CHAPTER 1
INTRODUCTION

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A) Historical background

In the early stages of human civilization, man preserved himself in a hostile environment by functioning as a bioelectrochemical machine, converting the solar energy stored in food via electrochemical reactions into muscle power. But recently man has linked himself more and more with machines that harness nuclear energy and the solar energy stored in coal and oil and has thereby satisfied has needs with increasing efficiency. Thus, an increasing use of machine power and a decreasing use of muscle power has marked the progress of civilization. After that the trend is clearly that man makes minimal use of his own biochemical energy converters and turns to insentient machines to effect the conversion of energy into convenient forms. Man is bound to lean increasingly on computerized mechanisms programmed to make energy derived from atomic fission and fusion reactions in the form of electricity do the work which he wants.

To make this vision a reality, the machines that do man's bidding and thus become the basis of the material aspects of civilization must be able to function without decay over years in the terrestrial atmosphere. Materials, mainly metals, used in fabrication must be stable. If the metals become unstable, then the machines fabricated partly from these metals undergo an undesired obsolescence. An industrial civilization depends in a crucial way upon the stability of metals in its moist (and often impurity-containing) atmospheres.

It is an interesting fact that a pieces of metal remains stable for an almost indefinite period of time provided that it is stored in vacuum. It appears that metals acquire stability when their surfaces are isolated from the normal terrestrial environment.

If this isolation is not achieved, metals become unstable in various ways. They develop cracks and break upon strain with catastrophic suddenness. They suffer fatigue, i.e., loss of strength when subjected to periodic stress. They undergo a process of embitterment. Their surfaces are transformed into oxides, which

peel off, or they just dissolve away. With the exception of the (hence) expensive noble metals, all metals are unstable to varying degrees in a terrestrial atmosphere. The most widely used metals, namely, iron, aluminum, copper, nickel, and alloys of these metals, all decay and lose good mechanical properties in unprotected contact with air.

One conclusion is obvious: the stability of metals is determined by the events at the interface between these metals and their environment. The internal strength of a metal (particularly a metal under stress) is influenced in the long run by happenings at its surface. If the surface of a metal is stable, its interior tends to remain so. The detrimental transformation of the bulk properties of a metal begins at its surface.

This, then, is a link between civilization, surfaces, and as will be seen electrochemical reactions.

B) General idea about corrosion process:

Corrosion of metals is defined as the spontaneous destruction of metals through their chemical, electrochemical or biochemical interaction with the environment[1-2].Corrosion is an undesirable and undeliberate process. The electrochemical dissolution of blister-copper anodes in copper-refining bath cannot be regarded as corrosion since it is a necessary and desirable link in the purification of copper. At the same time, the electrochemical dissolution of an iron anode in water electrolysis bath should be included in the category of corrosion processes since it is undesirable in this case. The erosion of the walls of iron tanks in which sulphuric acid which transported is considered corrosive destruction, whereas the dissolution of iron in sulphuric acid for the purpose of producing pure reactive iron sulphate is not regarded as corrosion, though both processes are based on the same phenomena.

Corrosion is spontaneous process occurring predominantly without application of an external current. This feature of corrosion is easy to understand considering that those metals (ferrous and nonferrous) are usually subject to corrosion which occur in nature as minerals or ores and not in the native state. The wining of these metals from ores minerals requires a certain amount of power. The same metals when corroded tend to revert to oxides, sulphides, carbonates and other compounds in which

they occur under natural conditions. Since the corrosion process results in the recovery of the original compounds, which are thermodynamically more stable than pure metals, it is accompanied by decrease in free energy and therefore proceeds spontaneously. Metals that occur in a native state (e.g. gold, platinum) usually do not corrode under conditions, which do not differ materially from those existing in nature. It is therefore not surprising that many metals are attacked rapidly, and losses due to corrosion sustained by all branches of the national economy are enormous. Five to twenty per cent of the ferrous metals produced annually are destroyed by corrosion. However great the direct loss due to corrosion, it cannot give an accurate idea of the actual damage caused by this process. Even a slight deterioration of a chemical apparatus by corrosion may put it out of service, upset and interrupt the technological process, lead to wastage of time and materials, etc. the associated expenses are much higher than the cost of replacement material. For example, the relatively low cost of an underground lead cable length destroyed by corrosion stands no comparison with the expenses on the work required to locate the damage, remove the ground and repair the cable.

The rate of corrosion is expressed by several ways. The first shows the weight loss (in grams or kilograms) per unit time (second, hour, day, year) referred to a unit area (square centimeter, square meter) of a test specimen. In the second case the corrosion rate is given in terms of current intensity (in amperes or mill amperes) per unit surface area of the specimen.

C) Types of corrosion

Corrosion can be classified in to three categories:

1-Chemical corrosion of metals is spontaneous destruction governed by the laws of ordinary heterogeneous reactions for examples: the destruction of metals which attack at high temperatures by aggressive gases which prevent condensation of moisture on the metal surface and also, the dissolution of metals in contact with nonconducting organic media.

2-Biochemical corrosion or biocorrosion is caused by the vital activity of various microorganisms using a metal as a culture medium or evolving products, which attack the metal. Biochemical corrosion usually accompanies other types of corrosion for example: soils of definite composition, stagnant

waters and certain organic products greatly favor the progress of biochemical corrosion.

3-Electrochemical corrosion is more frequently than other types of corrosion of metals and is most dangerous to metals. It may occur in a gas atmosphere, when moisture condenses on the metal surface (atmospheric corrosion), in soil (soil corrosion) and in solutions (liquid corrosion). Electrochemical corrosion is governed by the kinetics of electrochemical reactions. Its rate can be determined on the basis of Faraday's law.

A special case of electrochemical corrosion is electro corrosion, i.e., corrosion cause by an external electric current for examples: The corrosion of piplines with current-conducting liquids flowing through them, the dissolution of the walls of electrolytic baths, and underground metal structures under the influence of a direct current from bare electric lines (stray – current corrosion) where the stray currents may set up a potential difference between two portions of a metal structure, one receiving current from some external source of electrical energy (cathodic area)and other acting as the anode (anodic area), from which the current flows into the surrounding ionically conducting medium, the anodic portion being destroyed.

D)The mechanism of the corrosion of

ultrapure metals

On the basis of the local-cell theory, an ultrapure metal without impurity inclusions would be expected to be incorrodible. In general, the purer metal, the more stable it is in an aqueous environment. Wanger and Traud were suggested the basic mechanism for the instability of ultrapure metals in classic paper of 1938. the essence of their view is that, for corrosion to occur, the need not exist spatially separated electron-sink and source areas on there corroding metal. Hence, impurities or other heterogeneities on the surface are not essential for the occurrence of corrosion. The necessary and sufficient condition for corrosion is that the metal dissolution reaction and some electronation reaction proceed simultaneously at the metal-environment interface. For these two processes to take place simultaneously, it is necessary and sufficient that the potential difference across the interface be more positive than the equilibrium potential of the

$Mn^+ + ne = M$ reaction and more negative than the equilibrium potential of the electronation reaction $A + ne \rightarrow D$ involving electron acceptors contained in the electrolyte as shown in Fig. (1).
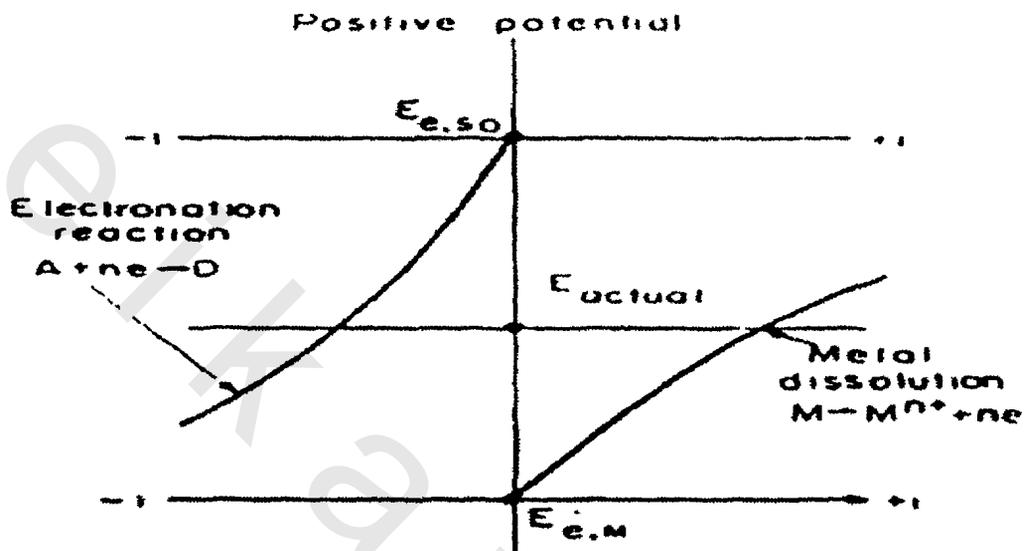

Fig.(1): Corrosion can occur always when the revisable potential of the metal dissolution is more negative than the actual potential of the metal and the potential of the electronation reactions is more positive.

Hence, the present view is a unified one. When the electron-sink and –source areas are distinct in space and stable in time, one has the local-cell, or heterogeneous, theory of corrosion as shown in Fig. (2a). On the other hand, when the metal-dissolution and electronation reactions occur randomly over the surface with regarded to both space and time, one has the Wangner-Traud. Homogeneous theory of corrosion as shown in Fig. (2b). The Wangner-Traud mechanism with its random and dynamic de-electronation and electronation sites requires a homogeneous metal surface. This is because heterogeneities tend to fix the de-electronation and electronation reactions to stable sink and source areas.

(a)   **(b)**

Corroding metal

Stable electron-sinks

Electrolyte

Homogeneous surface

Heterogeneous surface

Stable electron-sources

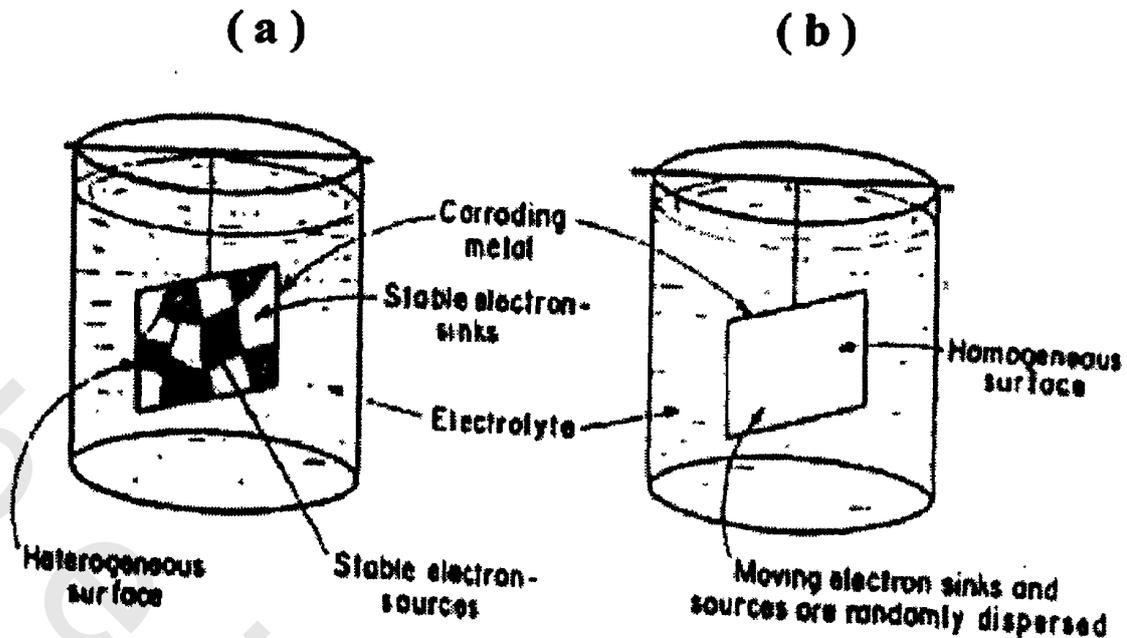Moving electron sinks and sources are randomly dispersed

Fig.(2): A metal can corrode (a) by a heterogynous mechanism if it contains areas of different electrodic properties or (b) by a homogenous one if the surface is uniform.

In some practical situations, however, there are heterogeneities of one type of another. Impurities are the most obvious type of heterogeneities but there are other type, e.g. different phases of an alloy, or metal with a no uniform stress distribution or with a no uniform access to electron acceptors. Thus, the local-cell, or heterogeneous, theory of corrosion has wide scope of applicability. The homogeneous theory of corrosion emphasizes that, irrespective of the presence or absence of impurities, metals become unstable because of different electrrodic charge-transfer reactions occurring simultaneously and in opposite directions at the surface.

E)Forms of corrosion:

1- Uniform attack

Uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction, which proceeds uniformly over the entire exposed surface [3]. The metals becomes thinner and eventually fails. In liquid, this form of corrosion involves an oxidation-reduction reaction. Anodic and cathodic areas keep shifting, so corrosion is spread more less

evently over the entire surface of the metal. This form of corrosion however, is not of too great concern from the technical stand point, because the life of equipment can be accurately estimated on the basis of comparatively simple tests. The usual solution to this problem involves the choice of more suitable materials inhibitors, protective coatings, or combinations of these expedients.

2- Galvanic or two – metal corrosion

When two dissimilar metals are in contact with each other and exposed to conductive solution, a potential is set up between these two metals and a current flow. Corrosion of the more resistant-material is decreased, the less-resistant metal becomes anodic and the more-resistant metal cathodic. This form of corrosion is called galvanic or two-metal corrosion.

Galvanic cells can form because of differences in the environment on the metal surface. These are called concentration cells. If is perfectly homogeneous and pure metal surface is exposed to an environment that is not identical at all points, anodic and cathodic areas may form and result in corrosion. The two most common galvanic cells are metal-ion cells and oxygen cells. This type is a shown in Fig. (3)
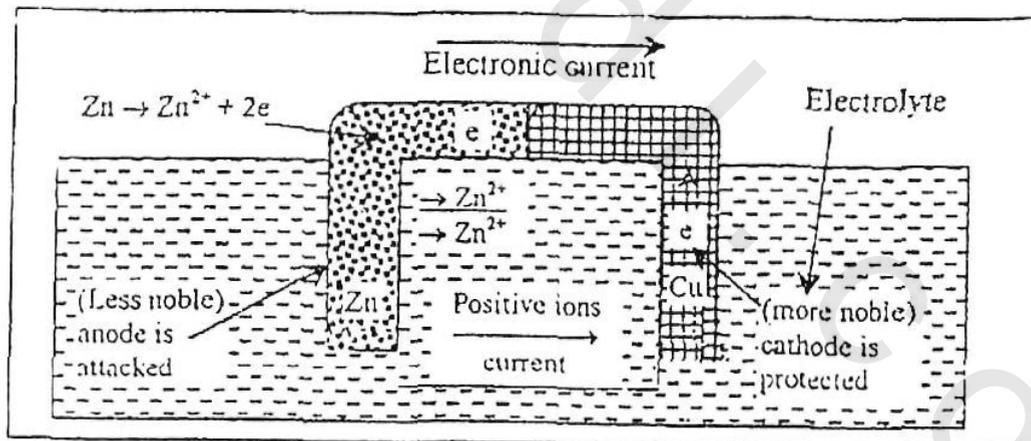

Fig (3) : Schematic diagram for Galvanic corrosion

(a)Metal ion cells

A metal tends to dissolve or corrode at a slower rate as the concentration of its ions in the solution increase. Metal in contact with the more dilute solution will become more anodic (active), and metal in contact with the more concentration solution will become the more cathodic (noble). Electrons will flow from the anode to the cathode and the anode area corrodes.

(b)Oxygen cells

Oxygen can effect corrosion rates of metals. The uneven distribution of dissolved oxygen on the surface of the metal will cause oxygen concentration cells. Areas poor in oxygen are anodic to areas rich in oxygen content.

3- Pitting corrosion

Pitting is form of extremely localized attack that result in holes in the metal. When the anodic area remains in one spot, corrosion occurs at this side and deep penetration results. Pitting is one of the most destructive and insidious forms of corrosion. It causes equipment to fail by perforation with only small percentage weight loss of the entire structure [4]. This type is obvious in Fig. (4)
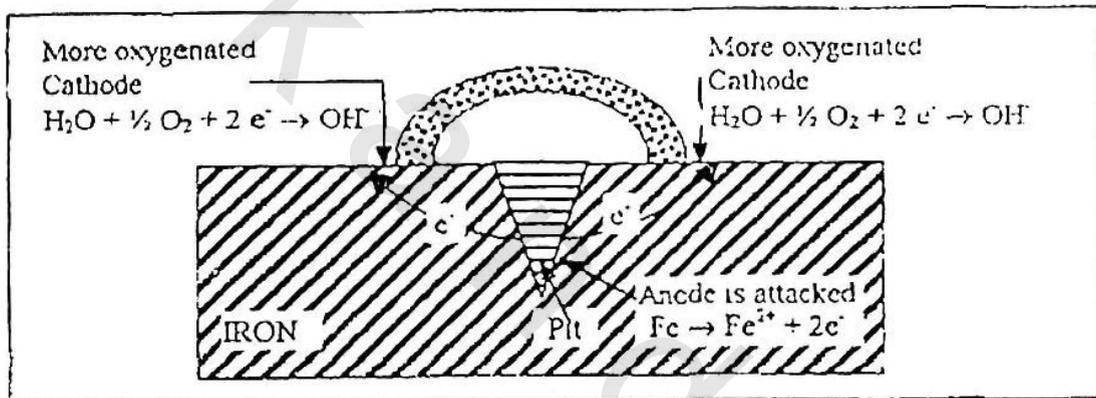

Fig (4) : Schematic diagram for Pitting corrosion at surface of iron.

4- Intergranular corrosion

Solid metals consists of grains and have a grain structure. Localized attack at grain boundaries, with relatively little corrosion of the grain, is intergranular corrosion. As corrosion proceeds, the grain fall out and the metal or alloy disintegrates this is a serious problem in some cases. The grain boundaries are usually anodic to the grain.

5- Parting

Parting is the general term used to describe the selective corrosion of one or more components from a solid solution alloy.

In one very common example it evolves the selective removal or dissolving of zinc from an alloy containing this element. This was first observed on brass, which is a copper-zinc alloy. Dezincification was the term commonly used in referring to such phenomena, but the referred term is parting. The commonly accepted theory explaining the mechanism of parting corrosion (dezincification) consists of the following steps.

(a)The brass dissolves (both copper and zinc),
(b)The zinc stays in solution and,
(c)The copper plates back on the piece.

Zinc has a high solution tendency and copper a high planting tendency. Zinc will naturally replace copper from a solution simply because copper is below it in the emf series.

Another example of parting is graphitization in which gray cast iron shows the effect selective leaching, particularly in relatively mild corrosion environments. The cast iron appears to become graphitized in that the surface layer has the appearance of graphite ant can be easily cut with penknife. What actually happens in graphitization is a selective leaching or dissolving of the iron matrix, an interlocking graphite network is left behind. The carbon is cathodic to iron and an excellent galvanic cell exists. The iron is dissolved, leaving a porous mass consisting of voids and complex iron oxides (rust). Such "graphitized" cast iron oxides loss strength and also loses its metallic properties. Graphitization does not occur in nodular or malleable cast iron simply because the graphite network is not present to hold the residue together, white cast iron has essentially no free carbon or graphite and therefore could not be subjected to graphitization.

6- Stress corrosion:

Stress and corrosion working together can cause failure of metals in two ways. The corrosion resistance of the metal or alloy is decreased and general corrosion occurs. This is called stress-accelerated corrosion. The second, and more important way, result in cracking or brittle failure of the metal. This is stress-corrosion cracking. Stress corrosion should be referred to as failure by cracking due to combined effects of corrosion and stress. These two parameters must work together of failure will not occur. One of the most important characteristics of stress corrosion is the absence of visual overall attack. The metal looks fine except it is cracked. This type is obvious in Fig. (5)
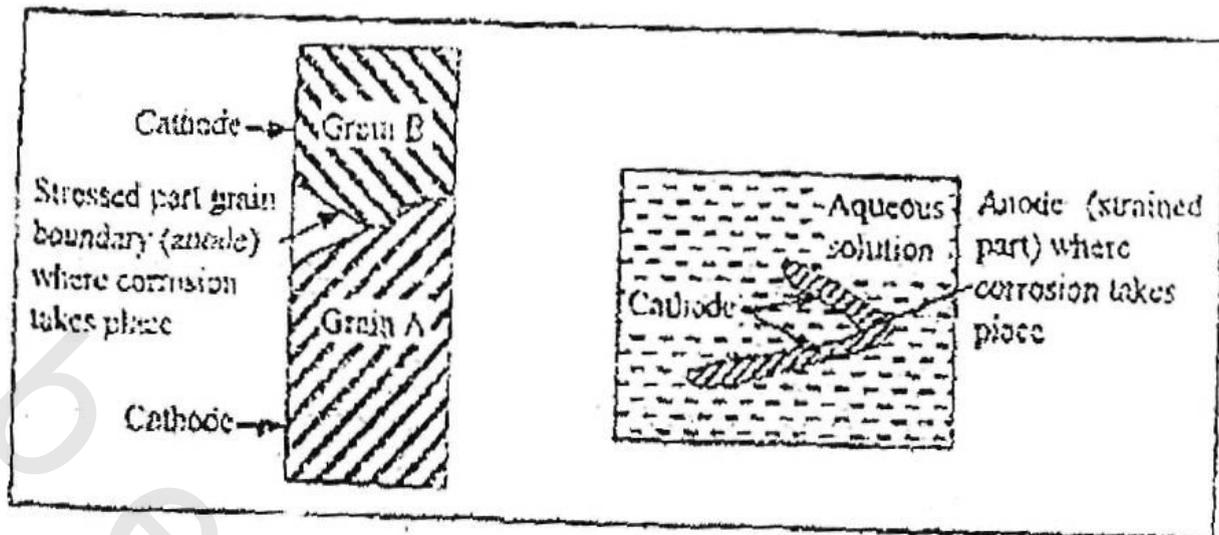
Fig (5): Schematic diagram for Stress corrosion

7- Hydrogen attack and hydrogen embitterment

Hydrogen attack or blistering due to H atom diffusion to the metal which produce by the cathodic reaction. H atoms combine to form H_2 inside the metal and results a blister which bursts and damages the metal. Embitterment due to the same diffusion of H atoms inside the metal but here the active H atoms combine with the metal to form metal hydride which is usually brittle, the metal hydride falls apart and the metal becomes a powder.

8- Erosion-corrosion

Erosion-corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosion fluid and the metal surface. Generally, this movement is quite rapid and mechanical wear effects or abrasion are often involved. These include gases, aqueous solutions, organic systems, and liquid metals. To defferentiate between corrosion and erosion-corrosion, the former is considered a purely mechanical effect.

Erosion-corrosion is characterized in appearance by grooves, gullies, waves, rounded holes and valleys and usually exhibits a directional pattern.

F) The methods used for corrosion studies

(1) Weight loss[5]

    a. Directly by measuring the loss of weight of a sample due to its corrosion.

    b. Indirectly by monitoring the free ions in solution (Fe^{2+}) by titrating it against $K_2 Cr_2 O_7$.

(2) Gasometry

In most corrosion processes either H_2 or O_2 is evolved and can by used as a measure for corrosion.

It is generally detected by collecting the gas over aqueous solutions and the volume the collected gas is read directly.

(3) Electrochemical Methods

The corrosion cell is deviced to follow the polarization processes either cathodically or anodically or both simultaneously [6-13]. Then using the well-known Tafel equation to obtain the corrosion parameters.

Tafel equation can be used for data treatment of electrochemical methods as follow. It is well known that three types of polarization effects. ohmic, concentration and activation.

The Tafel equation relates the activation polarization component of the overpotential to the current (i).

$$E = a \pm b \ln (i) \tag{1}$$

Where; a, b are constants.
        E is overpotential.
        i is current.

G) Metallurgical principles of steels

1- Iron-Carbon alloys [14]

Carbon steel alloys can be classified in to three categories, first is low carbon in 0-0.20% carbon range, second is medium carbon with 0.21 – 0.50% carbon, and the third is known as high carbon with carbon more than 0.50%. In this work, low and medium carbon steel with trace of vanadium were used. Carbon in the matrix presents as body center cube in ferrite phase, and as

iron carbide (Fe₃C) which known cementite in pearlite phase, where pearlite is double phase contains two types of lamina, ferrite and cementite lamina. Vanadium presents as vanadium carbide [15-17].

2- Cementite

Cementite represented by the formula Fe_3C which is the metastable Fe–C intermetallic compound. It has a negligible solubility limit in α-iron and contains 6.67 wt % carbon. It is ferromagnetic compound. In sharp construct to ferrite and austenite, cementite is hard and brittle. This is an industrial compound of low tensile strength but high compressive strength. It plays an important role in the hardening of many types of steel. It has an orthorhombic crystal structure with lattice parameters: a = 4.52 A°, b = 5.08 A° and c = 6.73 A° and 12 iron and 4 carbon atoms per unit cell. This type is shown in Fig. (6)
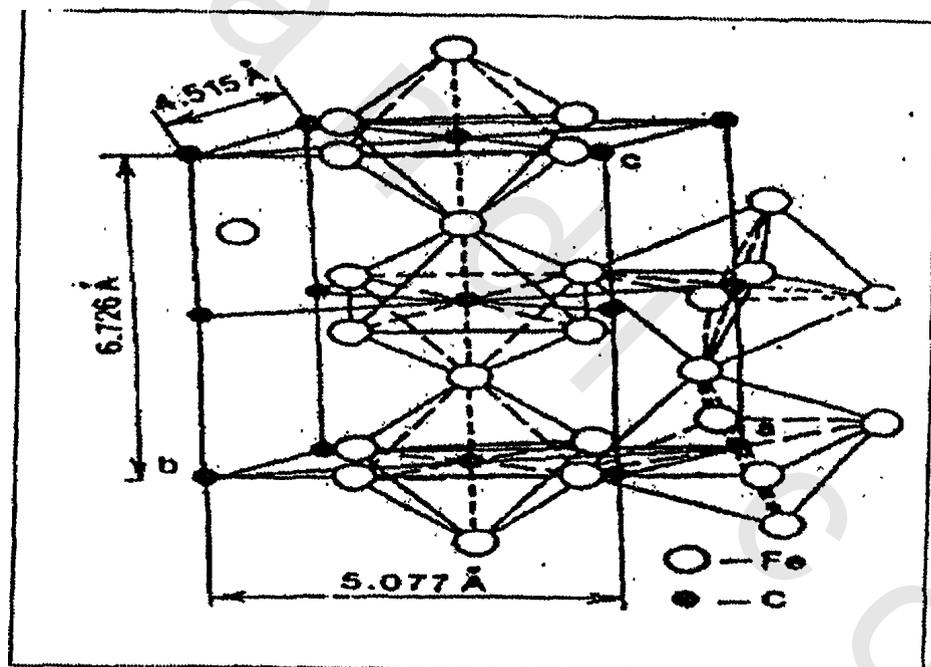

Fig (6): Schematic diagram for Cementite matrix.

3- Ferrite

Pure iron with carbon in steel. Alloy has the body centered cubic (bcc) structure at room temperature, also V, Mo, W and Cr have the same behavior with carbon, which is characterized by the unit cell as shown in Fig (7).
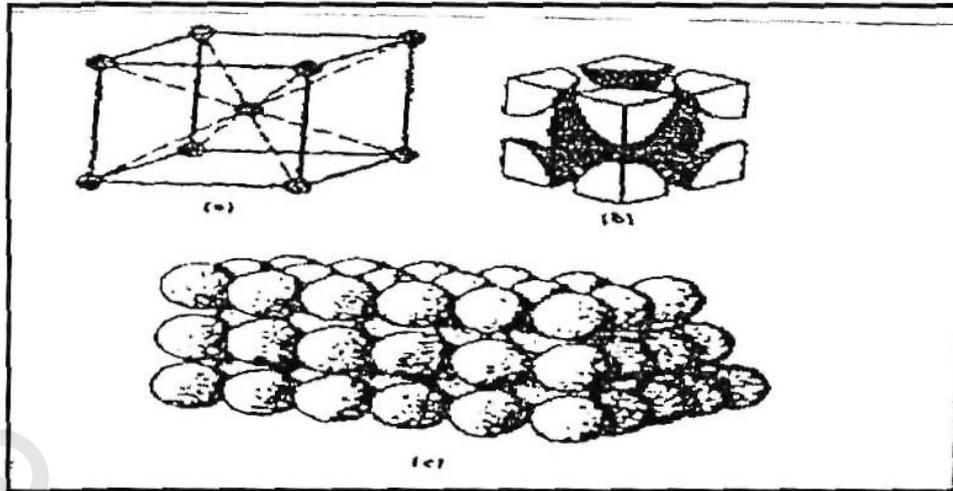
Fig (7) : Body-centered cubic of structure of a metal showing (a)the atomic-site unit cell , (b) the isolate unit cell , (c) the model made from hard balls .

The bcc structure of pure iron at room temperature, called either α-iron or ferrite, has one atom at the center of the cube and an atom at each corner of the cube and an atom at each corner of the unit cell and every cube includes 2 atoms of iron in the crystal net work. The atomic packing factor for this structure is 0.68 and represents the volume faction of the unit cell occupied by two atoms. The lattice parameter of α-iron at room temperature is 2.86 A°.

4- Pearlite[18]

Pearlite is double phase in lamellar structure of alternative ferrite and cementite. Pearlite has higher hardness and lower plasticity than ferrite as shown in Fig. (8).

Fig (8) :Microscopic view of lamellar pearlite structure

5- Heat treatment

Hardening by quenching in water is the regime which used for vanadium carbon steel samples. To get hard martensite phase in room temperature, with more hardness and less ductility[19-20]. But spheroidizing annealing regime in heat treatment to obtain cementite as spherical particles in the matrix. Otherwise, normalizing regime is used for obtaining fine pearlite.

H)Electrochemical nature of steel corrosion

Some of the basic principles of corrosion were investigated after the discovery of the galvanic cell [21-28]. We can considered the corrosion process as the result of the network of short – circuited galvanic cells on the metal surface. Metal ions go into solution at anodic areas in an amount chemically equivalent to the reaction at the cathodic areas, thus, in iron or steel corrosion, electrochemical reactions may take place as follows:

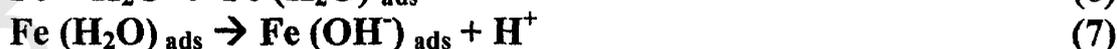$$Fe \rightarrow Fe_2^+ + 2e^- \qquad (2)$$

This reaction is rapid in most media, as shown by the lack of pronounced polarization when iron is made anode employing an external current. When iron corrodes, the rate is usually controlled by the cathodic reaction, which in general is much slower (cathodic control)[29-37]. In deareated solution, the cathodic reaction is:

$$H^+ + e^- \rightarrow \tfrac{1}{2} H_2 \qquad (3)$$

This reaction proceeds rapidly in acids, but slowly in alkaline or neutral aqueous media. The rate of hydrogen evolution at specific pH depends on the presence of absence of low hydrogen over Potential impurities in the metal. For pure iron, the metal surface itself may provides sites of hydrogen evolution, hence high purity iron continues to corrode in acids but at measurable lower rate than does the commercial iron. The cathodic reaction can be accelerated by dissolved oxygen in accordance with the following reactions (a process called depolarization):

$$2H^+ + \tfrac{1}{2}O_2 + 2e^- \rightarrow H_2O \qquad (4)$$
$$H_2O^+ + \tfrac{1}{2}O_2 + 2e^- \rightarrow 2OH^- \qquad (5)$$
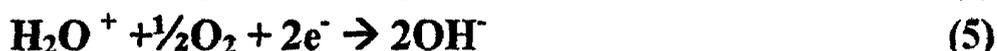
Although the overall anodic and cathodic reactions are those given in equations (1 to 4), it is usually considered that the equations take place in series of steps, one of which is the rate determining step (RDS). The reaction steps are the follows:

$$Fe + H_2O \rightarrow Fe\ (H_2O)\ _{ads} \tag{6}$$
$$Fe\ (H_2O)\ _{ads} \rightarrow Fe\ (OH^-)\ _{ads} + H^+ \tag{7}$$
$$Fe\ (OH^-)\ _{ads} \rightarrow Fe\ (OH)\ _{ads} + e^- \tag{8}$$
$$Fe\ (OH)\ _{ads} \rightarrow Fe\ (OH^+)\ _{ads} + e^- ----RDS \tag{9}$$
$$(Fe\ OH)^+ + H^+ \rightarrow Fe^{++} + H_2O \tag{10}$$

This mechanism postulates that the electron transfer step takes place in two stages with the oxidation of Fe (OH)ads. Being the rate determining step. The final concentration of Fe OH$^+$ and Fe^{++} is strongly pH dependent. The two ions will only be stable in acid or oxygen-free systems. In the presence of oxidants, the Fe^{++} will be oxidized to various insoluble ferric compounds such as Fe_3O_4, Fe_2O_3 and the hydrated oxides, α,β,γ Fe (OH) .The two main cathodic reactions involved in dissolution (and corrosion) reaction are the reduction of H$^+$ to H_2 and the reduction of dissolved O_2 to OH$^-$. The following schemes are the ones, which have been postulated [38-44].
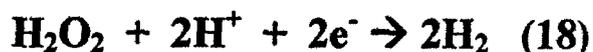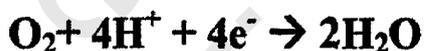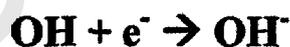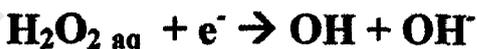
(a) Hydrogen ion reduction

$$H^+ + e^- \rightarrow H_{ads} \tag{11}$$
$$H_2O + e^- \rightarrow H_{ads} + OH^-_{aq} \tag{12}$$
$$H_{ads} + H_{ads} + e^- \rightarrow H_2 \tag{13}$$
$$H^+_{aq} + H_{ads} + e^- \rightarrow H_2 \tag{14}$$
$$H_2O + H_{ads} + e^- \rightarrow H_2 + OH^-_{aq} \tag{15}$$

At low pH's, reaction (11) and (14) will predominate over (12) and (15). The rate determining step depends in part on the catalytic properties of the surface. This is particularly true for the recombination reaction is more difficult than dissolution of atomic hydrogen into the metal and the following alternative reaction becomes the predominant one.

$$H_{ads} \rightarrow H\ metal \tag{16}$$

If catalytic sites for hydrogen atom recombination exist within the metal, such as inclusions, them H_2 gas is formed in the metal and blistering and rupture can occur.

(b) Oxygen reduction

$$O_2 + e^- \rightarrow O^-_{2\,ads}$$

$$O^-_{2\,ads} + H^+ \rightarrow HO_{2\,ads}$$

$$HO_{2\,ads} + e^- \rightarrow HO_2^-$$

$$HO_2^- + H^+ \rightarrow H_2O_{2\,aq}$$

$$H_2O_{2\,aq} + e^- \rightarrow OH + OH^-$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (17)$$

$$OH + e^- \rightarrow OH^-$$

$$2OH^- + 2H^- \rightarrow 2H_2O$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2 \quad (18)$$
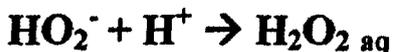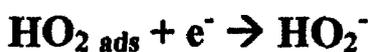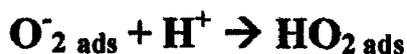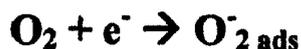
These reactions are all quite rapid in comparison to hydrogen evolution reaction and hence the oxygen is a better cathodic depolarizer than hydrogen ion [45-48].

I)Corrosion Inhibition[49-55]

1- Corrosion inhibitors

In general, any phase constituent whose presence is not essential to occurrence of an electrochemical process, but leads to a retardation of this process by modifying the surface state of the metallic material, will be called an inhibitor (this applies to electrolytic phases)[56]. Such modification of the surface state implies adsorption, the formation of "surface compounds" or a reaction between the metallic material and the inhibitor with separation of the corrosion products at the contact surface of the metallic material with the electrolytic conductor. Thus we can define corrosion inhibitors as substances that inhibit one or more of the partial processes of the corrosion process as a whole [57]. The electrochemical nature of the corrosion process leads to the realization of four distinct and separate basic process involved in corrosion, which are linked together by necessity of preserving electro neutrality in the overall reaction. These are:

a)Anodic or oxidative process.
b)Cathodic or reductive process.

c)Electronic charge transfer process in both directions across the interface,

d)Ionic charge transfer process which is required to maintain e.ectroneutrality on the electrolyte side due to disappearance of ionic charges in cathodic process and the formation of ionic charges in the anodic process.

One of these four reactions is usually the slowest and rate determining for the overall process[58].

2-Classification of Corrosion Inhibitors

(a) Anodic inhibitors[59-61]

Anions, such as phosphates, benzoates or tungstates, which precipitate the anodically dissolved metal and thus lead to the formation of adherent protective layers, or which are specifically adsorbed[62], may be regarded as anodic inhibitors. The inhibitor should be present in quantities sufficient to affect the reactions at all of the local anodes. Otherwise the attack on those remaining unprotected will be intensified, and pitting corrosion will result. Anodic inhibitors are thus particularly dangerous if their concentration is too low.

(b) Cathodic inhibitors[63-67]

Cathodic inhibitors act by preventing the combination of discharge H atoms to molecular hydrogen (reaction overpotential), by increasing the over potential of the discharge of H_3O^+ ions, or by delaying the diffusion of dissolved oxygen towards the cathode by forming an obstructing layer. Insufficient amounts of these inhibitors do not give rise to increased local corrosion as the anodic reaction. Cathodic inhibitors which can be reduced more readily than H_3O^+ should, however, be avoided, as these will enhance rather prevent corrosion.

3- Effect of inhibitor on the polarization behavior[68-76]

Mixed potential theory of an electrochemical corrosion process expressed graphically in the form of an Evans type polarization diagram is an extremely useful way to picture how an inhibitor works.

J)Literature survey

S.R. Selim and S.H. El-Nekhaly[77]. studied the effect of spheroidizing annealing of vanadium steel on corrosion rate in HCl solution, and they has been studying the effect of spheroidizing annealing of tow vanadium present carbon steel samples[0.081, 0.11%] and third one without vanadium. Polarization technique was used to deduce corrosion resistance.Generally corrosion resistance value reduced by increasing vanadium percentage, while it is increased after heat treatment for three samples. Increasing corrosion resistance value after heat treatment is due to phase transformation.

M.H. Ras and Pistorious,[78]. evaluated the possible mechanism for the improvement by vanadium of the pitting corrosion resistance of 18% chromium ferritic stainless steel, where addition of vanadium increase the pitting potential of 18% chromium ferritic stainless steel. Artificial pit measurements showed this is not related to any change in the dissolution kinetics in the pit acolyte, in construct with the effect of molybdenum, which lowers the dissolution rate strongly of the salt film in artificial pits in alloyed steel with vanadium. The slower dissolution is expected to contribute to the pitting resistance of the vanadium-alloyed steels.

A. Enver et al[79]. investigated effects of conventional heat treatment and abrasive wear and corrosion of steel types SAE 1010, SAE 1040, D2 and 304. Abrasive wear tests were carried out in wear cup model device sand of 1 mm diameter and the test duration was 40 hours with a velocity 0.157 m/s. Corrosion test were undertaken in 10% H_2SO_4 solution and temperature of 56 °C.

E.P.Kruglov and P.P.Toboienko[80], studied the corrosion resistant matenesitic [E1961 Sh, EP497Sh] And high speed tool (R18) steels which are quenched in vacuum furnace with cooling in medium of circulating argon. Mechanical properties of steel specimens [50mm in section] after hest treatment and computed cooling rate are reported. A sensitivity of R18 steel to cooling in rate in the temperature interval of carbides precipitation is ascertained.

V.Kuzuntsov et al[81], studied the influence of conditions of heat treatment on mechanical properties and corrosion resistance of 13GFA steel.

V.A.Alves and A.Cavalerio[82], evaluated the influence of heat treatment on the corrosion of high speed steel.

C. Garcia et al[83], investigated the effect of prior cold wok (CW) and sensitization heat treatment on the stress corrosion cracking (SCC) behavior of type 304 stainless steel using electrochemical test and magnesium chloride tests. The result indicated that the (SCC) behavior of the (CW) steel was essentially different from that of the annealed steel intergranular stress corrosion cracking.

T.M.C.Nogveria et al[84], have studied the effect of an annealing heat treatment on both the ductility and corrosion resistance of chromated hot dip 55mas % Al Zn coated steel sheet. With the result that the heat treatment improves coating ductility but impairs the over all corrosion resistance due to the decrease in the protective effect of the passivation layer.

G.Qieo[85], evaluated the influence of heat treatment on stress corrosion in H_2S. the effect of the intermediate treatment at 750-850 $^{\circ}$C on mechanical properties and stress corrosion resistance in H_2S medium was considerable. The result showed that the strength increases with increase of intermediate treatment temperature.

J.G.Gonzalez et al[86], have studied the effect of heat treatment on the stress corrosion cracking behavior of 403 martensitic stainless steel in 20% NaCl at 95 $^{\circ}$C. Heat treated specimens included water quenched, and tempered at 200 $^{\circ}$C, 400 $^{\circ}$C, 600 $^{\circ}$C, respectively. Other specimen of the same type of steel annealed at 850 $^{\circ}$C. the lowest elongation to failure and percentage reduction in area was shown by the quenched specimen and the highest by the annealed specimens.

A. Pyzalla et al[87], reported the rapid heat treatment surface layer with properties that are distinctly different from

those of the initial microstructure can be generated. In case of high nitrogen steels the rapid heat treatment aims at generating a hard surface with compressive residual stresses and high corrosion resistance. The residual stresses and especially the corrosion behavior of the rapid heat treated high nitrogen steel X30CrMoN15 and the reference steel X39CrMo17 are presented in dependence of the maximum heat treatment temperature and heating rate.

J. L. Albarran et al[88], evaluated the effect of heat treatment on the stress corrosion resistance of amicroalloyed pipeline steel. The pipeline steel exposed to sulfide stress cracking (SSC) from environment.

Mustafa et al[89], studied the use of molybdate and nitrite as corrosion inhibitors for mild steel galvanically coupled to copper in simulated cooling water (SCW), galvanic contact of copper is harmful to mild steel in acidic and alkaline pH ranges from 3 to 12. Galvanic contact is very harmful NO_2^-, or both are present at low pH, but it becomes less harmful as increases toward the alkaline region MO_4^{-2} alone in SCW was shown to inhibit corrosion of copper. Coupled mild steel at pH greater than equivalent to 6, and nitrite was shown to do the same at pH greater than equivalent to 4.5. Below these values, both accelerate galvanic corrosion.

Kumar et al[90], studied the corrosion protection of mild steel in 15% HCL and 3% HF used in acidization of oil well by some N- containing organic compounds. The corrosion rate of mild steel decreased appreciably even in the presence of traces of this compound. The extent of decrease in the corrosion rate was found to depend on the nature of the inhibitor and its concentration and recorded results of testing the additives in preventing corrosion of mild steel by the acid solution at different temperatures (30 to 70 °C) and exposure times (6h to 36 h) at fixed inhibitor concentration. Thermodynamic parameters like heat of adsorption and activation energies have been calculated in the absence and presence of these organic additives. The nature of the film formed on the metal surface was analyzed by infrared (IR) spectrum and relationship between structure of the organic compounds and inhibition efficiency has been explained.

Eswaran et al[91], used Modern analytical techniques such as Electron Spectroscopy for Chemical Analysis (ESCA), Infra Red Spectroscopy (IRS), particle size analysis and weight loss method for the evaluation of different inhibitors in demineralized water for carbon steel used in the process cooling water system of nuclear power plants. The results of the experimental finding have been discussed in the light of the kinetics of the corrosion and inhibition processes prevalent in the system..

Hettiarachi et al[92], evaluated the effectiveness of phthalocyanines as acid corrosion inhibitors for steel. Water soluble tetrasulfophthalocyanines are very poor corrosion inhibitors. Water insoluble tetraaminophthalocyanines serve as better corrosion inhibitors than the water soluble ones when the metal surface is coated with on adsorbed lyre of he pthalocyanine. Water insoluble polymeric phthalocyanine coatings based on Fe (III) centers gave inhibitor efficiencies as high as 82% as confirmed by both slow potentialdynamic technique and the ac impedance analysis.

Subramanyam et al[93], studied the corrosion of mild steel, in alkaline mine water containing various concentrations of hydrazine and 2.4- Dinitro phenyl hydrazine by weight loss and polarization techniques at 303 K. the degree of corrosion inhibition is a function of temperature, concentration and nature of the inhibitor. The hydrazine and substituted hydrazine inhibit corrosion effectively even at low concentration and/or complex formation by the inhibitions son the corroding mild steel surface. Thermodynamic parameters for adsorption are calculated by using the frumkin adsorption isotherm. These organic compounds act as anodic inhibitors.

Hariharaputhran et al[94], studied N- benzylidine phenylamine-N- oxide (nitrone) and eight of its derivatives with substituents in the Para position of the alpha phenyl group were synthesized and their inhibition of the corrosion of mild steel in 1N HCI by weight loss, potentiodynamic polarization, hydrogen permeation measurements, and impendence measurements. Determination of inhibition efficiency in the presence of these compounds at different temperatures clearly indicates that the dimethyl derivative shows the best performance even at temperatures as high as 70 ºC. potentiodynamic polarization

studies clearly reveal the fact that nitrone and its derivatives act as mixed type inhibitors. All of these compounds are found to reduce the permeation of hydrogen through mild steel in HCL solution. Values of double layer capacitance and charge transfer resistance were derived from Nyquist plots obtained from ac impedance studies. The adsorption of these compounds on the mild steel surface obeys Temkin's adsorption isotherm.

Shokry et al[95], investigated the corrosion inhibition by Schiff base compounds derived from diamines and o-hydroxy, o-methoxy aromatic aldehydes by weight loss, electrochemical measurements and surface analysis of SS 400 in various aqueous solutions such as tap water (LC), concentrated tap water (HC) and HCl solution. The maximum inhibition efficiency (eta) of N,N-bis (salicylaldehyde)-1,12- diaminododecane (Saldn) for SS 400 in HCl solution approached 93% the adsorption of Saldn on mile steel in HCl solution was obeyed langmuir's isotherm.

Abd-El-Kader et al[96], investigated the corrosion inhibiting effects of three additives, sodium benzoate, calcium gluconate, and sodium glycerophosphate, as co-inhibitors with Na_2WO_4 by measuring the corrosion weight loss of mild steel in distilled water and $10^{-3}M$ NaCl. In distilled water each of the substances completely inhibits the corrosion of steel at a definite concentration. In mixtures with Na_2WO_4 complete inhibition was achieved when the concentration of each component was considerably less than the minimum required to prevent corrosion when present alone (synergism). The result indicated further that organic additives could retard pitting corrosion.

Abd-El-Kader et al[97], had been studied the inhibition of corrosion of mild steel in aqueous solutions by sodium tungstate Na_2WO_4 in oxygen saturated, freely aerated, and fully deaerated solutions open circuit potential measurements were complemented by visual examination of the specimens. Curves of steady state potential versus log inhibitor concentration were constructed which revealed domains of corrosion and of passivation. Both O_2 and $(WO_4)^{-2}$ are physically adsorbed on the metal surface. Electrochemical measurements show that there is a direct relationship between the corrosion rate and the corresponding steady state potential.

Agarwal et al[98], studied the corrosion inhibition efficiency of a omega-benzoyl alcanoic acid model compound and compared to that of benzoic acid. Electrochemical testes showed that the electrolytes can significantly influence the performance of corrosion inhibitors. The experimental procedure coupled with the adsorption model was shown to provide a quantitative way of evaluating and ranking inhibitors.

Lahodny- sacra et al[99], investigated the inhibition of carbon steel in solutions of mixtures of calcium- and zinc fluconate with sodium benzoate. The influence of the concentration and the ratio of gluconate/benzoate on the anodic reaction and an observed cathodic effect, indicating slowing down the oxygen reduction process, relevant to the concentration of zinc ions, were demonstrated. The inhibition is enhanced by the cathodic polarization mechanism resulting in the precipitation of a zinc hydroxide film, due to the local cathodic gradient of hydroxyl ions.

Amalhay et al[100], determined the mode of action and the effectiveness of various inhibitors studied on reducing carbon steel corrosion in natural geothermal waters by using stationary and transitory electrochemical techniques.

Ajmal-Mohammed et al[101], have synthesized four macrocyclic compounds by condensing o-ethylene diamine and o-phenylene diamine with ethylacetoacetate and succinic acid their inhibiting action was evaluated on corrosion of mild steel in HCI and H_2SO_4 by weight loss and potentiodynamic polarization methods. A macrocyclic compound derived by condensing o-phenylene diamine with ethylacetoacetate exhibited best performance by giving IE of 98 percent at 500 ppm concentration. The potentiodynamic polarization studies revealed that the tested compounds are either mixed type or predominantly cathodic inhibitors. IE of all the investigated compounds increased significantly on addition of a small concentration KI in both acids due to synergism.

Rajendran-susai et al[102], evaluated the corrosion rates of mild steel in natural aqueous environment containing 60 ppm chloride in the absence and presence of polyacrylamide (PAA), phenyl phosphonate (PPA) and Zn^{2+} by weight loss method. The formulation consisting of 50 ppm PAA and 50 ppm Zn^{2+} and also

the 50 ppm Zn^{2+} to 300 ppm PPA system show synergistic effect (the inhibition efficiency of the latter is not decreased by addition of 50ppm PAA) while the formulation consisting of 50ppm PPA and 300 ppm PPA shows an antagonistic effect. The protective film has been analyzed using X-ray diffraction measurements, FTIR and luminescence spectra.

Hamid-Z-Abdel et al[103], investigated the inhibiting effect of cationic surfactant N, N-diethyl 4-methylbenzyl dodecyl ammonium chloride on mile steel in hydrochloric acid solution by surface and thermodynamic measurements, weight loss teats, polarization measurements and EDS techniques, The data obtained from surface and thermodynamic measurements with the inhibitor indicate that the area per molecule slightly increases with increasing temperature and both absorption and micellization processes are spontaneous. Weight loss measurement showed that the inhibition efficiencies increased with increasing surfactant concentration and attained a maximum around their critical micelle concentration. Polarization studies reveal that the inhibitor behaves as mixed type in hydrochloric acid solution and acted on the cathodic reaction. Without modifying the mechanism of the hydrogen evolution reaction. EDS measurement showed high coverage of surfactant on the mild steel surface.

Karman et al[104], studied the influence of phosphoric acid with Ca cation on iron surface in neutral aerated media 0.5 mol .dm^{-3} NaCIO$_4$ by electrochemical and surface analytical methods. X-ray induced photoelectron (XPS) and Auger electron spectroscopy (XAES) provided the possibility for identification of different chemical states of the corrosion protective layers. The presence of certain cation led to a synergistic effect. Is was found that calcium ions were incorporated into the film that developed on the mild steel surface, containing a mixed oxide and hydroxide complex. Electrochemical impedance Spectroscopy (EIS) was used to determine the inhibitor efficiency of phosphonic acid at different concentrations. The data obtained were fitted and modeled by an equivalent circuit model.

Heeg et al[105], studied on the persistency of inhibitor film under multiphase flow conditions using a jet-cylinder electrochemical cell. Optical Second Harmonic Generation SHG), Electrochemical noise and linear polarization resistance were used

to mentor the surface coverage $3CO_2$ corrosion inhibitors. It was found that slug flow conditions, generated by simultaneously applying a liquid jet and ultrasonic cavitations, can cause breakdown of the inhibitor film below inhibitor concentrations of several ppm. Removal of the inhibitor film was not found under jet-only or sonication-only conditions. Furthermore a jet of silica particles was also found to cause some striping of the inhibitor film.

Heeg et al[106], described a new jet-cylinder apparatus to study corrosion inhibitor film persistency under multiphase flow. A rotating cylinder electrode is used as the substrate and single phase flow conditions can be produced by firing a liquid jet at the cylinder. Multiphase flow conditions can be simulated by introducing ultrasonic cavities in the liquid jet. In addition, by introducing silica-particles in the jet, erosion-corrosion can be studied. Wall shear stress values for a rotating cylinder electrode have been estimated by computational fluid dynamics and compared with limiting current densities under various flow conditions. From this it is concluded that mass-transport is not necessarily proportional to wall shear stress under single and multiphase conditions for carbon steel in acidic (HCI) environment at higher flow velocities.

Shokry et al[107], investigated the effects of Schiff base-metallocomplex on the corrosion of mild steel by corrosion weight loss measurements, electrochemical measurements and surface analysis in various aqueous solution such as hydrochloric acid solution and pseudo cooling water. The maximum value of inhibition efficiency on the corrosion of mild steel in 1 mol. Dm^{-3} HCI solution was about 95.8% in the case of indium (III) left brace N,N-prime-bis (salicylaldehyde)-1,12-diaminododecane right brace complex. The molecules of Schiff base-metallocomplexes adsorbed on the surface of mild steels to depress the corrosion.

Gomma-Gamal et al[108], studied corrosion behavior of low-carbon steel in different concentrations $10^{-3} - 9 \times 10^{-3}$ M of benzotricazole (BTA) 1M H_2SO_4 by potentiodynamic polarization measurements at a scan rate of 0.166 mVs^{-1} it is found that passivation current, corrosion potential, passive potential and polarization resistance increase with increasing benaotriazole concentration, while critical current, corrosion current and

corrosion rate decrease it is established that the corrosion rate depends on the concentration of the inhibitor and chloride ions along with the sweep rate of polarization. A maximum inhibition efficiency (98.5%) was obtained at 9×10^{-4} M BTA are calculated.

Wang et al[109], described Acrylic latex was introduced into steel- reinforcing steel concrete as concrete admixtures or rebar coating in order to prevent corrosion of steel reinforcements. The results showed hat applying the latex by both methods took effect in different ways, while the latter was more noticeable. The corrosion prevention mechanism and the surface state of the steel rebar were also explored, based on which suggestion for enhancing the corrosion-resistant ability were made.

Gomma-Gamal et al[110], studied potentiokinetically, the concentration influence of benzotriazole on the electrochemical and corrosion behavior of steel with and without a copper cation. It found that benzotriazole increases the polarization resistance to a great extent it was found that the Cu cation, at concentration of 10^{-3} M, strongly inhibits the corrosion rate. The corrosion of the steel in 0.1 M H_2SO_4 is appreciably reduced by benzotriazole in combination with the metallic copper cation, as a result of co-adsorption. At a higher concentration of copper cation 10^{-2} M in association with benzotriazole, the dissolution of steel is increased owing to the cathodic reduction of the action to metal, and the potential is shifted toward the electropositive direction. In the presence of benzotriazole and lower metallic copper cation concentrations 10^{-2} M, the potentials shift in the electronegative direction, indicating suppression of the cathodic reaction by co-joint adsorption of the inhibitor and metallic cation. The kinetic and thermodynamic parameters were calculated at different temperature. The negative temperature coefficient for corrosion inhibition is assuming that the corrosion reaction is no longer the simple metal/acid reaction, owing to adsorption retardation.

Rajendran et al[111], described the formulation consisting of 300 ppm for 1-hydroxyethane-1,1 –diphosphoric acid (HEDP), 50 ppm polyacrylamide (PPa) and 50 ppm Zn^{2+} offered 99 per cent corrosion inhibition and 99 to 99.9 per cent biocidal inhibition to mild steel in neutral aqueous environment containing 60 ppm CI^{-1}, a situation commonly encountered in cooling water surface was analyzed using X-ray diffraction, UV visible reflectance, FTIR and

luminescence spectra. The film was found to be luminescence and to consist of Fe^{2+} HEDP complex, Fe^{2+} PPA complex and $Zn(OH)_2$.

Madhavan et al[112], studied the influence of thiophenol on the corrosion and hydrogen permeation 1 M HCI and 0.5 M H_2SO_4 has weight loss measurements, gasometric studies and other electrochemical techniques. Thiophenol inhibits the corrosion of mild steel in both the acids, but it is found to be more effective in H_2SO_4. it behaves predominantly as cathodic inhibitor. It brings down the permeation current in both the acids, but is more effective in H_2SO_4 . the adsorption of thiophenol on the mild steel surface from both the acids obey's Temkin's adsorption isotherm.

Vasudevan et al[113], studied the influence of pyridinium chloride (PC) and n-hexadecyl pyridinium chloride (HDPC) on the corrosion of mild steel in 5 N HCI and 5M H_2SO_4 using techniques such as weight loss and gasometric measurements, potentiodynamic polarization studies, linear polarization studies and small amplitude cyclic voltametric studies. It found that HDPC is more inhibitive than PC and both the compounds perform better in H_2SO_4. Polarization studies reveal that PC behaves as an anodic inhibitor in H_2SO_4 and as a mixed inhibitor in HCI. Measurements of values of polarization resistance (R_p)and double layer capacitance (C_{dl}) in the presence of these compounds also reveal the better performance of HDPC in both the acids. The adsorption of PC and HDPC on a mild steel surface from both the acids is found to obey's Temkin's adsorption isotherm.

Bastidas et al[114], investigated the corrosion of mild steel by acetic and formic acid vapors at 65,75, 85 and 100% relative humidity (RH) and its inhibition by dicylohexylamine nitric (DICAN). Electrochemical and gravimetric techniques. The corrosion rate of steel was in the range of less 10-145 mdd and less than 10-35 mdd for 225 ppm acetic and 300 ppm formic acid vapor, respectively, at 65-85% RH. Inhibitor efficiencies were 64% and 71% in acetic and formic acids, respectively, at 100% RH. There is reasonable correlation between inhibitor efficiencies estimates from weight loss, polarization and noise measurements. X-ray analysis of the corrosion products, in the presence and absence of DICHAN shows the presence of magnetite (Fe_3O_4), as principal constituent, along with alpha-FEOOH and gamma-FEOOH. The acetic corrosion product film was of porous nature.

Osman et al[115], investigate the corrosion of steel in sulphoric acid containing hexadecyl trimethyl ammonium bromide (HTABR) over the temperature range 30-60 °C at different inhibitor concentrations of 0.5 x 10^{-3} – 2.5 x 10^{-3} M/L multiplied by 10^{-3} M/L by the mass-loss method. Langmuir's adsorption isotherm fits the experimental data for the studied compound. Thermodynamic parameters for dissolution and adsorption were calculated. It is observed that HTABR can be used as an effective inhibitor.

Abd EL- Ghaffar et al[116],studies ploy (O-aminophenol), ploy (O -aminothiophenol), ploy (m-anisidine) and polyaniline which have been prepared by chemical oxidation of their monomers using ammonium persulfate at 0 °C. The polymers were evaluated as corrosion inhibitors for steel protection by measuring their corrosion rates in comparison inhibitors for steel protection by measuring their corrosion rates in comparison with the previously prepared polyaniline and the control sample. The polymers show a high performance as efficient corrosion inhibitors, and promising results were achieved when the polymers were incorporated in various paint formulations to replace a major part of the inhibitive pigments and to replace the classical toxic corrosion inhibitors of low molecular weights and low melting points. The polymers were characterized and their structures confirmed using elemental analysis and specteophotomeric measurements (FTIR, UV-VIS, HNMR, MS, XPD and TGA).

AIM OF THE WORK

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Vanadium building steel with two grades, low and medium carbon, usually heat treated before using to obtain better mechanical properties. Three heat treatment regimes used in this work, first was normalizing, second was spheroidizing, and the third one was quenching.

Two above types of carbon vanadium steel which heated and unheated treatment are used in manufacturing of concrete sanitary pipes.

Acidic liquid waste in sanitary pipes of industrial areas, can attack steel metal in reinforced concrete pipes by corrosion. Steel in concrete can be protected against corrosion inhibitors, which are soluble in water.

Eight samples from above two types of carbon vanadium (C.V.) steel were used in this stud, four specimens of every type have been used, one was kept without heat treatment, and the others were heat treated by using normalizing , spheroidizing, and quenching regimes.

N,N dihydroxyethyl acrylic acid amide(HEAA) studied in this work as inhibitor in HNO_3 as corrosion medium .

Both used vanadium steel types, were studied before and after treatment in HNO_3 solution in absence and presence of the (HEAA), to investigate corrosion behavior as follow:

1-The effect of temperature on the corrosion rate of vanadium steel in HNO_3 solution media and to correlate the protection efficiency of this organic compound with change both temperature and HNO_3 concentration.

2-Exploration of the protection efficiency from electrochemical data.

3-The application of fresh kinetic-thermodynamic model to obtain thermodynamic function (ΔG^o_{ads} , ΔH^o_{ads} and ΔS^o_{ads})for adsorption and activation energy (E^*)for dissolution that could be effectiveness of (HEAA) as inhibitor from quantitative point of view.

4-All above thermodynamic parameters of dissolution process and adsorption in presence or absence of (HEAA) were discussed in view of metal microstructure.