CHAPTER 8

ELECTROCHEMICAL STUDY

8.1 NEED

It is essential to predict the performance of a prepared specific material in a particular operating environment to determine the intrinsic corrosivity of the system. Such tests are often significantly different from those used for corrosion inhibitor qualification, particularly in the case of the corrosion testing of corrosion resistant materials. The prediction of corrosion rate is especially important when selecting a material may be applied subsea equipment and most of which is extremely challenging to replace or repair once it is installed. Corrosion testing is an extensively used method of evaluating a material’s ability to withstand specific environmental conditions. Corrosion in field conditions may be tremendously slow, thus accelerated test methods have been designed to enable prediction and evaluation of long-term corrosion behavior is a special task of researchers and scientists. Corrosion Testing determines the resistance of materials to corrosion under certain environmental conditions, including temperature and humidity, ocean type salt water. Since all metals and alloys are susceptible to corrosion, test results can help businesses make sound decisions. The effects of corrosion can be costly and devastating, so it generally makes sense to perform testing before damage occurs, often during product design. Corrosion analysis can also help identify a corroden or an environmental cause, if an unexpected corrosion problem occurs. The corrosion testing is conducted by exposing small samples of a prepared material to the designated environment for a comparatively short period of time and then evaluating the type and severity of corrosion in order to select materials or chemicals that will maximize the life of the part.
8.2 TYPES OF CORROSION

The major types of corrosion are categorized into general corrosion, localized corrosion, environmentally assisted cracking (EAC) and microbiologically influenced corrosion (MIC). General corrosion is the uniform loss of material from all environment-wetted surfaces of a part or component. As the surface corrodes, the component thickness may vary and thins. This is predominantly troublesome for load-bearing or pressure-containing components because they lose the ability to perform their functions. For instance, flow lines are designed with a corrosion allowance by considering this general corrosion. This corrosion allowance can be calculated based on results of conducted suitable tests and the desired life of the flow line.

One of the most dangerous forms of corrosion is environmentally assisted cracking because it led to catastrophic failures of system components. It is often undetectable by non-destructive evaluation (NDE) methods. Here the cracking is only possible when a liable material is under stress in an environment conducive to cracking. It includes stress corrosion cracking (SCC), sulfide stress cracking (SSC), hydrogen induced stress cracking (HISC) and similar cracking phenomena. The material susceptibility to EAC is decidedly by the surrounding environment. For example, Titanium undergoes hydrogen embrittlement, in the presence of methanol; carbon steel cracks in acidic sulfide-containing environments; and nickel–based alloys crack in low pH brines.

The two common forms of localized corrosion are pitting and crevice corrosion. The pitting corrosion remains localized to a small surface area, but can penetrate deeply and rapidly into a material’s bulk. It is generally detectable from simple visual evaluation of a corrosion coupon or tensile specimen surface. The crevice type corrosion can occur when fluid becomes trapped in or between components and cannot easily flow or refresh. This type
of corrosion is quite common in underneath washers, around nuts and bolts and underneath disbonded coatings etc.

When a material is in long-term direct contact with an environment that harbors growth of bacteria or microbes, some of these organisms can contribute more to corrosion processes. These stagnant conditions make worse the MIC phenomenon. For instance, sulfate reducing bacteria (SRB) can accumulate in water trapped in corners of carbon steel tanks or under scale buildup. These bacteria will reduce sulfate in the water to form hydrogen sulfide gas (H$_2$S), which is highly corrosive to steels and can promote EAC. Other microbes can produce slimes or bio-films that lead to crevice corrosion, or facilitate the oxidation of metal, accelerating the corrosion rate.

8.3 EVALUATION OF CORROSION

There are many different corrosion tests to evaluate specific type of corrosion. Interpretation of test results is not always straightforward. Implications of the test results are dependent on the type of test conducted and the design parameters of the system being simulated. The corrosion can be tolerated to an extent, but that extent depends on role of the material, its desired life span, and its design limitations. Understanding the capabilities of differences between each test is essential for correct interpretation of test results. The general corrosion tests are useful for determining corrosion allowance or evaluating the impact of environmental constituents on the integrity and life of a component. The cracking tests help to determine the material’s robustness in the simultaneous presence of stress and severe environment. The crevice corrosion tests help to predict the material’s ability to resist corrosion due to trapped fluids. The severity of localized corrosion can be evaluated by measuring the size and penetration depth of crevices or pits. The microbiologically influenced corrosion tests are useful to determine microbial species contacting material within a process stream can support the use of biocides or other mitigating methods. The existence of MIC is verified
by wide-ranging testing of produced fluids expected to contact a component that makes to identify bacteria types and its growth. The coupons of the material can also be placed in the process stream or area where MIC is suspected, then removed and evaluated using microbiological techniques, such as genetic tests or fluorescence microscopy to identify types and quantities of bacteria present in that material or component.

8.4 UNIT OF CORROSION RATE

The corrosion rate is measured in mm/yr or mils/year (mpy). One “mil” is equal to 0.001 inches, or 1 milli-inch. The acceptable corrosion rates depend on the design life of the applicable component and the permissible corrosion allowance. The corrosion testing is useful in identifying corrodents and environmental factors once an unexpected corrosion problem occurs with a product in service. The testing of corrosion provides the answers for corrosion needs as follows:

- Comparing and selecting appropriate materials for a need
- Evaluating protective treatments
- Estimating the life of products
- Determining if a material will meet its intended application
- Identifying corrodents and environmental factors responsible for corrosion attack
- Establishing the root cause of a product failure

8.5 TYPES OF ELECTRO ANALYTICAL METHODS

Electro analytical methods are the various techniques in analytical chemistry which study the constituents of chemical species or substance by measuring the potential (volts) and/or current (amperes) in an electrochemical cell containing the analyte. These methods can be broken down into numerous
categories depending upon the aspects of the cell are controlled and measured. The three major categories are potentiometry (the difference in electrode potentials is measured), coulometry (the cell's current is measured over time), and voltammetry (the cell's current is measured while actively altering the cell's potential). Three common types of electro-chemical methods are Potentio-dynamic polarization measurement, Electro-chemical impedance spectroscopy and Cyclic voltammetry measurement.

Polarization methods such as potentio-dynamic polarization, potentio-staircase, and cyclic voltammetry are generally used corrosion testing in laboratories. These techniques can provide significant useful information regarding the corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. Polarization methods involve changing the potential of the working electrode and monitoring the current which is produced as a function of time or potential.

8.5.1 Potentiodynamic polarization:

Potentio-dynamic polarization is a technique in which the potential of the electrode is varied at a suitable rate by application of a current through the electrolyte. It is probably the most frequently used polarization testing method for measuring the corrosion resistance and is used for a wide variety of functions. Potentio-dynamic refers to the measured change in the electrical potential (voltage) of a system. In electrochemistry analysis, this term is used in describing polarization methods in the corrosion industry. Potentio-dynamic polarization is often used for laboratory corrosion testing. It can provide significant useful information regarding corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. Polarization refers to the change of potential from a stabilized state as the result of the passage of current. It means that the change in the potential of an electrode during electrolysis, such that the potential of an anode becomes more noble, and that of a cathode more active, than their respective reversible potentials. If the potential shifts in the positive direction, it is anodic.
polarization. If the potential shifts in the negative direction, it is cathodic polarization. For example, when polarization is disrupted in a passive metal at a given point causes a very active anodic site. The resultant will be accelerated local corrosion, particularly if the metal was strongly anodically polarized. For a non-passive system (such as steel in seawater), anodic polarization always increases the corrosion rate. For systems showing an active-to-passive transition, anodic polarization will increase the corrosion rate initially, and then cause a drastic reduction in the corrosion rate. Anodic protection is essentially the application of anodic polarization to a corroding system.

Anodic Polarization

Anodic polarization refers to the change of an electrode's potential in the positive direction. It is caused by current flowing across an electrode-to-electrolyte interface, such as electrode polarization associated with an electrochemical oxidation or anodic reaction. In other words, the change in the initial anode potential results from current flow effects at or near the anode surface. Anodic polarization is used for measuring and protecting against corrosion. It can be used to determine the potential regions where materials are susceptible to rapid corrosion. Polarization of an anode, that is, the decrease in the initial anode potential resulting from current flow, is evident at or near the anode surface. The potential becomes more noble (more positive) because of anodic polarization. The change in potential of an anode is caused by current flow. In the context of corrosion, polarization refers to the potential shift away from the open circuit potential (free corroding potential) of a corroding system.

Anodic surfaces can be polarized by formation of a thin, impervious oxide layer. With most metals, however, the film formation must be aided by the addition of such anodic corrosion inhibitors as chromate, nitrite, etc. The long-term exposure of alloys at anodic potentials is shown to be accompanied by rapid failure, a remarkable decrease in tensile strength, significant loss of
plasticity and substantial uniform or inter-granular layer corrosion of the surface. Artificial aging improves the resistance of alloys to failure and corrosion.

Potentio-dynamic is also known as potentio-dynamic polarization experiments were conducted for the five prepared composite samples i.e. pure magnesium and variation of reinforcement weight percentage (2.5%, 5%, 7.5% and 10%).

Figure 8.1 Experimental set up

The potentio-dynamic polarization tests of magnesium based metal matrix composites are carried out using a potentio-stat (Gill AC) of ACM Instruments, UK. The 2.5% sodium chloride solution was selected as a electrolyte and the tests were conducted with an ambient temperature of about 25°C. The electrochemical cell consists of three electrodes. The prepared specimen forms the working electrode that is actually the sample being interrogate. In order to conduct the potentio-dynamic test an electrode with accurate potential is to be selected as reference electrode. In our experiment the saturated calomel electrode (Ag/AgCl) assumed as the reference electrode and provides a stable reference against the applied potential. The final functional electrode is the counter electrode, commonly called as the auxiliary
electrode, is an electrode used in a three electrode electrochemical cell used for other reactions in which an electric current is estimated to flow. The counter electrode serves as a source or sinks for electrons. The current can be passed from the external circuit through the cell. A platinum electrode serves as the counter electrode for our experiment that provides the path for the applied current into the solution.

The experimental setup is shown in Figure 8.1. An area of 1.5 cm$^2$ of the test specimen is exposed to the electrolyte to design the cell. In order to become stable the open circuit potential, a settling time of 10 min is assigned before every experiment. In electro-chemical analytical experiments an electronic hardware called as potentio-stat is used to control the three electrode cell. The potentio-stats are capable of controlling two or more working electrodes.

A portable computer is connected with potentio-stat for monitoring and controlling the experiments. The polarization data were captured by the portable computer. The polarization plot is obtained from the electro-chemical analyzer (CH604D) software which provides a special tool in order to manually extrapolate the values of corrosion potential ($E_{\text{corr}}$) and corrosion current density ($I_{\text{corr}}$) from the plot. The electro-chemical kinetics connecting the potential rate to the electrochemical reaction rate is represented by the Tafel equation. The Tafel plot explains as a diagram or illustration of the Tafel equation. The information like rate of pitting, passivity and corrosion susceptibility can be derived from the Tafel equation. This technique could be useful for the identification of corrosion current ($i_{\text{corr}}$) and can be used to compute the rate of corrosion. The values of corrosion potential and the corrosion current density were measured and plotted with the aid of a Tafel ruler and its associated software. The horizontal ruler is set at the junction of anodic and cathodic branches and the corresponding measured values are extrapolated in the Tafel plot. The experiments were conducted with a scan
rate of 0.01V/s. Polarization plots were obtained in the electrode potential range from −100 to +100mV versus corrosion potential ($E_{\text{corr}}$). The plot combined with the equation can be very useful in depicting the lifespan of materials used in various industries.

In electrochemistry, polarization is a collective term for certain mechanical side-effects of an electrochemical process in which isolating barriers build up at the interface between electrode and electrolyte. These side-effects influence the reaction mechanisms, in addition to the chemical kinetics of corrosion and metal deposition in a reaction. The electronic displacement in turn may be due to certain effects, some of which are permanent (inductive and mesomeric effects) and the others are temporary (electrometric effect). The effects which are permanently operating in the molecule are known as polarization effects.

8.5.2 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a powerful diagnostic tool that can be used to characterize limitations and improve the performance of fuel cells. EIS is a perturbative characterization of the dynamics of an electrochemical process. EIS is widely used as a standard characterization technique for many material systems and applications (corrosion, plating, batteries, fuel cells, etc.) computer based modern DSP electronics software packages now replace lock-in amplifier techniques for implementing EIS.

There are three primary sources of voltage losses in fuel cells. It includes charge transfer activation or kinetic losses, ion and electron transport or ohmic losses, and concentration or mass transfer losses. Among these factors, EIS is an important experimental technique that can be used to break up and enumerate these sources of polarization. The application of physically sound equivalent circuit models wherein physico-chemical processes happening within the fuel cell are represented by a network of resistors, capacitors and
inductors. It can be extracted into significant qualitative and quantitative information regarding the sources of impedance within the fuel cell. EIS is useful for research and development of new materials and electrode structures over and above for product verification and quality assurance in industrialized operations. EIS can be used for both diagnostic and application purposes. It is used to characterize changes at a surface under specific system parameters also tailoring the system parameters in order to obtain a desirable effect on a surface.

The application of EIS is to Exploit Faraday’s Law to characterize a chemical process in terms of electrical measurements. Electrochemical impedance is the response of an electrochemical system (cell) to an applied potential. The frequency dependence of this impedance can reveal underlying chemical processes. The response of electrochemical systems is very nonlinear.

The main advantages of EIS are:

- It gives information about the corrosion kinetics and produces an accurate and reproducible technique suitable for highly resistive environments
- It provides data about the electrochemical control mechanism, indicating the sources of corrosion occurs by activation, concentration or diffusion.
- It characterizes the morphology of the corrosion.
- Since it is a non-destructive and non-perturbative technique and the signals applied are of very small amplitude that will not affect the corrosion potential.
- It allows for monitoring of the evolution of the passive or active state over time and the measurements can be made under real-world fuel cell operating conditions, e.g., open circuit voltage or under load (DC voltage or current).
- Multiple parameters can be determined from a single experiment.
Relatively simple electrical measurement that can be automated.

Can verify reaction models, and characterize bulk and interfacial properties of the system, e.g., membrane resistance and electro-catalysts.

Measurement is non-intrusive – does not substantially remove or disturb the system from its operating condition.

A high precision measurement – the data signal can be averaged over time to improve the signal-to-noise ratio.

8.6 RESULTS AND DISCUSSION

8.6.1 Polarization techniques to determine corrosion rate

Tafel extrapolation and polarization resistance are commonly available methods to measure corrosion rates in composites. When considering other corrosion measuring techniques, polarization methods are more rapidly experimental techniques compared to conventional weight loss estimation. Tafel relationship with respect to activation controlled anodic and cathodic processes is presented in figure 8.2. The Tafel plot represents the illustration of Tafel equation. The equation connects the kinetics of over potential and its reaction rate. For an electrochemical reaction under activation control, polarization curves exhibit linear behavior in the E versus log (i) plots called Tafel behavior. Typical polarization behavior of metal matrix composites placed in sodium chloride solution in the presence of oxygen is illustrated below.

![Figure 8.2 Tafel plot with constants](image_url)
At the corrosion potential, $E_{corr}$, rate of cathodic reduction is equal to rate of anodic reaction (metal corrosion). Tafel constants ($\beta_a$ and $\beta_c$) are calculated from the anodic and cathodic slopes. Typical cathodic polarization curves with respect to Tafel behaviour are also represented in Figure 8.2. The curve indicates the extrapolation of cathodic and anodic Tafel slopes back to the corrosion potential ($E_{corr}$). The intersection point represents corrosion current density ($i_{corr}$) or corrosion rate $i_a = i_c = i_{corr}$ (mixed potential theory). Steady state polarization curves need be obtained to be more representative of
corrosion reactions. A plot of over potential against log i showing exchange current density is illustrated in Figure 8.3 and 8.4. The curves are plotted with an initial value of E (V) is -0.2 and corresponding final value of -0.8. The scan rate is fixed as 0.01 (v/s) and the quiet time is 2 seconds.

Figure 8.5 Potentiodynamic polarization curves

8.6.2 Electro-impedance spectroscopy analysis

The impedance is measured in a perturbative manner: Small amplitude (~10 mV) AC ripple on top of the controlled DC polarization potential. The complex response of the system is regularly displayed in Nyquist format, with the reactance inverted (since such systems are inherently capacitive). The principle of this technique is to apply an alternating signal of small amplitude (5 to 20 mV) to an electrode (rebar) inserted into an electrolyte.
The initial disturbance (applied) and the response of the electrode is compared by measuring the phase shift of the current and voltage components and by the measurements of their amplitudes. This can be done in the time domain or in the frequency domain, using a spectrum analyzer or frequency response analyzer, respectively. Importantly, the initial disturbance is a disturbance potential ($\Delta E$) of sinusoidal type, which must be imposed at steady state of the system and the electrode response is a current ($\Delta I$), also sinusoidal, but with a difference of phase ($\Phi$) to the applied signal. Therefore, the
impedance which is represented by $Z$, measures the relationship between $\Delta E$ and $\Delta I$. The EIS technique works in the frequency domain and is based on the concept that an interface can be seen as a combination of passive electrical circuit elements, i.e., resistance, capacitance and inductance. When an alternating current is applied to these elements, the resulting current is obtained using Ohm's law.

Figure 8.8 Bode plot for specimen 1

For the MMCs the information on several parameters can be obtained, e.g., the presence of surface films, characteristics of the composites, interfacial corrosion, and mass transfer phenomena. However, interpreting the results may be difficult and the use of an equivalent circuit, which can change according to the conditions of the material, makes the technique more suitable for laboratory studies. Potentio-static and galvano-static methods need be
compared to ascertain the choice of a better technique to determine corrosion rates. There are some demerits in Tafel extrapolation. Since polarization curves are not reversible and are influenced by experimental and environmental conditions, Tafel constants can vary from system to system. Often anodic curves may not exhibit linear behavior near $E_{corr}$. Friedrich (2006) and Hakamada (2007) stated that a thin surface film is formed when the magnesium and its alloys is in direct contact with moist air. This natural outer layer is not as denser and its corresponding Pilling-Bedworth ratio of 0.81 that indicates underlying metal cannot be completely covered. As a result, magnesium and its alloys are highly vulnerable to corrosion. The intervening factor of corrosion behavior of magnesium alloys prevents their applications in various fields in the past years.

Figure 8.9 Bode plot for specimen 2
But the attractive factor of magnesium alloys is they are acting as a substitute for polymers. The biggest problem of using polymers is that shortage of defined satisfactory recycling solutions.

Though the reduction of the dangerous contents of Ni, Fe, Cu etc. prejudiced the application of magnesium alloys and still lack the self-healing layer for protecting efficiently. In both manufacturing and alloying there is a need of efforts that directed towards composition and its corresponding microstructure involved the grain size and alloy temper/heat treatment to decrease the corrosion susceptibility. Also, according to the corrosion requirements, physical operations like grinding, polishing, abrading, particle blasting and brushing also the chemical treatments like organic solvents/emulsions, alkaline and acid treatment methods are usually taken.

8.7 CORROSION RATE

The corrosion rates for the developed samples were calculated and presented in the Figure 8.10. The values are based upon the corrosion potential, corrosion current and Tafel constants.

Figure 8.10 Graphical representation of corrosion rate
It clearly indicated that addition titanium dioxide particles effectively reduce the corrosion rates of magnesium composites. Hence the corrosion resistance can be improved by the incorporation of titanium particles in the composite. Potentio-dynamic polarization method is used to calculate the Tafel constants and further the corrosion resistance of developed samples. EIS method is used to determine the corrosion mechanism of the samples.

8.9 SUMMARY

There are several common test methods available for evaluating material degradation from corrosive processes. Different types of corrosion necessitate different test methods. Two methods were selected and the experiments were conducted for the determination of corrosion rate and corrosion mechanisms. Results of these tests in form design, materials, or chemical selection decisions that ultimately contribute to the efficient and effective operation of subsea equipment.