INTRODUCTION

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Corrosion is a term given to any process which causes a metal to loose its characteristics. It can, therefore, be defined as the destruction of a metal due to a reaction with its environment. The transfer of metal into a metal compound (i.e. Sulfide or Oxide) can not be looked upon simply as the union between metallic atoms with sulfur or oxygen atoms. These compounds are actually formed of metal, sulfide or oxide ions positioned in a definite lattice arrangement.

Corrosion is a spontaneous process and has an electrochemical nature. According to classical theory, a corroding metal consists of a heterogeneous surface with randomly destributed sites for the electronation reaction and sites for de-electronation reaction. This model of corrosion is often termed the local-cell theory of corrosion. In modern theory of corrosion, the description of corrosion phenomenon is based on modern electrode kinetic principle (mixed-potential theory). According to this theory, the corrosion reaction is the sum of an anodic and cathodic partial reactions occuring simultaneously on the metal surface at equal rates. The two theories are not conflicting but they merely are two different approaches.

Electrochemical reactions are the main cause of processes of degradation and deterioration of metallic constructions. Electrochemical techniques can be used for studying and predicting corrosion behaviour as well as passivation phenomenon. They permit rapid corrosion rate measurements and can be used for monitoring purposes. They could be used to accurately measure very low corrosion rates which are both difficult and tedious to perform with conventional weight loss or chemical analysis techniques. Electrochemical measurments focused on measuring potentials and currents. Corrosion today can be understood in terms of potential-PH (or Pourbaix) diagrams as well as in terms of potential-current (or Evans) diagrams. Corrosion occurs through the two simultaneous processes: metal dissolution (anodic) and cathodic reduction (H^+, O_2, H_2O .... etc.)

Another important phenomenon related to corrosion is passivity. The phenomenon is known over than a century. A passive metal is one that is active in the EMF series but which corrode at a very low rate. Passivation is the transformation from a corroding and unstable surface to a passive and stable surface. Passivation is a property underlying the useful natural corrosion resistance of many structural metals (i.e Al, Ni, St. St. ...). Some metals and alloys can be made passive by exposure to passivating environment or by anodic polarization at sufficiently high current densities (i.e. forced passivation). When a metal is anodically polarized, it normally dissolves as simple metal ions. This is then followed by a drop in the polarizing current, accompanied by an increas in anodic potential and consequently metal dissolution ceased and oxygen evolution takes place. Passivation refers to the loss of chemical reactivity experienced by certain metals and alloys under particular environmental conditions. Passivity effect can be quantitatively described by its polarization characteristic three regions (active - passive - transpassive) as well formation of a surface film.

Most corrosion research today is focused on the metallurgical and electrochemical characteristics of the metal, rather than on the chemical factors of the environment. Restricting attension to the part played by the metal upon corrosion, it is directly seen that metal atoms are transfered to metal ions. This transformation is simply an anodic reaction.

Electrochemical Behaviour of Copper Electrode in Aqueous Solutions:

Anodic dissolution of copper electrode in alkaline solution has attracted a great deal of attention due to its relevance to the understanding of corrosion mechanism of copper. The major part of the early work was performed using conventional electrochemical techniques and results are however, not in full agreement. Johnson(1) claimed four arrests in the anodic curve which were ascribed to (Cu_2O,

Cu_3O_4, CuO, Cu_2O_3). Miiller(2) claimed that metal dissolved as monovalent and then as a divalent ions which reacted with hydroxide ion precipitating the corresponding oxides (or hydroxides) once their solubility constant was exceeded. At very high potentials, Cu_2O_3 was formed which decomposed into oxygen and cupric oxide. Feitknecht and Linel(3) claimed the formation of Cu_2O with the simultaneous dissolution of copper and cuprous as cuprite ions leading to supersaturation with the deposition of Cu $(OH)_2$. Hickling and Taylor(4) using oscillographic technique observed two arrests which were ascibed to the formation of Cu_2O and CuO before oxygen evolution. The reverse cathode showed also the corrsponding two arrests (No evidence for the formation of Cu_2O_3). El-Wakkad and Emara(5) using potentiometric method claimed the successive formation of Cu_2O and $Cu(oH)_2$ (no evidence for Cu_2O_3). Bouillen et al.(6) using X-ray, electron differaction, optical and elecrtion microscope found that surface films are Cu_2O or $Cu(OH)_2$ or both depending on experimental conditions. Halliday(7) confirmed Bouillen results. Ohse(8) using galvanostatic technique showed one step which was ascribed to the oxidation of Cu_2O to CuO together with dissolution as cuprite ions.

The more recent work(9-11) was performed using cyclic voltammetry which affords more resolution than the conventional galvanic techniques. Abd EL-Halleem and

Ateya(12) performed a through study using cyclic voltammetry showed the presence of three anodic peaks with their corresponding three cathodic peaks. Anodic peaks were ascribed to the formation of monolayer of Cu_2O; a thick layer of CuO formed from the oxidation of copper and or oxidation of Cu_2O; and finally the formation of Cu_2O_3. Pyun and Park(13) using in situ spectro-electrochemical technique for identifying surface films and concluded that hydroxides of Cu (I) and Cu (II) were first formed by anodic oxidation at corresponding potentials and they transform to oxides upon aging. Miller(14) using a rotating split ring-disk method was able to identify a soluble Cu (III) species in the anodic region at the onset of oxygen evolution and passivation processes in the Cu (I) and Cu (II) oxidation regions were also analyzed. Recently, non electrochemical techniques had to be brought in to identify the actual composition of anodic product films. These techniques include ex-situ spectroscopic methods(16,17) and in situ techniques(18-21). Macdonald(11) study cyclic voltammetry of copper in lithium hydroxide solutions at elevated temperatures 25 to 250°C and found that the results are consistent with the formation of both soluble $Cu_2O_2^{2-}$ and insoluble Cu_2O and CuO products at the metal surface. The formation and reduction of Cu (III) was found to occur near oxygen evolution region at 25°C but not at higher temperatures due to a sharp reduction in the oxygen evolution potential with temperature.

The influence of anions on the electrochemical behaviour of copper in nearly neutral buffered solutions has been studied over a wide range of experimental conditions(22-24); generally implying an electrode surface initially covered by a protective layer consisting of an inner Cu_2O layer and an outer CuO hydrated layer (as revealed by ESCA and ISS)(16). When aggressive anions such as chloride, bromide or iodide are present in the solution, the passive film looses its protective characteristics and pitting corrosion occurs. This process starts when the applied potential exceeds a certain critical value i.e. pitting potential.

The effect of thiocyanate ions on the electrodissolution and passivation of copper was reported(25). It was claimed that, in 0.1 M KCN solution the electrode surface was covered by a thick layer of CuSCN. As the potential was gradually increased an inner layer made of Cu_2O and hydrated CuO was developed so that a complex film striucture was accomplished.

Copper does not normally displace hydrogen even from moderately concentrated acid solutions due to its position near the noble end of the electrochemical series of metals, and it is, therefore, virtually unattacked in non-oxidizing acidic media. Since most solutions that have to be handled contain dissolved air, however, this will cause cathodic depolarization and enable some corrosion to take place(26).

The medchanism of anodic dissolution of copper in aqueous acidified solutions of different anions was studied(27). It was found that, hydrogen ion accelerates the anodic reaction somewhat, by facilitating the removal of the formed Cu (II) ions from the surface through the formation of some protonated complex. On the other hand, Lee and Kennobe(28) studied the kinetics of copper electrodissolution in acidic chloride media. They found that, copper electrodissolution is essentially independent of variation in hydrogen ion concentration, but its rate increases as the chloride ion concentration was increased.

Electrochemical Behaviour of Nickel Electrade in Aqueous Solutions

The anodic oxidation of nickel electrode in alkaline solutions has been the subject of many studies(29). Such an electrode has been widely studied by conventional electrochemical technique because of its actual use as an active material in nickel alkaline battery(30) as well as its possible utilization in fuel cells(31). Visscher and Barendrecht(32) studied anodic oxidation of nickel in alkaline solutions using cyclic voltammetric and optical techniques. They found that the scanning potential affects the resulting voltammograms and that the layer on $Ni(OH)_2$ formed in the anodic cycle is only partially reduced by cathodic polarization. Weininger and Breiter(33) found that the first cyclovoltammogram of the nickel electrode differs from the sccessive voltammograms and they attributed those differences to the effect of some oxides remaining on the surface after the pretreatment. Somoilov et al(34) observed an oxidation and a reduction peak in the voltammogram for potential scans up to 0.3 V (vs rhe), the reduction peak shifts in cathodic direction for scan up to 0.7 V. This reduction peak was attributed to the reduction of adsorbed oxygen(35). Guzman et al(36) observed an anodic peak at 0.4 V during the first anodic potential sweep on a nickel anode and in the next potential sweep, this peak had disappeared. Boden et al(37). carried out their studies on nickel single crystal electrodes while Melendres and Xu(38) carried out some spectroscopic data but many points remained unanswered specially about deactivation. Bode et al(39). concluded the formation of at least two kinds of nickel hydroxides (α and β $Ni(OH)_2$) and two kinds of nickel oxyhydroxides (β an δ - NiOOH) and claimed that these various species differ by their electrochemical properties and by their crystalline structure. Arvia et al(36). showed the existance of another hydroxide species. Their physicochemical properties were studied by Leonardi et al(40). and the cystallographic structure was established by Braconnier(41). Hahn et al(42). investigated the nickel electrode-alkaline solution interface by in situ UV visible reflectance spectroscopic technique. They claimed that it would be more convenient to write ($Ni_2O_3 . XH_2O$) rather than (NiOOH), and gave some new insights concerning the reversibility of the electrochemical processes which occur on the electrode surface when varying potentials. They established the renewed Bode's diagram. According to the conditions imposed to the electrode, two main regions could be distingushed, corresponding to the formation of hydroxides and oxyhydroxide respectively. Gurzman et al(43). studied the kinetics of growth β-$Ni(OH)_2$ phase. It was reported that the growth of the β-$Ni(OH)_2$ film follows the formalism of cabrera-Mott(45) model of high field assisted formation of thin oxide film.

Abd EL-Haleem et al(46). investigated the behaviour of nickel in NaOH solutions using cyclic voltammetry technique. They suggested the oxidation of nickel to $Ni(OH)_2$ which was further oxidized to β-NiOOH and that the last oxidation step was the formation of NiO_2 during the oxygen evolution.

The corrosion behaviour of nickel heated in boiling NaOH solutions under atmospheric pressure was investigated(47). Nickel was attacked by caustic soda in the form of intergranular corrosion as well as uneven general corrosion when the corrosion potential was located in the active region. It was reported that(48), in LiOH, nickel was oxidized to hydroxide which was then deposited from solution onto the surface of the metal in a contineous, even film composed of highly oriented hexagonal crystals that provided excellent protection from corrosion.

Laser raman spectroscopy (LRS) was used to identify the films formed during the anodic corrosion of nickel in 0.15 N borate as well as in 0.15 N Na_2SO_4 solutions(49),at formation potentials in the region of secondary passivity. The spectrum observed was found to correspond predominantly to hydrated Ni_2O_3. The spectrum obtained upon anodizing nickel at 0.4 V ($Hg.Hg_2SO_4$) in 0.15N Na_2SO_4 was found to be the same as that found in borate solution indicating that the oxide film is of the same composition. This is significant in view of the previous assignment(50,51) that the film formed in this potential region and PH was NiO. The high anodic potential in the transpassive region was consistent with a Ni (III) species. The modulation reflection spectroscopy studies of Gobrecht et al(52)., as well as the ellipsometric measurments of Ord(53), also convincingly demonstrated a higher valency oxide than NiO in the region of secondary passivation.

Nishimura(54) studied the breakdown of passive films, potentiostatically, formed on nickel in borate and phosphate solutions of PH 8.42 and 11.5 in presence of NaCl. It was proposed that the passive film formed in these solutions consisted of two layers; an outer layer of $Ni(OH)_2$ and an inner layer of NiO. It was found that, pitting potential is a linear function of logarithm of Cl concentration, in the PH range of 4.0 to 10.0. The breakdown of nickel film was explained in terms of film thickness and ion selectivity, irrespective of solution pH and anion species.

The localized corrosion of pure and sulfur-doped nickel has been investigated in 0.25M Na_2SO_4 (pH 6.5), both with and without addition of chloride ions at 25°C.(55) Additon of more than 500 ppm chloride to Na_2SO_4 solution was found to cause pitting of annealed pure nickel.

Impedance measurments, potentiostatic quasi-steady state polarization data and scanning electron microscope studies were also used to investigate the dissolution of nickel in 0.5-18.8M sulfuric acid(56). An active-passive transition was observed with a single-stage reaction to divalent nickel occuring in the active region. The formation of the passivating film was shown to be associated with solid state mechanism.

Investigation on the passive behaviour of nickel in neutral and acid solutions have been reported(57-63). Potentiostatic current/potential for nickel anodes in H_2SO_4 solutions have been carried out by Kolotyrkin(63), Okamoto et al(64). and Vetter et al(65). There is no satisfactory agreement between the results of the above authors. According to Kolotyrkin(63), passivity begins at potential of 150 mv, with constant dissolution rate between 430 and 1350 mv. In contrary, the results of Okamoto et al(64). indicated that, passivation occurs between 400 and 700 mv. Ammar and Darwish(66) studied the passivity of nickel potentiostatically in 1.0 N H_2SO_4 solutions at 25°C through out the potential range from 760 to 2000 mv. The effect of Ni (II) ions on the potentiostatic behaviour of nickel was investigated in the passive and transpassive regions. According to the results obtained, Ni(II) ions had practically no effect up to the range of oxygen evolution. An addition H_3BO_3 was found to cause slight decrease of the stationary current density with increase of concentration from 10^{-4} to 10^{-1}M.

Electrochemical Behaviour of Copper-Nickel Alloys In Aqueous Solutions

Nickel has been used as an alloying metal with other metals specially copper to form high corrosion resistant alloys which could be used in aggressive environments. Some corrosion probelems appeared in power stations when Cu-Ni 70/30 was extensively used as heat-exchanger tubes where water is used as a cooling medium. For this reason, the behaviour of copper-base alloys had been the subiect of numerous previous studies(67-71).

It has been indicated that the corrosion behaviour of Cu-Ni alloys is strongly dependent on the nature and characteristics of the passive film formed on these alloys under various conditions. Beccaria and Crousier(72), studied corrosion behaviour of a series of Cu-Ni alloys (30-90% Cu) in natural sea water using electrochemical method and X-ray differaction techniques. Manfredi et al(73). studied the corrosion performace of different copper alloys including Cu/Ni, in polluted sea water.

Harvey et al(74). studied the effect of pH on corrosion and monotonic loading behaviour of 90 Cu-10 Ni alloy in 3.5% sodium chloride solution. They found that film formation was dependent on the applied current and the relative concentrations of the ionic species H^+, OH^- and Cl^- in solution which ultimately influenced the effects of substances such as sulfides(75,76), oxygen(68), ferrous ions(77) and chlorine(78) on film formation on (90/10) Cu-Ni alloy. Crassiania(79) studied and determined the effect of some adverse water addition. The influence of sulfide ions on corrosion rate(80-82) and its interfering with the normal passivation of the (70/30) Cu-Ni alloy(75,74-86) were studied.

Mukhopadhyay and Baskaran(87) studied the attack of sulphide in sea water on cupronickel 70/30(Fe) and examined the corrosion products formed. The corrosion behaviour of Cu-Ni10 (Fe) and Cu-Ni30 (Fe) alloy has attracted a great deal of attention because their widespread use for sea water pipe and its structure exposed to marine environment(88,89). De-Mele et al(90). studied the electrochemical behaviour of Cu-Ni30 (Fe) in natural sea water, artificial sea water, NaCl + Na_2SO_4, and NaCl solutions using potentiodynamic techniques as well as analysis of corrosion products in solution and in the surface deposits. Many investigation have been oriented for the study of de-alloying of copper based alloys. De-alloying of (Cu-Zn), (Cu-Mn), (Cu-Al) and (Cu-Au) was found to be the result of dissolution of zinc, manganese, aluminum and copper, respectevely(91-94).

Copper-nickel alloys have been widely studied in NaCl solutions with contradicting results. Some authors(95) have suggested that de-alloying is the result of selective removal of nickel, whereas others(96-98) have suggested that de-alloying is the result of copper dissolution. However, Efrid(99) in studies of 90-10 Cu-Ni and 70-30 Cu-Ni alloys in sea water claimed that these alloys were immune to dealloying at potentials more active than -220 mV (S.C.E.) at pH <8.5 for 90-10 Cu-Ni alloy and <7.8 for 70-30 Cu-Ni alloy.

Baccaria and Crousier(72) studied dealloying of a series of Cu-Ni alloy containing (30-90% Cu) in natural sea water using electrochemical methods, free corrosion tests and X-ray diffraction. They found that with alloys containing 90% and 70% Cu alloys, simultaneous dissolution of both components with copper re-deposited. With those containing 50% and 30%

Cu alloys, selective dissolution of copper took place.

The corrosion behaviour of Cu-Ni alloys in unpolluted and sulfide polluted sea water has been investigated(100,101). It was found that, when both sulfide and oxygen were present in the sea water, the corrosion of alloys was greatly accelerated. In aerated sulfide-polluted sea water, accelerated corrosion appears to be a result of the sulfide preventing the formation of a protective oxide corrosion product layer.

It was reported that(102), oxygen is the most important factor affecting the rate of corrosion of copper alloys by sea water, at temperatures between 180° and 250°F. At less than 5ppb oxygen, all alloys showed extremely low weight loss, while at 20-100ppb, Cu-Ni alloys showed lesser weight loss than the others. Banks(103) reported that, the presence of oxygen during the corrosion of 70/30 Cu-Ni alloy in carbonate solution increases the corrosion rate. Kato et al(104). and Hack et al(105). compared the Cu-Ni alloys with pure copper and concluded that, the most of the decrease in corrosion rate is due to a decrease in the rate of oxygen reduction. The good corrosion resistance character of the copper-nickel alloys in sea water is based on the low exchange current density of this reaction. Hack et al(105). demonstrated that removing of the outer porous layer of the film, which promotes oxygen reduction, has a larger effect on the 70/30 Cu-Ni alloy than on 90/10 alloy. Roberge and Beaudoin(106) used electrochemical impedence and spetectroscopic techniques as an errosion-monitoring for copper-nickel alloys. They suggested that, in the absence of passivation, copper dessolves as cuprous ions as an anodic reaction, while the cathodic reaction is the reduction of oxygen. Shortly after immersion into aerated sea water, copper-nickel alloy form a protective layer of corrosion products of Cu_2O in the inner and $Cu_2(OH)_3Cl$ in the outer(107). Wood et al(108). stated that, the dissolution rate of unfilmed surface is determined by the surface concentration of cuprous ions. Bianchi et al(109). have proposed that, the inhibition of corrosion of copper-nickel alloys results from the transformation of Cu_2O into sparingly soluble layer of atacamite $\{Cu_2(OH)_3\ Cl\}$.

Lenard et al(110). used the polarization resistance methode for monitoring the corrosion of specimens of 70/30 and 90/10 copper-nickel alloys during lengthy exposure to flowing sea water that was intermittently contaminated with sulfides. It was found that, exposure of 90/10 and 70/30 alloys to sulfides delayed or prevented the developement of a protective film during subsequent exposure to clean sea water. When ferrous salt was added to sea water the corrosion rate of both alloys was reduced. The conteneous aditions of ferrous ions caused a rapid development of a protective film on 70/30 alloy that was not affected by subsequent exposure to sulfides. Manfridi(78) reported that, the presence of ferrous ions in polluted sea water induces the deposition of a film of colloidal iron hydroxide (lepidocrocite) on the surface. He found that, when lepidocrocite is formed, the sulfide effect is weaker both on the cathodic and anodic currents. This situation implies a higher stability of this film in comparison with those naturally formed in clean sea water.

On the other hand, Chauhan and Gadiyar(111) investigated the corrosion behaviour and the composition of the surface films formed on Cu-10 Ni alloy in polluted and unpolluted sea water using XPS. They found that, the addition of ferrous sulfate to unpolluted sea water led to decrease in corrosion rate, while the addition of sodium sulfide enhanced the corrosion. Addition of ferrous sulfate to sea water polluted with 40 ppm Na_2S was not found to be beneficial, but instead increased the corrosion. An XPS study of the film formed in unpolluted sea water showed the outer most corrosion product to be Cu_2O with adsorbed water molecules. The inner film consisted of nickel ions in two different valence states and Cl^- ions, in addition to Cu_2O.

Passivation of Copper-Nickel Alloys in Aqueous Solutions

Chauhan and Gadiyar(112) investigated the passivation of 30/70 Cu-Ni alloy in 0.15 N Na_2SO_4 solution, in-situ, at various pH and potentials values. It was found that, the film responsible for passivation of the alloy is $Ni(OH)_2$ as was the case for pure nickel. In case of open solution (pH4) and dearated solution (pH8) a film conists of $Ni(OH)_2$ and Cu_2O was formed at low potentials. On the other hand, dealloying of copper has been found particularly in deaerated solution (pH4) at anodic potentials. The passivating film thickness for the alloy has been observed to be larger than that for pure nickel. The aloy was found to pasivate at more anodic potentials than pure nickel and occured without active dissolution. The film theckness was nearly a linear function of the electrode potential.

The effect of introducing of iron into copper-nickel alloy on their corrosion rate was investigated(113). Alloys of 90/10 Cu-Ni were plated with ^{52}Fe from an oxalate bath to give different iron percents and were corroded in a common salt bath (3.5% NaCl) at 70°C. The corrosion products were green on low iron content samples while black layer was formd on high iron content alloys. The percent of weight loss after corrosion showed that, the high iron content alloys exhibit a minimum in corrosion rate. The results showed that, only iron in solid solution in copper-nickel alloys is effective in reducing their corrosion rate. Several workers(114-116) suggested that, the corrosion films formed by 90/10 Cu-Ni (Fe) are composed mainly of the compounds FeOOH and Cu_2O along with its hydrates. Previous studies by several authors(116,117) have also shown that, the second phase; iron rich particles in 90/10 Cu-Ni, are preferentially corroded when exposed to anodic currents. These observation suggested that the first formed film is FeOOH. After the corrosion of iron particles is stabilished, copper and nickel atoms can then form compounds which result in formation of a protective film(74). Harvey et al(74). calculated the free energy of the formation reaction of FeOOH and stated that, this reaction is less likely to occur unless an external voltage is applied.

Manfredi et al(78). investigated the effect of addition of ferrous sulfate on the corrosion of different copper alloys in sea water. They found that the pitting potential of the 70/30 Cu-Ni alloy becomes more anodic when the surface has treated with ferrous ions and the surface remains passive within a broad range of potential. It was found that(114,118,119), the addition of ferrous sulfate induces the deposition of a colloidal iron hydroxide film on the surface. This film was found to be more protective than that naturally formed in contact with sea water. Manfredi et al(78)., reported also that, the formation of the passive film, on copper-nickel alloys, depends strongly on both oxygen concentration and pH value of the solution.

Inhibitors

A chemical substance which, when added in small concentration to an aggressive environment, effectively decreases or prevents the reaction of the metal with the environemt, is called corrosion inhibitor. Inhibitor was early defined by the National Association of Corrosion Engneers(120) as a substance which retards corrosion when added to an environment in small concentration.

Organic inhibitors can be classified as anodic, cathodic or both(121). This classification depends primarily on inhibitor reaction at the metal surface and how the potential on the metal is affected. The chemical structure of the inhibitor molecule plays a significant role and often determines whether or not a compound will effectively inhibits a specific system. However, an inhibitor which effective in one system, may not be effective in another.

Corrosion inhibitors could be classified also according to the mechanism of inhibition. In such classification there are inhibitors which form layers of considerable thickness, those form films by reaction with protected substrate and those which function by surface adsorption, with no significant reaction with substrate. Organic inhibitors usually are believed to inhibit corrosion by adsorbing at the metal solution interface. However, the modes of adsorption are depend upon the chemical structure of the molecule, the chemical composition of the solution, the nature of metal surface and the electrochemical potential at the metal-solution interface. There are three prencipal types of adsorption associated with organic inhibitors, namely, TT-bond orbital adsorption, electrostatic adsorption and chemisorption. Adrorption of organic inhibitors usually involves at least two types of adsorption simultaneously.

In addition to these classifications it is a recently descovered that, the organic molecule prevents the corrosion through the formation of organometallic complex layer. Fox et al(122). have suggested that the corrosion inhibition of copper by benzotriazole (BTA) results from the precipitation of the organometallic complex on to the surface of the metal, thus producing a barrier to the corrosion environment. The solution chemistry of 1:2:4 triazole (TRZ) was investigated in the range of solution concentrations in which the compound acts as a corrosion inhibitor for copper(123). Parallel photo-electron microscopic studies show that although a surface layer of Cu (I) complex is formed at low TRZ concentrations, this is ineffective as an inhibitor until at a critical concentration, a Cu (II) complex appears which provides effective protection. It was suggested that, the precipitation of Cu (II) hydroxychloride to which the TRZ is attached provides the protective layer. Walker(124) investigated the inhibition effeciency of benzotriazole for copper corrosion in different solutions using weight loss technique. It has been shown that benzotriazole is a good inhibitor for copper and brass when added to many acidic, neutral and alkaline solutions, and it appears to act as a weak buffer. He suggested that, when benzotriazole is in contact with copper and copper alloys, it is considered to be chemically adsorbed onto the surfaces, where it forms a stable, inert film that affords long term protection without the necessity to replenish the inhibitor. Copper surfaces pretreated with a hot solution of benzotriazole were found to have an increased resistance to staining in atmospheric environments and also to corrosion when immersed in many solutions of acids and salts.

Chadwick and Hashemi(125) studied the surface films formed by adsorption of benzotriazole (BTA) on copper and copper alloys using X-ray photo-electron spectroscopy (XPS). It was found that on both copper and copper-nickel alloys, benzotriazole forms a Cu (I) BTA surface complex. For the copper-nickel alloys the time taken to form the Cu (I) BTA film is dependent on the alloy composition. Surface films formed by BTA on 70/30 Cu-Zn alloy were found to contain both copper and zinc; the copper being in the Cu (I) state. A study of the adsorption of benzotriazole on cathodically reduced copper surfaces strongly suppports previous suggestions that the presence of Cu_2O facilitates formation of the surface film.

The effectiveness of (BTA) vapour as an inhibitor for copper in sulfiding atmospheres has been investigated(126). The corrosion products formed were analysed by coulometric method and by IR spectroscopy. It was found that, pretreatment with either alcoholic BTA solution or BTA vapour before expousre was necessary to ensure effective protection owing to the rapid attack of the unprotected copper oxide layer by the atmosphere. It was shown that BTA produces a protective layer by forming a complex with copper oxide rather than with metallic copper. It was concluded that this method of protection will be a practical use for copper and copper alloys devices exposed to tranishing sulfide pollutants. A typical application might be for the protection of electronic devices used in the vicinity of highly polluted sites.

Ekilk et al(127). used polarization technique to investigate the electrochemical behaviour of nickel in perchlorate aqueous and organic solutions, acetone, acetonitrile, methanal and ethanol, containing benzimidazole or its 2- substituted derivatives. It was found that the effects of benzimidazoles are caused by their adsorption, ability to complex formation and increase of pH.

A large number of compounds acts as corrosion inhibitors through adsorption on the surface without a significant reaction with the substrate. The surface active compounds represent the most important compounds in this category. Surfactants can be used alone as corrosion inhibitors(128), or in combination with other compounds such as transcinnamalbhyde or 1-phenyl-2-propyne-1-ol(129-131), to improve their performance as inhibitors. In such cases, surfactants are used at concentrations non of which acts as inhibitor in its own right. Abd EL-Fattah et al(130).studied the inhibitive effeciency of some polyethylene oxide fatty acid esters towards corrosion of admirality (90/10 Cu-Zn) alloy in 0.05 N HCl and 4.0 N HNO_3 solutions using potentiodynamic polarization technique. They found that, inhibition effeciency was increased with increase of inhibitor concentration and with increase of the number of oxyethylen units per ester molecule. These results was attribited to a decrease of interfacial tension which led to decrease of the bulk concentration of the inhibitor and its increase at the electrode surface-solution interphase. They stated also that, at the interphase the surfactant molecules orientate their hydrophilic group toward the metal and are adsorbed on its surface. The hydrophobic part is oriented away to the solution, repelling thus the aqueous fluid. Under such conditions a diffusion barrier to the chemical and/or electrochemical attack of the solution on the metal surface is established.

The inhibition of corrosion of mild steel in 0.05 N HCl by non-ionc surfactants polyethylen oxide-fatty acid condensate type was studied using the wight loss technique at 70°C(128). The percentage inhibition increased with the increase of additive concentration up to a certain values comparable with the critical micel concentration (CMC) of the surfactant, whereby, a constant effeciency was attained. Higher percentage inhibition values were obtained with increasing the molecular weight of surfactant. Moreover, the constant percentage inhibition value was reached earlier, the higher the molecular weight of the surfactant. Conformation with Langmuir adsorption isotherm suggested that, these compounds affect corrosion inhibition by being adsorbed on the metal surface.

The corrosion behaviour of steel in aerated aqueous 0.5M H_3PO_4 solution in presence of some surfactants was studied using potentiodynamic polarization technique(132). The surfactants used in this study were sodium lauryl sulfate (SDS), bis (2-ethylhexyl) sulfosuccinate sodium salt (SES) and centyltrimethylammonium bromide (CTAB). It was found that, the membrane inhibition effect due to the oxide layer was clearly increase by adding cationic surfactant (CTAB). Such compound is adsorbed at the metal surface and is incorporated within the protecting layer, leading to compact coverage.

Another way used for protection of metals and alloys against corrosion can be applied by introducing a small amount of metal cation to the solution in order to improve the passivation properties. Copper-nickel alloys selected for tubing in heat-exchangers used to cool exhaust steam from power plant turbines using salt water contain a small percentage of iron (usually 0.4 to 1.75%) because the iron significantly improves their corrosion resistance to salt water and boiler feed Water(199).

AIM OF THE WORK