
ANALYSIS OF POTENTIOSTATIC POLARISATION RESPONSES OF MILD STEEL IN ACID ENVIRONMENTS & SEAWATER

Bhupender Singh

Assistant Professor

Department of Chemistry

Pt. N.R.S. Government College Rohtak

Haryana

ABSTRACT:

Although pitting corrosion in passive materials is generally well understood, the growth of surface pits in actively-corroding materials has received much less attention to date and remains poorly understood. One of the key challenges which exist is repeatedly and reliably generating surface pits in a practical time-frame in the absence of deformation and/or residual stress so that studies on pit propagation and healing can be performed. Another pertinent issue is how to evaluate pitting while addressing general corrosion in low carbon steel. This paper investigates the corrosion behavior of mild steel in seawater. Seawater as corrosive media was taken from two different sites to compare the corrosion behavior of mild steel. Temperature data from both sites were recorded and two different studies conducted including weight loss analysis and polarization study.

KEYWORD: Mild steel, Polarization, Seawater

INTRODUCTION

There is increasing attention being given to deterioration of infrastructure exposed to actual hostile marine environments. As a result structural engineers and naval architects are increasingly interested in the rate of loss of strength of steel and hence in the loss of material in infrastructure systems. The loss of material even for short-term exposures is important in part because protective measures are not always wholly effective. Mild steel is the most versatile, least expensive and widely used engineering material which has found extensive application in various industries. It is used in large tonnages in marine applications, nuclear power and fossil fuel power plant, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction as well as metal processing equipment. However, the corrosion resistance of mild steel is relatively limited. This causes many corrosion problems to be arising in the related industries.

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 thickness 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 effective corrosion mitigation.

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 described by the abridged Kirchoff's second law:

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

Where $E_{c, \text{corr}}$, $E_{a, \text{corr}}$ 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 usually 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 unleashing severe attack at the base of breaks in coatings (Loto, 2013). Pitting corrosion takes advantage of the different 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 both 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.

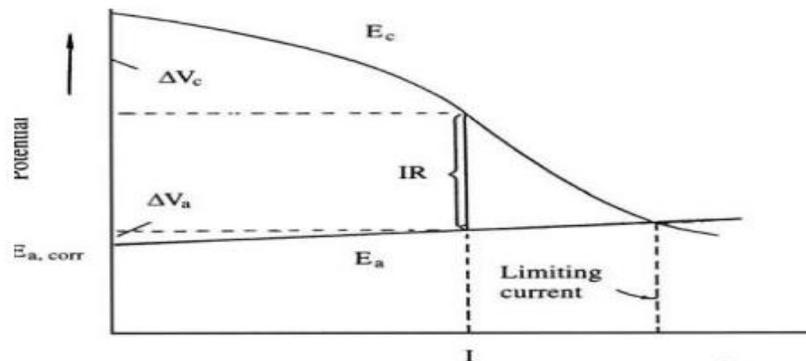


Fig.-1 Graphic estimation of galvanic current

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 conveys 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.

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 emission 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. %	0.22	0.10	0.61	0.02	0.02	0.04	0.10	0.00	0.01	0.00	0.00	0.00	98.8
	6	2	6	1	4	0	4	4	5	2	3	2	36

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 358mm² 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.

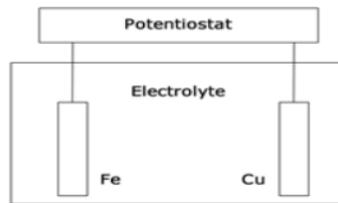


FIG 2. Potentiostat polarisation apparatus configuration

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 37⁰C while the electrolytic bath consists 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

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**.

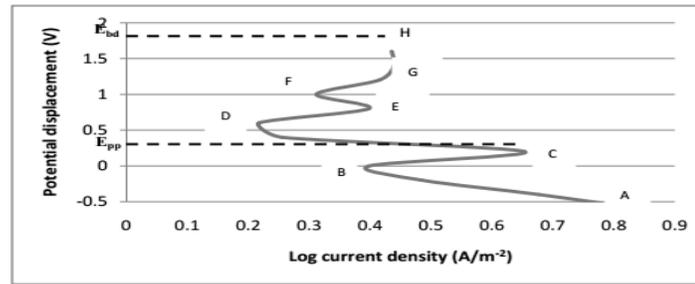


FIG 3. Potentiostatic polarisation behaviour of mild steel after 72 hours of immersion in 1M HCl at 37°C.

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).

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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