Chapter (I)

Introduction

1.1-Corrosion:-

1.1.1-Defination of corrosion:

Corrosion can be defined as the disintegration of a material or its properties by electrochemical reaction when interacting with its surrounding environment. Thus, according to Shreir (1), the definition of corrosion is the reaction of an engineering material with its environment leading to a consequent deterioration in properties of the material. For corrosion to occur three essential elements must be present:

(i) Electrolyte

(ii) Anode

(iii) Cathode

An electrolyte is a solution that can conduct electric current. An electrolytic liquid refers to any liquid that contains ions. Electrodes can be of different metals or the same metal with different sizes or areas. Corrosion occurs because there is a difference in electrical potential between them.

This circuit must be completed by a metallic path between the two electrodes.

1.1.2- Anodic Reaction (2):-

The anode is the site at which metal is corroded i.e. at which metal dissolution takes place. Metal is dissolved and transferred into the solution as metal ions. Positively charged atoms of metal detach themselves from the surface and enter into the solution or electrolyte as ions. The electrons flow, as an electrical current, to the cathode where they are consumed. This process is known as oxidation. The detached positive ions bear one or more charges.

For example in the corrosion of zinc, each Zn atom loses two electrons and Zn ions will carry two positive charges. The electrons travel through the metal to the cathode area.

$$M \rightarrow M^{n+} + ne^{-} \qquad (1.1)$$

Also in the corrosion of iron, the reaction may proceed by a single oxidation step for Fe into ferric ion.

$$Fe \rightarrow Fe^{3+} + 3e^{-} \qquad (1.2)$$

However, this is unlikely. In practice, two oxidation step processes occur in which iron is first oxidized to ferrous ion which depends on the anode potential,

$$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (1.3)$$

and then is oxidized into ferric ion

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-} \qquad (1.4)$$

The reactions above take place at the anode and must be balanced by other reduction processes that occur at the cathode.

There are other possible anodic reactions that may take place but these are dependent on the potential of the anode. Water is broken down into oxygen and hydrogen ions according to the equation below (at sufficiently high potential):

$$H_2O \rightarrow O_2\ (gas) + 4H^{+} + 4e^{-} \qquad (1.5)$$

If chloride ions are present, they will discharge at the anode giving:

$$2Cl^{-} \rightarrow Cl_2\ (gas) + 2e^{-} \qquad (1.6)$$

1.1.3- Cathodic Reaction (3):

Electrons reach the cathode by passing through the metal. At a cathode they may discharge, for example, H^+ ions present in acid electrolytes, forming hydrogen gas. This process is known as reduction. In reduction, electrons are consumed. Thus, a cathodic reaction is a reaction that consumes electrons. When proton reduction occurs, the concentration of hydrogen ions in the electrolyte decreases and thus this increases the alkalinity of the electrolyte in the area of cathode.

The main reactions that occur at the cathode are:

(i)Hydrogen evolution.

$$2H^+ + 2e^- \rightarrow H_2 \text{ (gas) in acid environment} \qquad (1.7)$$

(ii) If oxygen ions are present, oxygen reduction takes place

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{in alkaline and neutral solutions} \qquad (1.8)$$

The formation of OH^- at the cathode causes the pH here to be higher than in the bulk solution. Eventually, ion migration of OH^- occurs, towards the anode, which promotes the formation of ferric hydroxide in case of Fe corrosion, where,

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \qquad (1.9)$$

$Fe(OH)_3$ appears in the form of a reddish brown colloid. This ferric hydroxide may react further in presence of ferrous ions to produce Fe_3O_4.(4)

(iii) Another reaction.

$$2H_2O + 2e^- \rightarrow H_2 \text{ (gas)} + 2OH^- \quad \text{at all pH} \qquad (1.10)$$

(iv)Other possible reactions such as reduction of metal ions and reduction of carbonic acid (H_2CO_3) in oil and gas production.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (1.11)$$

$$Fe^{2+} + 2e^- \rightarrow Fe \qquad (1.12)$$

1.1.4- Several environmental factors can influence the corrosion rate:

1- If H^+ ions increase in concentration (pH drops), the corrosion rate will increase, because there are more H^+ ions to receive electrons at the cathode (i.e. the amount of oxidant increase).

2- If the solution is made more alkaline; the corrosion rate may be reduced (i.e. by passivation).

3-If the concentration of the dissolved material is lowered the conductivity of the electrolyte will decrease. The resistance is therefore increased which impedes the flow of current and thus reduces the overall corrosion rate.

1.2- Types of corrosion that can be inhibited:

1.2.1- General Corrosion (5,6):

In this form of corrosion, attack proceeds at about the same rate on the entire surface of metal, which undergoes a low, relatively uniform removal of material. Thickness is reduced uniformly. Conditions required for a metal to undergo general corrosion are:

- Metal and solution in the same environment.
- A chemical reaction between metal and water that forms soluble species.

Unexpected rapid uniform corrosion failure can occur if the surface of material changes from passive (low corrosion rate) to the active (high corrosion rate) state. The resultant increase in corrosion rate may be several orders of magnitude. This occurs if the passive surface film is disrupted by mechanical effects, flow rate changes, a chemical change in the environment.

Typical examples are rusting of carbon steel in atmosphere and dissolution of zinc in acid.

1.2.2: Localized Corrosion:

This type of corrosion occurs when there is a local breakdown of a passive, protective oxide layer, such as in aluminum or stainless steel leading to the formation of small anodic areas. Intense attack is visible at localized sites on surface. The rest of surface or area is corroding at lower rate. However, due to oxide film breakdown, the small anodic area compared with the larger cathodic area gives rise to a relativity big cathodic/ anode ratio. This ratio determines the degree of localized corrosion and the extent of pitting attack.

Localized attacks may also occur even when the material is protected with coating. If the coating contains few defects, these sites are not protected and exposed to corrosive environment. Furthermore, localized corrosion is also found under a deposit such as in between a belled joint. This small area has a very different environment from the bulk material and forms a so-called microenvironment. Then, the material is said to suffer from crevice corrosion.

Some key factors play a significant role in localized corrosion:

(i)Differential aeration:

Differential aeration occurs when the concentration of oxygen is not uniform in the corrosion cell, forming an area with a higher concentration of oxygen and another area with a lower value. Oxygen is transported through the solution by convection and diffusion process. When the rates of convection or diffusion are faster at one end, more oxygen is available there will be less oxygen at the other end. This will result in the former end as a cathode and the later as an anode. This phenomenon leads to a consequent localized attack; such a corrosion cell forms the basis of a crevice.

(ii) Variation in pH at cathode and anode sites:

Localized attack may be associated with pH changes that occur in near- neutral solution, which contains oxygen. As explained above, the cathodic reaction of dissolved oxygen gives rise to an increase in pH of the solution near the cathode. This is also applicable if the cathodic reaction involved is hydrogen evolution. The increment in pH and sufficient amount of dissolved oxygen promote passivation of the surface of the metal. The potential will increase substantially and favour the metal to become the cathode.

(iii) The cathode/ anode relationship:

A basic underlying principle of corrosion is that the sum of the rates of cathodic reactions must be equivalent to that of the anodic reactions regardless of the type of corrosion involved. In uniform attack, the assumption is that the areas of cathodic and anodic reactions are equal. Thus, the sums of both reactions are the same since both cathodic and anodic localized, the surface areas of cathode is larger than that of the anode, the larger the ratio anode: cathode, thus, the more intense the localization will be as briefly explained above.

(iv)Properties and effects of corrosion products or contaminants those are present on the surface of the metal and those that are formed as a result of the corrosion reaction.

1.3- Inhibitors:

Among the methods for corrosion control and prevention, certain types of chemicals may be needed to reduce the aggressiveness of the environment or to slow down the corrosion process. Inhibitors function occurs by adsorption of ions or molecules onto the metal surface. They reduce the corrosion rate by:

- Increasing or decreasing the anodic and/ or cathodic reaction.
- Decreasing the diffusion rate for reactants to the surface of the metal.
- Decreasing the electrical resistance of the metal surface.

The types of environment that can be modified include aqueous, partly aqueous and gaseous. Aqueous and partly aqueous conditions are often found at near neutral pH range such as acid picking to remove rolling scale as well as in the production and refinery of oil and gas. Inhibitors are often easy to apply and offer the advantage of in-situ application without causing any significant disruption to the process. However, there are several considerations when choosing an inhibitor:

- Cost of the inhibitor can be sometimes very high when the material involved is expensive or when the amount needed is huge.
- Toxicity of the inhibitor can cause jeopardizing effects on human-beings, and other living species.

- Availability of the inhibitor will determine the selection of it as if the availability is low, the material is often expensive.
- Environmental friendliness.

1.3.1-Types of Inhibitors:

There are several types of inhibitors available to the industries now, they are:

1.3.1.1- Volatile Inhibitors (7,8):

This type of inhibitors is also known as vapour phase inhibitors. As corrosion can also occur in vapour environment, it is useful to carry corrosion inhibitors into the system, which then need to be themselves, volatile. When the inhibitor molecules in the vapour come into contact with the surface of a metal, the adsorption of the inhibitor will occur. The moisture then hydrolyses it, hence protective ions may be released. These include species like amines and nitrites for inhibition of ferrous metal.

1.3.1.2- Passivating (Anodic) Inhibitors (9):

Passivating inhibitors are anodic inhibitors. They cause the anodic curve of polarization to shift such that less current flows. They have the ability to passivate the metal surface. There are two categories of passivating inhibitors. Namely, oxidizing anions and non-oxidizing anions. Oxidizing anions such have the ability to passivate metal in the absence of oxygen. Typical oxidizing anions are chromate, nitrite and nitrate. Non-oxidizing ones such as phosphate, tungstate and molybdate require oxygen to perform passivation. This kind of inhibitor is by far the most widely used and possesses higher efficiency than others. However, one major drawback of it is that in order to maintain sufficient passivation of the metal and thus providing sufficient inhibition, the concentration of the inhibitor must be kept well above a critical or minimum concentration. If the concentration is blew the minimum value, it is likely that the metal, which is to be protected in the first place, will suffer from localized corrosion such as pitting.

1.3.1.3- Precipitation Inhibitors (10):

These inhibitors are often film-forming in nature for instance silicates and phosphates. They are effective at blocking anodic and cathodic sites. They precipitate on the metal surface, forming a protective barrier. Hard water is rich in magnesium and calcium. When these salts precipitate on the metal surface, for example at the cathode where the pH is higher, they establish a protection layer on the metal. Film- forming types of inhibitors are often distinguished by two classes. The first one works by slowing down the corrosion without stopping it completely. The second ceases the attack completely. However, the efficiency of the inhibitor depends on the pH value and saturation index. The saturation index is then in turn determined by the water composition and temperature.

1.3.1.4- Cathodic Inhibitors (10, 11):

Cathodic inhibitors reduce the rate of cathodic reaction ,namely, oxygen reduction in near neutral environments and hydrogen evolution in acid solutions, respectively. These form species that precipitate on cathodic sites and thus, increase the surface impedance and lower the diffusion rate. The inhibiting action of cathodic inhibitors works by three mechanisms:

- **Cathodic poisons:**

In this case, the cathodic reduction process is suppressed, for example, by impeding the hydrogen recombination and discharge. But it may increase the tendency of the metal to be susceptible to hydrogen induced cracking. Hydrogen may be absorbed onto the metal during this process. It is essential to keep hydrogen in atomic form. Typical types of cathodic poisons are arsenic and antimony.

- **Cathodic precipitates:**

Compounds such as calcium and magnesium will precipitate as oxides to form a protective layer which acts as a barrier on the metal surface.

- **Oxygen Inhibitors:**

This mechanism functions by the removal of oxygen from the system to reduce corrosion. The compounds of oxygen scavenger react with oxygen presenting the system to form a product.

1.3.1.5- Organic Inhibitors (10):

This type of inhibitors is too film-forming in nature. They form a hydrophobic layer on the surface of the metal to prevent dissolution of the metal.

The efficiency of this inhibitor depends upon the chemical composition and molecular structure of the inhibitor as well as their affinity with the metal. They are used often when environmental issues are taken into account. They are classified into organic anions and cations. Inhibitors like sulphonates and phosphonates fall into the anions category. Chemicals with active groups such as aliphatic, aromatic and positively charged amine groups are organic cations. This type of organic inhibitor is often in the form of liquid or wax-like.

1.3.1.6-Inorganic Inhibitors (11):

The common inorganic inhibitors used are crystalline salts, for instance, sodium chromate and molybdate. The only active groups of these compounds that function to reduce corrosion are the negative anions they carry.

1.3.1.7- Mixed Inhibitors (8):

Corrosion inhibitors are rarely used as a single compound only. The formulation can be composed of 2 or more inhibitors which all carry different characters. This is due to three factors:

- A single inhibitor can only inhibit few number of metals. When the environments involve multi-metal system, the inhibitive action may sometimes cause jeopardizing effect to other metals.
- Advantages from anodic and cathodic inhibitors can be combined and optimized for best performance.
- Addition of halide ions improves the action of organic inhibitor in acid solutions.

1.3.2-Effect of molecular structure on corrosion inhibition:

The inhibition attributable to the initial compound is called “primary inhibition” and that brought about by the reduction products “secondary inhibition” (12, 13). The inhibition efficiencies calculated for different homologous series of organic compounds have sometimes underlined the difficulty of attributing the variation in inhibition within a series of mono functional substances to a single molecular property such as electron density. It is necessary to know the possible steric effect including molecular size and mode of interaction, which may provide a screening action on the reaction center for the adsorption of the molecule at the metal surface (14). Complexation between the organic molecule and the metal and the stability constants of the resulting complexes were taken in consideration. Kinetic and equilibrium processes in organic chemistry have been found to an empirical equation p-proposed by Hammett (15) and discussed and extended by Jaffe (16) and Taft (17). The family of relationships thus, obtained is a form of linear free energy relationship usually designated as the Hammett relation and is given by,

$$\text{Log } k / k_o \text{ or Log } K / K_o \ \rho\sigma \qquad (1.13)$$

where, k's = rate constants, or K's = equilibrium constants. The zero subscripts, refer to compounds = reaction constant and σ = substitution constant. By setting the reaction constant equal unity, for the substituted benzoic acid, the reaction can be further simplified to yield

$$\text{Log } k / k_o = (pk_o - pk) = \log K / K_o = \sigma \qquad (1.14)$$

This equation is then taken as the definition of the subsistent constant σ i.e. a subsistent is given a numerical value, which its effect is dependent on the pk of the substituted benzoic acid compared to benzoic acid. From this definition, hydrogen has σ of zero. Subsistent which increase ionization (i.e. weaken the O-H bond) have negative value. Therefore, σ is a measure of the electron density or distribution on an atom. This measure of the electron density or distribution at a specific atom in the molecule is justified on the basis of quantum-mechanical calculations of electron charge density of individual atom within a molecular orbital structure (18). Steric effects have not been considered since Hammett correlated only meta and para subsistent and aliphatic systems caused Tafel to develop σ scale. In general, this leads to rate or equilibrium equations, which are due to polar effects resulting from structural changes.

A comprehensive approach to corrosion inhibition was suggested by Fouda (19). according to this approach, metallic corrosion inhibition depends not only on the polar effect or the electron charge density of functional groups or adsorption active centers in the molecule, but also, on the molecular size of inhibitor, its mode of adsorption on the metal surface, its heat of hydrogenation, and its ability to form insoluble metallic complexes that can be incorporated in the oxide layer; thus, reinforcing it or soluble ones that enhance dissolution.

Review of Literature

1.4- Corrosion Behavior of Nickel in Aqueous solutions:-

Nickel and nickel alloys are important materials for the design vessels in different industrial processes. Nickel electrode is also used in different energy-producing cells in which aqueous or non-aqueous solutions are used as electrolytes. Nickel and it is alloys exhibit excellent corrosion resistance in aqueous corrosive environments, which are attributed to the ability of nickel to form stable passive film on its surface (20). Choice of Ni species is due to that Ni has electronic configuration $[Ar_{18}]$, $3d^8$,$4s^2$ hence 10 electrons outside the argon configuration. The relatively low energy in “s” and “d” levels make Ni compounds have the oxidation numbers from [0-IV]. However the most important one is II (21). Nickel occupies an intermediate position in the electrochemical series, so it is nobler than “Zinc” and “Iron” but less noble than “Tin”, “Lead” and “Copper” (22).

According to the potential- pH equilibrium Pourbaix′s (23) diagram, nickel would be stable in neutral and moderately alkaline solutions. The metal would be expected to dissolve as Ni^{2+} ions with the evolution of hydrogen, while in strong alkaline solutions, it would dissolve to form $[HNiO_2]^-$ ions. Anodic polarization curves of Ni obtained by potentiostatic, potentiokinitic or in earlier days by galvanostatic techniques have been reported by many workers; unfortunately a good agreement is not always found between data from different sources. The principle reasons for the discrepancies appear to lie in the nature and amount of impurities in the metal (24, 25) or in the solution (26), both of which may have a profound effect on the shape of the curves, and in the variation in experimental procedures (27-30).

The Pourbaix diagram (potential-pH diagram) for nickel at 25 - 300 °C was studied (21). Extrapolation of thermodynamic data to elevated temperature have been performed with the revised model of Helgeson-Kirkhom flowers, which also allows unchanged aqueous complexes, such as $Ni(OH)_2$ to be handled. At high temperature, thermodynamic data have been checked and fitted against experimental data at elevated temperature. The stable solid compounds if nickel are [NiH, β-Ni $(OH)_2$/NiO and higher oxides (β and γ phases)].

A theoretical impedance function for the anodic dissolution of nickel was studied (31). It is developed by considering the hypothesis that there are two competitive anions which participate in the stabilization of the electro generated Ni(II) species.

The experimental effect of chloride ions concentration on nickel electro-dissolution process is analyzed by means of a mechanism that considers this competency. It is observed that increase of Cl^- concentration causes an increase in Ni(I) surface concentration and decrease in kinetic constant rates of the considered mechanism. An increase in chloride concentration causes a flattening in low frequencies inductive loop in the Nyquist plot recorder at low potential. In active anodic dissolution/ passive transition potential range chloride ions favors a salt layer precipitation which interferes with passive layer formation.

Kamel et. al.,(32) studied the behavior of nickel amalgams of varying composition in NaOH solutions of different concentrations by galvanostatic technique. Two different oxidation patterns were distinguished. The first shows the behavior of concentrated nickel amalgams and the second the behavior of dilute nickel amalgams in NaOH solutions. The anodic curve for the concentrated amalgams showed regions for the charging of the anodic double layer, then oxidation of nickel and mercury, then oxygen evolution. NiO is first formed which is oxidized to Ni_3O_4, then to Ni_2O_3. For dilute amalgams the oxidation curves showed only one arrest corresponding to the system NiO/Ni_3O_4 before oxygen evolution. The relation between the polarizing current and the time of passivation was found to fit the equation:

$$\log t = A - n \log i \qquad (1.15)$$

where, A and n are constants. With cathodically pretreated electrodes the oxidation curves showed regions for the dissolution of the sodium amalgam formed during precathodization, the charging of the anode double layer and a prolonged indefinite arrest at the potential corresponding to the reaction:

$$3Ni + H_2O \rightarrow Ni_3O_4 + 2H^+ + 2e^- \qquad (1.16)$$

1.4.1- Corrosion Behavior of Nickel in Acidic Solutions:-

The passivation of nickel in acidic solutions is a feature not predicted by the potential-pH equilibrium diagram (22,23) and is one of the reasons why in practice the corrosion of the metal in acidic solutions is better than that indicated from consideration of the thermodynamic equilibria (22,23). A second and perhaps the more important reason lies in the fact that in the active region, the anodic polarization of Ni in acidic solutions is considerably greater than that of the most of other metals. This together with the fact that in the electrochemical series, nickel is only moderately negative with respect to H^+/H_2 equilibrium which means that in practice the rate of dissolution of nickel in acidic solutions is slow in the absence of oxidants. The anodic dissolution current density of nickel, in the active state, as a function of potential dose, however, depends on the rate at which the measurements are made (33 , 27) and on pH of the solution (27).

The study and inter-penetration of anodic behavior of nickel, which is fundamental to the understanding of corrosion processes, has been the subject of numerous publications (34-40). It has been suggested that the passive film formed on the nickel electrode in dilute H_2SO_4 solution is $Ni(OH)_2$, NiO, NiOOH or NiOH intermediates.

The dissolution of nickel in sulfuric acid solution using electrochemical quartz crystal microbalance was studied. The anodic polarization curve of electrodeposited nickel shows distinct three dissolution regions. i.e. two active dissolution regions at low anodic over voltage and the trans-passive dissolution region at high anodic over-voltages. The transient current indicates that the final products in the two active dissolution regions are almost Ni(II) and that the Ni(II) dissolution ratio to the total anodic charge in trans-passive dissolution region is smaller than that in the two active dissolution regions (41).

Kish et.al., (42) studied the corrosion of nickel in sulfuric acid solutions by using electrochemical techniques, complemented by weight change and X-ray spectroscopic measurements. It was found that, corrosion is a mass- transport controlled process with the convective diffusion of nickel cations from saturated $NiSO_4$ layer as a rate determing step. The oxidizing nature of acid solution leads to the formation of additional corrosion products including meta stable NiS and elemental sulfur along with $NiSO_4$ when present on the surface. NiS establishes a galvanic interaction with the uncovered metal, significantly polarizing the anodic metal dissolution reaction. Since corrosion is mass transport controlled, the resultant corrosion rate of metal is unaffected during the galvanic-induced polarization.

Cheng et.al., (43) studied the corrosion behavior and dissolution mechanisms of nickel in H_2SO_4 solutions with H_2S by using potentiostatic and galvanostatic techniques. Results show that, at lower anodic polarization range, the anodic current of nickel electrode with three dimential sulphide layer on it is surface was lower than that of the electrode without sulphide layer in solutions of H_2S. This is attributed to the corrosion-hindering effect of sulphide layer formed in the lower polarization potential increased into the higher polarization potential range, however, no obvious hindering effect of nickel sulphide layer on the anodic dissolution of nickel could be observed.

Zucchi et.al., (44) used the application of electrochemical quartz crystal microbalance to study the metal corrosion and its inhibition. Among the advantages of this techniques are, it is very highly sensitive and the possibility of simultaneous mass variation and voltammogram recording. These characteristics support the use of (electrochemical quartz crystal microbalance) for research in very low corrosion rate conditions. They reported the results of (electrochemical quartz crystal microbalance) measurements on the corrosion inhibition rates of Ni on 0.1M $HClO_4$ in absence and presence of inhibitors in free corrosion conditions.

Masaheda Iida et.al., (45) studied the nickel passive film in acidic sulfate solutions at pH 2.3 and 3.3 by ellipsometry. During anodic passivation followed by cathodic reduction, the roughness increase with dissolution of nickel being indicated by gradual decrease of reflectance.

Abd El Rehim et.al., (46) studied the electrochemical behavior of nickel in H_2SO_4 and HCl solutions of various concentrations by means of the potentiodynamic method. They found that in presence of very dilute solutions, the low anodic current is controlled by the presence of pre-existing film, while at higher concentrations, the passive film is removed and dissolution occurs. In H_2SO_4 solutions, pseudo-passivity, primary passivity, trans-passivity and secondary passivity are observed prior to oxygen evolution. In all these regions, the rate of dissolution increases with the acid concentration. In HCl solutions, the anodic polarization curves exhibit a current peak followed by a passivation region; the latter may not involve complete passivity. In the passive region, local attack in the form of pitting occurs. In both acid dissolution, the cathodic and anodic polarization curves satisfy Tafel's relation.

Stupnisek and Karsulin (47) studied the electrochemical behavior of nickel in a wide range of different concentrations of nitric acid by potentiostatic, potentiodynamic and weight loss measurements. The data of the potentiostatic-current potential curves were classified into three categories, according to the proportion of the nitric acid concentration. An increase of nitric acid concentration increases the influence of the cathodic reaction in the systems. The importance of cathodic reaction was investigated by eliminating HNO_2 by addition of p-nitro-aniline in the electrolyte. The coulostatic polarization has given distinct repassivation curves, indicating an intermediate state of nickel electrode between the active and passive states. In the first part of repassivating process, the potential value is more positive than the stationary potential of spontaneous passivation of nickel electrode in concentrated nitric acid. The return to the stationary potential of the passivity is a slow, time dependent process. According to the experimental result, it may be possible that in the beginning of the passivation process on nickel, $Ni(NO_3)_2.4H_2O$ forms which changes to NiO_2.

Abd El Haleem et.al., (48) studied the corrosion and passivity of nickel in nitric acid solutions, using the thermometric technique supported by weight loss and polarization measurements. It was found that, as the concentration of HNO_3 is increased from 2 to 9.4 M, the corrosion rate increased. This is indicated from thermometric measurements, the increase in the maximum temperature attained, T_{max} and the decrease in the time required to reach T_{max}. Dissolution of Ni in HNO_3 is proposed to take place according to an autocatalytic mechanism. Passivation sets in solution more than 9.4 M HNO_3. A parallel indication is obtained from weight loss measurements. That HNO_2 is involved in the autocatalytic cycle of Ni dissolution is shown by the results of addition of mono-methyl amine, hydrazine and urea to 6 M HNO_3. These compounds inhibit the metal dissolution due to adsorption and / or destruction of HNO_2 .The effect of varying concentrations of NaCl, HCl, Na_2SO_4 and $NaNO_3$ on the reaction number, (RN), of Ni in 6 M HNO_3, was examined. These additives inhibit dissolution due to the displacement of some cathodic depolarizing components, as NO_2, from the active sites on the metal surface. Addition of Cl^- ion to HNO_3 solutions in which Ni is passive causes the breakdown of passivity and the initiation and propagation of pitting corrosion.

1.4.2-Corrosion Behavior of Nickel in Neutral Solutions:-

The behavior of nickel in neutral solutions is of paramount importance from the practical point of view. The electrode behaviors of nickel in Ni^{2+} containing solutions have been repeatedly examined in connection with the problem of activity of nickel anode in nickel plating baths (49-57).

Mac Dougall et.al., (58) studied the oxide films formed on nickel in pH 7.65 borate solutions in both the passive potential and oxygen evolution regions which were analyzed by X-ray measurements. In the passive potential region, a highly epitaxed, single crystal NiO film is formed with a limiting thickness of ~12 A^0. In this potential range, even very long times of anodization do not alter the oxide epitaxy or increase its thickness. In contrast, polarization in the potential range where oxygen is evolved results in the development of considerable oxide misorientation and a significant increase in oxide thickness. While long times of polarization (>20hr) in this potential region produce oxide films hundreds of angstroms thick, the current efficiency for oxide growth is <1%. These thick anodic oxide films are quite different from those thermally prepared.

The mechanism of passive film formation in 0.15N Na_2SO_4 was studied using electrochemical polarization techniques (59). It was found that the passive film formed for nickel in 0.15N Na_2SO_4 (pH=4.0-12.0) is $Ni(OH)_2$. It is suggested that the film formed via a precipitation mechanism in the acid solutions subsequent to active metal dissolution. At low values of pH, this precipitated film, once formed, generally does not change in thickness as the potential is made increasingly anodic. Conversely, the $Ni(OH)_2$ film formed in higher pH solutions (pH=8.0 open, pH =12.0 open and de-aerated) grows by virtue of a solid state mechanism. Both NiO and NiOOH are observed to form subsequent to $Ni(OH)_2$ but only at higher values of pH. Although the films formed at alkaline pH values are thinner than those in the lower pH environments, they were found to be more protective.

Chao et.al., (60) studied the passivity of nickel over a wide range of pH (1.5-12.6) in Na_2HPO_4 solutions by polarization techniques. The results showed that solution pH had a strong effect on the formation and the growth of the passive films. In basic solutions (pH 9.1- and 12.6) and in moderately acidic solution (pH 4.5), the passive film exhibits different growth behaviors. The film formed in the basic solutions dose not grow, but the film formed in pH 4.5 solution increases in thickness with time. In an acidic solution of pH 1.5, the passive film is composed of two layers: a base layer of partially dehydrated $Ni(OH)_2$, and an upper potential-dependent film. The two- layer film evolves with time.

Differential reflectometry in conjunction with electron spectroscopy for chemical analysis techniques are used to identify various surface films which formed electrochemically on nickel in $0.15NNa_2SO_4$ electrolyte (61). The film observed on Ni in a $0.15NNa_2SO_4$ electrolyte has been identified to be $Ni(OH)_2$. At different values of pH and potential, NiO has been found to form simultaneously with $Ni(OH)_2$. At solutions with pH >8, the $Ni(OH)_2$ film partially transforms into a third oxide, presumably NiOOH, which can only be observed.

Abd-El- Kader and Shams El-Din (62) studied the variation of open circuit potential of nickel in strongly aerated solutions of different concentrations of a large number of neutral anions. The steady state potentials were approached from negative values denoting film repair and thickening except in relatively concentrated Cl^- media, no Ni^{2+} ion detected in solutions. The plot the electrode potential (E) of Ni and logarithm of immersion time (t), are linear satisfying the straight line relation ship:-

$$E=a_1+ b_1\log t \qquad (1.17)$$

where, a_1 and b_1 are constants. This equation was derived theoretically taking into account the conducting properties of NiO and assuming that the adsorption of anion on the oxide film generates the electric field necessary to promote the diffusion of Ni^{2+} ions through the oxide. The rates of oxide thickness in the presence of different concentrations of the various anions were computed and the expression are deduced relating the steady state potential variation with the logarithm of the molar concentration of various anions according to the relation:-

$$E_{st} = a_2 - b_2 \log C \qquad (1.18)$$

This relation is reached from consideration of the structure of double layer and effects produced there on when the anions are specifically adsorbed on surface of the electrode.

1.4.3-Corrosion Behavior of Nickel in Alkaline Solutions:-

The anodic oxidation of nickel in alkaline solutions has been the subject of many studies connected in particular to the reactions that take place in the nickel- alkaline battery (63, 64). There is a clear evidence that nickel in contact with aqueous alkali hydroxide solutions is spontaneously covered by a layer of $Ni(OH)_2$. The study of the electrochemical behavior of nickel in that medium indicates that it behaves like a hydrated nickel hydroxide electrode. This sort of electrode is widely used in different batteries (65-70).

Armstrong et.al., (71) studied the passivation of nickel in alkaline solutions by using galvanostatic measurements. They suggested that, the passivation of nickel is due to formation of a monolayer of $Ni(OH)_2$. This layer is probably formed by a solid state process involving nucleation and growth.

Wolf et.al; (72) studied the growth kinetics of thin anodic oxide films at nickel electrodes in 0.1N KOH solutions at room temperature under potentiodynamic and galvanostatic conditions. At electrodes that have been mechanically polished and cathodically reduced, growth of the lower oxidation state phase β-$Ni(OH)_2$, follows under both experimental conditions. The potential at which β-$Ni(OH)_2$ begins to grow,V_0 = -0.39Vvs(SHE), is identified as the reversible potential of the phase. It is, however, 270 mV positive than the reversible potential listed in literature for $Ni(OH)_2$ formation in solutions of the same pH. It is suggested that the observed reversible potential refers to the β-$Ni(OH)_2$ phase. The exchange current density for the oxide film growth is $2.3x10^6$ Acm^{-2}. The activation energy for the growth of the β-$Ni(OH)_2$ phase is 21Kcal/mole.

Bohe et.al., (73) studied the electrochemical behavior of nickel in 0.5M K_2CO_3. They used simple and combined potentiodynamic techniques in potential regions of the $Ni(OH)_2$/Ni and Ni(III) /Ni(II) redox couples. The diffusion controlled hydrated $NiCO_3$ precipitation interferes with the electro-formation of the $Ni(OH)_2$ pre-passive layer. Both anodic and cathodic peaks multiplicities are observed in the potential rang of the Ni(III)/Ni(II) electrode. The presence of CO_3^{2-} ions are associated with a change in the hydration of composition $Ni(OH)_2$ layers with HCO_3^- ions coming out from the CO_3^{2-}/HCO_3^- equilibrium, which depend on the local change in pH produced during the corresponding anodic and cathodic reactions.

Grden et.al., (74) examined two kinds of metallic nickel electrodes [freshly deposited and subjected one] in basic solutions from potential negative of -500mV to potential positive vs. (S.C.E) and reverse. The irreversible phase transition between various forms of Ni(II) compounds takes place. Oxidation of fresh Ni electrode is accompanied by mass increase smaller than that expected for proposed production of Ni oxidation $Ni(OH)_2$ and NiO. Adsorbed species, i.e. H_2O/OH^-_{ads} participate in generation of Ni(II) compounds .Obtained result indicates the existence of bulk hydrogen adsorption in fresh Ni electrode at sufficiently negative potentials.

Desouza et.al., (75) studied the oxidation of nickel in alkaline solutions using spectroscopic ellipsometry and cyclic voltammetry. Electrode surface films were formed by air exposure and by electrochemical oxidation at various potentials during the first voltammetric scan. Using a self-compensating ellipsometer and a previously developed data fitting program, it was found that oxide layers formed during the polishing of nickel in air have a significant optical effect and normal polishing conditions can produce NiO of 10A° thickness. During the positive-going sweep at potentials between-0.9V and –0.4V vs. (Hg/HgO), a compact film of β-$Ni(OH)_2$ is formed. The surface layer that appears after the second anodic peak at +0.5V contains a mixture of $Ni(OH)_2$ and NiOOH with an over layer of β-NiOOH. This over layer is completely reduced after the cathodic peak, at +0.2V, is reached during the negative-going sweep, and the layer remaining at this potential consists of a mixture of $Ni(OH)_2$ and NiOOH. At very cathodic potential (-0.9V) NiOOH is still found on the electrode surface, and some electrode roughness appears. During a potentiostatic hold at this potential, NiOOH is reduced to $Ni(OH)_2$, which is very slowly reduced to Ni with a decrease in electrode roughness.

Alkaine et.al., (76) investigated the passivating films at the Ni(II) potential region in alkaline solutions, qualitatively by voltammetry. One anodic (a_1) and two cathodic (c_1 and c_2) peaks were observed. It is shown that the peak at more negative potential (c_1) corresponds to the reduction of a film formed previously during preparation of the electrode. Peaks (a_1 and c_2) correspond to the same films, which is attributed to NiO. As a consequence, the presence of the passivating film increases the hydrogen over potential. The total cathodic charge densities have been always found to be smaller than the anodic one. And Ni anodic film growth quantitatively (77).

1.4.4-Pitting Corrosion of Nickel:-

Pitting corrosion is observed most frequently in chloride containing solutions although other ions are also known to act as pitting agents. For a given metal, the value of critical potential above which pitting is observed, depends on the ratio of “aggressive” to “non-aggressive” ions (78). Pitting corrosion is observed most frequently in chloride containing solutions like (1N $NaClO_2$, 1N NaCl and mixtures of the two electrolytes). The presence of chloride ions led to pitting and also to an increase in anodic dissolution rate. Apparent current efficiencies based on divalent nickel formation even exceed 100 percent (79).

Strehblow et.al., (80) examined the potential range in which passive metals show pitting by different aggressive anions. For the most metals, pitting potential (E_{pit}) was found below which pitting corrosion did not occur. Further more, inhibition potential (E_{inh}) was found in presence of inhibitors which no pitting could be observed. The pitting potential (E_{pit}) and inhibition potential (E_{inh}) values depend on the concentration of aggressive anions (C_{agg}) and the inhibitor (C_{inh}) according to following equations:-

$$E_{pit} = a_3-b_3\log C_{agg} \qquad (1.19)$$

$$E_{inh} = a_4+b_4\log C_{inh} \qquad (1.20)$$

For the inhibition potential, large values of (b) were observed. The critical potentials determined by galvanostatic and potentiostatic measurements were explained by the adsorption of aggressive anions on the metal surface and their competition with the inhibitor. These critical potentials depend on the logarithm of concentration of aggressive anions and inhibitors.

Abd El Aal (81) investigated the effect of Cl^-, Br^- and I^- anions as aggressive agents on the anodic behavior of the nickel electrode in $Na_2B_4O_7$ solutions by using galvanostatic polarization technique. At low concentrations of aggressive anions there is no effect on the mechanism of nickel passivation, but high aggressive anions concentrations cause break down of passive film and initiated pitting corrosion. As the temperature increases, the breakdown potential is shifted towards the more negative direction. On the other hand, as pH of solution increases, the breakdown potential is shifted toward more positive direction, including increased protection of the passive film.

Mac Dougall et.al., (82) used the galvanostatic anodic charging technique to study the pitting of nickel in acid and neutral Na_2SO_4 solutions containing various concentrations of Cl^-. Pit initiation is indicated by a change in potential in the cathodic direction. This potential being substantially higher than that required to sustain pitting. The steady state potentials are in the passive rather in the active potential region, a result that can be explained by the highly localized nature of the pitting process. Increasing the $[Cl^-]$ lowers the potential for pit initiation. The influence of anodic charging rate on pit initiation depends on the $[Cl^-]$ in solution. At high $[Cl^-]$, the charging curves are similar expect for the potential shift with anodic charging rate, while at low $[Cl^-]$ pit initiation is more difficult. The minimum $[Cl^-]$ required for pit initiation of pitting corrosion increases with decreasing solution temperature. The potential for pit initiation tends to be higher at lower solution temperature and/ or at higher pH. The [Cl^-], anodic charging rate, solution temperature and pH influence pit initiation by affecting the efficiency of oxide repair at local break down sites in the passive oxide film.

Nishimura (83) studied the pitting corrosion of nickel covered with films formed potentiostatically at various potentials in borate and phosphate solutions at pH 8.42 and pH 11.50 in NaCl solutions at a constant potential of 0.395 V (SHE) higher than the critical pitting potential of 0.295 V in the same solution. The time t, obtained from the logarithm plots for pitting current (i_p) or amount of electric charge passed (Q_p) vs. time curves was found to be the transition time from pit nucleation to pit growth. The transition time value was a linear function of potential in the passive region and showed a rapid increase at potential in the secondary passive region, irrespective of anion species and solution pH in which the film was formed. From the linear relationship between transition time and total film thickness in the passive region, it was proposed that the passive film formed in solutions consists of two layers: an outer layer of $Ni(OH)_2$ and an inner layer of NiO. Thereby, the pit nucleation time was assumed to be the period that continues until the inner layer is perforated by attack of Cl^- ion.

1.4.5-The Corrosion-Inhibition of Nickel:-

Inhibition means, the reduce of the corrosion process. The use of inhibitors to protect metals against corrosion is based on the ability of certain individual chemical compounds or mixtures of them to reduce the rate of corrosion process or to completely suppress it when they are added in small amounts to corrosive medium. Addition of certain inhibiting compound to corrosive solutions greatly diminishes their aggressiveness to metals. The result obtained by separate inorganic inhibitors and organic inhibitors, the action mechanisms are quite different.

1-Dodecylpyrrole (Pych3) and 12-(pyrrol-1-yl) dodecane-1-thiol(pysh) films have been electrochemically polymerized on nickel electrode from acetonitrile solutions containing the monomer and lithium per chlorate as supporting electrolyte. The electrochemical study of the polymer growth has been carried out by cyclic voltammetry detecting the nickel dissolution during electro-polymerization. Furthermore, N-substituted pyrrole derivatives exhibited some corrosion protection properties for nickel in neutral NaCl solution (84).

Muñoz et.al., (85) studied the influence of [NO_2^-] on the corrosion of Ni in acid phosphate solution by means of potentiodynamic scans and impedance spectroscopy under electrode rotation. The adsorption of NO_2^- near corrosion potential has several consequences: (i) it brings about a lower surface coverage of NiOH decreasing rate of Ni active dissolution. ii) Its preferential adsorption against that of passivating species, such as NiOH and $Ni(OH)_2$ hinders the formation of the pre-passive layer at pH-values increasing the passivation current.

Zucchi et.al., (44) investigated the corrosion inhibition of nickel in 0.1M$HClO_4$ in absence and presence of different inhibitors: acridine, benzyl quinolinium chloride, dodecyl quinolinium bromide, tri-butyl ammonium iodide and potassium iodide using application of the electrochemical quartz crystal microbalance . The corrosion rate reduced considerably by potassium iodide and tri-butyl ammonium iodide. Dodecyl quinolinium bromide showed a good inhibition, while benzyl quinolinium chloride had only a small effect in the surface of Ni electrode.

The aqueous extract of the leaves of henna (lawsonia) was tested as corrosion inhibitor for nickel in acidic, neutral and alkaline solutions using galvanostatic polarization technique (86). It was found that the extract acts as a good corrosion inhibitor in all tested media. The order of inhibition efficiency increases as the added concentration of the extract is increased. The order of inhibition efficiency depends on the type of medium and increases in the order:

alkaline < neutral < acid.

The extract act as mixed inhibitor, and the inhibitive action of the extract is discussed in view of adsorption of lowsonia molecules on the metal surface. The adsorption process follows Langmuir adsorption isotherm.

The effect of aprotic solvent additive on the anodic behavior of nickel in aqueous sodium chloride solution is studied (87). A three parameter equation correlating the physicochemical properties of the medium (conductivity, polarity and polarizability) with the electrochemical dissolution rate of the metal is formulated. A substantial rate of conductivity agrees with the diffusion control of the processes under investigation.

The corrosion inhibition of nickel in acidic medium by phenformine hydrochloride was studied (88). This compound inhibits the dissolution process due to the adsorption of the organic cation on the metal surface, although it dose not protect the metal from pitting corrosion. Electrochemical impedance spectroscopy data allowed the proposal of physical model for the role of chloride ion in the dissolution and passivation processes of nickel electrodes.

Mun□oz et.al., (89) studied the inhibition efficiencies of nitrite for the corrosion of nickel in acidic phosphate solution using atomic force microscopy and interpreted in light of electrochemical responses. At low nitrite concentrations, the competition of absorbed species leads to the appearance of rough surface with protrusions, cavities and cathodic reaction regions. With increasing nitrite concentration, N-species adsorb displacing passivating species.

The role of iron deposits on the surface of nickel electrodes with respect to electrode activity during alkaline water electrolysis was studied (90). Nickel electrodes were sputtered with a smooth iron layer to determine the effect of metallic iron on the electrode surface without significantly changing the electrode surface area. The iron coating prevents the surface phase from forming and hence prevents deactivation of the electrode.

The inhibition of Ni electrodissolution in H_2SO_4 solutions containing carbon monoxide, ethylene or acetylene after adsorption equilibrium at room temperature was studied (91). The interaction of these molecules with Ni was followed by the anodic stripping of adsorbed residues. The Ni electro-dissolution inhibitory effect caused by the different adsorbates increases in the following order:

ethylene <carbon monoxide < acetylene.

The corrosion of nickel in acetic acid solutions was studied using polarization measurements at 30 °C (92). The polarization curves for nickel showed active-passive and trans-passive behavior in the entire compounds range of water-acetic acid solutions. Anodic dissolution of nickel in acetic acid solutions is markedly decreased with an increase in the acid concentration. In order to prevent the corrosion of nickel in acetic acid solutions (20 mol %) some organo-tin compounds; di-butyl-tin-dichloride , phenyl-tin-trichloride, di-phenyl-tin-dichloride and tri-phenyl-tin-chloride were used as inhibitors and their inhibition efficiency and surface coverage were evaluated. Tri-phenyl-tin chloride gave the highest inhibition efficiency and all inhibitors are held on the surface most probably by physical adsorption.

Frignani et. al., (93) studied the inhibition of nickel corrosion by means of 3-methyl-1-butyne-3-ol(H), its halo-derivatives, and 1-octyn-3-ol using solution analysis polarization technique and electrochemical impedance spectroscopy in deaerated 1N HCl or H_2SO_4 solutions at 70 °C. It has been found that the inhibiting effects of the additives tested are similar to those determined in the case of iron-acid corrosion. It is assumed that on both metals the inhibitors form polymeric films by the same mechanism. These compounds are more efficient than (H), but the efficiency of the latter can be improved by replacing the acetylenic hydrogen atom with halogen atoms, chiefly iodine, which provides higher inhibition of the anodic reaction.

The effect of some mono-substituted phenyl N-phenylcarbamates derivatives as corrosion inhibitor for nickel in 1M/perchloric acid using galvanostatic polarization was investigated (94). The inhibition appears to function through general adsorption isotherm. However, galvanostatic polarization data show that in the case of all inhibitors used both anode and cathode are polarized under the influence of an external current. Electrocapillary measurements have also revealed that the tendency of the inhibitors tested to adsorb on metallic surface follows the same order of efficiency.

The corrosion inhibition of nickel in acid solution by 2-(triphenyl phosphoranlidene) succinic anhydride, using polarization technique was studied (95). The percentage inhibition was up to 85 percent at a concentration 400µM 2-(triphenyl phosphoranlidene) succinic anhydride. The inhibitor used was found to shift the corrosion potential to less negative values and to decrease the anodic dissolution of nickel and hydrogen evolution. The effect, however, was more pronounced on the anodic rather than on the cathodic process. The passivation current density (i_p) and the capacitance of the double layer (c_d) were also affected by 2-(triphenyl phosphoranlidene) succinic anhydride. Experimental findings reported show that at the critical concentration of 25 µM of (triphenyl phosphoranlidene) succinic anhydride, these parameters attain their lowest values and that subsequent increase of inhibitor concentration does not lead to any significative change of either i_p or c_d.

Mac Donald et.al., (96) studied the localized corrosion of nickel metal in aqueous media and showed that it can be inhibited by illumination with electromagnetic radiation. Irridation of nickel in a chloride-containing borate buffer solution of pH 9.2 with white light yielded a pitting potential 34±8 mV more positive than in the dark. A similar anodic shift in pitting potential was found for nickel alloy in the same medium and under the same conditions of illumination. The number of pits initiated under illumination for the same observation time was reduced by a factor 3±1 for both materials. The effect of light on passivity breakdown was explained in terms of point defect model for the growth and breakdown of anodic films. The point defect model predicted that, if the electric field could be suppressed by a factor >85, practically useful photo-inhibition of the nucleation of localized corrosion on nickel and alloy might be realized.

The corrosion inhibition characteristics of organic heterocyclic compounds like, pyridine, pyrole, furan and thiophene during acid corrosion of nickel have been investigated (97). It has been found that, the results can not be explained only on the basis of their structural parameters like aromaticities, charge densities on the heteroatoms, ionization potential, basicities, and the simple chemisorptions mechanism. Rather protonation of the heterocyclic ring and subsequent chemical transformation into some other species determine the route of inhibition mechanism in some cases. Pyridine, pyrole and furan were found to inhibit the acid corrosion of nickel whereas thiophene catalyzed the dissolution process. Pyrole in acid solution was found to form polymeric product which effectively protects the metal surface while thiophone was found to be decomposed into sulphide leading to higher dissolution of nickel.

Abdallah. et. al.,(98) studied the inhibition of nickel electrode in 1.0 M H_2SO_4 using non-ionic surfactant, namely, tween 20, 40, 60 and 80 where, weight loss, potentiostatic polarization and cyclic voltammetry techniques were used in this study. It was found that all the used four compounds act as good inhibitors for acid corrosion of nickel. The inhibition efficiencies obtained by the three techniques were almost the same, and increase with increasing the hydrocarbon chain length, the presence of a double bond in the chemical structure of the surfactant and with increasing the surfactant concentration. The polarization studies show that the tween compounds act as mixed inhibitors. The inhibition action of these surfactants is interpreted in view of their adsorption on the metal surface making a barrier to mass and charge transfer. It was found that the adsorption of only tween 20, and 40 follows Langmuir adsorption isotherm. The cyclic voltammetry shows that there is only one anodic peak corresponding to the dissolution peak and was used also for corrosion rate measurements and in evaluation of inhibition efficiencies of the used compound.

In the line of conducting polymer on oxidizable metal, electropolmerization of 3.4- ethylene- dioxythiophene was performed in ammonium oxalate aqueous solution on nickel (99). The advantageous effect of the oxalate ions on the electro-polymerization process as well as on the physical characteristics of the resulting polymer film has been evidenced. Among these properties, adhesion has been drastically improved. Hybride nanowires nickel/ 3.4-ethylene-dioxythiophene have been elaborated to highlight the nickel-3.4-ethylene- dioxythiophene adhesion. The protective effect of the 3.4- ethylene- dioxythiophene film against corrosion in NaCl is nevertheless very slight.