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Electrochemical corrosion behaviour of austenitic stainless steel (type 304) in dilute hydrochloric acid solution

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Abstract

The effect of sodium chloride concentrations on the electrochemical corrosion behaviour of austenitic stainless steel (type 304) in dilute HCl solution at ambient temperature was studied with the aid of potentiodynamic polarization technique. Results show that increase in concentration of sodium chloride causes a proportionate increase in corrosion rate in 2M HCl solution. At 5M HCl, progressive increase in sodium chloride concentration initially resulted in sharp increase in corrosion rate before decreasing proportionately. Observation reveals that at a threshold concentration increase in sodium chloride concentration does not result in increase in corrosion rate and it was found that the addition of chloride ion destroyed the protective passive film on the surface and increased the corrosion current density. The kinetics of dissolution in the acid chloride solution resulting in pitting and general corrosion was also studied.

Keywords: corrosion; hydrochloric acid; sodium chloride; steel

1. Introduction

Corrosion is the electrochemical degradation of a material especially metallic alloy due to interaction with its environment. This phenomenon is characterized by the removal of atoms from the metal to form deleterious compounds in the presence of water and gases. The effects and consequences of corrosion has been known to man since the earliest metallurgical times and has been a constant drain on his productive activities, as such, purposeful attention have been focused on the problem both by scientists and engineers[1]. It is a major industrial dilemma which results in millions of dollar lost each year on mechanical breakdowns, maintenance and repairs [2]. Much of this loss is due to the corrosion of iron and steel. Stainless steel is a versatile material with wide spread applications in numerous corrosive conditions. Austenitic stainless steels are an extraordinary family of stainless steel alloys that have exceptional corrosion resistance and equally impressive mechanical properties which allowed them to be used as a construction material in various aggressive environments such as heat exchanger systems, drilling platforms, wastewater treatment, and desalination plants. The most popular austenitic grades have been type 304[3]. The corrosion initiation process and propagation mechanism on stainless steels is of great importance due to its complication and insidious nature. The corrosion resistance of stainless steels is through the formation of thin, passive protective films on their surfaces which coats the base alloy. The film formation occurs instantaneously within an oxidizing environment. Despite these attributes they are vulnerable to specific corrosion types in astringent atmospheres such as pitting and uniform corrosion. Acidic solutions are specifically aggressive to this film causing severe pit formation and growth in addition to general corrosion [4, 5]. Pitting is a localized form of corrosion in which metallic dissolutions occurs at vulnerable sites and/or regions on the metal surface resulting in the formation of cavities in passivated metals or alloys that are exposed to aqueous, nearly neutral solutions containing aggressive anions. It generally occurs in chloride, halide or bromide solutions. If a fault in the passive layer or a surface defect results in the local destruction of the former, dissolution of the steel underneath leads to a build-up of positively charged metallic ions, which in turn causes negatively charges (e.g. chloride ions) to migrate near the defect. A significant number of researches have been done in order to study the initiation and the growth of pitting on traditional materials [6-11]. The highly corrosive nature of aqueous mineral acids on most metals requires degree of restraint to achieve economic maintenance and operation of equipment, minimum loss of chemical product and maximum safety conditions. In many industries, maintenance costs can be related directly to the cost of corrosion [12]. Mineral acid solutions such as hydrochloric acid are widely used for various treatments of materials in industry.

Hydrochloric acid is used in the chemical industry as a chemical reagent in the large-scale production of vinyl chloride for PVC plastic, and MDI/TDI for polyurethane. It has numerous smaller-scale applications, including household cleaning, production of gelatin and other food additives, descaling, and leather processing. About 20 million tons of hydrochloric acid are produced worldwide annually. Hydrochloric acid is a strong inorganic acid that is used in many industrial processes. One of the most important applications of hydrochloric acid is in the pickling of steel, to remove rust or iron oxide scale from iron or steel before subsequent processing, such as extrusion, rolling, galvanizing, and other techniques [13-14].This study aims to investigate the corrosion resistance reactions phenomena of type 304 stainless steels in hydrochloric acid at specific concentrations of sodium chloride (NaCl) addition to enhance the breakdown of passivity by the chloride ions. The usefulness of hydrochloric acid is to simulate many industrial applications/conditions.

2. Experimental procedure

2.1 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 18mm.

2.2 Test Media

2M and 5M hydrochloric acid with 1-5% recrystallized sodium chloride of Analar grade were used as the corrosion test media.

2.3 Preparation of Test Specimens

The cylindrical stainless steel (18mm dia.) was mechanically cut into a number of test specimens of dimensions in length ranging from 17.8mm and 18.8mm coupons. The two surface ends of each of the specimen were ground with Silicon carbide abrasive papers of 80, 120, 220,800 and1000 grits. They were then polished with 6μm to 1μm diamond paste, washed with distilled water, rinsed with acetone, dried and stored in a desiccator for further weight-loss test and linear polarization.

2.4 Linear Polarization Resistance

Linear polarization measurements were carried out using, a cylindrical coupon embedded in resin plastic mounts with exposed surface of 254mm^2. The electrode was polished with specific grades of silicon carbide paper, polished to 6μm, rinsed by distilled water and dried with acetone. The studies were performed at ambient temperature of 25^{o}C with Autolab PGSTAT 30 ECO CHIMIE potentiostat and electrode cell containing 200ml of electrolyte, with and without inhibitor. A graphite rod was used as the auxiliary electrode and silver chloride electrode (SCE) was used as the reference electrode. The steady state open circuit potential (OCP) was noted. The potentiodynamic studies were then 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.

3. Calculation

The corrosion current density (j_{corr}) and corrosion potential (E_{corr}) were determined from the Tafel plots of potential *versus* log *I*. The corrosion rate (*R*) was calculated as follows:

$$R = \frac{0.00327 * i_{corr} * E_{\mathrm{q}}}{D} \qquad (1)$$

where i_{corr} is the current density in μA/cm^2, D is the density in g/cm^3;Eqis the specimen equivalent weight in grams and 0.00327 is a constant for corrosion rate calculation in mm/year

4. Results and discussion

4.1. Polarization studies

Potentiostatic potential was cursorily examined from –1.50 to +1.50 V vs. Ag/AgCl at a scan rate of 0.0166 mV s^{-1}.The effect of the addition of sodium chloride on the anodic and cathodic polarization curves of austenitic stainless steel type 304 in 3M HCl solutions at 25 °C was studied at ambient temperature. Figure1shows the polarization curves of the stainless steel in presence of specific concentrations of sodium chloride in 2M HCl while figure 2 shows the polarization curves of the stainless steel in presence of specific concentrations of sodium chloride in 5M HCl.

Electrochemical variables such as, corrosion potential (E_{corr}), corrosion current (i_{corr}) corrosion current density (I_{corr}), cathodic Tafel constant (*bc*) and anodic Tafel slope (*ba*), were calculated and given in Tables1& 2. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were determined by the intersection of the extrapolating anodic and cathodic Tafel lines, %*IE* was calculated from Eq. 6:

$$\%IE = \frac{R_1 - R_2}{R_1}\% \qquad (2)$$

Table 1: Data obtained from polarization resistance measurements for austenitic stainless steel in 2M H_2SO_4at (1-5) % NaCl concentration

Sample	NaCl (%)	*ba* (V/dec)	*bc* (V/dec)	E_{corr}, Obs (V)	j_{corr} (A/cm^2)	i_{corr}(A)	Corrosion Rate(mmpy)	Polarization Resistance(Ω)
A	0	0.033	0.058	-0.365	0.0004	0.0011	4.3	8.583
B	1	0.051	0.074	-0.364	0.0006	0.0016	6.6	8.023
C	2	0.081	0.054	-0.361	0.0010	0.0027	10.7	5.278
D	3	0.161	0.222	-0.380	0.0013	0.0033	13.5	12.119
E	4	0.168	0.104	-0.372	0.0014	0.0036	14.7	7.668
F	5	0.160	0.086	-0.361	0.0017	0.0043	17.2	5.680

Table 2:Data obtained from polarization resistance measurements for austenitic stainless steel in 5M H_2SO_4 at (1-5) % NaCl concentration.

Sample	NaCl Concentration (%)	*ba* (V/dec)	*bc* (V/dec)	E_{corr}, Obs (V)	j_{corr} (A/cm^2)	i_{corr} (A)	Corrosion rate (mmpy)	Polarization resistance (Ω)
A	0	0.046	0.132	-0.373	0.0008	0.0019	7.9	7.599
B	1	0.159	0.095	-0.360	0.0031	0.0078	31.7	3.282
C	2	0.139	0.102	-0.368	0.0015	0.0039	25.9	3.213
D	3	0.211	0.136	-0.371	0.0021	0.0052	21.2	3.853
E	4	0.089	0.162	-0.363	0.0027	0.0068	17.4	3.677
F	5	0.117	0.056	-0.387	0.0011	0.0029	11.7	5.677

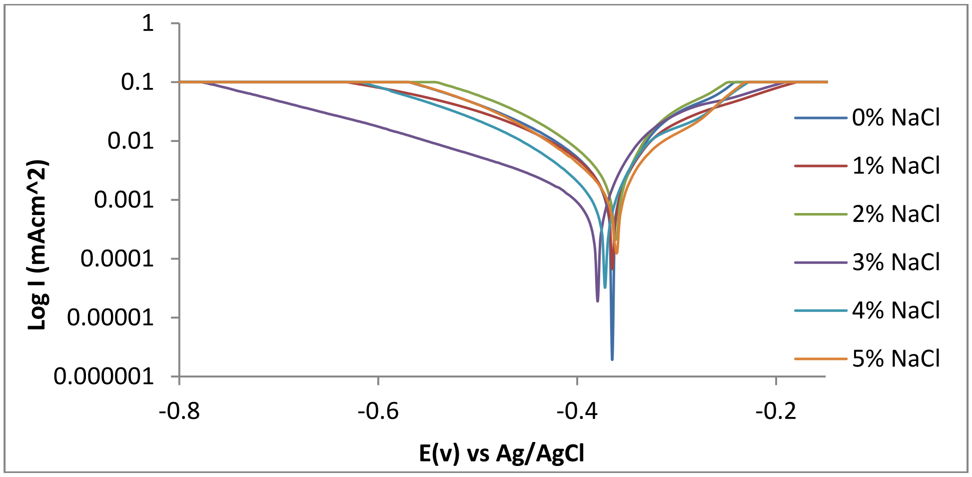

Figure1: Polarization scans for ASS in 2M H_2SO_4 at (1-5) %NaCl concentration

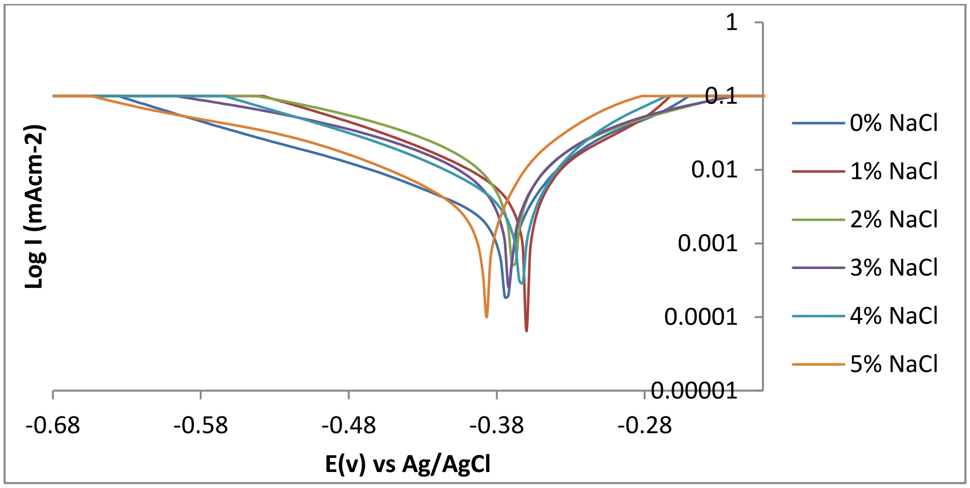

Figure 2: Comparison plot of potentiodynamic polarization scans for ASS in 5M H_2SO_4 with (1-5) %NaCl concentration

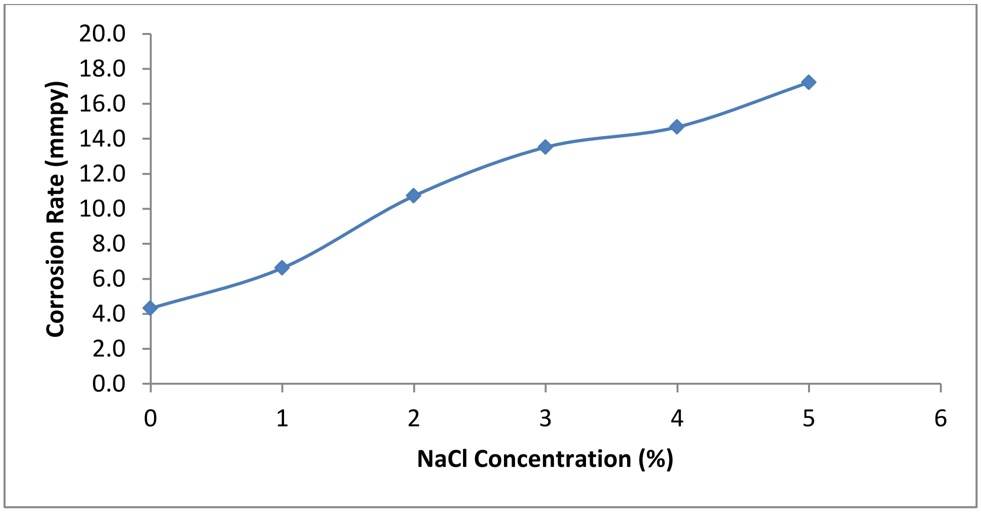

Figure 3: The relationship between corrosion rate and NaCl concentration for polarization test in 2M H_2SO_4 with (1-5) %NaCl concentration

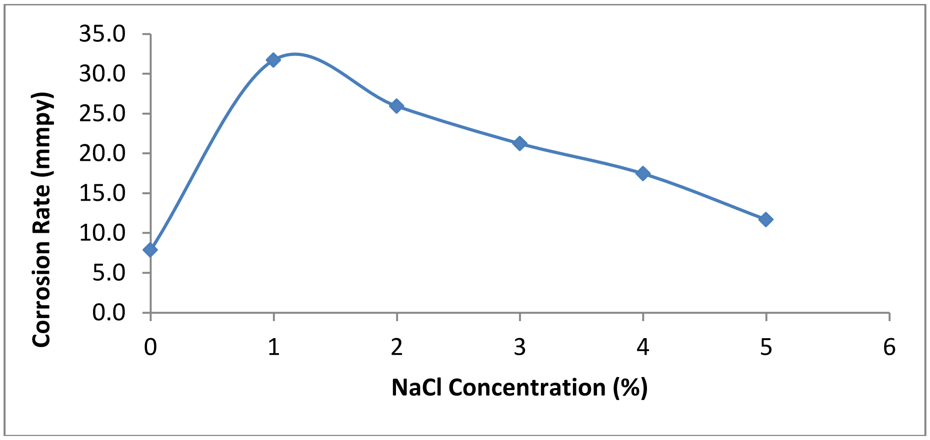

Figure4: The relationship between corrosion rate and NaCl concentration for polarization test in 2M H_2SO_4 with (1-5) % NaCl concentration

Absorbed oxygen is responsible for passivation of ASS due to the ability of its uncoupled d electrons to create a stable bond with oxygen, thereby hampering the kinetics of metal dissolution. Adsorption of the aggressive ion on the metal surface and simultaneous displacement of oxygen results in pitting and general corrosion of the steel. Pitting corrosion is controlled by the same factors responsible for any electrochemical reaction; charge-transfer processes, ohmic effects, and mass transport considerations. The role of many of the environmental and material parameters that are critical to the pitting process, such as electrochemical potential, alloy composition, electrolyte concentration, and temperature, can be explained by their effects on pit growth stability for austenitic stainless steels.

Observation of Table 1 and figure 3 shows the linear relationship between the chloride concentrations and corrosion rates due to increased electrolytic action and activity of chloride (Cl^-) ions. This results in increased anodic dissolution and hydrogen evolution reactions. In localized corrosion, the rate of anodic reaction usually varies with position along the corroding surface owing to variations in potential, alloy composition and solution concentration within the pitted regions. The anodic and cathodic processes are distributed in a non-uniform manner along the corroding surface. The observations in Table 2 and figure 4 are quite contrary to the previous observations probably due to decrease in oxidizing power of the solution concentrations. At sample B, the maximum concentration was reached for increase in corrosion rates as a result of solution saturation, beyond this the corrosion rate decreased progressively to sample F.

The polarization resistance of the samples in table 1 varied considerably with increase in corrosion current density indicating accelerated metal dissolution, these values contrast the results in Table 2 where the polarization resistance decreased progressively with differential values of corrosion current most probably as a result of decreased electrolytic action of the hydrochloric acid solution with increase in sodium chloride concentration. Differential redox reactions occurred in both solutions irrespective of the solution concentration causing alloy degradation due to breakdown of the passivating film on the alloy at region. The corrosion rates show specimen failure in the test media, with greater intensity in 2M HCl as the chloride concentration increases. Regardless, large current densities are necessary at the instant of film breakdown, and, at least for the case of stainless steel; a high local chloride concentration would be needed to achieve such a high current density. Due to applied potential, chloride ions migrates to the metal/oxide interface and forms a metal chloride phase that cracks the overlying oxide as a result of its large specific volume. The chloride phase would then provide a ready source of chloride ions to stabilize pit growth from the onset.

Another factor that enhances chloride attack and increased reactivity of the anions is the possibility of a pre-existing defect at that interface due to mechanical stress. Mechanical stresses at weak sites or flaws resulting from electrostriction and surface tension effects may cause the local breakdown events, which rapidly heal in non-aggressive environments. In chloride-containing solutions, however, there is a lower likelihood for such a breakdown to heal because of the hindrance to repassivation by chloride. The chloride ions undoubtedly caused more deleterious degradation on the stainless steel, the consequence of which was that of severe active corrosion reactions of anodic dissolution of the tested alloy. In the presence of the reacting species (Cl^-), at high concentrations, the ability of the stainless steel to repair its protective film was drastically reduced and the protection was lost. The relative concentration of metal cations in within the pit solution increases with increase in chloride concentration which results in increase in the dissolution rate of the steel.

Through an autocatalytic process pit forms and becomes continuously loaded with positive metal ions from anodic dissociation. 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 which combine to release hydrogen gas. At this region the passive film is electrochemically unstable, undergoing potential-dependent transpassive dissolution. Progression from the passive state to pitting corrosion phase can also be explained on the basis of competitive adsorption interaction between the Cl^- and the elemental atoms responsible for passivity whereby Cl^- ions migrate to the metal/liquid interface under high electric field intensity resulting from an impressed current sequentially reaching the critical potential (E_{pit}), which corresponds to the Cl^- concentration necessary to displace adsorbed oxygen species and facilitate the oxidation of iron atoms. The presence of adsorbed Cl^- increases the potential difference across the passive film thereby enhancing the rate of Fe^{2+} diffusion from the metal/film interface to film/solution interface.

Studies of the structure of the passive film on stainless steels have shown that the properties of steels are due to the selective dissolution of chromium metal and accumulation of Chromium (III) oxide (Cr_2O_3) on the passive film [15]. The understanding of the passive film as being self activating, instead of a rigged structure, is critical to the indepht knowledege of the mechanisms of passive film breakdown and pit initiation. This can be assessed under three mechanisms such as passive film penetration, film breaking and adsorption mechanism. The penetration mechanism involves the diffusion 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 bare metal surface to the electrolyte and the related very intense metal dissolution that leads to the formation of pits. The adsorption mechanism refers to agitated electrochemical diffusion of metallic cations from the passive film to the electrolyte due to the reactivity of corrosive ions and chromium depletion causing the collapse of the passive film.

Pit creation on metals is incalculable though there is preference for sites associated with flaws or cracks. In harsh conditions, general corrosion of stainless steel is inconsequential. The inception of pitting corrosion on occurs in two phases (nucleation and collapse of passivity) leading to oxidation and anodic dissolution. Inhomogeneities on the surface of the alloy are initiation sites for pit formation. The necessary condition for an active pit is the presence of an aggressive environment inside the pit. Under this condition, the pit remains active, behaving as a small anode, while the surrounding surface acts as a large cathode. The rapid production of metal ions within the pit induces the diffusion and migration of anions such as Cl^- chiefly responsible for breakdown of the passive film. Figure 5 below depicts a propagating pit in an iron based alloy containing chromium in a chloride containing environment.

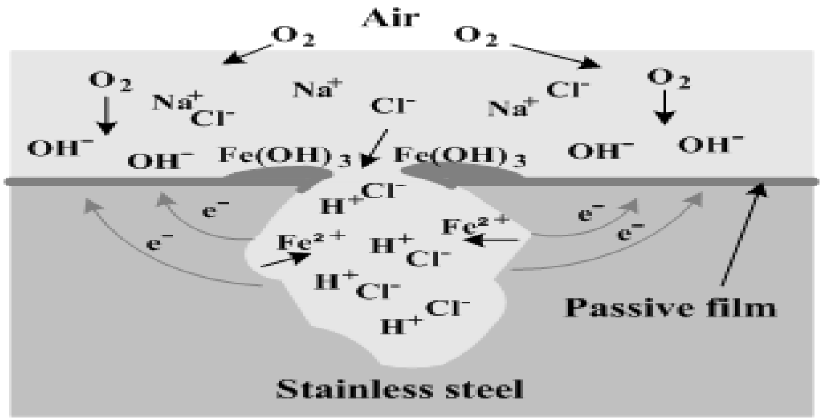

Figure 5: Schematic of an actively growing pit in iron [16]

Anodic reactions inside the pit:

$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e$ (3)
$Fe \rightarrow Fe^{2+} + 2e^-$ (dissolution of iron) (4)
$Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+$ (5)
$3Fe(OH)^+ + H_2O \rightarrow Fe_3O_4 + 5H^+ + 2e$ (6)

In the presence of Cl^-, the hydrolysis of Fe^{2+} is accelerated, as shown in the reactions below;

$Fe^{2+} + Cl^{2-} \rightarrow FeCl_2$ (7)
$FeCl_2 + H_2O \rightarrow Fe(OH)^+ + H^+ + 2Cl^-$ (8)
$Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+$ (9)

The electrons given up by the anode flow to the cathode (passivated surface) where they are discharged in the cathodic reaction:

$\frac{1}{2} O_2 + H_2O + 2e- \leftrightarrow 2(OH^-)$ (10)
$H^+ + e \rightarrow H$ (11)
$2H^+ + 2e \rightarrow H_2$ (12)

Electrochemical diffusion of chloride ions within the pit activates the redox reactions. This increases the entropy of the ions and electrolytic reactions in the pit, including hydrogen evolution reactions (eqn. 11 & 12) thereby accelerating the confined corrosion process on the steel. The corrosion process is due to the induced ionization of metallic atoms in the pit which as cations thus attracting the negatively charged Cl^- ions. The differential size between the anodic and cathodic sites catalyzes the rate of corrosion and the aftermaths of the process i.e. the formation of $FeCl_2$, $Fe(OH)_3$etc within and at the outer regions of the pit. Breakdown of the passive film can be seen partially dependent of the circumstances associated with pitting corrosion. At a particular potential the passive film perforates due to anion adsorption. Once a pit nucleates, metal dissolution self-propagates causing the film to lose its capacity to repassivate.

4.2 Electrochemical Influence of chloride concentration

Chloride is a strong electronegative ion, relatively small and easily diffuses through perforations or pores. Metallic cations ionizes and reacts strongly in chloride solutions.Increment in NaCl concentration influences the redox portion of the polarization curve resulting in higher values of i_{corr} and less noble values of E_{corr}. The Cl^- ions are aggressive enough to attack and initiate pitting corrosion on the steel samples. Cl^- ions are capable of penetrating through the passive layer under induced corrosion. This propagates the diffusion of Cl^- ions into the pits to perpetuate electrical neutrality and breakdown of the corrosion products within it thus obstructing repassivation. The mechanism is under activation control due to increased acidity which accelerates the corrosion rates.

The effects of Cl^- concentrations on the potentiodynamic polarization curves as well as on the Tafel lines of the stainless steel samples in the acid chloride media is shown in Tables 1& 2 which displays the values of the electrochemical parameters: j_{corr}, E_{corr}, and E_{pit} at specific concentrations of the acid chloride. For the samples studied in table 1, the values of I_{corr} increases with increase in NaCl concentration. Moreover, an increase in NaCl concentration has insignificant influence on the corrosion potential of the sample studied.

It can also be hypothesized that chloride attack on passive film results in the formation of cracks. The reduced interfacial tension as a result of Cl^- attack on the surface of the passive film increases the electrostriction pressure above a critical value to bring about breakdown leading to corrosion. The cohesion of the passive film depends on the electrochemical action of Cl ions which results in differential deterioration of metal originating from flaws on the passive film. The selective precipitation of Cl^- ions at high concentration at particular sites accelerates metal dissolution and pit formation. Basically the chlorides ions interfere with the repassivation process due to their electro-active nature and diffusion into the metal solution interface.

4.3 Passivity Studies

The passive film formed on the stainless steels is composed of chemical combination of iron and chromium oxides in addition to hydroxides and oxyhydroxides. At the onset of passivation there is a chemical reaction between metal cations and water to form hydrated species resulting in the formation of the oxide film by de-protonation of the hydroxyl ion [17-21]. Under anodic polarization the stainless steels samples acquired a passive state. Pitting corrosion is induced by an attack of the Cl^-ions diffuse into the passive film through electrochemical migration under electrostatic influence. The electrolytic transport of chloride ions through the film is due to the selective nature of the layer on the passive film in the solution. The chlorides accumulate in the region leading to the formation of pits.

During pit initiation, the passive film is bombarded and attacked by the chloride ions causing breakdown mostly at specific sites e.g. non-metallic solutions, impurities etc. This results in hysteries in current density due to chloride adsorption. Under this circumstance the electrostatic intensity at the boundary layer reaches a critical value. During the oxidation process chromium aggregates at the metal/oxide interface but are unable to reinforce the passivation characteristics of the metal specimen in the acid chloride solution, thus the metal dissolution process continues.

4.4 Influence of Oxygen

Corrosion pit nucleates on ferrous alloys in the absence of oxygen. Oxygen depletion prevents the production of hydroxyl ions. This electrochemical mechanism causes the accumulation of ionized metal atoms on the surface creating strong electrostatic affinity from the chloride anions resulting in accelerated metal dissolution within the pit. The experimental condition was well aerated to aid the passivation of the steel samples. The stainless steels were unable to repassivate in the presence of atmospheric oxygen in addition to reciprocal alterations which depletes the protective film. The oxygen in solution oxygen reacts with metal cations from the anodic dissolution process to form protective oxides on the metal interface. This reduces anodic oxidation responsible for corrosion; however decreased supply of oxygen caused the propagation and progression of micro pits. Under induced corrosion, the impressed current evokes the diffusion of chloride species to the pit interior, destroying the passive film in the process, thereby accelerating the mechanism of corrosion reaction.

Conclusion

The corrosion behaviour of type 304 austenitic stainless steel in 2M and 5MHCl solution with sodium chloride addition showed that increase in concentration of sodium chloride caused a proportionate increase in corrosion rate in 2M HCl solution coupled with increase in corrosion current density, however at 5M HCl, increase in sodium chloride concentration initially resulted in instantaneous increase in corrosion rate before decreasing progressively. Observation reveals that at a threshold concentration increase in sodium chloride concentration does not result in increase in corrosion rate and it was found that the addition of chloride ion reduces the growth of protective passive film on the surface and increase corrosion current.

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