

On-Line Corrosion Monitoring and Survey Using Electrochemical Impedance.

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ABSTRACT

On-line corrosion monitoring and surveillance of process plants and equipment should really involve a technique for continuous measurement of corrosion rate of engineering materials during their service or operational life. Aluminium, mild steel and nickel alloys were used as suitable examples.

The correlated response of the corroding system to a series of small voltage perturbations was effectively expressed as electrochemical impedance from which the charge transfer resistance and hence, corrosion rate could be evaluated. This has obvious advantages over the conventional linear polarization (polarization resistance) technique to the effect that it can be used to investigate a wide range of materials and environments.

Corrosion measurements need not be confined to the region of the corrosion potential but can be obtained at any point on the potential versus current polarization curve. The various factors favouring or hindering corrosion were effectively highlighted.

I. INTRODUCTION

Theoretical and instrumental developments over the past few decades have demonstrated the feasibility of using impedance measurements to monitor and control corrosion reactions. The conventional weight loss determination tests seem rather tedious and could not be satisfactorily employed in the measurement of extremely low corrosion rates (less than 0.1 mpy) often encountered in noble or passivating metals, inhibited environmental media and in the chemical and food-processing industries where product contamination constitute serious problems. Thus, over the years, much attention has been directed towards the use of the so-called polarization resistance method which is primarily based on the fact that for small polarizations up to

20 mV from the corrosion potential, a linear relationship seems to exist between the applied current density (i) and the electrode potential (E), in accordance with the well-known Stern & Geary Equation:

$$R_p = \frac{\Delta E}{\Delta i} = \frac{\beta_a \beta_c}{2.3 i_{\text{corr}} (\beta_a + \beta_c)}$$

Where R_p is the polarization resistance, i_{corr} is the corrosion current and β_a and β_c are the anodic and cathodic Tafel slopes, respectively.

The Electrode Impedance Theory:

In view of the electrochemical nature of corrosion, it is not surprising that measurement of the electrical properties of the metal/solution interface, i.e., the electrical double layer, has been gainfully utilized in the study of corrosion. The impedance concept assumes that a corroding electrode exhibits an intricate behaviour which is dependent upon several factors, namely: the ionic and electronic resistance of the solution and the bulk of the electrode film ($R\Omega$), the double layer capacitance ($C(\text{dl})$) resulting from interfacial build-up of water dipoles, adsorbed ions and organic molecules, the charge transfer resistance (R_o) arising from the anodic and cathodic reactions, the relative effects of diffusion (Warburg Impedance, W) and that of reactant and product adsorption on the electrode surface. The overall response can thus be represented by a network of circuit elements (Randles Equivalent Circuit) comprising resistance, capacitance, inductance, etc., similar in behaviour to the corroding electrode (1-4). The cell impedance (Z) may be treated as a vector in the complex plane by specifying the magnitude of its real and imaginary components. Using complex number notation: $Z = Z' + jZ''$ where Z' is the real or resistive component, Z'' is the imaginary or reactive component and j , the complex operator = $(-1)^{1/2}$.

For a purely activation-controlled corrosion behaviour, the electrode impedance can be

represented by a parallel combination of the charge transfer resistance (R_0) and the double layer capacitance (C_{dl}) in series with the solution resistance (R_Ω), Fig. 1(a) and 1(b). This is usually represented by a semicircle on the Argand plot, wherein the impedance at any one frequency corresponds to a point on the semicircle, Fig. 2(d). Expressed mathematically:

$$Z = R_\Omega + \frac{R_0}{1 + \omega^2(C_{dl})^2 R_0^2} - j \frac{(l)C_{dl} R_0^2}{1 + (l)^2(C_{dl})^2 R_0^2}$$

This means that at extremely high frequencies, the capacitor (C_{dl}) conducts easily and effectively shorts out R_0 so that only solution resistance (R_Ω) is measured. However, as frequency decreases, C_{dl} tends to conduct less and less and the response following the semicircle until zero frequency ($(l)-0$) or d.c. is approached. Thus, the electrode impedance is the sum of R_Ω and R_0 , R_0 , being equal in magnitude to the diameter of the semicircle. The maximum capacitive effect corresponds to the frequency at the very top of the semicircle and is given by

$$(l) = \frac{1}{R_0 C_{dl}}$$

from which the double layer capacity is computed (5-9).

Many corroding system exhibit an impedance due to diffusion control (concentration polarization). This is known as Warburg impedance (W), Fig. 1(c). Solution of Fick's second law of diffusion, taking into account the appropriate

boundary conditions, defines this impedance as: $W = \sigma \omega^{-1/2} + j \omega^{-1/2}$

Where σ is the Warburg coefficient. The electrode impedance for this system can thus be mathematically represented as follows;

$$Z = R_\Omega + \frac{1}{j\omega C_{dl} + \frac{1}{R_0 + \sigma \omega^{-1/2} - j\sigma \omega^{-1/2}}}$$

Separating into real and imaginary parts:

$$Z = R_\Omega + \frac{1}{(C_{dl} \sigma \omega^{-1/2} + 1)^2 + \omega^2 (C_{dl})^2 (R_0 + \sigma \omega^{-1/2})^2} - j \frac{\omega C_{dl} (R_0 + \sigma \omega^{-1/2})^2 + \sigma^2 C_{dl} + \sigma \omega^{-1/2}}{(C_{dl} \sigma \omega^{-1/2} + 1)^2 + \omega^2 (C_{dl})^2 (R_0 + \sigma \omega^{-1/2})^2}$$

Two borderline cases are of particular interest

A. At very low frequencies ($\omega = 0$), the electrode impedance reduces to:

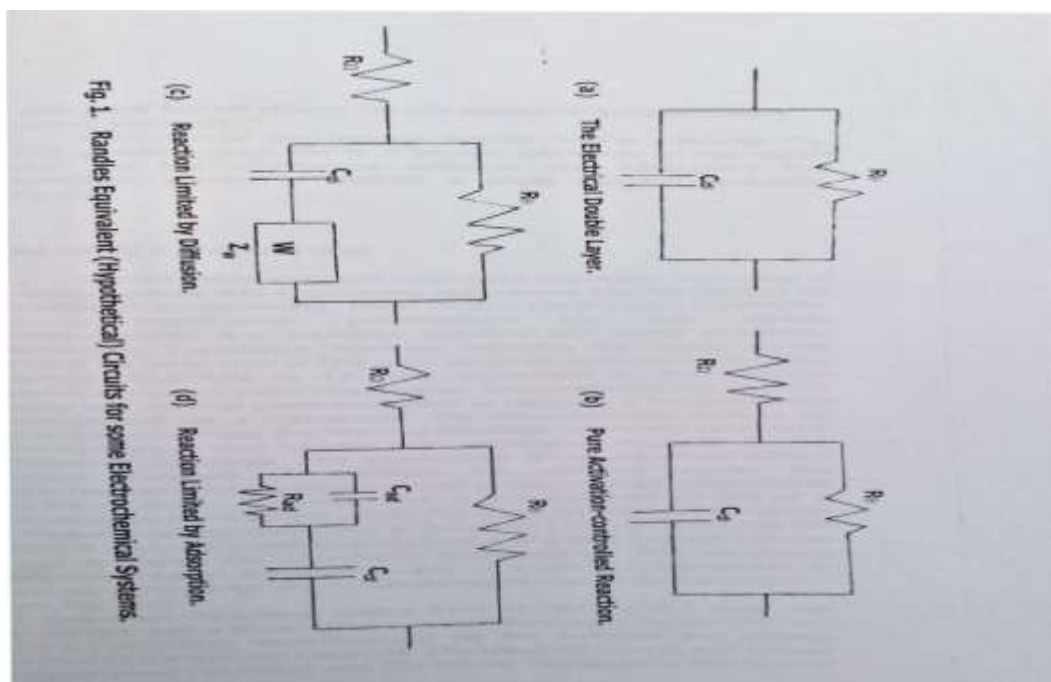
$$Z = R_\Omega + R_0 + \sigma \omega^{-1/2} - j(\sigma \omega^{-1/2} + 2\sigma^2 C_{dl})$$

Which is a straight line of slope 45° and intersecting the real

Axis (Z') at $(R_\Omega + R_0 - 2\sigma^2 C_{dl})$ as shown in fig 2(e)

B. At very high frequencies ($\omega = \infty$), diffusion and hence, W , can be neglected and the electrode impedance reduces to

$$Z = R_\Omega + \frac{R_0}{1 + \omega^2(C_{dl})^2 R_0^2} - j \frac{\omega C_{dl} R_0^2}{1 + \omega^2(C_{dl})^2 R_0^2}$$



which is the familiar charge transfer resistance (pure activation control) semicircle.

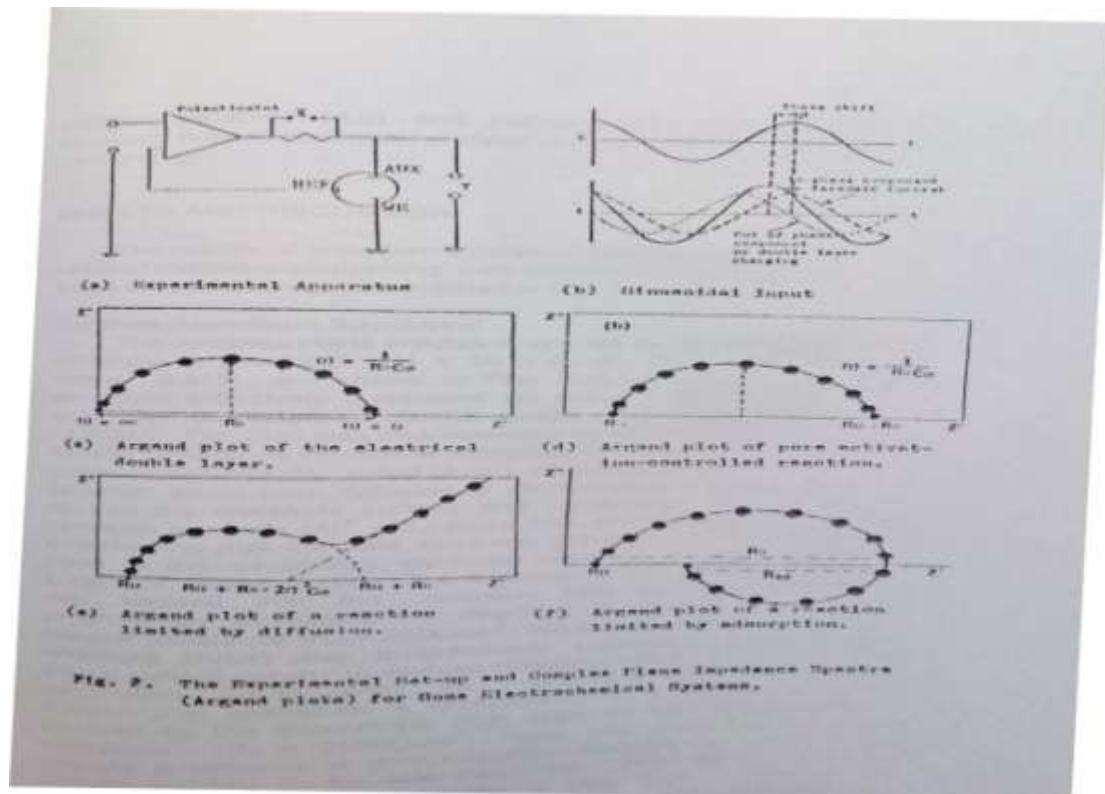
Adsorption of electroactive species on the electrode, Fig. 1(d), generally gives rise to a second semicircle on the argand plot. The two phenomena (diffusion and adsorption) may sometimes interact to produce a single distorted semicircle, Fig. 2(f).

II. MATERIALS AND METHOD

Several electrochemical techniques commonly accessible in various science and engineering applications can be adapted for impedance measurement. These include oscilloscopic techniques, lock-in amplification, potentiostatic and time domain measurements, a.c. corrosion monitors and digital correlation techniques. Experience, however, indicates that measurements should be taken over a frequency range of some seven decades, namely: 10.0 KHz to 1.0 mHz, dependent on the particular corrosion system under investigation. Measurements can be taken using two identical plane electrodes or perhaps, a three-electrode arrangement via a potentiostat. The three-electrode system, for example, comprises the Working electrode (corroding specimen), the Auxiliary or inert

(usually platinum) counter electrode and the Reference electrode. The potentiostat is an electronic control device designed to maintain the potential across the specimen/solution interface constant at any required value relative to the reference electrode. This is accomplished by use of a negative feedback control circuit, Fig. 2(a). An automated Transfer Function Analyzer comprising a "Solartron 1172" or "S.E. Labs SM 2001 A" frequency response analyzer and a data transfer unit was used to obtain the impedance measurement. This equipment employs modern digital technique of wave form generation to impress a frequency and amplitude stable signal into the corrosion cell, Fig. 2(b).

A downward frequency sweep from 10 KHz to 0.1 mHz was employed, with a sinusoidal a.c. input perturbation signal of 10 mV (r.m.s.) amplitude superimposed on the constant d.c. voltage applied to the working electrode. The resultant current and voltage outputs were correlated and the results displayed in the form of complex variables (a,b) and subsequently analyzed with a computer. A fresh specimen surface was used for each impedance measurement.



III. RESULTS AND DISCUSSION

The results of impedance measurements conducted on selected materials comprising pure aluminium, mild steel and nickel alloy specimens are outlined in Fig. 3.

The pure Aluminum Specimen:

The complex plane impedance spectra for the pure aluminum specimen in 3% NaCl (pH = 10.5) from -1700mV to 1500mV, versus S.H.E., are shown in Figs 3(a) to 3(d). As expected, aluminium effectively underwent an active - passive, transition within the aforestated potential range. The impedance plot at -1700mV, Fig. 3(a) was characterized by a clearly distinct charge transfer resistance semicircle indicative of an activation-controlled corrosion process ($R_0 = 480 \Omega\text{cm}^2$), albeit limited by diffusion. This limitation arose from diffusion of electroactive species (OH^- , Cl^- , etc.) to the electrode surface and conversely, the diffusion of corrosion products (Al^{3+} etc.) away from the electrode. It is worth emphasizing that the

said electrode potential (-1700mV) is very close to the equilibrium electrode potential of pure aluminium (-1660mV versus S.H.E.). The impedance plot at -1500mV, not only showed that the corrosion rate (anodic dissolution) progressively increased, as depicted by the smaller charge transfer resistance ($R_0 = 250 \Omega\text{cm}^2$) but that the effect, of diffusion (Warburg factor) also progressively increased. Apparently, a critical current density (maximum reaction rate) is reached prior to passivation. Subsequently, the impedance plot at -1000mV showed that aluminium is undoubtedly in a passive state as depicted by the exceedingly high value of the charge transfer resistance ($R_0 = 3500 \Omega\text{cm}^2$). Here, the dominant electrode process is diffusion or pore migration through the passive film, possibly $\text{Al}(\text{OH})_3$. On the other hand, the impedance plot recorded at 1500mV, Fig. 3(d), exhibited a very high corrosion rate ($R_0 = 100 \Omega\text{cm}^2$) owing to oxygen evolution and transpassivity. Oxygen evolution is believed to occur at potentials above 1230mV. This apparently involved an intermediate adsorption stage.

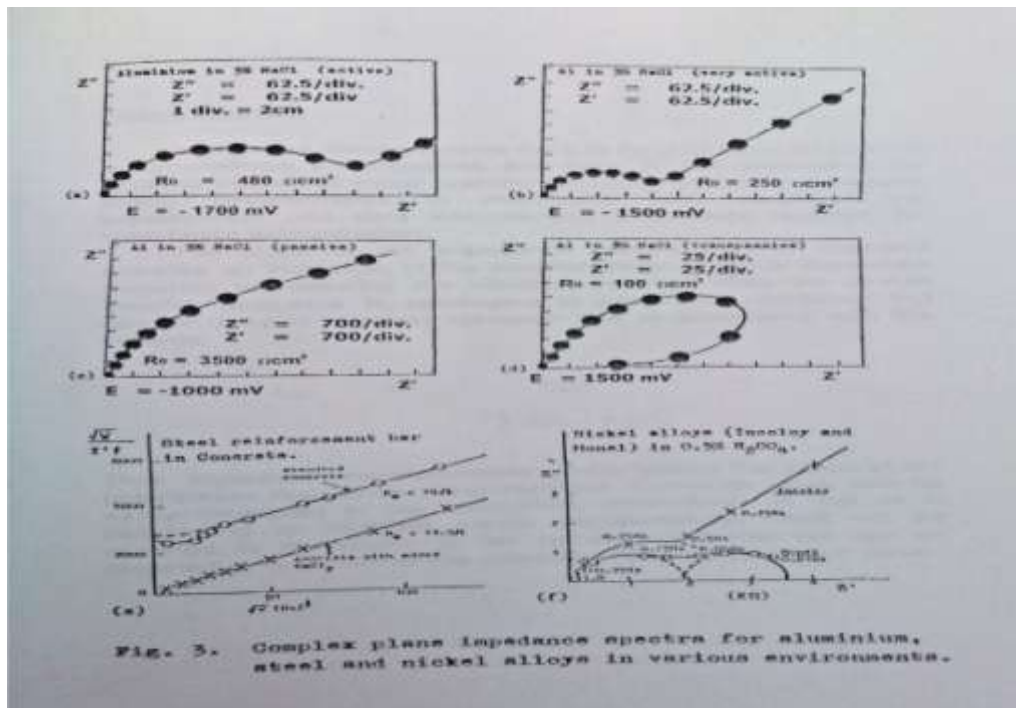


Fig. 3. Complex plane impedance spectra for aluminium, steel and nickel alloys in various environments.

IV. CONCLUSIONS

Impedance measurements have in the part been confined to electrochemical investigations and there is little information on systems related to more practical corrosion problems. However, recent developments in electronics have simplified the experimental and data interpretation procedures required for impedance determination.

The slope of the impedance spectra (Argand diagram) provides an indication of the conjoint electrochemical processes favouring or hindering the corrosion reaction while the charge transfer resistance, R_0 (analogous to polarization resistance, R_p) can be used to evaluate corrosion rate in accordance with the scheme:

$$i_{\text{corr.}} = \frac{\beta_a \beta_c}{2.3 (\beta_a + \beta_c) R_0}$$

Thus, impedance measurements greatly extend the scope of the polarization resistance measurements. Corrosion rates can be easily measured in low conductivity electrolytes as well as in passivating or inhibited media. Measurements need not be confined to the region of the corrosion potential but can be obtained at any point on the potential - current polarization curve.

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