Potentiostatic Polarisation Responses Of Mild Steel In Seawater And Acid Environments

O. I. Sekunowo, S. O. Adeosun, G. I. Lawal

ABSTRACT: The imperative of secondary corrosion response evaluation in real-time to prevent catastrophic failure in service continues to be at forefront of research efforts. In this paper, electrochemical polarisation response of mild steel in acid and seawater media was studied. Specially prepared mild steel plate coupons were immersed in seawater and 1M hydrochloric acid respectively at a scan rate of 0.2 volts per second while the corrosion potentials varied from -0.6 volts to +1.6 volts. The electrode polarisation response data obtained is used to analyse the material relevant electrochemical parameters. The results demonstrate the well established corrosion phenomenon of carbon steel (mild steel) occasioned by chloride ions aggressiveness coupled with the acidic nature of the corrosion product. Thus, the continuous corrosion without any passive time-lag of the mild steel in seawater is predicated on the large concentration of chloride ions. It is concluded that corrosion mitigation of mild steel in seawater and hydrochloric acid entails either an entire prevention of accumulation of corrosion product or an efficient neutralisation of its acidic nature.

Keywords: Electrochemical polarisation, hydrochloric acid, mild steel, seawater

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INTRODUCTION
Most exposed metallic surfaces in air are usually covered with oxide film thereby limiting spontaneous degradation. However, when a metal is immersed in an aqueous solution, the oxide film tends to dissolve. Sometimes the thichness of such oxide film may be up to 0.84nm with the tendency to thicken further as days of exposure increases (Alexander, et al., 2002). In particular, the corrosion of mild steel pipes in acid and saline environments has been a major challenge with regard to processed products (oil, gas, chemicals, etc) transportation due to its devastating effects (Ismaeel and Turgoose, 1999). Although the corrosion behaviour and passivation characterisation of mild steel have been extensively investigated (Lise, et al., 2006) but, electrochemical methods are rarely employed. Electrochemical polarization method is often preferred because it enables the determination of instantaneous reaction rates at electrode or solution interface in a single experiment while other methods require multiple measurements over time to obtain the required corrosion rate data (Kear, et al., 2004). Further, the data generated from such study is broad and can be analysed in many forms thus, serving as the basis for an effective corrosion mitigation.

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Given that electrochemical polarisation resistance technique is relatively short time dependent, it aids the selection of best protective measures to be used thereby saving cost. The transportation of processed crude oil and gas including other petrochemical products on shore or off shore often takes place using mild steel pipes which are joined severally. In practice, coupling of pipes requires the use of dissimilar metals which often results to galvanic corrosion in the presence of electrolyte (Zhang, X. G. 2011). Electrolytes are electrically conductive solutions such as sea water which contains chloride thereby making the marine environment a veritable source of chloride contamination. Generally, the coupling of two dissimilar metals in the presence of an electrolyte causes a salty bridge as one of the metals becomes anodic with reference to the other and the potential difference creates corrosion current causing the more anodic metal to corrode. Thus, in a galvanic couple, it is imperative to evaluate the relative contributions from the polarisation of the coupled metals and the electrolyte resistance as discribed by the abridged Kirchoff's second law:

$$E_{c, corr} - E_{a, corr} = \Delta V_c + \Delta V_a + IR \text{ -------------------------1}$$

Where $E_{c, corr}$, $E_{a, corr}$ are the uncoupled corrosion potentials of the cathode and anode respectively, ΔV_c, ΔV_a are the ohmic potential drop at cathode and anode respectively while I is the impressed current and R is the resistance of electrolytic portion of the galvanic circuit. Equation 1 is ususally illustrated in a typical anodic and cathodic polarisation curves as developed by Zhang (2011) which is used in the estimation of galvanic current (Fig 1). According to Zaharani, et al., (1988), three prerequisites exist for galvanic corrosion to occur namely (i) the two metals must be far apart in the electrochemical series (ii) the metals must be in electrical contact and (iii) the metals must be bridged by an electrolyte. Thus, one of the most effective measures against galvanic corrosion is avoidance of dissimilar metals that are far apart in the electrochemical series applicable to the environment. Pitting corrosion is another ubiquitous form of degradation to which mild steel pipes are susceptible. This phenomenon is often aggravated in the presence of chlorides by unleaching severe attack at the base of breaks in coatings (Loto, 2013). Pitting corrosion takes advantage of the different

139

metallurgical phases present on the surface of most common alloys such as mild steel. Generally, pitting occurs as a result of localized anodic dissolution where the anodic portion of the corrosion cell is dwarfed by the larger cathodic portion. However, the severity of pitting tends to vary with the logarithm of the bulk chloride concentration (Leckie and Uhlig 1966). According to Galvele (1981), the

reasons for chloride aggressiveness bother on its characteristics in terms of solubility, size and diffusivity. Chloride is an anion of a strong acid and many metals cations exhibit considerable solubility in chloride solutions. With regard to size, chloride is a relatively small anion with high diffusivity hence it easily interferes with passivation.
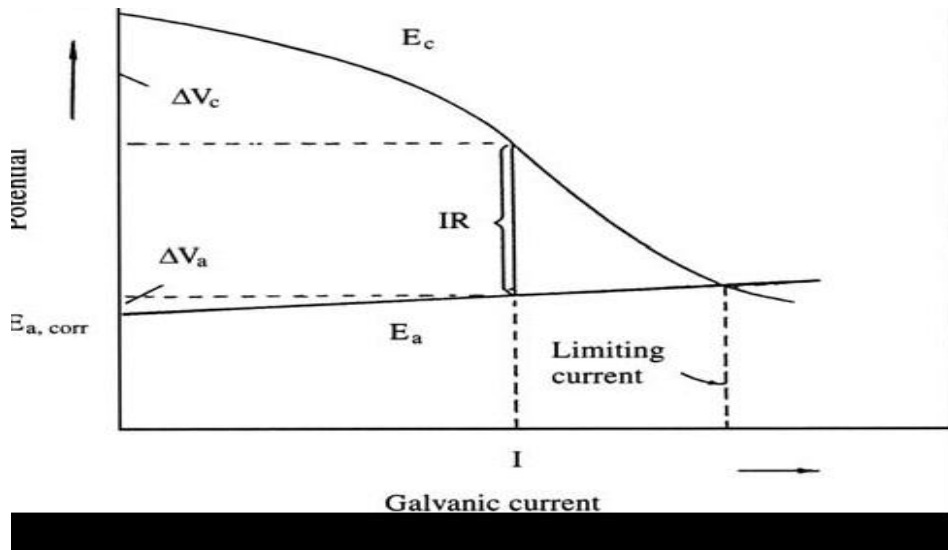

FIG 1: Graphic estimation of galvanic current (Source: Zhang, X. G. 2011; Galvanic Corrosion)

The challenges pose by the combined effect of stress and aggressive corrosive media continue to take their toll on engineering infrastructures (Bjerken and Ortiz, 2010). In particular, stress corrosion cracking occurrences due to pipe-walking phenomenon is currently receiving intense attention (Olunloyo, et al., 2007). This is because stress variations occur as the pipe convey products under intense pressure in the presence of solutions of chloride ions which often leads to brittle cracking of the pipe. Under such conditions, a plethora of fast propagating incipient cracks often ensued in such pipes. Bolted joints as common in pipe couplings are spots where oxygen or air flow is grossly deficient resulting in the accumulation of salts, acids and moisture leading to the formation of a close corrosion cell. Consequently, a small anode is created at the joint with the remainder of the pipe body acting as a large cathode leading to concentrated corrosion at the bolted joint. Mild steel is known to exhibit passive behaviour in aqueous solutions hence its corrosion is known to depend on the aggressiveness of the environment (Videm and Koren, 1993). However, due to the wide spread utility of mild steel in various environments, the evaluation of its corrosion responses in marine (seawater) and acid environments is of immense

relevance especially in the petrochemical industry. For example, in the oil industry, the presence of hydrocarbon is a major determining factor coupled with the continuous accumulation of corrosion products on the surface which often cause severe damage leading to the loss of some critical equipment. Therefore, this study investigates the corrosion responses of mild steel pipes in marine (seawater) and acid environments through electrochemical polarisation technique. The aim is to profer corrosion mitigating measures for mild steel pipes that enhance their reliability is service.

EXPERIMENTAL PROCEDURE

Materials and equipment

The materials used consist of chemical reagents namely; acetone, 1M HCl (hydrochloric acid solution), seawater of pH 8.3 and commercial mild steel with its chemical composition determined by atomic emmission spectroscopy (AES) and the results presented in Table 1. Major equipment employed include voltmeter, rheostat and inverter as the current source.

Table 1. Chemical composition of mild steel coupon

Element	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	V	Pb	Zn	Fe
Wt. %	0.226	0.102	0.616	0.021	0.024	0.040	0.104	0.004	0.015	0.002	0.003	0.002	98.836

Specimen preparation

The mild steel coupons were mechanically machined and dimensioned to 76mm x 22mm x 3mm with two 8mm diameter holes bored at one end of each coupon for firm attachment to a fixture placed above the plastic bowl containing the test media (See Fig 2). The coupons configuration have 358mm^2 exposed surface area. Cleaning of the coupons was carried out using a rough abrasive paper of 320 grits followed by a smooth abrasive paper of 600 grits. In order to ensure a rust-free surface, the coupons were pickled in a dilute HCl acid and rinsed with de-ionised water, degreased with acetone and dried. The coupons were then stored in a dessicator prior to polarisation experiment.

Electrochemical polarisation campaigns

The electrolytic media simulated for the electrochemical analysis consists of dilute 1MHCl solution and one litre of seawater having pH 8.3 as the second test medium. The electrochemical analysis with the set-up shown in Fig 2 was carried out at 37^{0}C while the electrolytic bath consits of a two-cell arrangement with copper as the auxiliary electrode. Both coupons were connected to the terminals of a potentiostat with mild steel and copper at positive (+) and negative (-) terminals respectively. The coupons were then immersed in the electrolytes (HCl solution and seawater in succession) at 20cm immersion depth. Electrode polarisation was accomplished from -0.6V to +1.6V at a scan rate of 0.2V/s and the corrosion currents recorded.
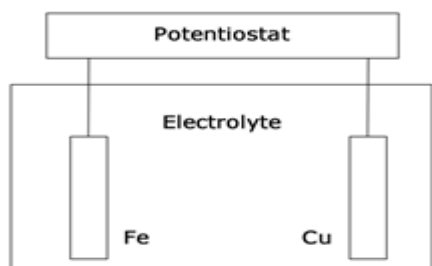

FIG 2. Potentiostat polarisation apparatus configuration

RESULTS AND DISCUSSION

Polarisation analysis

The critical polarization dynamics of mild steel are shown in Fig 3. The Figure illustrates the linear polarization response of mild steel in 1M hydrochloric acid. Point **AB** represents the typical cathodic behaviour in line with Tafel curves while **BC** is the active zone with its characteristic anodic dissolution reaction. It is also observed that at potentials more than -2v (point **B**), corrosion rate increases and reach a maximum at the passivation potential, **D.** This point is usually referred to as the passivation potential, E_{pp}. However, transition from the active dissolution occurs from **D** to **G**. Within this region, it appears a protective film has begun to form resulting in sudden drop in corrosion current density. Thereafter, the corrosion current density is maintained at a steady level until point **H.** Beyond this point the breakdown of protective film formed starts. Hence, the likelihood of eventual specimen failure is rife at this point. Often, the potential at this stage of protective film breakdown, E_{bd} is a useful parameter used in assessing the oxidation-passivation properties of materials. However, this is not an absolute parameter because it varies according to certain metallurgical and electrochemical conditions of the material under investigation (Loto, 2013).
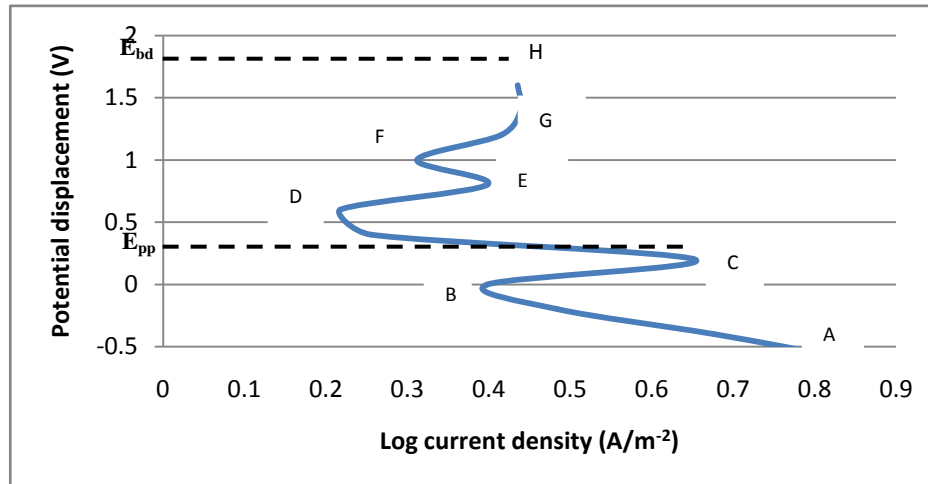
FIG 3. Potentiostatic polarisation behaviour of mild steel after 72 hours of immersion in 1M HCl at 37^0C.

In Fig 4, there appears to be no specific periods of specimen passivation as the curve represents continuous severe active corrosion reaction of the mild steel. The higher concentration of chloride ions (Cl⁻) in the electrolyte (seawater) must have been responsible for this observation. Given the relatively high presence of chloride ions resulting in increase aggressiveness, the ability of the mild steel to repair its protective film (if any) is drastically impaired hence the loss of protection. The continuous accumulation of corrosion products on the specimen surface further aggravates the reaction of positive metal ions with water to form a hydroxide corrosion product and H^+ ions. This makes the corroding specimen surface weakly acidic thereby accentuating the corrosion process.
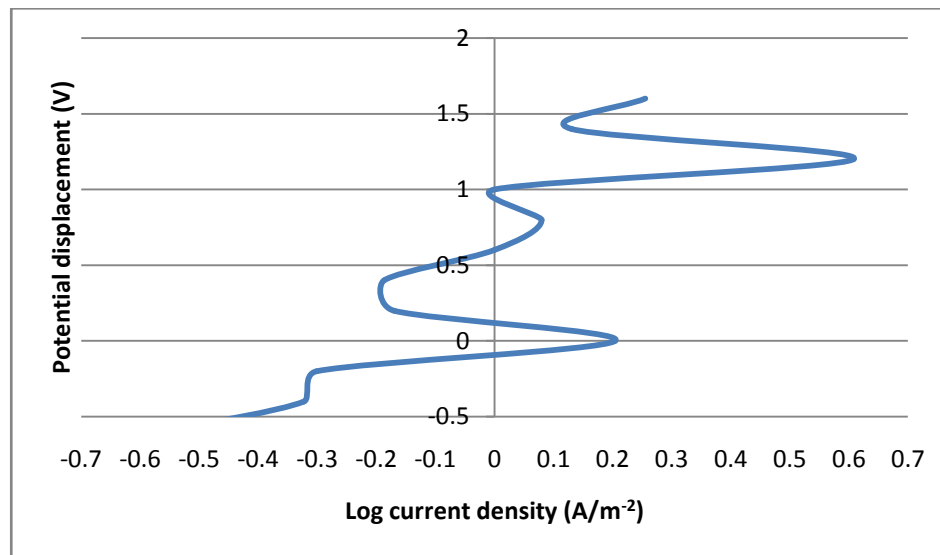

FIG 4. Potentiostatic behaviour of mild steel in after 72 hours of immersion in seawater environment at 37^0C.

Studies on the formation and stability of passive film on mild steel have shown that it is dependent on dissolution matrix of constituent elements (Schmuki, et al., 1994). The polarization curve in Fig 3 indicates a material exhibiting no intrinsic passivation. This connotes the absence of reliable protective film on the specimen surface at the various passivation potentials such as at E_{pp} and other regions. Consequently, breakdown easily occurs immediately an attempt is made to form any protective film during upward scanning. This agrees well with established studies to the effect that passive film structure is dynamic (Fattah-alhosseini, et al., 2011). With regard to the effect of chloride ion, its aggressiveness stems from its relatively small anion which confers on it a rather high diffusivity. This enables chloride ions to easily interfere with passive film culminating in a deleterious contamination of passive film structure and its eventual breakdown. According to Zhang, et al., (1998), passivation breakdown potential, E_{bd} is sometimes used as an accelerated laboratory test to determine the relative susceptibility of a material to localized corrosion for iron based alloys in a chloride environment.

Polarisation dynamics

The other relevant electrochemical parameters such as corrosion current (i_{corr}), corrosion potential (E_{corr}), corrosion current density (I_{corr}) and corrosion rate (**CR**) are determined for both acid and seawater media and presented in Table 2. The corrosion rate was calculated using Faraday's law in term of penetration rate (**CR) is** given as:

$$\text{CR (mm/yr)} = \frac{k.\ I_{corr}.\ EW}{\rho} \quad \text{----------------------- (2)}$$

Where, k is 0.00327 (mm.g/A.cm.yr), I_{corr} is corrosion current density (A/cm^2), ρ is density (g/cm^3) and EW is equivalent weight for mild steel which is considered to be dimensionless in this calculation. The mild steel equivalent weight is estimated to be 28.25 (detail calculation is shown in the appendix).

Table 2. P**olarisation resistance parameters of mild steel in (A) 1 M Hydrochloric acid (HCl) and (B) Seawater at 37^0C.**

Hydrochloric acid (**A**)				Seawater (**B**)			
E_{corr} (V)	i_{corr} (A)	I_{corr} (A/cm^2)	Corrosion rate (mm/yr)	E_{corr} (V)	i_{corr} (A)	I_{corr} (A/cm^2)	Corrosion rate (mm/yr)
-0.6	7.0	0.196	2.306	-0.6	0.275	0.008	0.904
-0.4	4.75	0.133	1.565	-0.4	0.475	0.013	1.565
-0.2	3.05	0.085	1.0	-0.2	0.500	0.014	1.643
0	2.51	0.070	0.825	0	0.625	0.017	2.054
0.2	4.52	0.126	1.486	0.2	0.675	0.019	2.219
0.4	1.81	0.051	0.595	0.4	0.650	0.018	2.137
0.6	1.65	0.046	0.542	0.6	1.000	0.028	3.287
0.8	2.52	0.071	6.502	0.8	1.200	0.033	3.944
1.0	2.05	0.057	5.287	1.0	1.011	0.028	3.323
1.2	2.61	0.073	0.858	1.2	1.150	0.032	3.781
1.4	2.75	0.077	0.904	1.4	1.352	0.038	4.444
1.6	2.78	0.078	0.717	1.6	1.801	0.050	5.921

Corrosion rates

Fig 5 compares corrosion rates in both media under polarization. As scanning increases, corrosion of the mild steel in seawater occur spontaneously without mitigation, though a brief period of passivation is observed at low potentials but immediately thereafter, corrosion rate increased continuously. In hydrochloric acid solution, similar corrosion response is observed until about 0.51 potential when corrosion rate increased sporadically and reached a peak at 6.502mm/yr. However, the formation of a stable passive film brought down the corrosion rate to 5.287mm/yr and reduce further to 0.717mm/yr at 1.6V. The overall behaviours appear to have stemmed from the ubiquitous action of chloride on the corrosion propensity of mild steel both in hydrochloric acid and seawater.
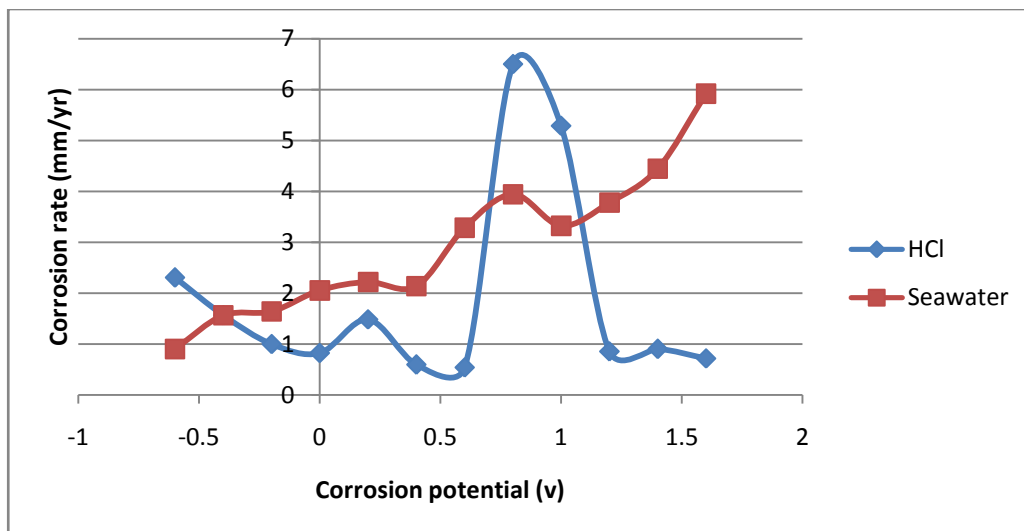

FIG 5: Mild steel polarisation behaviours in hydrochloric acid and seawater media

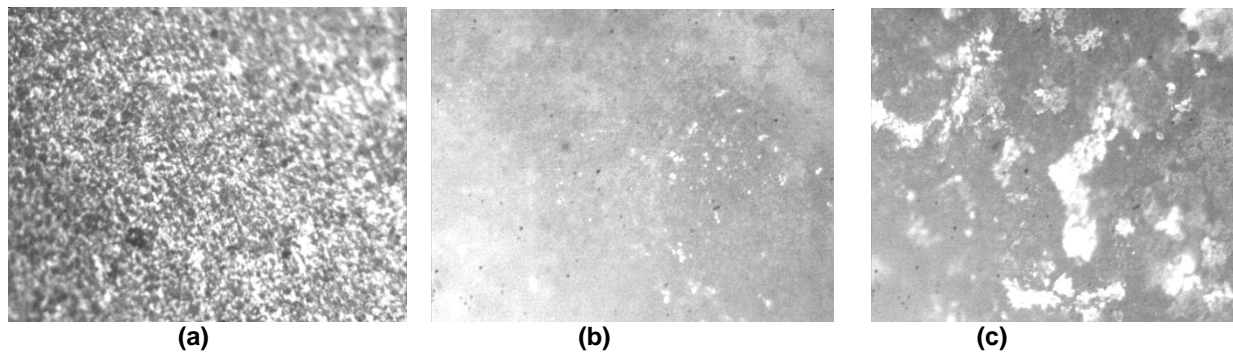**Microstructures of polarised mild steel coupons**

| (a) | (b) | (c) |

FIG 6: Micrographs of mild steel as observed under an optical microscope for (**a**) unpolarised (**b**) polarised in concentrated hydrochloric acid and (**c**) polarised in seawater.

The polarized specimens' exhibit extensive erosion of their morphological phases indicating that severe corrosion had taken place. In particular, the micrograph of the specimen polarized in seawater (Fig 6c) reveal selective leaching of the constituent pearlite thereby depicting the ferrite matrix in a sort of pit. This invariably is capable of compromising the desirable mechanical properties of the steel. Similarly, the polarised specimen in hydrochloric acid as shown in Fig 6b exhibited massive erosion of different segments of the structures leaving some ferrite islands while the cementite could hadly be revealed due to severe damage to its texture. In contrast, the unpolarised specimen (Fig 6a) shows homogeneous dispersion of the pearlite in fine ferrite matrix. The differences in the specimens micrographs indicate that corrosion often adversely impact materials microstructures which is the leading cause of failure in service. According to Kruger, et al., (1992), microstructural changes during corrosion have been shown to affect the stability of passive films on metals.

CONCLUSION

The potentiostatic polarization of mild steel in hydrochloric acid and seawater has been investigated. Mild steel intrinsic characteristics approximated by its constituent elements significantly impacted the corrosion responses. Given that both media contain chloride ions as the most aggressive specie, the acidity of corrosion product appears to have distinguished the corrosion rates of the mild steel in each of the environment simulated. The acid nature of corrosion product in this study adversely affected the stability of protective film. It may be concluded that any effort made to reduce corrosion product acidity and its accumulation will go a long way in mitigating corrosion of mild steel in both media.

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APPENDIX: Calculation of mild steel equivalent weight

According to standard ASTM (G. 102-89 of 1999) practice for calculation of corrosion rates and related information from electrochemical measurements, the calculation of equivalent weight (EW) for alloys entails that only elements above 1 mass percent are included. Hence, in the case of mild steel, iron (Fe) is the only relevant element (see Table 1). Equivalent weight is therefore calculated according the relation:

$$Fe \ (equivalent) = \frac{wt.\% \ . \ Valence \ value}{Atomic \ wt.} \quad -------------------- \ (3)$$

Where; wt. % is 98.89 (see Table 1), Valence value is +2, atomic wt. is 55.8 and substituting these values give 3.54. Therefore, the mild steel equivalent weight is 100/3.54 = 28.25