

Evaluating Corrosion and Passivation by Electrochemical Techniques

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Abstract—In this study, the electrochemical techniques used to analyze corrosion behavior and passive films are introduced in detail. These electrochemical techniques include Linear Sweep Voltammetry (LSV), Cyclic Polarization (CP), Cyclic Voltammetry (CV), Tafel Extrapolation (TE), and Electrochemical Impedance Spectroscopy (EIS). The advantages and disadvantages of these techniques are also introduced in this study. As an example to examine the efficiency and performance of these techniques, electrochemical measurements were carried out in a three-electrode system whereby a commercial copper nickel alloy, C70600 was used as the working electrode. These measurements were performed in natural seawater and in artificial saline solutions with different sulphate content. The results obtained from these electrochemical investigations were compared with the results from conventional immersion tests reported in previous studies. The results conclude that these techniques provide a very convenient and efficient way to evaluate the corrosion and passivation processes in both the laboratory and field within a very short time.

Index Terms—linear sweep voltammetry, cyclic polarization, cyclic voltammetry, Tafel extrapolation, electrochemical impedance spectroscopy, copper-nickel alloys

I. INTRODUCTION

A. Electrochemical Techniques

There are various electrochemical techniques used to analyze the corrosion behavior and passive films formed on metal and metal alloys surfaces. These electrochemical techniques include Linear Sweep Voltammetry (LSV), Cyclic Polarization (CP), Cyclic Voltammetry (CV), Tafel Extrapolation (TE), and Electrochemical Impedance Spectroscopy (EIS) among many others. The advantage of these methods is that they can be used in both laboratory and field. In addition, corrosion resistance can be measured in a very short time (few minutes) as opposed to conventional weight loss measurements that require several days or longer. Electrochemical techniques are very useful for kinetic studies and are very sensitive to different conditions such as a change in temperature. Another advantage is that electrochemical measurements may be repeated

numerous times using the same electrode. Electrochemical impedance spectroscopy is used beside the polarization techniques to investigate the nature of a passive film formed on the material and for conducting electrochemical kinetics studies. The different electrochemical techniques are summarized in Table 1.

B. Linear Sweep Voltammetry (LSV)

LSV is a technique that provides information about the passivation process and gives an indication of the ability of a material to resist corrosion in a specific environment by forming a film on the surface of the material to act as a barrier film. Evidence for the formation of a passive film on a material surface is observed by a decrease in the current density value. This indicates that the electrochemical reactions decrease to a lower rate as can be seen in Fig. 1 [1].

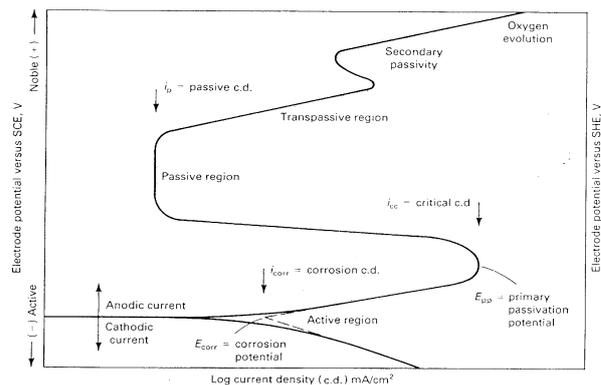


Figure 1. Passivation and transpassivation processes [2]

C. Cyclic Polarization (CP)

By reversing the potential reading in the previous technique (LSV) at the same scan rate (from a high potential value to lower one), a loop is observed as can be seen in Fig. 2 [2]. The potential at which the current density crosses the passive range at the reverse scan is called the protection potential (E_{prot}). The protection potential refers to the potential at which passivity, once broken down, will be re-established [2]. This indicates that increasing the difference between the corrosion potential and the protection potential enhances the protection on the material.

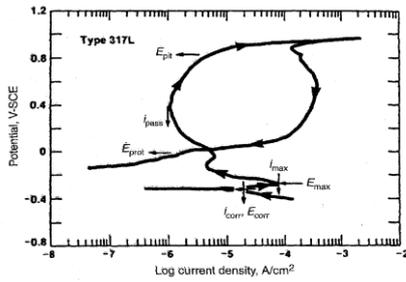


Figure 2. Cyclic polarization curve [2]

D. Cyclic Voltammetry (CV)

CV is an electrochemical technique which is used to identify the mechanism of the electrochemical processes, which take place at an electrode surface. The potential is scanned linearly between an initial potential E_1 to a second potential value E_2 followed by reversal of the potential scan back to the initial potential value as seen in Fig. 3. The sweep rate might range from a few mV/s to thousands mV/s. The anodic peak current (i_{pa}), the cathodic peak current (i_{pc}), the anodic peak potential (E_{pa}), and the cathodic peak potential (E_{pc}) values can be obtained and can be used to identify the diffusion coefficient of the ionic species involved.

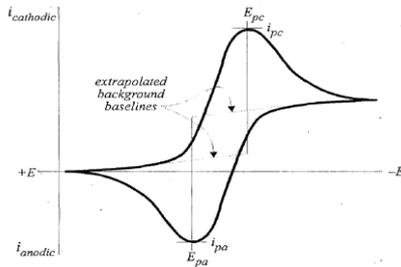


Figure 3. Cyclic voltammogram [5]

E. Tafel Extrapolation (TE)

TE is an electrochemical technique where the potential is swept from a cathodic to an anodic value. The resulting data is recorded as a $\log(i)$ vs. E plot. The corrosion current and the corrosion potential are obtained from this technique. The corrosion rate is calculated from the corrosion current (i_{corr}). A Tafel extrapolation plot is shown in Fig. 4 [3].

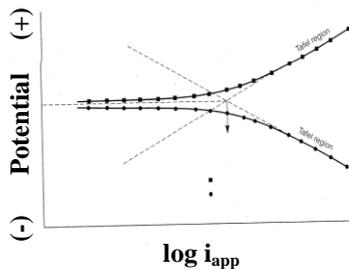


Figure 4. Tafel Extrapolation plot [3]

F. Electrochemical Impedance Spectroscopy (EIS)

EIS is a technique used for corrosion monitoring, passivation monitoring and for conducting electrochemical kinetics studies. The principle of impedance (Z) measurements is based on the analysis of a low amplitude alternating potential signal of a widely varying frequency that is applied to the electrode/electrolyte interface. The current flowing through the cell is measured and the phase relationship between the current and voltage signals is established digitally. The electrochemical impedance response of the corroding electrode may be modeled in terms of simple electrical circuit elements, as seen in Fig. 5 [4], and estimates of corrosion rates and mechanisms are possible. There are many kinds of plots to represent the variation of the impedance, Z , as a function of frequency. The Nyquist Plot is the most common, shown in Fig. 6 [3], a function of the real part, Z' , on the X-axis, against the imaginary part, Z'' , on the Y-axis. The impedance behaves as a semicircle path, and at very low and very high frequencies, the imaginary value of the impedance is zero.

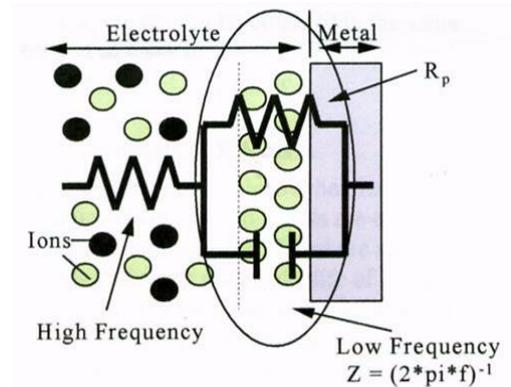


Figure 5. An electrical circuit representation of EIS [4].

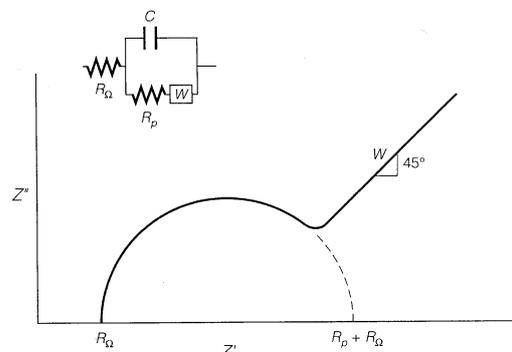


Figure 6. Nyquist plot [3]

TABLE I. ELECTROCHEMICAL TECHNIQUES

Electrochemical Technique	Applied	Plots	Obtained Results
Linear Sweep Polarization (LSP)	Potential	E vs. $\log(i)$	Passivation potential range
Tafel Extrapolation (TE)	Potential	E vs. $\log(i)$	Corrosion rate
Cyclic Polarization (CP)	Cyclic Potential	E vs. $\log(i)$	Corrosion & protection potential
Cyclic Voltammetry (CV)	Cyclic potential	E vs. i	Electrochemical reaction nature
Electrochemical Impedance Spectroscopy (EIS)	AC with a wide range of frequency values	(Z vs. Z')	Thickness and number of layers of the passive

G. Experimental Procedure

The experiments in the present work were conducted using a commercial alloy, C70600. All experiments were carried out in aerated electrolytes and at room temperature ($22\text{ }^{\circ}\text{C} \pm 1.1\text{ }^{\circ}\text{C}$). The average oxygen dissolved was 8.2 mg/L. The pH of the natural seawater was 7.8, and for the synthetic saline solution the pH ranged between 4.76 and 6.75, depending on the sulphate content. Materials, equipment, and experimental procedures used in this work are described in the following sections. **Materials:** Samples were cut to 1 cm^2 surface area and were ground using 600 grit SiC paper and polished using 1 and 0.05 micron alumina. The commercial alloy was 88.62 wt% Cu, 9.86 wt% Ni, 1.11 wt% Fe, 0.13 wt% Zn, 0.01 wt% Mo, 0.005 wt% Co. **Electrolytes:** Seawater was used as an electrolyte. It was analyzed and contained 17400 ppm Cl, 8560 ppm Na, 2260 ppm SO_4 , 316 ppm K, 105 ppm Mg and 33 ppm Ca. In addition to the seawater, artificial saline solutions were prepared using distilled water mixed with 2.86 wt% NaCl and different amounts of sulphate (0, 50, 100, 200, 300, 400, 500, 600, 700, 800, 1000, and 2260 ppm). **Electrochemical Measurements:** A potentiostat was used for the different electrochemical techniques including TE, LSV, CP, and CV by using a three-electrode electrochemical cell. Only 1 cm^2 of the Cu-Ni sample surface was subjected to the electrolyte, a graphite rod with a surface area of 16.32 cm^2 was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The potential range versus SCE and the scanning rate for LSV were -0.25 to 0.75 V and 1 mV/s respectively, they were -1.5 to 2.5 V and 1 mV/s for CP, -0.5 to 0.02 V and 1 mV/s for TE, and -1.5 to 1.5 V and 10 mV/s for CV.

II. RESULTS AND DISCUSSION

A. Tafel Extrapolation and Corrosion Rates

The cathodic and anodic slope constants, the corrosion potential, and the corrosion current were estimated from the Tafel plots as seen in Fig. 7. The corrosion rate initially decreased with increasing amounts of sulphate in the solution from 0 ppm to 400 ppm, before the corrosion rate could increase drastically. The corrosion rate ranged from 0.03 mmpy in the 0 ppm sulphate artificial saline solution to 0.046 mmpy in the sea water/seawater environment. Similar results were obtained for the same alloy in a previous study (0.03 mmpy) at very low concentration of sulphide (0.01 mg/L) [5]. The corrosion rate in the absence of sulphate has been reported as 0.048

mmpy [6], 0.043 mmpy [7], 0.03 mmpy [8], and 0.023 mmpy [9]. G. Kear et al. [10] reported that the corrosion rate varied between 0.01 mmpy and 0.24 mmpy. When adding sulphate up to a concentration of 600 ppm, there was no significant change in the corrosion rate values, but if more than 600 ppm was added, the corrosion rate increased to a relatively high value. Addition of sulphate to a level of 1000 ppm caused the corrosion rate to reach 0.039 mmpy. The corrosion rate calculations were 0.042 and 0.046 mmpy for the 2260 ppm sulphate and the N.S. seawater, respectively. **Linear Polarization and Passivity Potential:** The linear polarization plots for the commercial alloy C70600 in different artificial saline solutions and in N.S. seawater are shown in Fig.8. The electrochemical behavior of the commercial alloy depends on the amount of sulphate in the solution. In the absence of sulphate in the artificial saline solution and at low concentrations of sulphate (less than 400 ppm), the C70600 alloy has a good passivity in the potential value range from $+0.1$ to $+0.75\text{ V/SCE}$. This can be explained by the decrease in the passivation current density value at $+0.1\text{ V/SCE}$ to a lower value, which then remains approximately constant until the potential reaches a value of $+0.75\text{ V/SCE}$. This indicates that the passive film has good integrity and there is very limited or no pitting corrosion at low sulphate concentrations to destroy the passivity of the film. Similar results in the 0 ppm sulphate artificial saline solution were reported in another study [11]. By increasing the sulphate content of the solution to more than 400 ppm, a transpassive region appeared, which is an evidence of the breakdown of the passive film, and the current density starts to increase again. This results in a decrease in the passivity potential range (the difference between the passivation potential and the transpassive potential value). In addition to the change in the potential values, the passivation current density values also increased by raising the amount of sulphate above 400 ppm. The behavior of the commercial alloy in the N.S. seawater environment was very close to the behavior of the alloy in the 2260 ppm sulphate artificial saline solution. **Cyclic Polarization and the Protection Potential:** Fig. 9 shows the cyclic polarization plots for the commercial alloy C70600 in artificial saline solutions containing various amounts of sulphate and in N.S. seawater. The electrochemical behavior of the commercial alloy depends on the amount of sulphate in the solution. By adding up to 400 ppm sulphate to the solution, the potential difference between the corrosion potential (varied between -0.401 V/SCE and -0.409 V/SCE) and the protection potential (varied between -0.138 V/SCE and -0.144 V/SCE) remained

approximately the same. By adding more than 400 ppm of sulphate, the potential difference became smaller, which indicates that the commercial alloy becomes less protected. This result is consistent with the results obtained by linear polarization, where 400 ppm of sulphate led to a significant change in the behavior of the alloy. The smallest potential difference was observed for the commercial alloy in the 2260 ppm artificial saline solution and in the N.S. seawater. The corrosion potential shifted to a more negative value in the solution containing up to 400 ppm sulphate (from -0.401 V/SCE in the 0 ppm sulphate artificial saline solution to -0.409 V/SCE in the 400 ppm sulphate artificial saline solution). Starting from the artificial saline solution with 400 ppm sulfate as the electrolyte, the corrosion potential starts shifting to less negative values. It had a value of 0.391 V/SCE in the 600 ppm sulphate artificial saline solution, -0.373 V/SCE in the 2260 ppm sulphate artificial saline solution and approximately -0.375 V/SCE in the N.S. seawater. In contrast to the results obtained by another study [12], the corrosion potential for the commercial alloy in N.S. seawater was -0.220 V/SCE but the electrolyte (the seawater) in this case was stagnant unlike the previous report where the flow velocity of the seawater was 0.5 m/s. The behavior of the commercial alloy in the 2260 ppm artificial saline solution was the same as that of the commercial alloy in the N.S. seawater, and these plots were similar to those reported by others

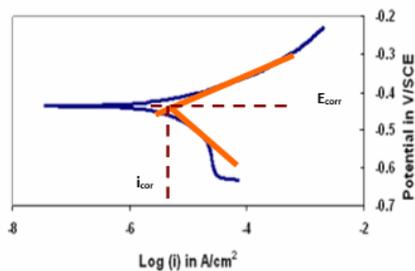


Figure 7. A Tafel extrapolation plot for commercial alloy C70600 in 0 ppm sulphate artificial saline solution.

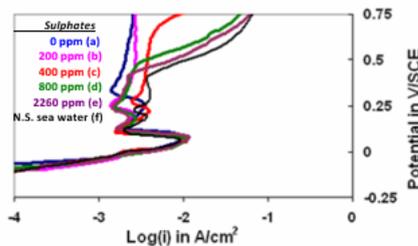


Figure 8. Linear sweep polarization plots for commercial alloy C70600 in N.S. seawater and in artificial saline solutions with various concentrations of sulphates.

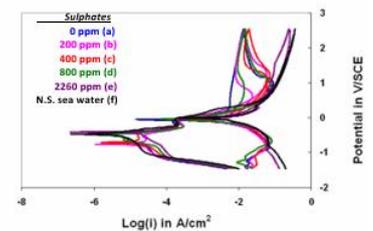


Figure 9. Cyclic Polarization plots for commercial alloy C70600 in artificial saline solutions for various concentrations of sulphates and N.S. seawater.

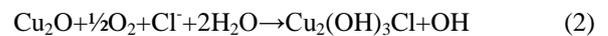
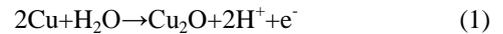
III. CONCLUSIONS

Electrochemical methods are highly efficient for the evaluation of corrosion and passivation processes. There are many advantages of these methods over the conventional immersion tests such as saving time, giving accurate results, and the ability to use these techniques in both the laboratory and the field. By using these techniques, it was concluded that the behavior of the commercial alloy C70600 depends on the amount of sulphate in the saline solution.

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[13]. **Cyclic voltammetry:** The voltammogram in the 0 ppm solution is similar to one produced in a previous study for a 85 wt% Cu, 15 wt% Ni alloy [14]. This suggests that the reactions taking place in this system are not ideally reversible because the anodic current peaks are not equal to the cathodic current peaks. The peaks that appear could be attributed to the following reactions:



In the artificial saline solution with 2260 ppm sulphate, the peaks became more complicated and distorted, which made it difficult to separate the peaks from one another. The behavior of the commercial alloy in the N.S. seawater was similar to the behavior of the alloy in the 2260 ppm sulphate artificial saline solution. It can be noted that the current density values of the anodic peaks were approximately constant up to a 400 ppm sulphate artificial saline solution, then they started to increase when more sulphate was added, causing a distortion in the cyclic voltammogram. These increases in the current density values can be explained by increases in the corrosion rates in these conditions, and was consistent with the linear polarization data.

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He has worked for about 25 years as an instructor and Scientific researcher in different universities and higher education institutes in both Libya and Canada. Dr. Abulmaali has served as a consultant to many organizations on a wide range of problems related to materials engineering in both Libya and Canada. He has received many awards, including an award for the best oral presentation in the 2008 graduate research symposium (Dalhousie University), an award for the best SEM image in the 2008 IRM annual meeting and was the recipient of a Dalhousie University award (Dalhousie University certificate in university teaching and learning). At the current time his research focuses on the corrosion behavior of steels and copper nickel alloys in the marine environment, corrosion in concrete, laser alloying and hardening and memory shape alloys.