each curve in order to compute Ic, βa and βc. The behavior of iron in 1 N sulfuric acid solutions at 25 °C was examined by carrying out polarization curves of the potentiodynamic type at potential sweep rates of 120, 300 and 600 mV min−1 and collecting simultaneously the values of the current and electrode potential. Each run lasted about 15 h; potentiodynamic polarization curves were performed over the potential interval [Ec − 90, Ec + 60]mV, starting from the cathodic region, at regular time intervals. NOLI method was successful in processing all the experimental data. The experimental results show that the corrosion current density is a monotonic increasing function of the potential sweep rate. The corrosion rate of iron was underestimated when the potential sweep rates of 120 and 300 mV min-1 were used. The best result was obtained using a potential sweep rate of 600 mV min−1. In this case electrochemical and direct determinations of the corrosion rate are in good agreement and the apparent dissolution valence takes the value of 1.93, which confirms the fact that iron dissolution occurs through the formation of Fe2+ ions [11].

The corrosion of metals occurs primarily by electrochemical processes involving metal oxidation and simultaneous reduction of some other species. The fundamental understanding of these processes has allowed the development of a number of electrochemical techniques for the study of the corrosion phenomena and assessment of the corrosion rate. In fact, electrochemical techniques are so ingrained in the field that many practitioners think of corrosion rates first in terms of current density rather than thickness or mass loss per unit time. Standard approaches for electrochemical corrosion rate determination are commonly used in the field for on-line monitoring of systems and facilities. Electrochemistry also provides powerful tools for developing fundamental understanding of corrosion phenomena. However, there are some limitations to the abilities of current electrochemical techniques and some needs for the future. This paper describes the status of electrochemical techniques, their limitations, where nonelectrochemical methods are required, and future needs in the field 12].

Tafel slopes and corrosion rates determined from data obtained in the pre-Tafel region of polarization curves was followed by a description of the approach taken in the POLFIT program. Several examples were given of the application of this program including the use of factorial design experiments to determined the optimum conditions for formation of a chromate free conversion coating on hot dipped galvanized steel [13].

The polarization resistance technique exists as a laboratory tool for the measurement of corrosion rates. A simple method of making measurements using this technique had been developed, making it usable for plant corrosion monitoring. Its effectiveness had been demonstrated by comparing the results with potential/time curves. The processes of film breakdown and repair were shown to be accompanied by corresponding variations in corrosion rate [14].

MATERIALS AND METHODS

Nearly all metal corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte solution. Corrosion normally occurs at a rate determined by equilibrium between opposing electrochemical reactions. Because corrosion occurs via electrochemical reactions, electrochemical techniques are ideal for the study of the corrosion processes. In electrochemical studies a metal sample a few cm² in surface area is used to model the metal in a corroding system. Direct current techniques for corrosion monitoring were utilized using Gamry DC 105 software. The DC105 provides a modern set of tools for DC electrochemical corrosion testing. It offers a unique combination of flexibility, power, and ease of use. The DC105 includes techniques for measuring the rate of general corrosion, determining corrosion mechanism, measuring the susceptibility to localized corrosion, and measuring galvanic corrosion rates.

Standard tests in the DC105 are as follows:

- Polarization Resistance
- Tafel Analysis
- Potentiodynamic
- RpEc Trend
- Cyclic Polarization
- Galvanic Corrosion
- Critical Pitting Potential
- Potentiostatic
- Galvanodynamic
- Galvanostatic
- Corrosion Potential
- Reactivation

Among above, in our current study we make use of some of them namely, polarization resistance, Tafel analysis, corrosion potential and corrosion behaviour diagram to measure corrosion behaviour of locally avaiable mild steel and stainless steel materials.

Tafel Technique

The Tafel technique is used to obtain an accurate estimate of the corrosion rate of a metal in a solution. Cell current is measured during a slow sweep of the potential. The sweep typically is from -250 to +250 mV relative to Eoc. A fit of the data to a standard model (Butler-Volmer Model) yields an estimate of Icorr which is used to calculate a corrosion rate. The graphical output of the experiment is a plot of log current versus potential. Analysis of the curve can yield the following types of information:

- Corrosion potential.
- Corrosion current and corrosion rate.
- Kinetic information (Beta coefficients) for the anodic and cathodic reactions.

Polarization Resistance

The polarization resistance technique is used to obtain a rapid estimate of the corrosion rate of a metal in a solution. Cell current readings are taken during a very short, slow sweep of the potential. The sweep typically is from -20 to +20 mV relative to Eoc. Over this range, the current vs. voltage curve is roughly linear. A linear fit of the data to a standard model yields an estimate of the Polarization Resistance Ru. Ru is then used to calculate Icorr and corrosion rate.

Analysis of the curve can yield the following types of information:

- Corrosion potential.
- Corrosion current and corrosion rate.

Corrosion Potential

The Corrosion Potential technique is the simplest of the DC105 techniques. It is the only technique in which there is no current flow through the sample. The DC105 just measures the open circuit potential, Eoc of the sample as it changes over time.

Corrosion Behavior Diagram

The Corrosion Behavior Diagram (CBD) technique is used to examine the overall corrosion behavior of a system. It's a complex technique that acquires data during three sweeps of the potential. The advantage of the CBD over other techniques is its generality. It will work both with spontaneously passive systems that are difficult to study otherwise as well as with more traditional systems.

The graphical output of the experiment is a plot of log current versus potential. The data from three scans are shown on one graph. Analysis of the curve can often yield the following types of information.

- Corrosion potential.
- An estimate of corrosion current.
- Potential region for passivity.
- Mechanistic information.

Corrosion Cell

All experiments were performed in a three-electrode cell (a glass beaker of capacity 100 ml was utilized) containing working electrode (mild steel and stainless steel rods, a quasi-reference (carbon black rod) and a reference electrode. The electrodes were immersed into the solution of tap and saline water (3.5 % salt solution).

Electrodes

1. Working Electrode

Mild steel and stainless steel rods were obtained from local market shaped into disk electrode with area 0.1256 cm2 and 0.071 cm2 were used as the working electrodes.

2. Counter Electrode

A carbon black, A = 0.1256 cm^2, was used as the counter electrode.

3. **Reference Electrodes**

Silver/silver chloride, chloride ion electrode (Ag/AgCl, saturated KCl):

Silver wire was coated with silver chloride by providing a potential of 0.21 V for 45 minutes in 10 % hydrochloric acid solution. Then the inner reference compartment with a fine sinter at its one end was filled with saturated potassium chloride solution. The outer bridge also terminating in a sinter was filled with background electrolyte. Construction was similar to silver-silver chloride electrode.

Polishing of Working Electrodes

Polishing of working electrodes was done on a fine grained emery paper. Thorough rinsing with distilled water followed polishing.

Instrumentation

Direct current corrosion techniques was carried out using Gamry, Instrument Inc, PC4 potentiostat. Data was acquired using Gamry Framework and finally processed using Echem Analyst Research Software on a dedicated PIII micro–processor coupled to the potentiostat.

RESULTS AND DISCUSSION

Tafel scan provide quantitative information for measuring corrosion rate. Normally, the working electrode is polarized cathodically and anodically. Figures 1-3 shows Tafel scans for mild steel and stainless steel specimen in tap water and saline water respectively. Fitting of the data results in various parameters used to measure corrosion rate quantitatively are summarized in Table 1-3. Similarly, polarization resistance method is also quantitatively used to determine corrosion rate. Polarization resistance curves for iron samples were presented from figures 4-6. Best fitting of these resistance curves generate parameters summarized in tables 4-6. Moreover, corrosion potential set of experiments were also conducted, which is the most simple set of experiment in corrosion monitoring and corrosion behavior of iron specimen were evaluated indicated in figures 7-9. Overall corrosion behavior of the system was visualized by running corrosion behavior diagram set of experiments as evident from figures 10-11. Corrosion behavior diagram provide useful information about corrosion potential, an estimate of corrosion current, potential region for passivity and mechanistic information. Similarly, figure 12 indicates a typical cyclic polarization curve for iron specimen and provide qualitative information about pitting susceptibility of the system under consideration (iron).

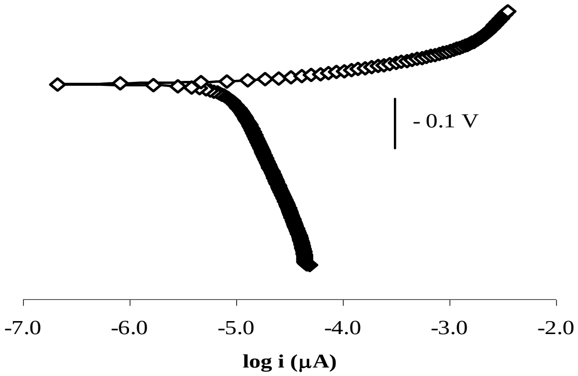

Figure 1: Tafel plot for mild steel in tap water

Table 1: Tafel fit for mild steel as per Figure 1

Sr. #	Tafel analysis Active	Results
1	β_a	25.25e-3 V/decade
2	β_c	377.5e-3 V/decade
3	I_{corr}	8.0 μA
4	E_{corr}	-277.0 mV
5	Corrosion Rate	29.11 mpy
6	Chi Squared	2.504

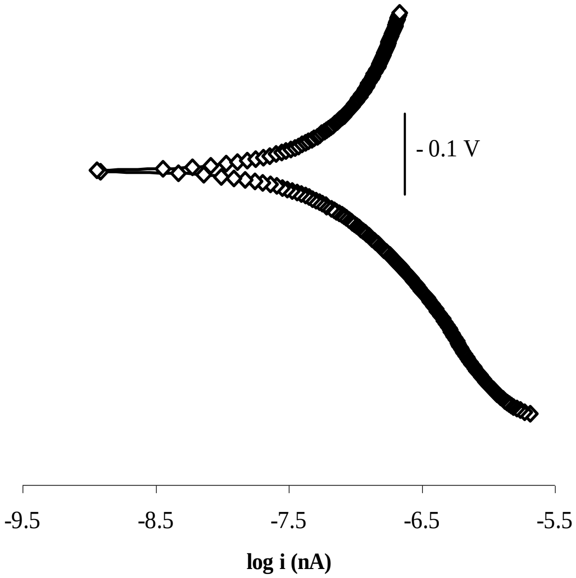

Figure 2: Tafel plot for stainless steel in tap water

Table 2: Tafel fit for stainless steel as per Figure 2

Sr. #	Tafel analysis Active	Results
1	β_a	476.2e-3 V/decade
2	β_c	260.3e-3 V/decade
3	I_{corr}	94.20 nA
4	E_{corr}	-208.0 mV
5	Corrosion Rate	347.76e-3 mpy
6	Chi Squared	102.8e-3

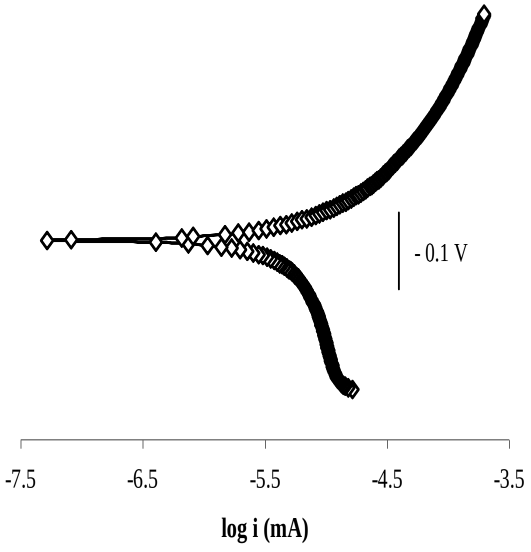

Figure 3: Tafel plot of mild steel in saline water

Table 3: Tafel fit for mild steel as per Figure

Sr. #	Tafel analysis Active	Results
1	β_a	162.5e-3 V/decade
2	β_c	3.158 V/decade
3	I_{corr}	10.50 µA
4	E_{corr}	-635.0 mV
5	Corrosion Rate	38.12 mpy
6	Chi Squared	5.923

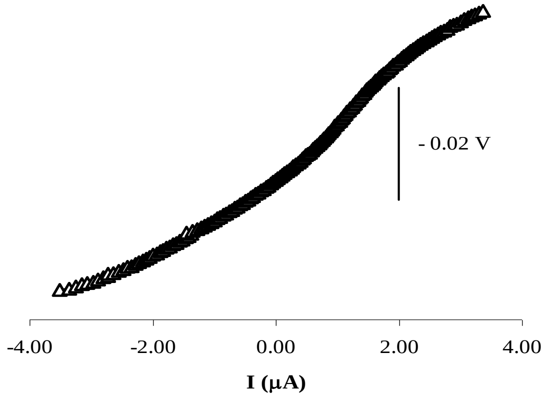

Figure 4: Polarization resistance plot for mild steel in tap water

Table 4: Polarization resistance fit for mild steel as per Figure 4

Sr. #	Polarization analysis Active	Results
1	β_a	120.0e-3 V/decade
2	β_c	120.0e-3 V/decade
3	I_{corr}	3.782 µA
4	E_{corr}	-675.1 mV
5	R_p	6.889 kohms
6	Corrosion Rate	13.76 mpy

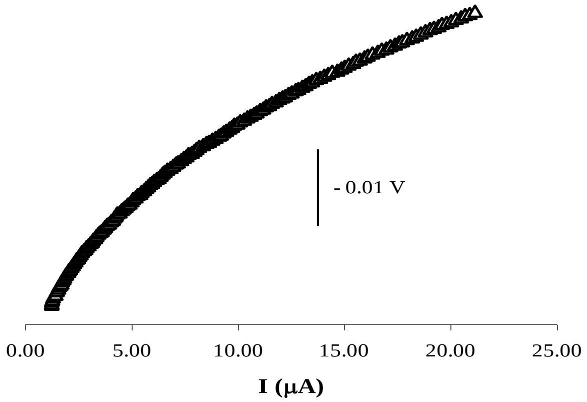

Figure 5: Polarization resistance plot for mild steel in saline water

Table : Polarization resistance fit for mild steel as per Figure 5

Sr. #	Polarization analysis Active	Results
1	β_a	120.0e-3 V/decade
2	β_c	120.0e-3 V/decade
3	I_{corr}	136.5 µA
4	E_{corr}	-387.1 mV
5	R_p	190.8 ohms
6	Corrosion Rate	496.8 mpy

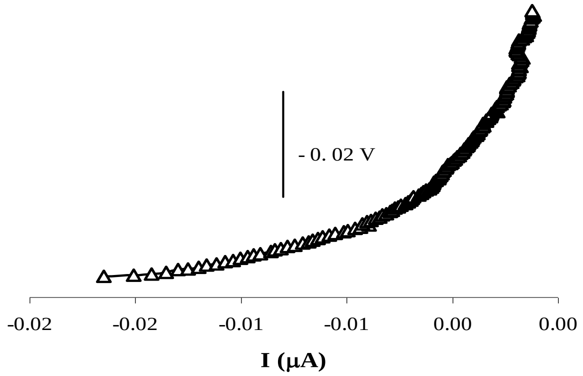

Figure 6: Polarization resistance plot for stainless steel in saline solution

Table 6: Polarization resistance fit for mild steel as per Figure 6

Sr. #	Polarization analysis Active	Results
1	β_a	120.0e-3 V/decade
2	β_c	120.0e-3 V/decade
3	I_{corr}	84.55 nA
4	E_{corr}	-282.8 mV
5	R_p	308.1 kohms
6	Corrosion Rate	307.6e-3 mpy

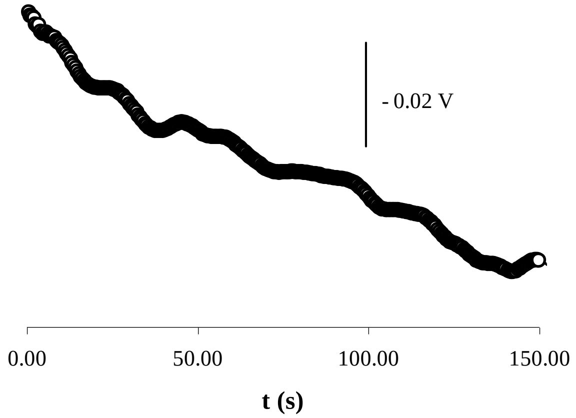

Figure 7: Corrosion potential plot of mild steel in tap water

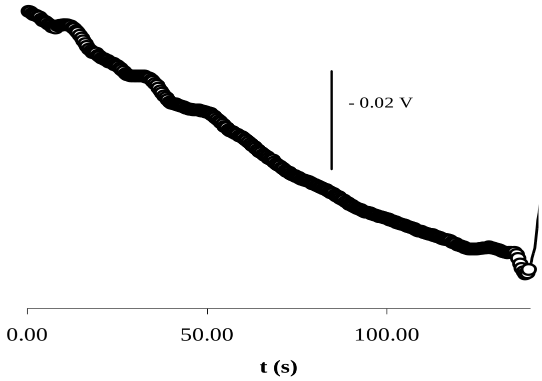

Figure 8: Corrosion potential plot of mild steel in saline water

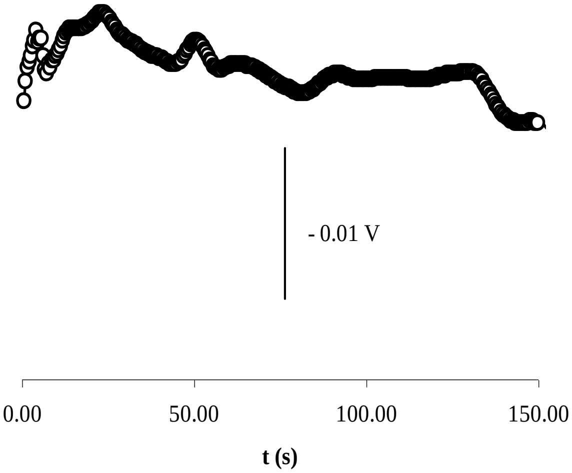

Figure 9: Corrosion potential plot of stainless steel in tap water

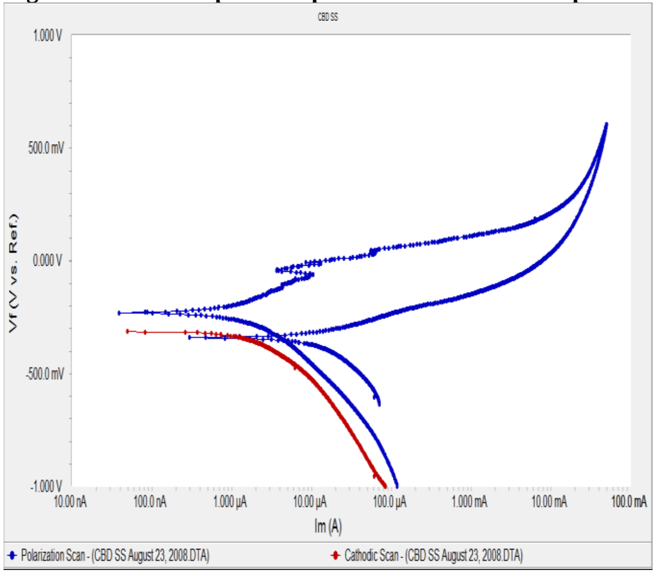

Figure 10: Corrosion behavior plot for stainless steel in saline water

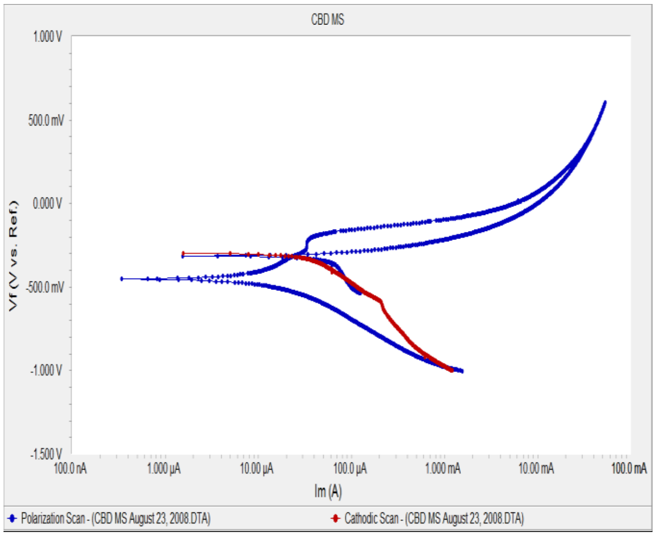

Figure 11: Corrosion behavior plot for mild steel in saline water

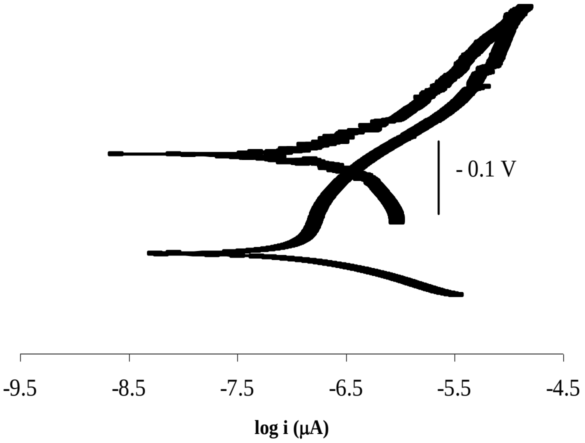

Figure 12: Cyclic polarization plot for stainless steel in deionized water

CONCLUSIONS

Corrosion measurement is the quantitative method and use to predict the shelf life of the system under consideration. In our current studies we make use of direct current electrochemical techniques to quantitatively estimate the corrosion rates of Mild steel and stainless steel specimen.

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