Pitting corrosion evaluation of austenitic stainless steel type 304 in acid chloride media

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Abstract

The resistance of austenitic stainless steel type 304 to pitting corrosion was studied in solutions of sulphuric acid (2M and 5 M) with and without sodium chloride addition by linear polarization technique. The pitting and passivation potentials, corrosion rate and current density were analyzed with respect to the chloride ion concentration. Under anodic polarization the stainless steels in sulphuric acid solution acquired a passive state, with breakdown at the transpassive region (pitting potential), however this was greatly reduced with the addition of sodium chloride which led to a sharp increase in current at potentials significantly lower than the value that necessitates pitting in the acid media due to rapid breakdown of the passive film and development of local pits. Results obtained establish the dynamic relationship and interaction between the sulphate/chloride ion concentration and electrochemical potentials in the corrosion behavior of the ferrous alloy at ambient temperature.

Keywords: Pitting, Corrosion, Stainless steel, Sodium Chloride, Sulphuric acid

Introduction

Corrosion causes a variety of problems, depending on the conditions under which engineering alloys applied. Steel corrosion is an electrochemical process, initiated by certain electrolytic conditions in the proximity of the steel member. Stainless steels are generally very corrosion resistant and will perform satisfactorily in most environments. The limit of corrosion resistance of a given stainless steel depends on its constituent elements when exposed to a corrosive environment; however under exposure in certain industrial conditions stainless steel corrodes in the form of localized attacks (pitting), due to inclusions or a breakdown of the passive film. Pitting corrosion is an accelerated form of chemical attack in which the rate of corrosion is greater in some areas than others. It occurs when the corrosive environment penetrates the passivated film in only a few areas as opposed to the overall surface. Pit type corrosion is simple galvanic corrosion, occurring as the small active area is being attacked by the large passivated area. This difference in relative areas accelerates the corrosion, causing the pits to penetrate deeper [1]. Pitting corrosion is particularly insidious; a component can be perforated in a few days with no appreciable loss in weight on the structure as a whole. It is most aggressive in solutions containing chloride, bromide or hypochlorite ions; iodides and fluorides are much less harmful. The presence of sulfides and H_2S enhances pitting corrosion as well and systematically impairs the resistance criteria for this type of attack. The presence of an oxidizing cation (Fe^{+3}, Cu^{+2}, Hg^{+2}, etc.) enables the formation of pits even in the absence of oxygen. However, in the presence of oxygen, all chlorides become dangerous, and this is also true in the presence of hydrogen peroxide [2]. This form of corrosion is often more detrimental than general corrosion, due to local dissolution which can cause rapid penetration of the metal thickness. In many cases pitting corrosion is not detected until severe damage occurs, such as complete penetration in sheet or tube material. This is due to the very small pit holes formed on the surface and to the fact that the metal surfaces in many applications become covered with precipitates from process fluids or with thick layers of more or less

protective corrosion products. The corrosion products from a pit attack are often found to create a lid on top of the pit, with only a very small opening. When examining the metal surface for pits it should therefore be thoroughly cleaned in order to reveal the pitted areas. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. A small, narrow pit with minimal overall metal loss can lead to the failure of an entire engineering system. The rate of penetration may be 10 to 100 times greater than that by general corrosion.

Austenitic stainless steel is the largest and most important group in the stainless steel range. These steels, which exhibit a high level of weldability, are available in a wide range of compositions which are used for general stainless steel fabrications, elevated temperature applications and resistance to pitting corrosion respectively. This material has good corrosion resistance due to the formation of passive film of chromium oxide. The film is stable, invisible, thin, durable, extremely adherent and self-repairing. Passivation reduces the anodic reaction involved in the corrosion process, but quite severe pitting corrosion can occur in acidic environments [3]. The failure of some stainless steels resulting from pitting, corrosion is sometimes considered a technological problem [4]. Consequently, much effort has been expended in attempting to understand and overcome pitting, corrosion, thus many stainless steel /environment combinations have been studied [5]. Perhaps the greatest research effort has been concentrated on the localized corrosion of stainless steel in chloride, bromide, chloride/sulphide, bromide/ sulphide and chloride/thiosulphate media [6-12] reflecting the preeminence of austenitic stainless steel as construction material for many industrial process plants applications. This research aims to investigate the resistance of austenitic stainless steel type 304 to pitting corrosion in sulphuric acid + chloride media by potentiodynamic measurement test.

Experimental procedure

Material
Commercially available Type 304 austenitic stainless steel was used for all experiments of average nominal composition; 18.11%Cr, 8.32%Ni and 68.32%Fe. The material is cylindrical with a diameter of 1.80cm (18mm).

Test Media
2M sulphuric acid, 5M sulphuric acid, 2M and 5M sulphuric acid with $(1-5)$ % recrystallised sodium chloride of Analar grade were used as the corrosive medium

Preparation of Test Specimens
The cylindrical stainless steel (18mm dia.) was mechanically cut into a number of test specimens of the same dimensions, manually mounted and ground silicon carbide abrasive papers of 80, 120, 220,800 and1000 grits. They were then polished with $6.0 u$m to $1.0 u$m diamond paste, washed with de-ionized water, rinsing with acetone before been dried and stored in a dessicator for weight-loss measurement.

Weight-Loss Measurement
Each experiment in weight loss measurement was carried out in a flat plastic bowl containing 200 mL of the dilute corrosive solution (sulphuric acid with and without sodium chloride) in the specified concentrations. Twelve clean and previously weighed coupons were hanged and immersed vertically in the vessel. The cleaning procedure consisted of washing with de-ionized water and then rinsed with acetone. Weight loss was determined by weighing the cleaned samples before and after hanging the coupons into the acid solutions at ambient temperature after the elapsed time. The average weight loss of the coupons was taken to calculate the corrosion rate.

Linear polarization Resistance
Linear polarization measurements were carried out using cylindrical stainless steel coupon embedded in resin plastic mounts with exposed surface of 254 mm^2. This working electrode was metallographically prepared with different grades of silicon carbide paper, then polished to $1 u$m using diamond paste, rinsed with de-ionized water and dried with acetone prior to electrochemical analysis. The studies were performed at ambient

temperature with Autolab PGSTAT 30 ECO CHIMIE potentiostat with corrosion cell containing 200ml of the various electrolytes (test media). A graphite rod was used as the auxiliary electrode and silver chloride electrode (Ag/AgCl) was used as the reference electrode while the steady state open circuit potential (OCP) was noted. The potentiodynamic studies were made from -1.5V *versus* OCP to +1.5 mV *versus* OCP at a scan rate of 0.00166V/s and the corrosion currents were registered. The corrosion current density (j_{corr}) and corrosion potential (E_{corr}) were determined from the Tafel plots of potential *versus* logarithm of corrosion current density i.e. applied current (*log I*). The corrosion rate r was calculated as follows

$$r \ (mm/py) = \frac{0.00327 * i_{corr} * eq.wt}{D} \ldots\ldots\ldots\ldots eqn.1$$

Where j_{corr} is the current density in uA/cm^2, D is the specimen density in g/cm^3; *eq.wt* is the specimen equivalent weight in grams.

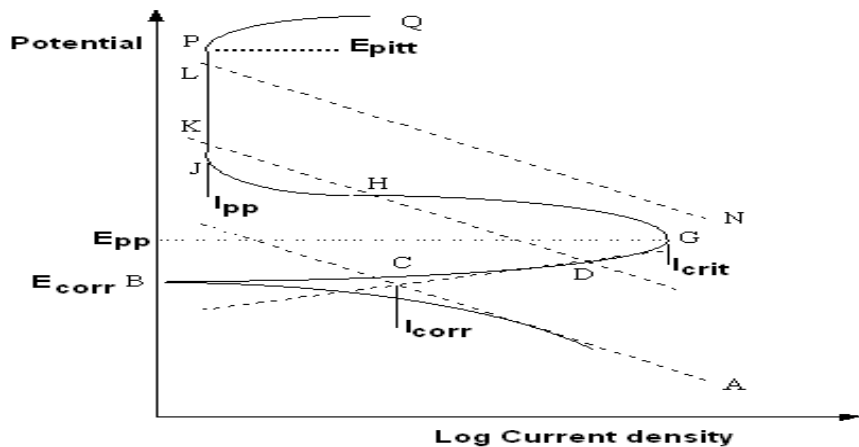## Results and discussion
Polarization studies

Figure 1 Schematic variation of potential E with log current density

The solid line in Fig.1 is a schematic diagram of the variation of potential E with log Current density for austenitic stainless steel in the dilute sulphuric acid + chloride media.

- AB represents cathodic behaviour,
- BG is the active zone (anodic dissolution reaction). The metal is not passivated at its corrosion potential, B.
- AC and DC are Tafel-type straight lines drawn for the reduction and oxidation reactions of the normal metal dissolution ($M = M^+ + e^-$).
- At potentials more positive than B, corrosion rate increases, and reaches a maximum at the passivation potential, G, which is often given the symbol, E_{pp}.
- The transition from active dissolution occurs in the region G to J. A protective film begins to form and causes a sudden drop in corrosion current density.
- From J to P, the passive zone, the current density is maintained at a steady, low level, until point P
- At P (pitting potential E_{pitt}), breakdown of the protective film begins. It is here that the likelihood of pitting is greatest, and consequently specimen failure.

- The potential E_{pitt}, often called the critical pitting or breakdown potential is a useful parameter in assessing pitting properties of materials. It should be noted that it is not an absolute parameter, and varies according to both metallurgical and electrochemical conditions.
- At potentials more positive than P, the current density begins to rise as more and more pits propagate.

The electrochemical parameters such as, corrosion potential (E_{corr}), corrosion current (i_{corr}), corrosion current density (I_{corr}), cathodic Tafel constant (**bc**), anodic Tafel slope (**ba**) and corrosion potential (E_{corr}) were determined from linear polarization as shown in table 1.

Table 1 Data obtained from polarization resistance measurements for austenitic stainless steel in dilute H_2SO_4 at different concentrations of the NaCl

Sample	Solution concentration (Molarity)	E_{corr} (V)	i_{corr} (uA)	I_{corr} (uA/cm²)	bc (V/dec)	ba (V/dec)	Rp (Ω/cm²)	Corrosion Rate (mm/py)	Pitting Potential (V)	Current at E_{pitt} (A)
A1	2M	-0.386	0.00010	0.00430	0.382	0.139	2.129	4.380	1.168	0.001
A2	2M + 1%	-0.427	0.00057	0.00043	0.016	0.032	8.057	4.944	0.746	0.002
A3	2M + 2%	-0.349	0.00058	0.00043	0.130	0.040	23.04	5.040	0.688	0.003
A4	2M + 3%	-0.410	0.00061	0.00046	0.030	0.035	11.96	5.337	0.446	0.018
A5	2M + 4%	-0.334	0.00062	0.00047	0.081	0.056	23.13	5.437	0.346	0.010
A6	2M + 5%	-0.331	0.00014	0.05413	1.119	0.890	3.145	5.561	0.653	0.034
B1	5M	-0.314	0.01800	0.00730	0.344	0.242	1.961	7.454	0.336	0.004
B2	5M + 1%	-0.415	0.00099	0.00075	0.010	0.030	3.200	8.671	1.003	0.013
B3	5M + 2%	-0.352	0.00104	0.00078	0.010	0.144	24.55	9.093	0.988	0.001
B4	5M + 3%	-0.412	0.00105	0.00079	0.035	0.044	8.014	9.155	0.985	0.015
B5	5M + 4%	-0.363	0.00105	0.00079	0.141	0.054	16.06	9.185	0.946	0.003
B6	5M + 5%	-0.322	0.02356	0.00930	0.349	0.163	1.050	9.518	1.044	0.056

Observation of table 1 shows the linear relationship between the sulphuric acid/sodium chloride concentrations and corrosion rates due to increased electrolytic action and activity of sulphate (SO_4^-) and chloride (Cl^-) ions. This results in increased anodic dissolution and hydrogen evolution reactions. Sample B1 showed the highest corrosion rate while sample A1 showed the lowest corrosion rate, thus the higher the solution concentration, the greater the corrosion rate due to the aggressive nature of the ionic species. The polarization resistance of the samples [Fig.3 (a-f) and Fig.4 (a-f)] varied considerably with increase in corrosion current density accompanied by inconsistent cathodic and anodic Tafel constants indicating differential redox reactions irrespective of the solution concentration. This results in variable alloy degradation due to breakdown of the passivating film on the alloy. The corrosion rates show specimen failure in the test media, with greater intensity as the chloride concentration increases. The combined chloride and sulphate ions undoubtedly caused more deleterious corrosion reactions, the consequence of which was that of severe active corrosion reactions of anodic dissolution of this tested alloy. In the presence of these reacting species, (Cl^- and SO_4^-) the ability of the stainless steel to repair its film was drastically reduced and the protection was lost. The presence of chlorides significantly aggravates the conditions for formation and growth of the pits through an autocatalytic process. The pits become loaded with positive metal ions through anodic dissociation and the Cl^- ions concentrates in the pits for charge neutrality and encourage the reaction of positive metal ions with water to form a hydroxide corrosion product and H^+ ions. Now, the pits been weakly acidic accelerates the corrosion process.

In many studies of the structure of the passive film on chromium stainless steels it has been demonstrated that the properties of the steel is due to the selective dissolution of Cr alloy and accumulation of Cr_2O_3 on the surface of passive layer, i.e., practically the formation of a chromium passive layer [13]. The polarization curves in Fig. 3 and 4 shows a spontaneously passive material, meaning that a protective passive film is present on the metal surface at the different passivation potentials (E_{pp}, region G). During upward scanning, breakdown occurs, and a stable pit starts growing at the pitting potential (E_{Pitt}) in the transpassive region of the polarization curve, where the current increases sharply from the passive current level.

The view of the passive film as being a dynamic structure, rather than static, is critical to the proposed mechanisms of passive film breakdown and pit initiation. Theories for passive film breakdown and pit initiation have been categorized into three main mechanisms that focus on passive film penetration, film breaking and adsorption [14,15].

The penetration mechanism involves the migration of aggressive Cl^- ions from the electrolyte through the passive layer to the oxide–metal interface under the influence of the high electrical field strength of most passivating films. The film-breaking mechanism starts with cracks in the passive layer under induced corrosion activity, exposing small areas of the bare metal surface to the electrolyte and the related very intense metal dissolution that leads to the formation of a pit. The adsorption mechanism refers to the increase in the transfer of cations from the passive film to the electrolyte due to the complexing properties of the aggressive anions and chromium depletion. This process causes the thinning and final removal of the passive layer, thus the metal.

The stabilization of the growth of corrosion pits may be influenced by several complicating factors depending on the state of their development. The rate of growth is controlled by diffusion of the dissolving metal cations from the pit interior, the surface of which is saturated with the metal chloride. This process is independent of electrode potential. All pits, whether metastable, or destined to become stable, grow initially in the metastable condition i.e. within the passive region [16].

Alloying metals are very important factors to stabilize an alloy against general and localized corrosion, among these; Cr plays a very important role for iron and nickel base metals. It accumulates in the passive layer because of its extremely small dissolution currents even in strongly acidic electrolytes [17]. The figure below (figure 2) depicts a propagating pit in an iron or nickel based alloy containing chromium in a chloride containing environment.

Anodic reactions inside the pit:

$Fe \leftrightarrow Fe^{2+} + 2e^-$ (dissolution of iron) …………eqn.2
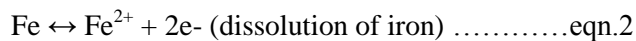
The electrons given up by the anode flow to the cathode (passivated surface) where they are discharged in the cathodic reaction:

$\frac{1}{2} O_2 + H_2O + 2e^- \leftrightarrow 2(OH^-)$…………..eqn.3
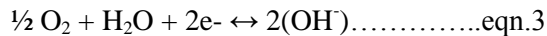
As a result of these reactions the electrolyte enclosed in the pit gains positive electrical charge in contrast to the electrolyte surrounding the pit, which becomes negatively charged. The positively charged pit attracts negative ions of chlorine Cl^- increasing acidity of the electrolyte according to the reaction.

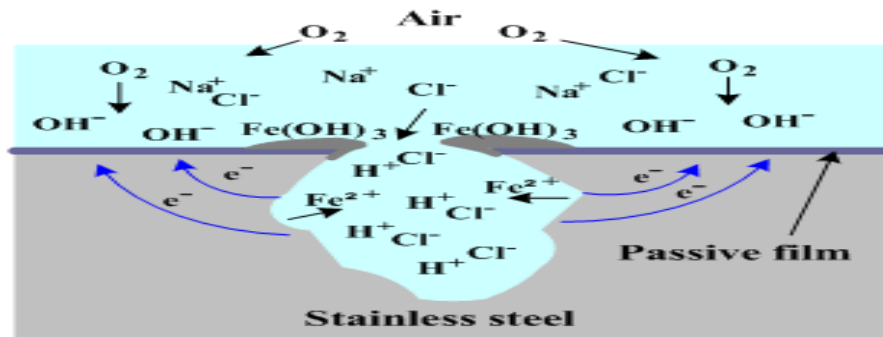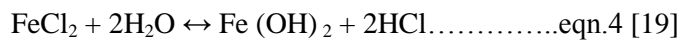$FeCl_2 + 2H_2O \leftrightarrow Fe(OH)_2 + 2HCl$…………..eqn.4 [19]

Figure 2 Schematic of an actively growing pit in iron [18]

The pH of the electrolyte inside the pit decreases which causes further acceleration of the corrosion process. Large ratios between the anode and cathode areas favors increase of the corrosion rate and the corrosion

products (Fe(OH)$_3$) which forms around the pit resulting in further separation of its electrolyte; however the formation of a pit does not require the complete dissolution of the inclusion. It has been proposed that the special chemistry within the pit electrolyte with the formation of sulfur containing compounds such as sulfides, sulfur, sulfites, and even sulfates has a strong influence on localized corrosion.
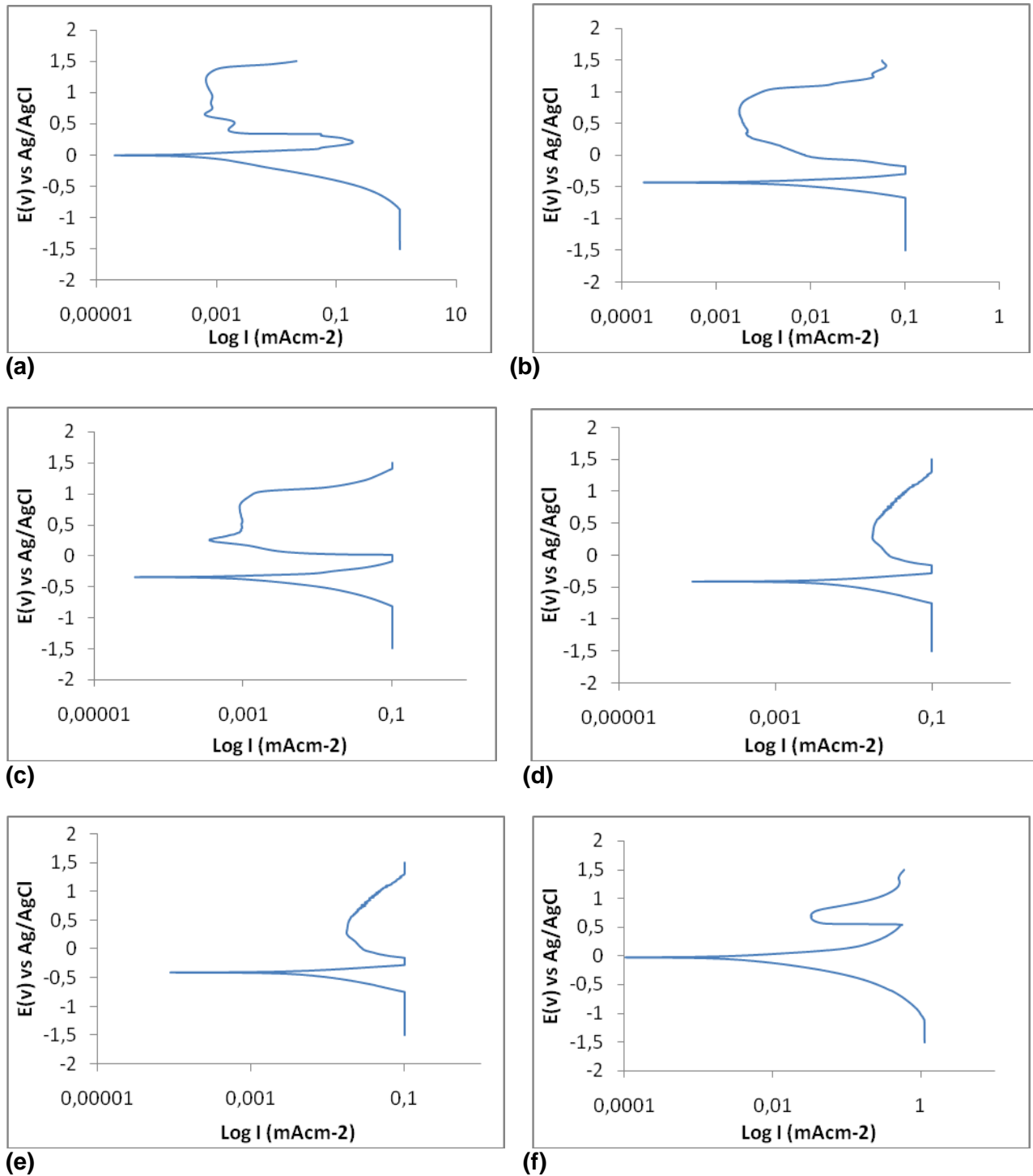

Figure 3 Polarization Curve of austenitic stainless steel (a) 2M H$_2$SO$_4$, (b) 2M H$_2$SO$_4$ + 1% NaCl, (c) 2M H$_2$SO$_4$ + 2% NaCl, (d) 2M H$_2$SO$_4$ + 3% NaCl, (e) 2M H$_2$SO$_4$ + 4% NaCl, (f) 2M H$_2$SO$_4$ + 5% NaCl

Pit forms on the surface in the absence of oxygen. The depletion of oxygen inside the pit slows down the generation of hydroxyl ions. The accumulation of positive charges in the form of Fe^{2+} then attracts negatively charged chloride ions. The resulting ferrous chloride hydrolyzes to produce insoluble ferrous hydroxide plus excess hydrogen and chloride ions, these ions accelerate the corrosion at the bottom of the pit [19]. Therefore, stainless steels usually have poor corrosion resistance in low-oxygen environments. When deprived of oxygen stainless steel lacks the ability to re-form a passivating film of chromium oxide. In the worst case, almost all of the surface will be protected, but tiny local fluctuations will degrade the oxide film in a few critical points. Corrosion at these points will be greatly amplified, and can cause corrosion pits of several types, depending upon conditions. While the corrosion pits only nucleate under fairly extreme circumstances, they can continue to grow even when conditions return to normal, since the interior of a pit is naturally deprived of oxygen [20].

Breakdown of the passivating film on the steel metal by the aggressive anions causes the formation of micro anodes of active metals surrounded by large cathodic protective areas of the passive metal. This fixes the position of anode and results in pitting corrosion. Once a pit is nucleated, pit growth and propagation proceeds via an active dissolution mode leading to breakdown of the passivating film at higher anodic potential as shown in the transpassive region of the polarization curves. It is supposed by some that gravitation causes downward-oriented concentration gradient of the dissolved ions in the hole caused by the corrosion, as the concentrated solution is denser. This however is unlikely. The more conventional explanation is that the acidity inside the pit is maintained by the spatial separation of the cathodic and anodic half-reactions, which creates a potential gradient and electromigration of aggressive anions into the pit [21].

The cause of pitting is not always completely local in nature although alterations or intrinsic defects at the metal-solution interface (e.g. inclusions emerging through the passive film in stainless steels) often represent nuclei for local dissolution, all such potential nuclei are not attacked, but galvanic coupling can be established between the discontinuous zones, which form small anodes where metal dissolution occurs, and the remainder of the surface where the cathodic reaction takes place [21]. The reason for the aggressiveness of chloride has been pondered for some time, and a number of notions have been put forth. Chloride is an anion of sodium chloride and strong acids, and many metal cations exhibit considerable solubility in chloride solutions due to its strong electronegativity [22]. Chloride is a relatively small anion with a high diffusivity which interferes with passivation, and it is ubiquitous as a contaminant.

Pitting potential

Pitting potential (E_{pitt}) is the potential at which pitting starts and this is noticed when the current of the polarization curve suddenly rises [23]. E_{pitt} is frequently used as an accelerated laboratory test to determine the relative susceptibility to localized corrosion for iron-base alloys in a chloride environment [24-26]. The more noble the E_{pitt} obtained at a fixed potential, the less susceptible the material to the initiation of localized corrosion. The E_{pitt} for austenitic stainless steel occurs at the point when the anodic current increases sharply as shown in table 1 and the polarization curves (figure 3 & 4) due to stable pitting; indicating sustained localized corrosion [27]. The E_{pitt} values (table 2) decreases with increase in chloride ion concentration from sample A1 to A6 and from B1 to B6. The pitting values indicate aggressive degradation due to high corrosion rate.

Table 2 Values of Pitting potentials and Sodium chloride concentration for the investigated samples of austenitic stainless steel.

Sample	Pitting Potential	NaCl Concentration (C)	Sample	Pitting Potential	NaCl Concentration (C)
B1	1.336	0	A1	1.168	0
B2	1.123	0.00017	A2	0.746	0.00017
B3	0.988	0.00034	A3	0.688	0.00034
B4	0.885	0.00051	A4	0.446	0.00051
B5	0.746	0.00069	A5	0.346	0.00068
B6	0.532	0.00086	A6	0.653	0.00086
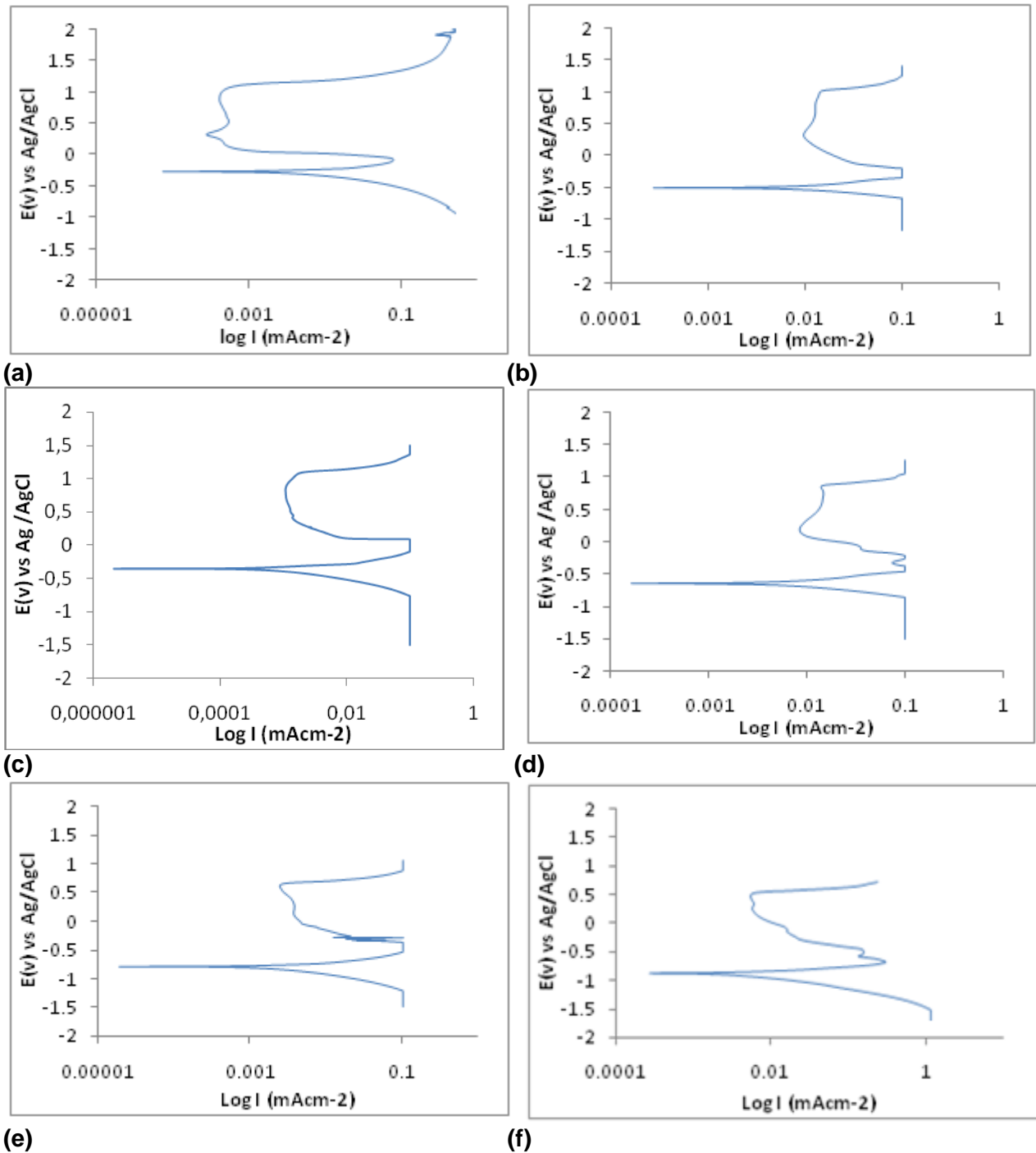
Figure 4 Polarization Curve of austenitic stainless steel (a) 5M H_2SO_4, (b) 5M H_2SO_4 + 1% NaCl, (c) 5M H_2SO_4 + 2% NaCl, (d) 5M H_2SO_4 + 3% NaCl, (e) 5M H_2SO_4 + 4% NaCl, (f) 5M H_2SO_4 + 5% NaCl

According to the present understanding of the pitting corrosion process the E_{pitt} represent a critical threshold value, where metastable pit nuclei within the passive state of the stainless steel may be transformed into stable growing pits when the passive formation breaks down. In this case the stable pit is reached when activating conditions are established within the pit such as high chloride concentration (salt film formation) which is necessary to maintain the pits over an extended time [28].

The linear dependence of E_{pitt} on log [Cl$^-$] represented by

$E_{pitt} = A + B$ log [Cl$^-$]……….eqn.5

Where a and b are two empirical constants depending on the corroding system and the composition of the alloys.

Fig. 5 shows the linear relationship between pitting potential and logarithm of chloride concentration. The higher the chloride concentration, the lower the potential at which pitting occurs. The values of E_{pitt} at any given Cl$^-$ ion concentration depend upon the chemical composition of the sample. However in this investigation the value of Epitt strongly depends on the sulphuric acid concentration of electrolytic medium as indicated in the value of E_{pitt} at different concentrations of the sulphuric acid. Increased sulphate ion concentration at 5M of sulphuric acid in the chloride containing solutions reduced the pitting corrosion risk of the stainless steels, i.e. pitting occurred at a higher potential; this can be seen as an increase in the critical pitting potential in the acid chloride solution. When considering the inhibitive effect of sulphate it must be kept in mind that precipitation of sulphates can substantially change the ionic ratio between sulphates and chlorides [29]. It is generally known that the localized corrosion susceptibility of stainless steels increases with increasing chloride concentration and decreases with increasing sulphate to chloride ionic ratio [30-31]. It is proposed that sulphate inhibits pitting corrosion, because it adsorbs on the metal surface preventing the ingress of chlorides [32]. However, the sulphate concentration can remarkably decrease and the sulphate to chloride ionic ratio reduces if precipitation of sulphate compounds occurs. At very high potentials passive to transpassive transition occurs and the corrosion rate increases again. For stainless steel this potential is near the oxygen evolution potential, where the Cr rich passive film is unstable. However, the presence of sulphate SO_4^{-2} in the aqueous solutions plays an important role in the passivation process [33-35]. They tend to reduce the susceptibility of stainless steel to pitting in chloride solutions. Although sulphate ions are well known to facilitate film growth and act as pitting inhibitor, the presence of these ions together with chloride ions leads to stronger attack and produces larger pits compared to those obtained in sulphate free chloride solutions [36-39].
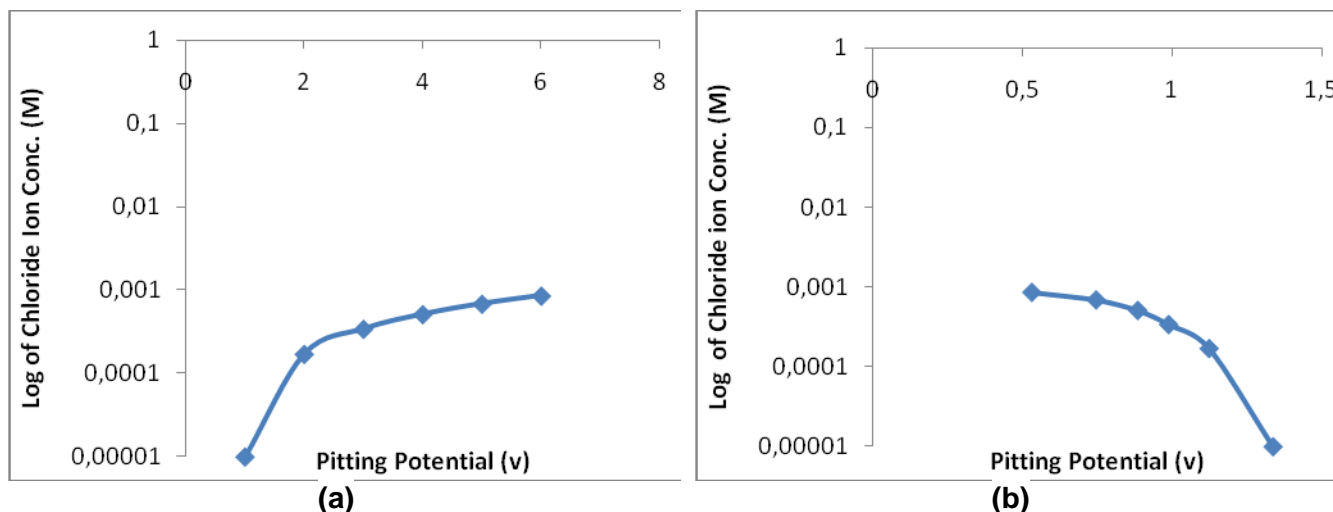

Figure 5 Variation of logarithm of chloride concentration with pitting potential (a) samples A1- A6 in 2M H_2SO_4 at varying concentration of NaCl, (b) samples B1- B6 in 5M H_2SO_4 at varying concentration of NaCl

Table 2 indicates that increase in SO_4^{-2} ion concentration shifts the value of E_{pitt} to more positive potentials which is commensurate with an increase in the alloy resistance to passivity breakdown. At E_{pitt}, the initiation of pitting attack at high anodic potential could be ascribed to competitive adsorption between Cl$^-$ ions and the passive species (OH$^-$ and H_2O dipoles). The Cl$^-$ anions displace the adsorbed passivating species at some

locations and accelerate localized anodic dissolution. On the other hand, the initiation of pitting attack could be due to the ability of Cl^- anions to penetrate the passive film with the assistance of a high electric field across this film and to attack the base metal surface [40].

Effect of chloride concentration

It is well known that Cl^- ions are aggressive enough to attack steel and initiate pitting [41-45]. The small size of Cl^- ions enables penetration through the passive oxide film under the effect of an electric field. Migration of Cl^- ions into pits is enhanced to maintain electrical neutrality and hydrolysis of the corrosion products inside pits causing acidification, and hence prevents repassivation. The mechanism is autocatalytic because the increased acidity accelerates the dissolution rate inside pits.

The effects of Cl^- ion concentration on the potentiodynamic polarization curves as well as on the Tafel lines of the stainless steel samples in different concentrations of sulphuric acid media is shown in Table 1 & 2 which shows the values of the electrochemical parameters: j_{corr}, E_{corr}, and E_{pitt} at different concentrations of the sulphuric acid. For all samples studied the value of I_{corr} increases with increase in NaCl concentration. Moreover, an increase in NaCl concentration shifts E_{pitt} of all samples towards more negative (active) direction, indicating a decrease of pitting corrosion resistance. In the absence of NaCl the steel electrode is passive over a wide potential range. Addition of Cl^- shifted the polarization curves in the active direction and recorded current increase due to pitting corrosion while the steel electrode is passive over a short range. The results in Figure 3 and 4 reveal that in the absence of Cl^- pitting occurs only in the transpassive region at higher potentials due to the effect of chromium oxide (CrO_4). However with the addition of Cl^- ions pitting occurs in the passive region resulting in a shift of the polarization curves in the active direction.

It is clear that the passive region in all cases extends up to a certain critical potential, (pitting potential E_{pitt}), at which the small passive current density increases rapidly without any sign for oxygen evolution, indicating initiation of pitting corrosion. Once a pit nucleates, pit growth and propagation proceeds in active dissolution mode. The stability of passive films and the reactions taking place in the transpassive potential region depend on the nature of the anode potential and the anion present. According to the work of Cieslak and Duquett [46] Cl^- did not enter the film or was weakly bonded to the film in the passive state; they suggested that Cl^- ions may just interact with the weak points of the film during the passivity breakdown. Chloride ion incorporation can be strongly detected within the passive film, especially when the critical pitting potential is reached. The activity of Cl^- ions determines the stability of the passive film and it is explained that it plays its role in two ways [47].

First, it may replace OH intermediate compounds within the film and result in the formation of a soluble Cl^- complex. This replacement results in the self-repairing action of the film and inhibits the breakdown of the passivity in terms of a reduction of the metal dissolution. It has a small effect in the passive and transpassive potential regions [48-50], and its presence increases the efficiency of the passive film formation. Secondly, Cl^- may provide a rapid selective dissolution of metal ion in the bulk when both ions meet at a weak site. The high Cl^- concentration around the preferred weak sites accelerate the dissolution of the metal ion and result in the full development of pitting. Consequently, the effects of its incorporation in pit initiation is limited and is not a necessary condition to thinning or a break in the passive film; but rather it simply interferes with the reformation of the film.

Conclusion

The pitting corrosion resistance of austenitic stainless steel was investigated in dilute sulphuric acid contaminated with NaCl solution. Comparison of the polarization curves in 2M and 5M sulphuric acid with those containing sodium chloride shows that chloride ions significantly reduces the potential at which pitting occurs, thus initiates early pit formation and accelerates its process. The higher the molarity of sulphuric acid, the greater the potential at which pitting occurs. This is due to its inhibitory effect which delays pit formation when competing with the chloride ions despite the high corrosion rate. Results show a decrease in the passive

regions in the sulphuric acid + chloride media compared to the sulphuric acid solution only due to the breakdown of the passive film of chromium oxide owing to the high diffusivity of the chloride ions through cracks and film breakage faster than the rate of repassivation causing the formation of pits by autocatalytic mechanism. Increasing the concentration of sulphuric acid only delays the formation of pits but still enhances the rate of corrosion.

Acknowledgement

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