INTRODUCTION

INTRODUCTION

Investigation of the mechanisms involved in corrosion process and the development on the basis of these mechanisms of new effective methods for protection of metals against corrosion is of paramount importance to the national economy of any country. The study of corrosion can be considered as an independent branch of science, within the scope of physical chemistry, which deals with the deterioration of structure of solid bodies through physico-chemical reactions that takes place with the surrounding environmental media.(1)

Aqueous corrosion can take many forms. Apart from general corrosion which results in a relatively uniform removal of a surface, specific features in a metal surface may be preferentially or selectively attacked. Such features include grain boundries, precipitate and metal/inclusion interface. The presence of films on a metal surface may give rise to highly localized regions of corrosion attack, resulting, perhaps, in pitting(2).

The thermodynamically possible process of metal transition into oxide or ionic state by reacting with surrounding medium, i.e., the corrosion process, can proceed by a chemical or electrochemical route, or by both taking place simultaneously. However, it can be assumed that with electrical-conducting media (electrolytes), the electrochemical mechanism prevails to such an extent that the purely chemical mechanism can be eleminated. The basic difference between the electrochemical and chemical mechanism is that the over-all reaction of the metal with the surrounding environment, in the former, takes place through the independent processes namely, anodic and cathodic.

Modern corrosion science stems from the local cell model was proposed by **Evans**(3) and the concept of mixed corrosion potential was proved by **Wagner**(4). These two magnificent achievements have combined into what is called the electrochemical theory of corrosion. This theory describes metallic corrosion as a combination of an anodic oxidation such as metal dissolution producing metal ions and a cathodic reduction such as oxygen ionization or discharge of hydrogen ions.

Recently(5), the corrosion process, however, consists not only of oxidation reduction reactions but also of acid-base reactions. The anodic dissolution of metal is an oxidation process producing metal ions. The metal ions thus produced are transferred into aqueous solution to form hydrated aquo-metal ions or amino-complexes of metal ions. Therefore, the acid-base character involved, that makes the corrosion process diversified, depending not only on the oxidizing agent and the electrode potential but also on the acid-base species such as basic anions present in the environment.

The most important factors that control the dissolution of metals in aqueous environment are the type and concentration of the present anions. There are, however, many cases where the dissolution rate of metal in acid solutions depends not only on the concentration of hydrogen ions participating in the process, but also on the nature and concentration of the anions which, at first sight, do not seem to take-part. The work carried out by **Kolotyrkin, et al.**(6-10), has shown that the changes in the anion composition can influence both cathodic (hydrogen evolution)(6-9) and the anodic processes.(10,11)

The influence of anions on the anodic process is connected frequently with their action on the state of the passivating film carried by the metal surface, i.e. on the dissolution barrier.(12) Evidence has been accumulated to indicate that anions contribute directly to the discharge reactions and to the formation of metallic ions.(10,11,13-17)

In explaning the mechanism of the influence of anions on the kinetics of eloctrode processes, it is necessary to study their effect on the structure of the electrical double layer produced by adsorption of these anions at the metal/solution interface, with the subsequent appearance of the negative ψ -potential. If these alone are taken into consideration, there will be no satisfactory explanation for much of the experimental data available at present. It is obvious, in praticulary that a change in ψ-potential should cause the same change in the rates of the direct (anodic) and reverse (cathodic) reactions, and consequently, to a change in the exchange current density. However, as was shown by **Kolotyrkin**(10), such a parallism is not observed. From the data available at present, it can be concluded that the direct participation of the solution components in the elementary action ionization of metallic atoms appears to be inevitable stage in these processes. It is important to mention that, the components possessing the greatest affinity for the electrode metal are those which take part predominantly in the process. **Losev**(11) showed that such a part could be played not only by specifically adsorbed anions, but also by neutral molecules such as water. It was found that, the rate of anodic dissolution of iridium amalgam in the acidified solutions of perchlorate, which are not known to display any tendency for specific adsorption, decreases as the concentration of free water in solution becomes less. These results seem to show that the hydration of metallic ions, at least in part, takes place before its transition from metallic lattice into the solution.

The stimulating action of a certain anions on the anodic dissolution process is manifested only after a certain critical potential has been reached at which the strength of the covalent bond between the surface atom of the metal and the adsorbed ion equals the covalent bond strength in the corresponding individual compound.

Evidently, the different anions must have different values of critical potentials. If at a given potential several components of the solution are adsorbed, then not all the surface complexes can pass into the solution, but only those the strength of whose chemical bond has attained the required value.(18-21)

A- Corrosion Behaviour of Iron and Steel in Acid Solutions :

The anodic behaviour of iron has been widely examined(22-24). In general there is an agreement with regard to the experimental results, however, theoretical interpretation often differs. **Müller**(22) investigated the anodic behaviour of iron and also some other metals. His experimental results and his theoretical interpretation are very useful in the study of the anodic polarization of iron, especially in H_2SO_4. The first stage of the anodic polarization of iron in H_2SO_4 consists of covering the surface of iron with crystalline layer of hydrated $FeSO_4$. More recently the investigation by **Bartlett and Stephenson**(25) and **Froment et al.**(26) have given deeper insight onto the process of the anodic deposion of $FeSO_4$ on iron in H_2SO_4 solutions.

The crystal structure of $FeSO_4 \cdot 7H_2O$, was determined by **Baur**(27) and also the structure of $FeSO_4 \cdot 1\ H_2O$ was given by **Pistorius**(28). From the solubility data for $FeSO_4$ in H_2SO_4 and the experimental results it was concluded that the passivating layer consists of only $FeSO_4 \cdot 7\ H_2O$ at H_2SO_4 concentration up to 7N. In

7N H_2SO_4 there is simultaneous deposition of $FeSO_4.7H_2O$ and $FeSO_4.1\ H_2O$, while at still higher concentrations the layer consists of $FeSO_4.1\ H_2O$ only.

Taking into account only the species formed by anodic polarization of iron in H_2SO_4 solutions, such as hydrated specimens, $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_4]^{2+}$, and $[Fe(H_2O)_5OH]^{+}$ and the hepta- and monohydrates, the following mechanism of the anodic polarization of iron in H_2SO_4 was proposed:(27)

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad \ldots\ldots\ldots\ldots \quad (1)$$

The electrons then react with H_2O molecules as :

$$2e^- + 2H_2O \longrightarrow H_2(\text{partly } 2H) + 2OH^- \quad \ldots\ldots\ldots \quad (2)$$

According to **Mileuch and Olszewsky**(29) hydration of the Fe^{2+} ion follows:

$$Fe^{2+} + 4\ H_2O \longrightarrow [Fe(H_2O)_4]^{2+} \quad \ldots\ldots\ldots \quad (3)$$

Further, the complex formation reaction can take place according to the following equation :

$$[Fe(H_2O)_4]^{2+} + 2\ OH^- \longrightarrow [Fe(H_2O)_4\ 2OH] \quad \ldots\ldots \quad (4)$$

The complex then reacts with H_2SO_4

$$[Fe(H_2O)_4\ 2OH] + H_2SO_4 \longrightarrow [Fe(H_2O)_5OH]^+ + HSO_4^- \quad \ldots\ldots\ldots \quad (5)$$

Finally :

$$[Fe(H_2O)_5OH]^+ + HSO_4^- \xrightarrow{+H_2O} Fe(H_2O)_6 \cdot H_2O.SO_4.. \quad (6)$$

With the heptahydrate as the final product. The formation of nuclei were observed and described by **Bartlett and Stephenson**(25) and also by **Froment et al.**(26). They added that, on the active parts of the iron surface crystalline $FeSO_4.7H_2O$ and $FeSO_4.1\ H_2O$ are formed covering the iron surface with porous layer.

The dissolution of iron in H_2SO_4 - Na_2SO_4 and HCl-NaCl solutions was studied by **Kolotyrkin and Co-workers**(30,31) using galvanostatic technique. In both systems an increase in the anion concentration is accompanied by corresponding increase in the dissolution rate of iron. They concluded that, both the SO_4^{2-} and Cl^- ions participate in the dissolution of iron, and both have an accelerating effect. By addition of Cl^- ions to 1N H_2SO_4, the dissolution rate of iron was found to decrease with increasing the concentration of Cl^- ions up to 0.1N. However, further increase in the Cl^- ion concentration increased the dissolution rate. The interpretation of these results, was based on the competitive adsorption of Cl^- and SO_4^{2-} ions on the iron surface. The retarding effect observed when Cl^- ions were added to H_2SO_4 solution was attributed to the displacement of SO_4^{2-} ions by Cl^- ion on the iron surface.

The corrosion behaviour of cast iron was investigated potentiostatically in 2.5M H_2SO_4 in temperature range from 303^0K to 333^0K. The rate of corrosion in 2.5M H_2SO_4 at various temperatures (T) for the equilibrium, active and passive states were obtained from the corresponding values of the current density (i) at such temperature. Activation energy (E) of the corrosion process in each state was derived. It was found that the corrosion behaviour of cast iron in HCl was very much similar to that in H_2SO_4, but in HNO_3 there is a less tendency for corrosion as compared with H_2SO_4. Also, the corrosion rates for equilibrium, active and passive states depend on temperatures for the same medium (2.5M H_2SO_4).(32)

The corrosion behaviour of steel has been extensively studied in mineral acids. However, there is scant work done in relation to the corrosion of steel in organic acids.(33-37) **Morris and Bryan**(33) attributed the corrosion of steel in citric acid solutions to the diffusion process of hydrogen through the mild steel.

Gouda et al.(38) studied the corrosion behaviour of steel in stagnant de-aerated citric and oxalic acid solutions (10^{-5}-10^{-1}M) in pH range (2-6). They concluded that in dilute organic acid solutions in pH range 2-5, the corrosion behaviour of steel is similar to that obtained in neutral solutions. In these solutions the corrosion process is dependent on the breakdown of the pre-immersion oxide film.

Thus the destruction of the film leads to an increase of the anodic areas at the expense of the cathodic ones. The corrosion process in these dilute acid solutions becomes controlled by the anodic reaction because there is a negative shift in the corrosion potential and an increase in the corrosion rate with the increase of acid concentration. But in concentrated acid solutions (10^{-2}, 10^{-1}M) the corrosion process is controlled by the cathodic reaction because there is a positive shift in the corrosion potential and an increase in the corrosion rate with the increase of the acid concentration.

B- Corrosion Behaviour of Iron and Steel in Alkaline Solutions :

A potentiostatic investigation of the corrosion behaviour of cast iron has been performed in NaOH solutions in temperature range from 303°K to 333°K. The rate of corrosion at various temperatures (T) for the equilibrium, active and passive state were obtained from the corresponding values of the current density (i) at such temperature. Activation energy (E) of the corrosion process in each state was derived. It was found that dilute alkali solutions do not corrode cast iron at any temperature, but hot solutions exceeding about 30% concentration will attack it.(32)

The processes occuring during anodic polarization of iron in alkaline solutions have long been established(39-42). After the initial charging of the double layer, two arrests are observed before oxygen evolution. These may be attributed, to the formation of a layer of $Fe(OH)_2$ and the oxidation of ferrous hydroxide to ferric hydroxide(39). A mechanism of dissolution and passivation of iron in pure alkaline solutions, based on the formation of an electrochemically active layer of adsorbed oxygen (or oxide), has been investigated.(39)

A galvanostatic investigation of corrosion behaviour of iron in pure NaOH solutions, and in alkaline solutions containing Cl^-, Br^- and I^- ions has been studied(43). It was found that, the presence of these ions leads to the formation of XO^- ions on the surface covered with patches of an oxide or a hydroxide. The potential at the oxide/electrolyte boundary is more positive than that at the metal/electrolyte interface particularly when the oxide or hydroxide is not a good electron conductor. This higher positive potential may enable the discharge of X_2 (results from the discharge of X^-) on the oxide or hydroxide patch, while dissolution (hence, hydroxide formation) continues at the spots of bare metal. X_2 has a dual function. In the first case, it attacks the oxide by chemical interaction. Secondly, it produces XO^- ions which acts as oxidizing agents.

$$X_2 + 2OH^- ==== X^- + XO^- + H_2O \text{ .... } \quad (7)$$

The glavanostatic technique was often applied to investigate the iron passive system especially in alkaline solutions.(44-49) Most of the work in this domain was devoted to infer the passive film structure and composition through the analysis of the potential arrests in the chronopotentiometric curves under constant cathodic current.

The electrochemistry of iron and carbon steel in hydroxide solutions has been studied extensively at both ambient(50-58,39) and elevated(59-65) temperatures. In spite of these extensive studies, unanimous agreement on the mechanism of oxidation of iron in hydroxide solution has not been obtained. In particular, doubt exists as to identity of the oxide/hydoxide phases which are formed under different conditions, and as to the sequence with which they appear as a function of potential. Attempts to identify the various phases which formed on iron and carbon steel in alkaline solution using X-ray and electron diffraction(50,53-55) and electrochemical methods(51,59) have concluded that $Fe(OH)_2$, Fe_3O_4, γ-F_2O_3 and γ-$Fe_2O_3.H_2O$ are formed under a variety of conditions.

The anodic oxidation products of iron in concentrated hydroxide solution was reported by **Geronov and Co-workers**(57). They used Mossbauer spectroscopy to identify the phases in situ during the cyclic galvanostatic oxidation/reduction of iron in 5M KOH. Two anodic arrests were observed; the first due to the formation of $Fe(OH)_2$ and the second due to the formation of β-FeOOH. Unreacted $Fe(OH)_2$ was also detected at the end of the second arrest. Upon cathodic charging from a potential which is noble to that for the second arrest, it appears that β-FeOOH is first reduced to $Fe(OH)_2$, which then undergoes reduction to metallic iron.

The potentiostatic transient behaviour of carbon steel in 1M NaOH at 20 ± 2^oC was studied.**(66)** The data obtained suggests that the initial film on the metal surface forms by a nucleation and lateral growth mechanism. Film thickening and reduction transients were found to obey the empirical relationship.

$$i = Kt^{-n} \quad \text{..} \quad \textbf{(8)}$$

Where "i" is the transient current in mA, "t" is the time in sec., "n" is constant depends on the potential and the constant K depends on the potential, structure and the morphology of the surface film.

Wikjord et al.(67) found that, corrosion product formed on a rotating disc electrode in oxygen-free sulphide solution changes from iron- rich to sulphide-rich phases, according to the sequence Mackinawite ——> Ferrous sulphide ——> Troilite ——> Pyrohotite ——> Pyrite, the latter phase being thermodynamically favoured. The growth of mac- kinawite on an iron electrode surface in alkaline sulphide solution is preceded by a fast growth of a thin imperfect film of magnetite**(68)**. Nucleaction of mackinawite patches on the electrode surface starts at the fault sites in the oxide film, and the rate of coverage is controlled by the rate of the oxide removal.

Voltammetric studies(68,69) of iron and steel in alkaline sulphide solutions indicated that, the passivation of the metal is due to the presence of a defective oxide layer. The sulphide anions are apparently able to inhibit the oxide growth process by competitive adsorption with the hydroxy anions. The competitive adsorption between SH^- and OH^- anions for corrosion and passivation of iron and in alkaline sulphide solution is based on their concentration. If SH^- anion concentration is much greater than the OH^- anion concentration, the mackinawite layer is instantaneously formed on the electrode and the metal surface attack is mainly uniform. On the other hand if SH^- concentration is greater than OH^- anion concentration, an oxide film with sulphide species is located at certain sites of the metal surface. Finally when the SH^- and OH^- anions concentration are approximatly alike, the metal passivation or repassivation is then favoured.(70)

C- Corrosion Behaviour of Iron and Steel in Neutral Solutions:

The corrosion behaviour of mild steel has extensively studied in neutral solutions, propably as a result of its wide use in handling of natural waters.(71-73) One of the most important environmental constituents affecting both the nature of the corrosion attack and the corrosion rate, is dissolved oxygen(74,75). A lower corrosion rate and more uniform attack can be obtained by decreasing the oxygen concentration. High oxygen concentrations may favour steel passivation, but the intensity of attack at active sites when present is increased. In aerated solutions(75) the partial spread of active sites from local points of initiation gives rise to a macroscopic distribution of attacked and unattacked areas on steel. These areas may represent the anodes and cathodes of a corrosion cell, and the cell current is considered to be responsible for the protection afforded to the unattacked cathodic area (termed the mutual protective effect).

Glass(76) investigated the corrosion behaviour of mild steel in oxygen saturated 0.01M $NaHCO_3$ solution at 65 ^{o}C. He found that the corrosion rate depends strongly on the change in the surface conditions produced by the anodic or cathodic reactions. It was found also that the adsorbed intermediates and products of oxygen reduction reaction stimulate the formation of passive film on the unattaked cathodic areas by a direct metal-solution reaction. Oxygen was found to be screened from the anodic area by the precipitated corrosion products. Much of the overpotential stimulating metal oxidation will be lost as an ohmic potential drop across this precipitated product. The development of the protective films at the anodic areas is thus likely to involve further precipitation.

The electrochemical behaviour of carbon steel in 3% sodium chloride solution has been investigated using a rotating disk electrode.(77) Both steady-state (diffusional current vs. the disc angular velocity plots) and transient (frequency analysis of the electrohydrodynamical impedance) measurements, which specifically sample mass transport phenomena, have been carried out. It was found that oxygen transport takes place not only in the liquid phase but also through a porous layer of corrosion products. From the electrochemical impedance measurements, it was found that at the corrosion potential the oxygen reduction reaction is under either diffusional or mixed (activation + diffusion) control depending on both the electrode rotation speed and on the hold time at the free corrosion potential. In addition, it was shown that the oxygen consumption occurs not only by electrochemical reduction but also chemical oxidation of ferrous to ferric ions.

The anodic polarization curve, the static passive potential, and the behaviour of the decay of the polarized passive potential of iron were examined in neutral boric acid/borate solutions with and without Fe^{2+} ion in solution.(78) It was found that the passivation potential is a function of the $[Fe^{2+}]$ and pH and corresponds to the equilibrium potential of the reaction :

$$\gamma\text{-}Fe_2O_3 + 6H^+ + 2e^- == 2Fe^{2+} + 3H_2O \text{ ....} \qquad (9)$$

The polarized passive potential in the steady state is related to a pesudoequilibrium potential that corresponds to a higher deffect concentration in the oxide surface and to a lower $[Fe^{2+}]$ at the oxide/solution interface. The potential gradient across the film appears to be very small. The decay of the polarized passive potential on open circuit is explained as due mainly to the change in the defect-concentration and consequently of the film composition at the oxide/solution interface either by the outward migration of iron through the film or by the reaction with Fe^{2+} ion in the solution when the latter had been added or supplied by a small amount of self-corrosion.

The effect of chemical species in solution on the passivation of iron in phosphate-borate buffer solution was studied, especially the effect of the anions containing oxygen.(79-82,45) It was found that, iodate and borate or phosphate ion facilitate the passivation of iron by taking a part in the anodic process(79, 45). The incorporation of borate into the passive film was also confirmed by determing, the depth profile of the film using electron spectroscopic analysis.(83.84) On the other hand, sulphate or arsinite was found to inhibit the growth of the passive film in neutral solutions, which was verified by chronopotentiometric analysis.(79) In general, chemical species in the solution affect the passivation of iron at different stages depending on the nature(79) of each stage: adsorption, hydroxide formation, complex formation and film growth.

D- Passive Film Formation on Iron and Steel :

In electrolytic solutions, passivity of metals results from the formation of an interface which prevents the direct contact of the metal with the electrolyte. The behaviour of the interface depends on its thickness, chemical composition, conductivities, potential maintained and rate of dissolution.(85) Measurements of metal tendency to be passive are important for determining the electrochemical corrosion characteristics of the metal. These measurements are available from the potential-current anodic polarization curves.

The passive interface on iron has been examined by many investigators. Most of their experimental techniques required air-drying and/or removal of the passive layer from the metal substrate. The results then do not necessarily disclose the nature of the passive layer as it exists on the metal surface. The assignment of specific potentials was ignored. More accurate results should be obtained with the passive layer remaining in sites.

Nagayama and Cohen (86) showed that the films gave an electron diffraction pattern characteristic of either γ-Fe_2O_3 or Fe_3O_4 on iron in neutral borate buffer solution. Cathodic reduction results indicated a composition of a cation defect γ-Fe_2O_3 at the surface with Fe_3O_4 next to the surface.

Sato et al. (87) showed that the passive film formed in neutral solution is a two-layer structure of γ-Fe_2O_3 next to the metal formed by direct oxidation and FeOOH at the oxide solution interface formed by deposition from Fe^{2+} ions in solution.

Cohen and Co-worker(88) showed that iron which is passivated in an Fe^{2+}-free borate buffer solution forms a substantially anhydrous "Fe_3O_4- γ Fe_2O_3" film. The presence of Fe^{2+} ions in the solution leads to the additional formation of a mixed hydrated "iron born oxygen" compound which is amorphous [$FeOHB_4O_7$]. Small amounts of waters or hydrate may be present in or on the films due to adsorption from the solution. However, this water probably dose not play a major role in the protectivness of the film.

At present, two models are utilized in interpreting the data obtained on passive films on iron in borate buffer solution (pH=8.4)(89,90) In one view(91-93,86,55) the film is considered polycrystalline and anhydrous, the only water in the film being that adsorbed in the surface region.(94,95) Passivity in this model is understood in terms of the nature of the crystalline oxide present (either a duplex layer consisting of an inner layer Fe_3O_4 and an outer layer of γ-Fe_2O_3(95) or γ -Fe_2O_3(91,55) alone). In the second model (98-100) the passive layer is regarded as an amorphous hydrated ferric oxide represented by $Fe_2O_3.H_2O$ (99). According to this model the bound water is essential element in the passive film cementing the polymeric iron oxide chains together(100) forming a network structure.

Cohen (101) has presented a mechanism for passive film growth on iron in neutral solutions. He stated that, when an anodic potential is applied to a film-free iron specimen, iron oxidized to form both a film of magnetite and ferrous ions in the solution. When the applied anodic potential is above the range where γ-Fe_2O_3 is stable, γ-Fe_2O_3 is formed on the top of the magnetite, and any excess ferrous ions in the solution over the equilibrium value are also oxidized at the oxide/solution interface to form γ-Fe_2O_3. In the initial stages, the film is then so that there is a high potential gradient across the film and thickening occurs rapidly. As the potential gradient decreases with thickening, the rate of migration also decreases and the anodic current drops.

Sarver(102) has found that in NaOH solution of pH 12 as in borate solution(103) the composition of the film is probably closer to FeOOH than to Fe_3O_4 or Fe_2O_3.

When a metal corrodes in aqueous solutions the metal is often covered with precipitate films of corrosion products such as hydroxides or hydrous oxides of the metal. The precipitate films act as gel-like electrolytes in contact with the metal or with the passive oxide layer that cover the metal surface. These precipitate films exhibit in most cases the characteristic of ion-selectivity.(104-109)

The ion-selective properties of hydrous ferric oxide precipitate films has been investigated by measuring the membrane potentials which arise across the precipitate membranes of hydrous ferric oxide with and without adsorbed MoO_4^{2-} ions in solutions of NaCl, KCl, $MgCl_2$, $CaCl_2$, $BaCl_2$, $AlCl_3$ and $FeCl_3$. The hydrous ferric oxide membrane was only permeable to Cl^- ions in chloride solutions (anion-selective films which accelerates the corrosion process), whereas the membranes with adsorbed MoO_4^{2-} ions were permeable to cations, H^+ ions in NaCl and KCl (cation-selective) films which inhibits the corrosion), and to both Cl^- ions and cations in the presence of multivalent cations (bipolar films which also inhibit the rate of corrosion).(110)

E- Breakdown of Passivity of Iron and Steel :

The electrochemical study of corrosion reactions is simplified considerably when it occurs uniformaly over the electrode surface. In the homogeneous theory of corrosion the microscopic sites for oxidation and reduction are assumed to distribute randomly. A site does not influence the neighbouring ones. Reduction sites change over to oxidation sites and vice versa in random fashion. Thus, both cathodic and anodic reactions take place over the entire surface, and the metal apparently corrodes uniformly. Such a state of affairs accounts for the corrosion of very pure metals or amalgams in solid solution. Heterogeneous corrosion, on the other hand, takes place through spatially divided, localized anodic and cathodic areas. Attack is, therefore, nonuniform as observed in the dissolution of a metal containing noble inclusions.

Among all the specific types of corrosion pitting holds a special place. It is one of the most dangerous and insidious type of attack, since perforation by a single pit can cause complete failure.

It is known at present that the passive state of a metal or an alloy can be destroyed by introducing into the solution certain anions such as Cl^-, Br^- and I^- ions. These ions in many cases cause nonuniform corrosion which gives rise to pits on the metallic surface (111-119).

Pitting may be divided into two distinct steps mainly pit initiation or surface breakdown and pit propagation (grouth) in depth and volume.

Some authors(120-122) claim that, there is no fundamental difference between initiation and propagation steps, since direct contact between the bare metal and the electrolyte occurs instantaneously upon the immersion of the passive metal. The aggressive electrolyte instantaneously penetrates the film at these flaws and reacts with the bare metal giving rise to a rapid metal dissolution.

Janik-Czachor(123) distiguished between initiation and propagation steps in pitting process for iron. He stated that, halide ions agglomerate and adsorb on the oxide surface specially at the defects or inhomogenties on the surface. The chemisorbed halides may replace oxygen ions on the passivating film. These adsorbed halide ions cause a localized decrease in the film thickness before the pit nucleation potential followed by complete local removal of the film at sufficiently high anodic potential (pitting potential). This potential was found to be decreased as the concentration of the halide ions increases.

However, **Galvele**(124) stated that the main reason for passivity breakdown at the initial stages of pit growth is the localized acidification due to the metal hydrolysis.

Pitting potential is a characteristic parameter for pitting. It was found that, the pitting potential considered as the minimum potential at which localized acidity could be maintained inside a pit(125). On the other hand **Strehblow**(126) defined the pitting potential as the potential corresponds to a critical coverage of film by halid ions above which there are sufficient aggressive ions at the surface to breakdown the film.

An interesting feature of pitting corrosion by halogen ions is that it does not start directly after the addition of the depassivating agent. A certain time, the so called induction period, elapses before dissolution.(127-130) Induction period varies with the concentration of halide ions as follows :

$$1/\tau = K\,C_{X^-}^{n} \qquad \ldots\ldots\ldots\ldots \qquad (10)$$

Where τ is the induction period, K and n are constants. The constant n is 1 for iron in chloride solution(131), suggesting that the reaction leading to pit nucleation is first order with respect to chloride ion concentration. This value estimates the rate of the breakdown process. This means that the rate of dissolution of passivating film increases linearly with Cl^- ion concentration. **Heusler and Fischer**(130) found that, τ , (induction period) varies with the potential according to the relation :

$$Ln\,\tau / \tau_0 = E_0 / \Delta E \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

Where τ_0 is the minimum induction period, for $\Delta E = E - E_p \longrightarrow \infty$ τ_0 does not depend on halide concentration but does depend on its kind and is an order of magnitude higher for I^- than the other halides. The slope $E_0 = \partial\, Ln\,\tau / \partial\,(1/_{\Delta E})$ diminishes with halide ion concentration.

Pit growth has been described in some details in the literature(111,112). **Sato** (132) stated that the pit is considered stable and grow with time if the local ion concentration (halide ion concentration) build up at pit sites exceeds a certain critical value. **Okada**(133) on the other hand, found that the fluctuation of concentration of ionic species or the electrical field in the solution would thus play a major rule at the initial stage of pit nucleation. At higher halide ion concentration and a more positive potential or a large electric field in solution, the pit is considered stable and growth with time.

Oranowska et al.(134) studied the behaviour of iron in a saturated $Ca(OH)_2$ solution of pH 12.5 with and without 0.05 or 0.1M $CaCl_2$ added. They found that, in presence of Cl^- ions, breakdown of passivity occurred by a spontaneous onset of uneven general corrosion. Breakdown took place as the potential of iron attained a critical value. **Alvarez et al.**(135) reported pitting of iron in NaOH + NaCl solution above a certain critical potential which was more positive than that found in neutral NaCl solution.

Localized corrosion of iron has, also, been studied in the presence of typically aggressive anions such as chloride, bromide and iodide. However, the information on the effect of fluride ions on the passivity breakdown of iron and steel in neutral buffered solution containing NaF was also discussed.(136,137) At a certain constant ionic concentration, the pitting potential become more positive with the halide ions size ($F < Cl^- < Br^- < I^-$). At potentials greater than the breakdown potential, pit initiation was attributed to the reaction of the adsorbed halide with the metal surface.

The influence of different anions on the pitting corrosion of iron was also studied in neutral buffered solutions by **Ogura and Ohama**(138). These results showed that the breakdown potential becomes more positive in, the following order $SO_4^{2-} < Cl^- < Br^- < I^- < F^-$. For halides, the species related to pitting were assigned to a complex of the form $[FeX_4]^{2-}$.

The breakdown of passivity of iron in alkaline sulphide solution is a two-step process. The first involves the nucleation of mackinawite patches at faults in the oxide film and their subsequent growth by dissolution of the oxide. The second step is associated with the growth of pits under these patches. At higher positive potential, mackinawite may be oxidized to Fe_2O_3 and sulphur with simultaneous formation of pyrite. The resistance of passive films to breakdown is affected not only by its thickness but also by its composition.(139)

Moll et al.(140) studied the localized corrosion of mild steel in alkaline solution containing a salt with sulphur-containing anion (Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$,KSCN and Na_2S) using potentiostatic and potentiodynamic techniques complemented with scanning electron microscopy. Alkaline solutions containing one of these salts produce pitting corrosion of mild steel at potential more positive than those of the active-passive transition of iron in anion-free solution. In the presence of either SCN^- or $S_2O_3^{2-}$ anion, the pitting of iron takes place through sulphide formation which reacts at the electrode surface yielding, poorly protective ferrous sulphide. Both sulphide(141,67) and sulphate ions(142,143,138) in solution and elemental sulphur(144) produce pitting corrosion of iron and mild steel. Sulphide ions promote corrosion of stainless steel by chloride ions(145,143). A similar effect is observed for stainless steel in a mixture of chloride and thiocynate ions as well as chloride and thiosulphate ions(146). In both cases, at a constant chloride ion concentration, the increase of sulphur containing anion concentration shifts the corresponding breakdown potential towards more negative values.

F- The Use of Organic Compounds as Corrosion Inhibitors :

Most organic inhibitors function by forming adsorbed layer on the metal surface. Probably no more than a monolayer in thickness which essentially blocks of H^+ discharge and dissolution of metal ions. Compounds serving as inhibitors require, a favorable polar groups by which the molecules can attach itself to the metal surface. These includes the organic nitrogen, sulfur and oxygen groups in which nitrogen, sulphur and oxygen atoms is regarded as the reaction centers for the stablishment of the adsorption process.(147)

At first the force of interation between the metal and the organic molecule may be weak electrostatic force (physical adsorption)(148). However, the process of chemisorption involving charge transfere, takes place more slowly and with high heat of adsorption. In this respect adsorption is specific for certain metals and is not completely reversible.

According to the adsorption theory of **Uhlig,**(149) any substance adsorbed on the metal surface and capable of sharing electrons with underlying metal would acts as inhibitor. The adsorbed species may: (i) block the active site, (ii) displace from the surface any catalyst for the anodic dissolution reaction on (iii) by virtue of the net charge of the adsorbed ion have some effect on the potential and corrosion of the metal.

Many investigators(150-158) supported a theory for inhibition based on the adsorption of organic additives on the cathodic sites of the metal surface. Mann(159) suggested that the cathodic areas are blanketed by the organic inhibitors due to the electrostatic attraction. He suggested also that the organic inhibitors function by increasing the true ohmic resistance. A major weakness in this theory is that many inhibitors are of mixed type. It is difficult, if not impossible, for many inhibitors to undergo cathodic reduction under conditions existing in the corrosion process. Several other authors have reported that organic inhibitors induce both anodic and cathodic effects(160-163). Hoar(164) suggested that organic inhibitors function through the general adsorption of molecules.

De(165) has formulated a general theory of inhibition by adsorption, in both neutral and acid solutions, based on the electrocapillary properties of anions. It is well known that capillary-active anions are preferentially adsorbed on mercury along the positive branch of the electrocapillary curve, depressing it and shifting the maximum to slightly more negative value. It is assumed that these ions are adsorbed into the electrical double layer at the metal/ solution interface. Similary cations are prefrentially adsorbed along the negative branch of the curve, and the neutral molecules at potentials round that of the electrocapillary maximum (or "zero charge potential") depressing thus the upper portion of the curve. This formulation may expected to be the case for the behaviour of iron. However, the zero-charge potential of iron is not known with any certainty, a value of about -0.37 V (hydrogen scale) for iron in sulphuric acid has been reported by **Aiazian**(166).

Balezin et al.(167) proposed a theory to explain the inhibiting action of resins and polymers which form stable complexes with metal ions. According to this theory, inhibition is due to the formation of organometallic-type complexes which were produced by the reaction between the metal, the inhibitor and the corrosive ions. The solubility of such corrosion products determines whether the organic compound acts as a corrosion inhibitor or stimulator corresponding to low and high solubilities.

The nature of metal(168) to be protected can determine the choice of inhibitor, i.e., an inhibitor effective for one type of metallic material can stimulate attack on a different material. Thus, amines and amine salts, which inhibit the atmospheric corrosion of iron and steel, can stimulate attack on non-ferrous materials.

Donnelly et al.(169) studied the relationship between the physical properties of the inhibitors and their inhibition efficiency, on the basis of "the principle of hard and soft acids and bases". They found that, for organic inhibitors of the same structure with oxygen, nitrogen and sulphur as a functional groups (e.g. benzoxazol, benzimidazole and benzthiazole), the inhibition efficiency should follow the sequence: O < N < S. Depending on this principle sulphur atom is considered the active center in thio-compounds even if nitrogen is also present(170). Adsorption through sulphur atom could be predicted from the principle of hard and soft acids and bases.(171) The metal surface having atoms in oxidation state zero is a soft acid and sulphur compounds (containing sulphur atom of high polarizability) of the type used as soft bases. An "electrostatic attraction" leading eventually to a certain type of bonding between the soft acid Fe^0 and soft base sulphur compounds would be more favourable than between the soft acid Fe^0 and the other possible active centers in the compounds, the nitrogen atoms which would be classified as hard bases (low polarizable). Since the sulphur atom has d orbitals of symmetry compatible with some of the d orbitals of the metal atoms, d electrons may to some extent overlap with sulphur d orbitals forming a partial $d_\pi - d_\pi$ bond decreasing the residual positive charge on the sulphur atom and the negative on Fe atoms, with partial formation of a further bond or at least strengthening of the original electrostatic bond. Oxygen and also nitrogen(172), atoms having no d orbitals available (the next energy level being 3S) will not be able to form such a π bonding and therefore the decrease of the negative residual charge at the centre of adsorption will only be allowed by concentration of the charge at the cathodic site.

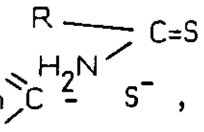
Comparative measurements(173) carried out on amines as corrosion inhibitors with equal numbers of carbon atoms in the chain. and with double bond or branched chains have shown that the greatest inhibiting power is obtained with straight-chain saturated derivatives. Primary amines were found to be more effective than tertiary. The mechanism of their action has been interpreted by assuming the formation of a compact monolayer by adsorption of the compound on the metal surface through the polar function group, with hydrocarbon chain oriented towards the aqueous phase. The coverage and water repellent characteristics of the film ensure protection against corrosion. The greatest coverage density can be obtained with saturated long-chain compounds rather than with those having branched chains because of their lateral orientation.

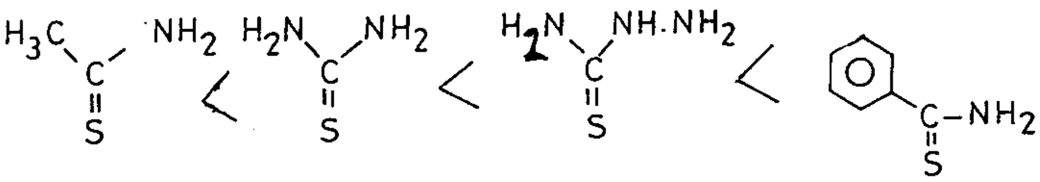
Hackerman et al.(1976)(174) who investigated the inhibiting properties of pyridine and its derivatives found that inhibition increases when electron density at the nitrogen atom is increased in the sequence pyridine < 3-picoline < 2-picoline = 4-picoline. He devolped a theory for inhibition in the presence of a series of secondry aliphatic amines and cyclicimines as inhibitors for iron in acid media.(175) It was concluded that, the greater the percentage of π -orbitals of the free electron on the nitrogen atom the more effective is the corresponding inhibiting action. Therefore, cyclicimines would be of more inhibiting efficiency than the corresponding aliphatic amines.

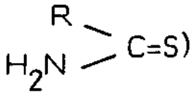
Thiourea and some of its derivatives were used as inhibitors for corrosion of iron and steel in acid media.(176-180) There are many conficting reports on the mechanism of inhibition by thiourea. Thus it has been characterized as either anodic, cathodic or mixed inhibitor.(181,161,162)

The inhibiting efficiency of thiourea increases as its concentration in the solution is increased up to a critical value where the efficiency begins to decrease. Some workers(177) have attributed this loss of efficiency to reduction of thiourea to yield corrosion promoting species e.g. SH^- ions. Others(182) attributed this behaviour to protonation, on the assumption that the protonated species catalyzes the hydrogen evolution reaction and hence the corrosion reaction. **Ateya et al.**(183) registered that thiourea inhibits the hydrogen evolution reaction via adsorption of both protonated and predominant molecular species. While the molecular species inhibits via a blocking mechanism, the protonated species inhibits via a ψ (zeta potential) effect, in addition to its blocking effect. The protonation of thiourea does not seem to be the reason underlying the loss of inhibiting efficiency at high concentrations, but rather to the decomposition of thiourea to produce presumably SH^- ions which promote the hydrogen evolution reaction and hence the corrosion reaction via a ψ effect.

The inhibiting efficiency of some thioacetamines on corrosion of mild steel in sulphuric acid solution was investigated.(180) It was found that the molecules which include a thiocarbonyl group e.g. thiourea, thioacetamide and thiosemicarbizide exhibit much higher protection than the corresponding compounds e.g. semicarbazide, guanidine and aminoguanidine. Above a certain concentration both thiourea and thiosemicarbazide loss their efficiency and eventually become promotors due to the presence of H_2S and SH^- ions as the decomposition product of thiourea or hydrolysis product of thiosemicarbized.

Donnelly et al.(169) investigated the inhibition properties of some derivatives of thiourea. They found that the first factor affecting the inhibiting properties is the availability of electrons to the anchoring atom. Thus for a system  $\begin{matrix} R \\ H_2N \end{matrix}\!\!>C{=}S$ a localization of electrons to form the canonical form $\overset{H_2N}{>}C - S^-$, will facilitate the bonding of the sulphur atom to the active sites of the metal surface in acid media. For a series of inhibitors they found that, the inhibiting efficiency increase in the sequence :



They also discussed the efficiency of another series of inhibitors in which -R group (in  $\begin{matrix} R \\ H_2N \end{matrix}\!\!>C{=}S$) is pyridyl group. The inhibiting efficiency of this group of compounds increases in the order: 2-thiocarbamoylpyridine = 4-thiocabamoylpyridine < 3-thiocarbamoylpyridine. This is due to the protonation of pyridine in acid medium which causes a high degree of positive character to the 2-, 4-carbon atoms. It is worth noted that for the three thiocarbamoylpyridine only 2-isomer has the ability of acting as chelating agent(184), while the two other isomers can only behaves as bidentate or even tridentate ligands(185). There seems, therefore, to be no relation between the chelating and inhibiting properties of these ligands.

Desai et al.(186) gave an account of the performance of some carbonyl compounds (furfuraldehyde, anisaldehyde, vanilin, cyclohexanone, acetylacetone and diacetone alcohol) as corrosion inhibitors of mild steel in HCl solutions (1-6N). They reported that, the first four compounds are excellent inhibitors, while the last two compounds are not so good in protecting the corrosion of mild steel.

Shiff bases(187) have been found to be very effective inhibitors for corrosion of mild steel in HCl solutions. The inhibitive effect of Shiff bases in greater than that obtained for their corresponding aldehyde (benzaldehyde, anisaldehyde, salicylaldehyde and cinnamaldehyde) or amines (aniline or ethylenediamine). All compounds seem to function by being adsorbed on the metal surface.

AIM AND SCOPE OF THE PRESENT WORK

From the point of view of corrosion susceptibility and resistance, iron and steels have attracted the attention of many workers. It appears from the literature survey given in the introduction of this thesis that, the electrochemical behaviour of iron and steels has been extensively studied because of their various industrial applications and their remarkable economic importance.

The studies included in this thesis deals with the electrochemical behaviour of three carbon-steel samples in sulphuric acid solutions in comparison with that of pure iron in the same solutions in order to elucidate the mode of their passivation and the effects of the carbon content on their susceptibility to general as well as pitting corrosion.

In part I of this thesis the electrochemical behaviour of iron and steel samples I, II and III in aqueous oxygenated H_2SO_4 solutions is established using the open-circuit potential measurements. The study extended to show the effect of some organic amines (aniline and some of its para-substituted derivatives) on the electrochemical behaviour of iron and steel samples.

In part II of this thesis, the galvanostatic polarization technique (Tafel lines) was used to study the dissolution kinetics of iron and steel samples in deareated solutions of H_2SO_4. The study included also the effect of the same organic amines used in part I on the kinetic parameters of dissolution of iron and the different steel samples.

Part III of this thesis is devoted to the stablishment of the electrochemical behaviour of iron and the different steel samples in H_2SO_4 solutions using the cyclic voltammetry technique under variety of experimental conditions of concentration, scanning rate and addition of Cl^- ions as pitting corrosion agent. Also the potentiodynamic polarization technique was used to study the pitting corrosion of iron and steel samples in 0.1 M H_2SO_4 solutions in the presence of aggressive Cl^- ions, together with the possibility of inhibiting such type of attack using the same organic amines.

PART I

VARIATION OF THE OPEN-CIRCUIT POTENTIAL OF IRON AND CARBON STEEL IN H_2SO_4