Corrosion – Occurrence & Prevention

Iqra Zubair Awan
Research Fellow, Institute Charles Gerhard, Ecole Nationale Superieure de Chimie,
(34040) Montpellier, France.
iqrazubair@gmail.com*

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Summary: This is a brief review of the problem of corrosion, the menace and its remedy. Corrosion costs not millions but billions of dollars in damages to equipment, accidents, failures of equipment, bridges, pipelines etc. Corrosion is the caustic attack by a metal/alloy by agents such as rain, polluted air, sea water or aggressive chemical agents. The process of corrosion and various methods of prevention have been discussed.

Keywords: Corrosion, Menace, Prevention Methods, Losses, Cathodic, Anodic, Protection, Electrochemistry.

Introduction

"Many metallic articles are usually used under conditions where they are attacked or applied by the atmosphere and by moisture – hence corrosion by the attack of these two media is the most familiar kind. Corrosion is the destructive attack upon a metallic article by agents such as rain, polluted air, or sea water. The rusting of iron and steel is the most common and best-known example of corrosion, and the continuous painting of steel bridges and slumps illustrates that protection against rust / corrosion is an ever-present problem. It has been estimated that billions of dollars more are spent each year all over the world in protecting iron and steel and on wastage [1] and replacement of corrugated metal articles.

"The 2004 worldwide direct cost of corrosion, representing costs experienced by owners and operators of manufactured equipment and systems was estimated to be $900 billion US dollars per annum or 2% of the world GDP. The 2004 global indirect cost of corrosion was estimated to be US$ 940 billion annually. Thus the total cost to the global economy in 2004 was probable to be ca. US$ 1.9 trillion per annum. The larger contribution was from the US at 31%, Japan 6% and Germany 5% [2]. We would like to emphasize that corrosion must be distinguished from erosion which is caused by mechanical erosion, although corrosion and erosion are often jointly responsible for the destruction of metallic structures and components." [1].

In practice, sometimes the conditions in which a metal/alloy gives service are of a severely corrosive nature, like the steel-work of a pier at the seaside tends to become badly corroded since the intermittent immersion in seawater with the increase and decrease of the tide causes even more intense corrosion. If the steel structure was covered permanently in seawater, the corrosion would be much less. We are told that the spread of corrosion is affect by marine growths, viz., seaweed, barnacles and bacteria. Rapid corrosion is usually caused by sewerage water, by effluvia and contaminated water produced by (chemical) factories. Steel structures in rural areas last longer than in tunnels due to moisture (humidity, exhaust fumes etc)." [1].

"It is interesting to note that not all corrosion is considered as undesirable. For example, the appearance of bronze statues or copper roofs is often enhanced by a patina of a bluish-green corrosion commonly referred to as verdigris". [1]

According to Marcus [2], two major fields are commonly prominent in the corrosion of metals and alloys, viz, (1) where the metal/alloy is exposed to a liquid electrolyte, usually water, leading to aqueous corrosion, (2) where the corrosion occur in gaseous environment called oxidation high-temperature oxidation and called gaseous corrosion. These two types corrosion are usually referred to as wet and dry corrosions. In wet corrosion the electrochemical process is the dominant factor in contrast to the thick oxide layer in air or other oxidizing environment, at higher temperature with rapid transport processes by solid state diffusion through a growing oxide layer. According to Marcus [2] the division between the two processes should not be overemphasize, as these are many similarities and analogy between the two, e.g., (1) The first stages of reaction involves the absorption of chemical agents on the metallic surface that can be described by

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*To whom all correspondence should be addressed.

Gibbs equation for both liquid and gaseous atmospheres. (2) The nucleation and growth phenomenon of oxide layers and other compounds. (3) The use of surface analytical techniques.

Definition of Corrosion

According to Revie and Uhlig [3, 4], Corrosion is the caustic attack of a metal by chemical or electrochemical reaction in a certain environment and deterioration by physical cause is not called corrosion but erosion, galling or wear. In some instance, chemical attack goes with physical wear tear. Rust or rusting is usually referred to corrosion of iron and steel. Nonferrous metals usually corrode but do not rust".

Corrosion Science

The word Science means the systematic study of the structure and behavior of the physical and chemical world through observation and experiment. In short it means why, how and when some phenomenon takes place and this is exactly what the corrosion science is all about.

The problem of corrosion may be tackled by initially considering the chemical action on the surface of a metal by atmospheric gases. These gases form chemical compounds with the metals. We know that atmospheric oxygen can form iron oxide on the surface of oxide. Wet or humid atmosphere causes rapid corrosion whereas if it is stored in dry air, it will be safe for a much longer time. This shows that water plays an important role in the rusting of iron.

Since corrosion has much to do with chemical reaction, a corrosion scientist/engineer must be quite familiar with the principles of chemistry rather electrochemistry, sequentially to grasp corrosion reactions. And since the structure, composition and properties of metal are usually responsible for corrosion behavior, knowledge of physical metallurgy is essential.

"The corrosion scientist must know the corrosion mechanism to understand the cause of corrosion and the methods to minimize the damage cause by corrosion. The corrosion engineer's main task is to apply the scientific knowledge to control corrosion by using preventive measures such as cathodic protection, special paints, cladding, coating etc. The scientists and engineers have to work together as a closest team to combat the menace of corrosion and erosion". [4]

The corrosion of iron and steel is the most observed corrosion (chemical) phenomenon in everyday life. This, as we can imagine, is due to the wet corrosion of iron and steel. As a matter of fact, the atoms of iron react with oxygen from the air and humidity. This happens in accordance with the well-known following chemical reaction: [5]

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (a)$$
$$Fe \rightarrow Fe^{2+} + 2e^- \quad (b)$$
$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (c)$$

All the above-mentioned 3 equations could be considered to the following equation:

$$4Fe + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_3 \quad (d)$$

It is not as simple as it looks from the reactions and several other reactions also take place since it is affected by several other atmospheric agents such as CO_2, SO_2, NO_2 and Cl^- in addition to composition of iron/steel along with the process of the corrosion products which have significant influence [6].

In order to remove the rust/corrosion (iron oxides), the components are pickled (unmerged) in baths of aqueous solution containing about 16% HCl or 10% H_2SO_4. One needs intermittent rinsing with clear water to remove the grease from the alkaline water to protect the acid from neutralizing. The oxides are removed as they react with the acid and form water-soluble salts (in the case of H_2SO_4 sulphuric salts are produced [6].

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O \quad (1)$$

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \quad (2)$$

$$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 3HO \quad (3)$$

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \quad (4)$$

The reaction taking place in (3) is rather slow and, as a matter of fact $Fe_2\ O_3$ (magnetite) is not soluble in HCl and H_2SO_4. But still, it is washed away with the other oxides as it is partly converted to Fe_2O_3 from H_2 which is generated from reaction shown in (4). The dissolution of the rest of the oxides leads to the break-up of the lattice that supports Fe_2O_3. [6].

Electrochemical reaction

The corrosion reactions processes are mostly electrochemical (hence a good knowledge of electrochemistry is essential for corrosion scientists and engineers) and therefore we will discuss this topic in some detail to understand the corrosion process properly. In aqueous solution, the corrosion reactions are similar to those occurring in a flashlight battery or cell which is made up of a central carbon electrode and a zinc cup electrode in an electrolyte consisting of ammonium chloride solution [4].

Two electrical electrodes (conductors) absorbed in an electrolyte is called a galvanic cell in honour of Luigi Galvani, a physician, a physicist, a biologist and a philosopher, a former student of the (and still one of the oldest and functional international educational institute in Europe), University of Bologna, Italy. He had published his studies of electrochemical action in 1791 AD. The first author (IZA) is lucky to be a Research Fellow under Erasmus Mundus Split Ph.D Program in Sustainable Industrial Chemistry at the Universities of Bologna in Italy and Montpellier in France.

"Since corrosion is a process involving chemical/electrochemical action in which the metal transfer electrons to the environment and undergoes a valence change from zero to a positive value. The background may be liquid, gas or hybrid soil-liquid. These environments are called electrolytes as they have own conductivity for electron transfer. The electrolyte is a conductive solution and the corrosion process then becomes chemical or electrochemical due to a current flow and acquires at least 2 reactions that must occur in a particular corrosive environment and these reactions are classifies as anodic and cathodic reactions and are defined below for a metal M immersed in sulphuric acid, H_2SO_4, solution. The metal oxidation takes place by an anodic reaction and reduction takes place through a cathodic reaction:

$$M \rightarrow M^{+Z} + Ze^- \quad \text{(Anodic = Oxidation)} \qquad \text{(a)}$$

$$2H^{+Z}SO^-_4 + Ze^- \rightarrow Z/2\,H_2SO_4 \quad \text{(Cathodic=Reduction)} \qquad \text{(b)}$$

$$M + ZH + ZSO^- \rightarrow M^{+Z} + Z/2\; H_2SO_4 \quad \text{(Redox)} \qquad \text{(c)}$$

where M = Metal,
H^+ = Hydrogen cation
Z = Valence or Oxidation slate
M^{+Z} = Metal cation
SO^-_4 = Sulphate anion

The explanation of the above equations means that an anodic reaction (oxidation) reaction gains Ze^- electrons for reducing the relevant ions. Thus, both the anodic and the cathodic reactions combined in a corrosion reaction, i.e. adding (a), (b) gives (c). This way, Redox (Red = reduction and Ox = oxidation) give the resultant reaction (c), and exhibits the overall reaction at equilibrium where the anodic and cathodic reaction rates are equal. The equation (d) below shows that the metal reaction takes place to the right for oxidation or to the left for reduction.

$$M = M^{+z} + Ze^-$$

The concepts of metal oxidation and metal reduction or electro deposition are systematically shown in Fig. 1" [7].

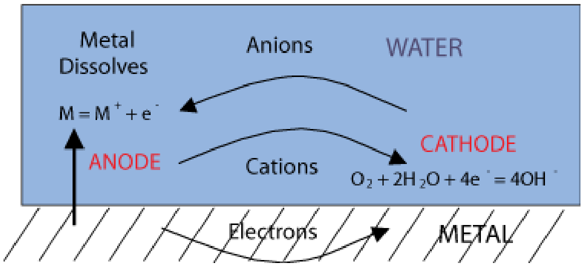

Fig. 1: (a) Oxidation of a metal in an aqueous environment [17].

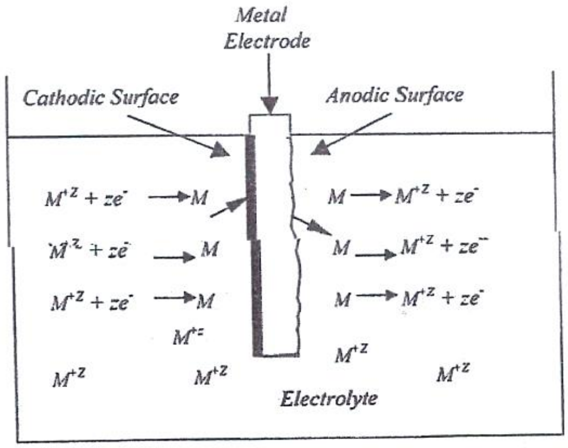

Fig. 1: (b) Schematic electrochemical cell [17].

The galvanic cell represents all the corrosion cells in which combination of two electrodes (conductors) are absorbed in an electrolyte. The electrode at which chemical reduction occurs (or + current enters the electrode is called the cathode. And the electrode in which chemical oxidation occurs (or + electricity leaves the electrode is called the anode.

"In galvanic cells, the cathode is the positive pole, whereas the anode is the negative pole.

However, it is important to note and remember that current is connected to a cell from a generator or an external battery (as in electroplating) reduction take place at the electrode connected to the negative pole of the external current source, and this positive pole of the generator becomes the anode". Revie & Uhlig (4) advice that it's remember anode and cathode as negative and positive electrodes or vice versa, but remember the cathode as the electrode in which the current enters from the electrolyte and the anode as the electrode at which the current leaves to return to the electrolyte. Moreover, cations are ions which migrate toward the cathode when electricity flows through the cell (e.g. H^+, Fe^{2+}) and are always positively charged whether current is drawn from or supplied to the cell. Likely, anions are always negatively charged (e.g. Cl^-, OH^-, SO^{2-}_4) [4]. Example of the cathode reactions as given by Revie & Uhlig (4) are:

$H+ \rightarrow \frac{1}{2} H_2 - e^-$

$Cu^{2+} \rightarrow Cu - Ze^-$

$Fe^{3+} \rightarrow Fe^{2+} - e^-$

and example of the anode reactions are (4):

$Zn \rightarrow Zn^{2+} + 2e^-$

$Al \rightarrow Al^{3+} + 3e^-$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

Types of Cells

According to Revie & Uhlig (4), there are 3 main types of galvanic cells which are operational in corrosion reactions.

(A) Dissilimar Electrode Cells

These include the dry cell, (Fig. 2). When the circuit is open (left) the cell may stay intact for years. On short-circuiting the cell with a good conductor, the Zinc cup will perforate by corrosion within a few hours.

A metal contains electrically conducting trace elements on the surface of the metal as a separate phase (c) a copper pipe associated to an iron pipe and (d) a bronze propeller in contact with the steel hull of a ship. Different electrode cells also include cold worked metals in contact with the same metals annealed, grain-boundary metal in contact with grains and even a single crystal of definite orientation in contact with another crystal of dissimilar orientation.

(B) Concentration Cells

There are cells with two similar electrodes, each in contact with an electrolyte of dissimilar composition. These are 2 kinds of concentration cells. The first is called a salt concentration cell. For example one copper electrode is immersed in a concentrated copper sulphate solution and the second one in a dilute copper sulphate solution (Fig. 3) and if they are short-circuited, copper will dissolve (i.e. $Cu \rightarrow Cu^{2+} + 2e^-$) from the anode (i.e. electrode in dilute $CuSO_4$) and plates out on the cathode (i.e. $Cu^{2+} + 2e^- \rightarrow Cu$). After some time, the 2 reactions tend to bring the two electrolytes to the same or equal concentration."

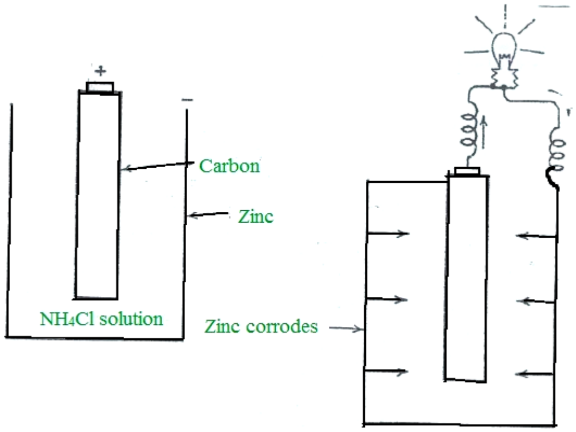

Fig. 2: Dry cell [4].

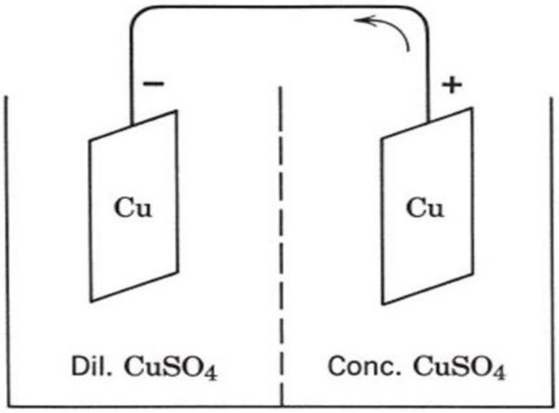

Fig. 3: Salt concentration cell [4].

According to Revie & Uhlig [4] a more important another kind of concentration cell is the differential aeration cell. It may includes two iron electrodes in dilute NaCl (Sodium Chloride) the electrolyte around one electrode thoroughly aerated (cathode) and the other deaerated, for example agitating the electrolyte with bubbling nitrogen through the electrolyte and potential difference is created due to the difference in oxygen concentration and it creates current to flow (Fig. 4). The formation of such cells cause pronounced damage at cracks, crevices, hence the true crevice corrosion. In engineering studies crevices are quite common at the border of two pipes that are coupled together and at junctions made y threaded pieces. In such places the concentration of oxygen is rather low making it anodic with respect to the areas outside the crevices. This results in the formation of differential aeration cells causing pitting corrosion under rust (Fig. 5) and also at the water line, i.e. at the water-air interface (Fig. 6). In this case the Oxygen coming in contact with the metal (covered by rust etc) is less than the quantity that comes into contacts with other portion where the porous or permeable coating layer is either very thin or not present. Differential aeration cells are prone to causing localized corrosion at pits (crevice corrosion) in materials such as stainless steel, aluminum, nickel and other passive metals when they are in contact with seawater etc.

(C) Differential Temperature Cells

This cell consists of electrode components of the same metal, but both the electrodes at different temperatures inverted in a homogenous electrolyte. These cells are commonly used in heat exchange, boilers, immersion healers etc. The electrolyte, usually copper sulphate, the copper electrode at the high temperature works as cathode, and the copper electrode at the lower temperature works as the anode [8]. On short-circuiting the cell, copper is deposited on the hot electrode, cathode, and dissolves from the cold electrode, anode. Lead also acts in the same way but if you use silver, the cathode becomes anode and the anode becomes cathode. A rather strange behavior is of iron immersed in dilute aerates NaCl solutions. The hot electrode works as anodic to the colder metal (cathodic) of the same composition. But, after several hours, depending on the aeration condition, stirring speed and the two electrodes are short-circuited, the polarity may reverse [9, 10].

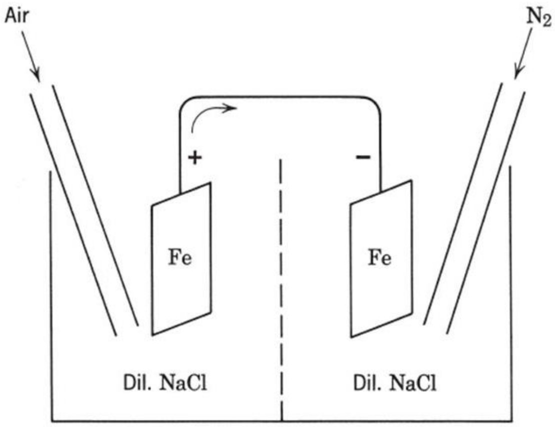

Fig. 4: Differential aeration cell [4].

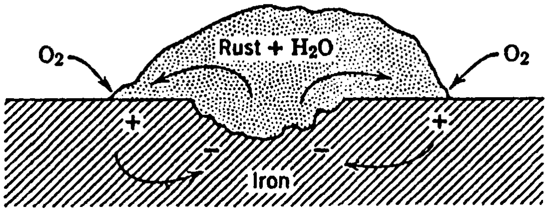

Fig. 5: Differential aeration cell formed by rust on iron [4].

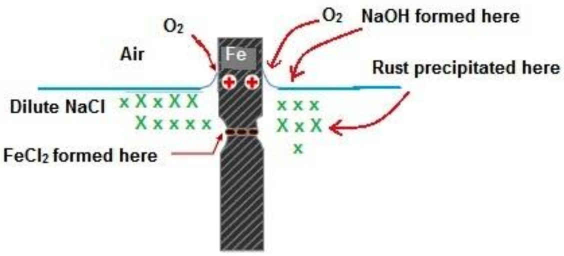

Fig. 6: Water-line corrosion, showing differential aeration cell [4].

Corrosion – Occurrence & Classification

Fontana [11] has classified corrosion forms in which they manifest themselves. This basis of this classification is the appearance of the corroded materials. Usually, an experienced engineer/scientist can easily identify the form of the corrosion just through observation by naked eye or by using a magnifying glass. One must not clean the surface of the corroded material before inspection.

Fontana [11] has mentioned 8 forms of corrosion, more or less all related to each other. The 8 forms are (1) Uniform or general attack (2) Galvanic or two-metal corrosion (3) Crevice corrosion (4) Pitting corrosion (5) Intergranular erosion (6) Selective leaching or parting (7) Erosion Corrosion and (8) Stress Corrosion. These 8 types cover practically all types of corrosion failures and problems. We now briefly discuss these 8 forms of corrosion, their characteristic, mechanisms and remedial measures.

Winston Revie & H.H. Uhlig [4] have more or less classified the corrosion types as: (1) General Corrosion or Uniform Attack, (2) Pitting, Fretting, Cavitation-erosion, (3) Dealloying Dezincification and Parting, (4) Intergranular corrosion, (5) Cracking.

As we can see both the classifications are more or less the same with slight modification/ difference in nomenclature. We would now briefly discuss the various forms of corrosion mentioned above. Fig. 7A gives the schematics of the common forms of corrosion [23].

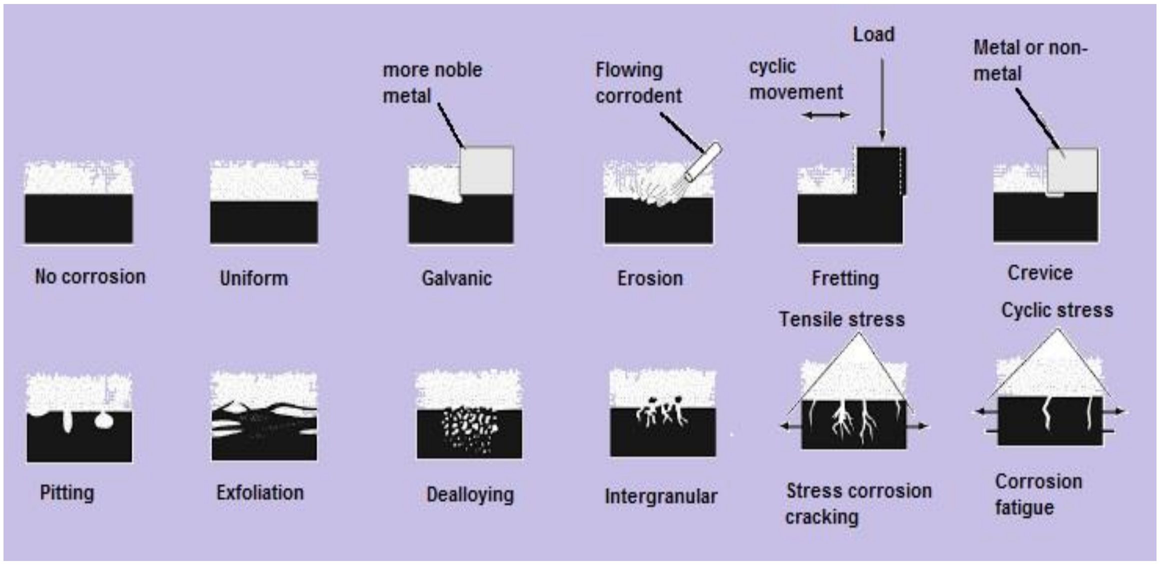

Fig. 7: (a) Schematics of common forms of corrosion [23].

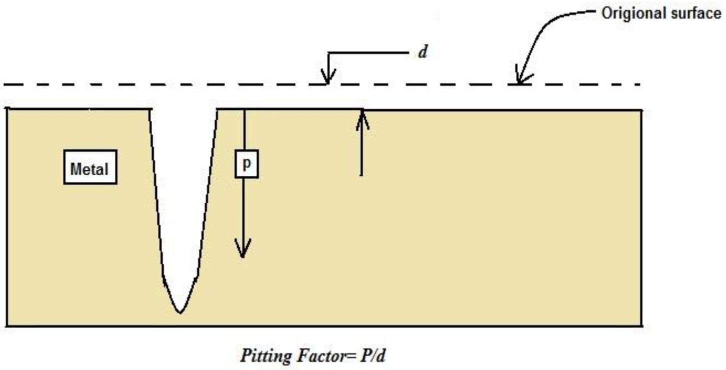

Fig. 7: (b) Sketch of deepest pit in relation to average metal penetration and the pitting factor [4].

General or Uniform Corrosion

It is general kind of corrosion, usually associated with electrochemical reaction that spreads uniformly over the complete open or expose surface. The metal loses its thickness and finally fails (cracks or breaks).

Uniform corrosion usually results in the greatest loss of metals. This loss, however, can be minimized by using proper materials protective coating inhibitors. There are a number of rare type of corrosion are unpredictable and can cause premature or unexpected failure of components.

Pitting, Fretting Corrosion and Cavitation-erosion

This type of corrosion is usually localized. Sometimes the attack is localized and appreciable and the pits are deep (acting as anode). The depth of a pit is exposed by pitting factor (Fig. 7). Iron (pipes, rods, structures) buried in earth corrodes forming shallow pits. But if stainless steel components are in touch with seawater corrode forming deep pits. Similarly, high speed liquids cause pitting and is designated as corrosion-erosion. Similarly, when two metallic surface are in relative motion, it leads to many pits at the interface.

Similarly, when a metal is exposed to cavitation by exposure to loss of material which is caused by production and collapse of water/vapour bubbles at a active metal-liquid surface interface (just as in rotors of pumps etc). This results in many pits, occasionally looking like a honeycomb of rather small cracks.

Dealloying, dezincification and parting

Yellow brass (70% Cu + 30% Zn) shows red or copper colour of Zinc is reduced in those areas. Two types of dezincification usually take place and one can easily recognize both of them: One is uniform, other whole surface creating a layer and the other is localizer or plug-type [11]. Parting is like to dezincification wherein one or more elements in an alloy corrode preferentially and leave a porous mass. Parting usually happens in noble metal. Copper-aluminum, iron, cobalt, chromium, aluminum, silver, copper etc are removed. This is also known as selective leaching [11].

Integrated Corrosion

This is a localized type of corrosion. Many alloys have precipitates at grain boundaries causing stresses there. These areas set as anodes, and the larger remaining areas act as cathodes. The attack is usually fast and since it is at the joint of crystals, it can cause rapid failure. Duraluminium and 18-8 stainless steels (improperly heat-treated) are common to face intergranular corrosion results – due to melting of some phases resulting in drastic failures. This happens in nickel-base alloys when they are subjected to sulphur-containing gaseous atmosphere resulting in the formation of nickel sulphide causing drastic failure [4].

Erosion Corrosion

It is an accelerated in the rate of corrosion (deterioration) hit on a metal because of relative movement between corrosive fluid and metal-surface. Usually, the movement is fast resulting in metallic wear and abrasion. The high speed fluid tears away the metallic particles from the surface. This may include solid corrosion products which sweep away by high speed flow.

Erosion-corrosion is characterizes visible grooves, gullies, waves, circular holes, valley and usually share a directional pattern. “Fig. 8 shows a typical shape of an erosion-corrosion failure. Fig. 9 is a sketch to explain the same phenomena [11].

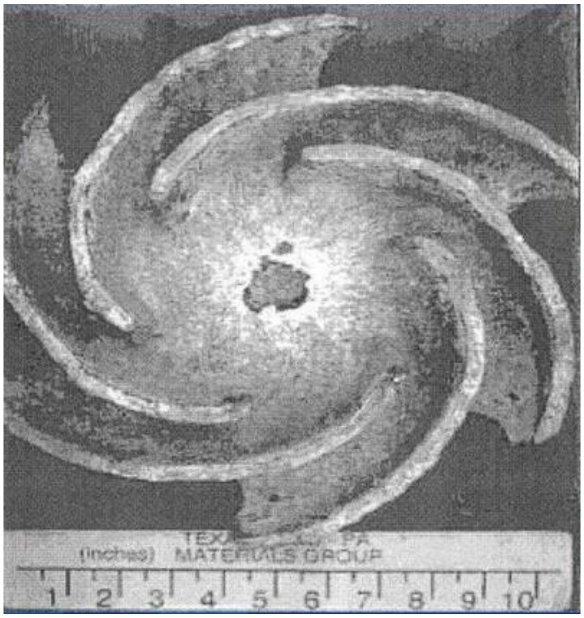

Fig. 8: Erosion-corrosion of a cast stainless steel pump impeller after exposure to hot concentrated sulfuric acid with some solids present. Note the grooves, gullies, waves, and valleys common to erosion-corrosion damage [11].

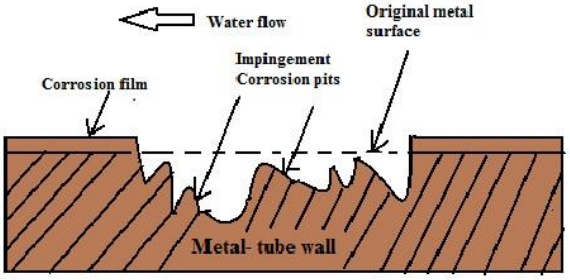

Fig. 9: Erosion corrosion of condenser tube wall [11].

Fontana [11] has explained briefly the erosion-corrosion behavior of metals and alloys, the circumstances under which this happens, the various corrosive medium (gases, aqueous solutions, organic systems, liquid metals etc). According to him, all kinds of equipment exposed to dynamic fluids are prone to erosion-corrosion, viz. piping systems, bends, elbows, tees, valves, pumps, blowers, centrifuges, propellers, impellers, agitators, heat-exchanger (tubes, heaters, condensers, measuring instruments such as an orifice, turbine blades, nozzles, ducts, vapour lines, scrapers, cutters, wear plates, grinders, mills, baffles and equipment subject to spray. Since corrosion is an essential factor in this process all factors must be considered. Fontana [11] has further mentioned surface films, velocity, role, turbulence, impingement, galvanic effect, etc and has also mentioned remedial measures to combat the erosion-corrosion problem. He has also describes the role of cavitations and fretting in erosion-corrosion problem. Figs 10-19 and Table-1 and 2.

Table-1: Corrosion of metals by seawater moving at different velocities [11].

	Typical corrosion rates, mdd*		
Material	**1 ft/sec†**	**4 ft/sec‡**	**27 ft/sec¶**
Carbon steel	**34**	**72**	**254**
Cast iron	**45**	**-**	**270**
Silicon bronze	**1**	**2**	**343**
Admiralty Brass	**2**	**20**	**170**
Hydraulic bronze	**4**	**1**	**339**
G bronze	**7**	**2**	**280**
Al bronze (10% Al)	**5**	**-**	**236**
Aluminum brass	**2**	**-**	**105**
90-10 Cu Ni (0.8% Fe)	**5**	**-**	**99**
70-30 Cu Ni (0.5% Fe)	**2**	**-**	**199**
70-30 Cu Ni (0.5% Fe)	**<1**	**<1**	**39**
Monel	**<1**	**<1**	**4**
Stainless steel type 316	**1**	**0**	**<1**
Hastelloy C	**<1**	**-**	**3**
Tatanium	**0**	**-**	**0**

*Miligrams per square decimeter per day.
†Immersed in tidal current.
‡Immersed in seawater flume.
¶Attached to immersed rotating disk.
Source: International Nickel Co.

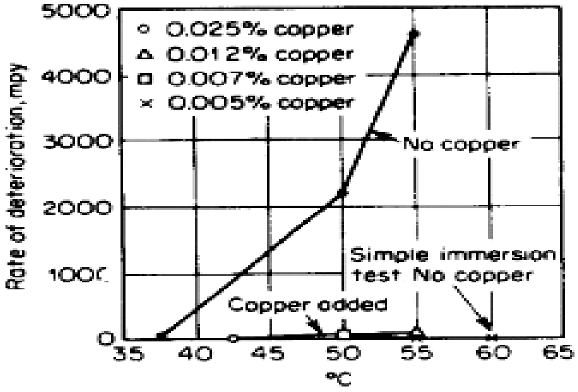

Fig. 10: Effect of temperature and copper-ion addition on erosion corrosion of type 316 by sulfuric acid slurry (velocity, 39 ft/sec) [11].

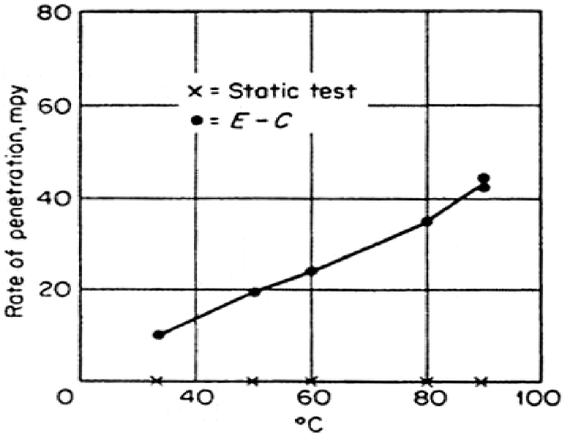

Fig. 11: Erosion corrosion of hard lead by 10% sulfuric acid (velocity, 39 ft/sec) [11].

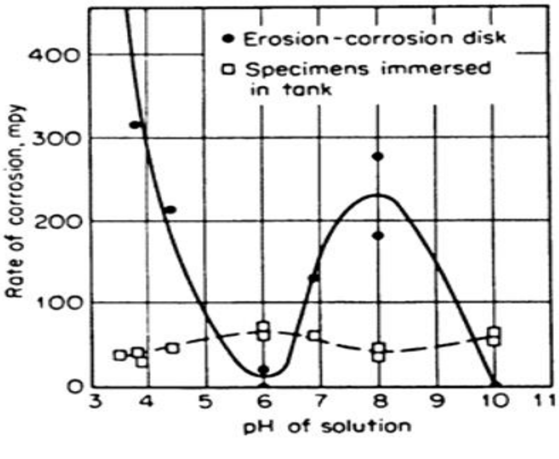

Fig. 12: Effect of pH of distilled water on erosion corrosion of carbon steel at 50°C (velocity, 39 ft/sec) [11].

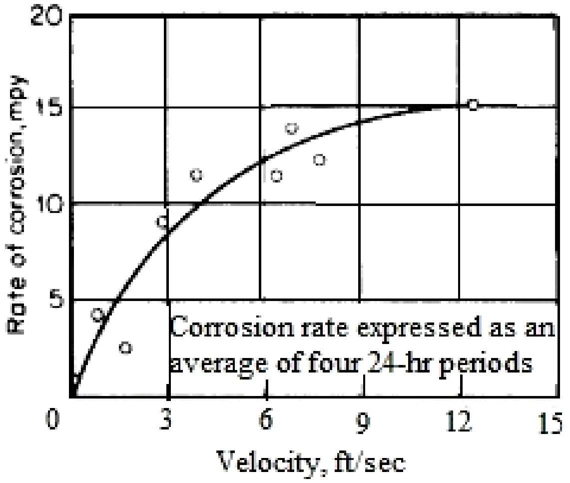

Fig. 13: Erosion corrosion of 3003 aluminum by white fuming nitric acid at 180°F [11].

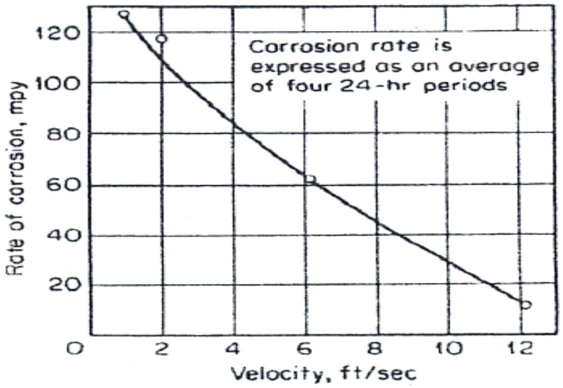

Fig. 14: Erosion corrosion of type 347 stainless steel by white fuming nitric acid at 108°F [11].

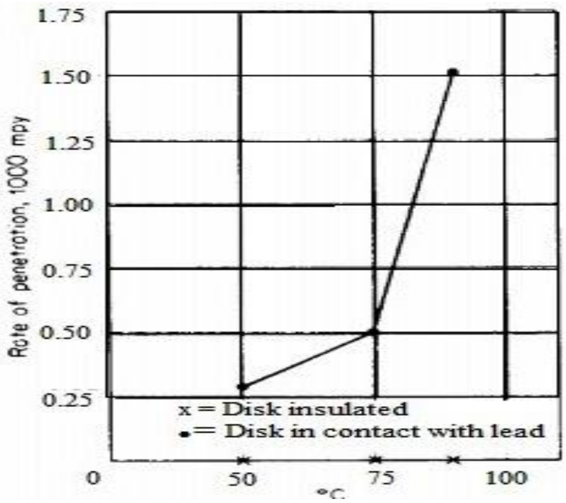

Fig. 15: Effect of contact with lead on erosion corrosion of type 316 by 10% sulfuric acid (velocity, 39 ft/sec) [11].

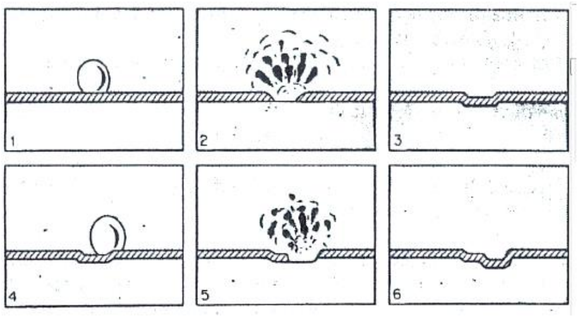

Fig. 16: Schematic representation of steps in cavitation. (R. W. Henke) [11].

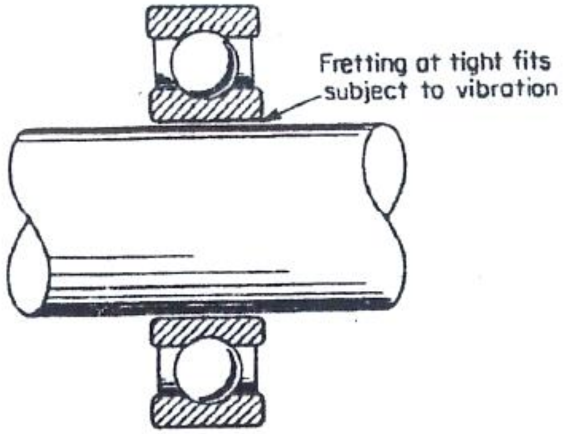

Fig. 17: Example of typical fretting corrosion location [11].

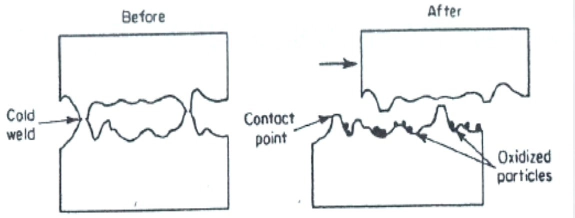

Fig. 18: Schematic illustration of the wear-oxidation theory of fretting corrosion [11].

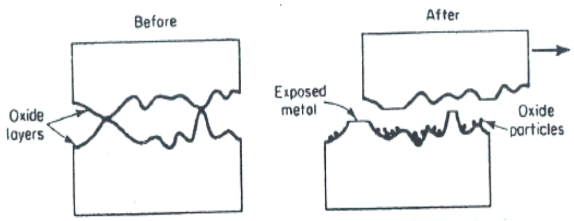

Fig. 19: Schematic illustration of the oxidation-wear theory of fretting corrosion [11].

Table-2: Fretting resistance of various materials.

Poor	Average	Good
Aluminum on cast iron	Cast iron on cast iron	Laminated plastic on gold plate
Aluminum on stainless steel	Copper on cast iron	Hard tool steel on tool steel
Magnesium on cast iron	Brass on cast iron	Cold-rolled steel on cold-rolled steel
Cast iron on chrome plate	Zinc on cast iron	Cast iron on cast iron with phosphate coating
Laminated plastic on cast iron	Cast iron on silver plate	Cast iron on cast iron with coating of rubber cement
Bakelite on cast iron	Cast iron on copper plate	Cast iron on cast iron with coating of rubber cement
Hard tool steel on stainless	Cast iron on amalgamated copper plate	Cast iron on cast iron with coating of tungsten sulfide
Chrome plate on chrome plate	Cast iron on cast iron with rough surface	Cast iron on cast iron with rubber gasket
Cast iron on tin plate	Magnesium on copper plate	Cast iron on cast iron with Molykote lubricant
Cast iron on cast iron with coating of shellac	Zirconium on zirconium	Cast iron on stainless with Molykote lubricant

Source: J. R. McDowell, *ASTM Special Technical Publication No. 144*, p. 24, American Society for Testing Materials, Philadelphia, 1952.

Fig. 20: Cross section of stress-corrosion crack in stainless steel (500 x) [11].

Stress Corrosion Cracking

Many structural components in service are influenced by a mixture of tensile stress and corrosive media. They can hastily fail at a stress below the yield strength. The stress corrosion cracking also encompasses Hydrogen-induced cracking (HIC) and Corrosion-Fatique Cracking (CFC). The environmentally influenced cracking is classified as EIC.

The stress corrosion cracking takes place under slow strain rate and chlorine. It takes place only when the tensile strain rate is in a narrow, critical range, or else the metals are immune to stress corrosion cracking either to the rehabilitation of the protective film or fracture due to high strain velocity. Fig. 21 shows the stresses necessary for stress corrosion cracking compares with the total range of strength capability for SS304. Exposure to body $MgCl_2$ (310°F) reduces the strength capability to about that available at 1200°F [11]. Fig. 22 shows Parkins′ classical stress strain curves [12].

According to Kim and Wilde [13], they exists a lower and an upper limit of strain rate at a constant applied potential and a potential range at a constant strain rate for ductile materials, as schematically separated in Fig. 23.

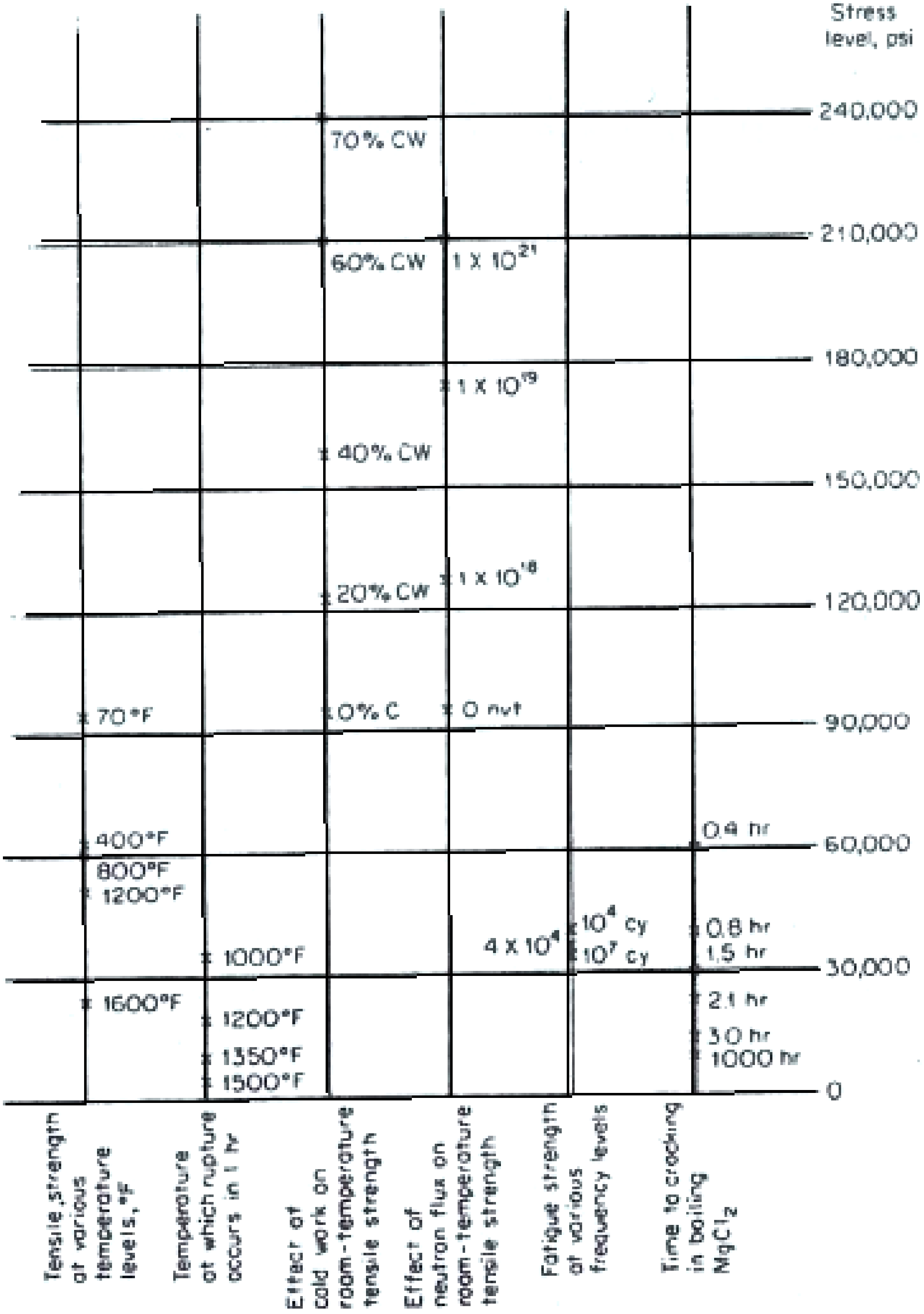

Fig. 21: Comparison of fracture stress by various techniques compared with stress-corrosion cracking. Material: type 304 stainless. (Courtesy Dr. R. W. Staehle, Ohio State University) [11].

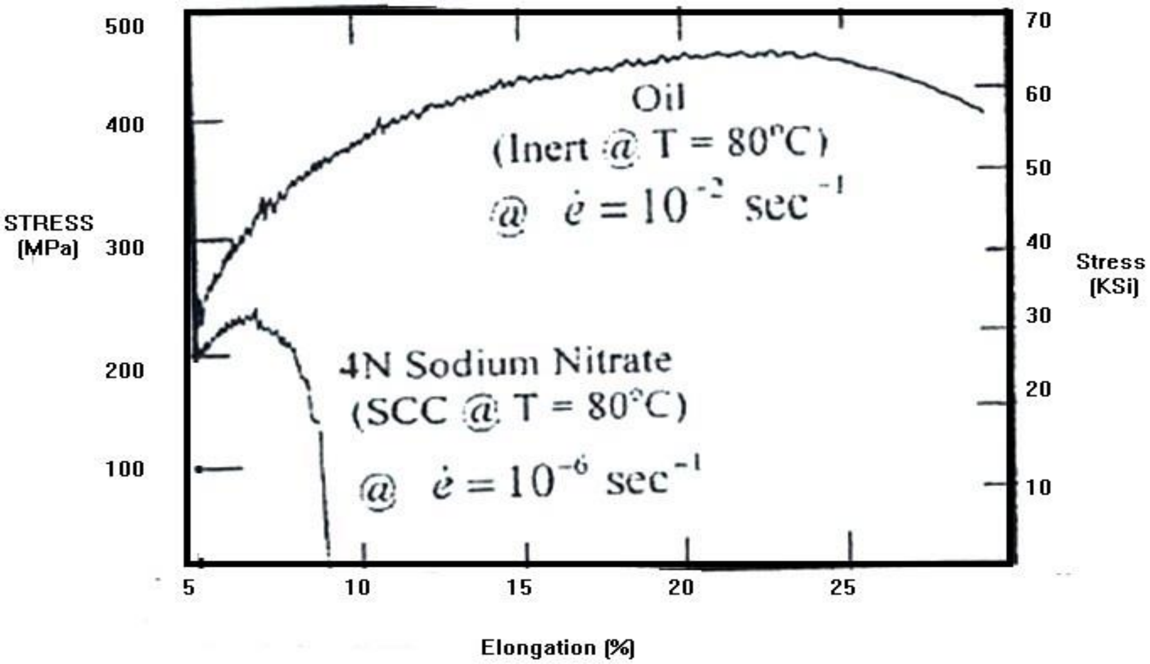

Fig. 22: Stress-strain curves for carbon steel in hot oil and hot sodium nitrate. [12]

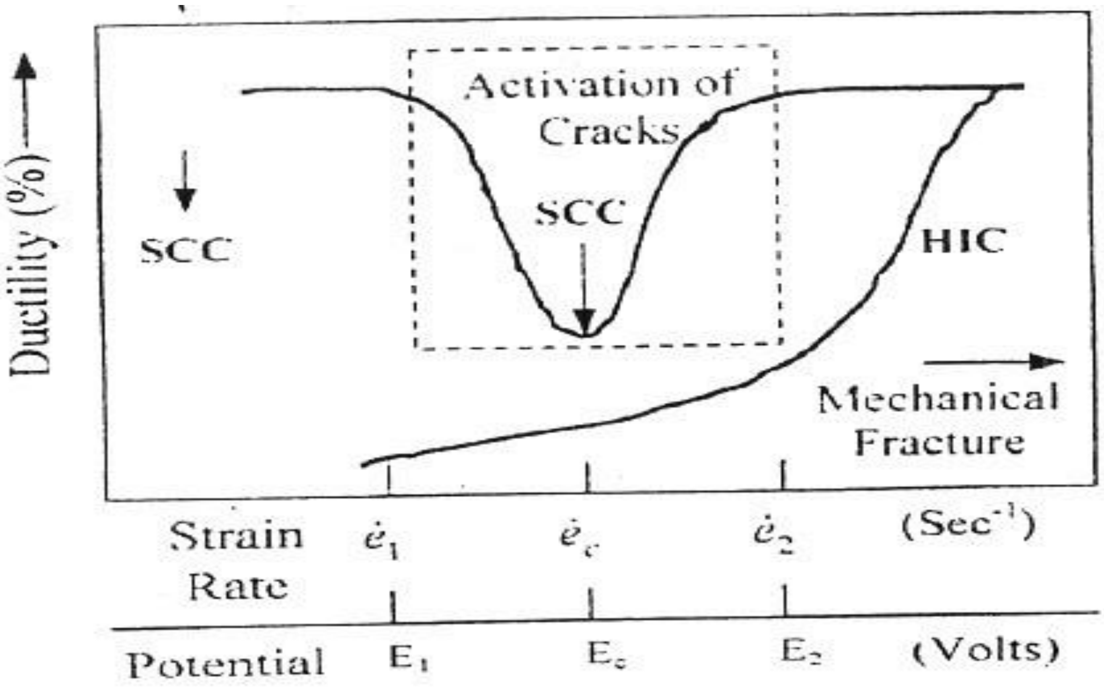

Fig. 23: Schematic effect of strain rate on ductility using a slow strain rate testing method [13].

Experimental verification of the stress corrosion cracking curve by Kim and Wilde [13]. Fig. 24 for a quickly solidified alloy AISI 304 under tension testing in O.I0N H_2SO_4 solution at room temperature [14].

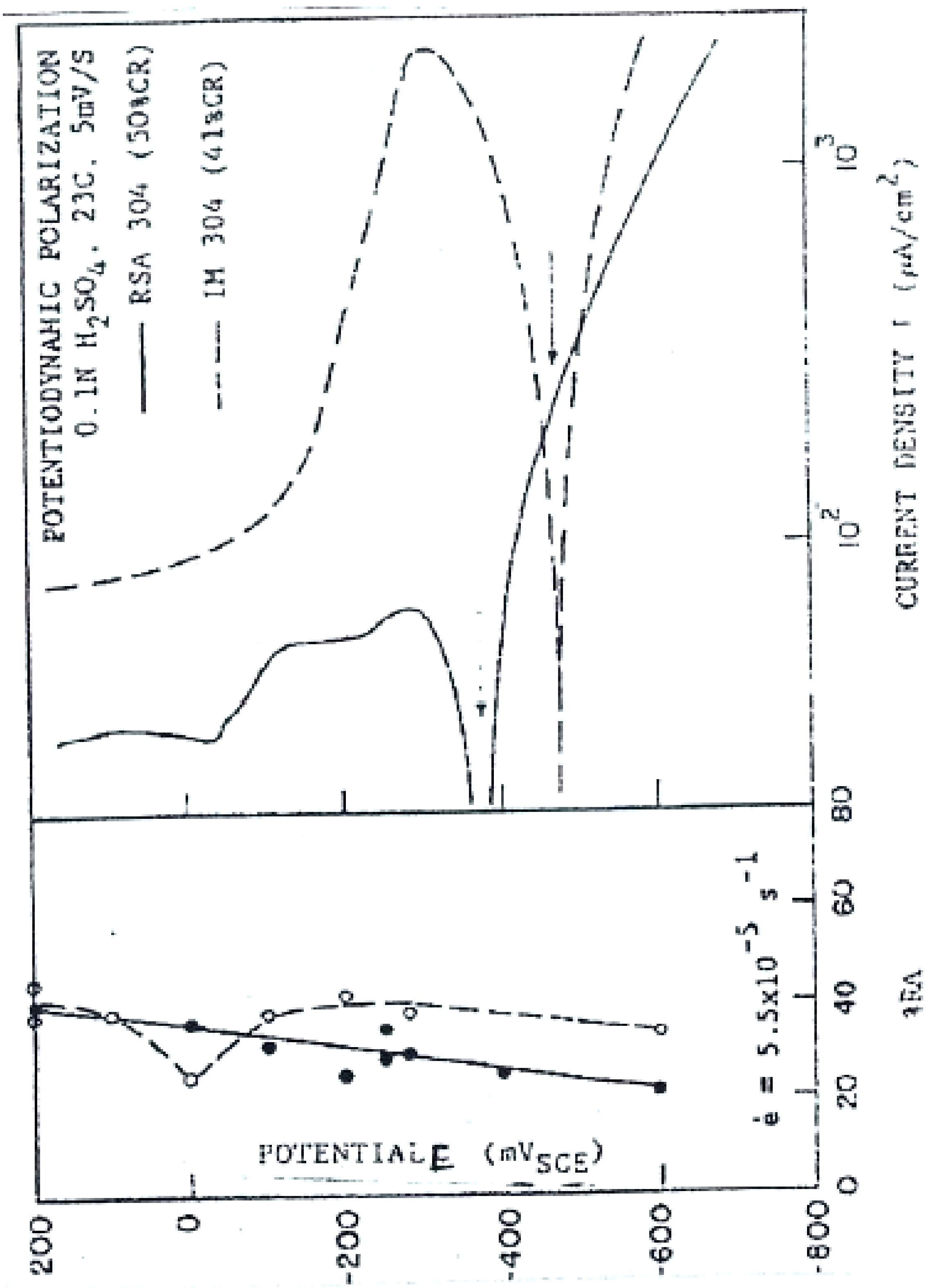

Fig. 24: Influence of the slow strain rate technique and the applied potential on the ductility of 41% cold rolled and annealed AISI 304 S.S. at 1000ºC for 24 hours. The applied strain rate was 5.5.x10−5sec–1 [14].

Fontana [11] has described in detail the stress corrosion cracking phenomena and crack morphology, stress effect, time to cracking, environmental factors, metallurgical factors, mechanisms and classification of mechanisms, methods of prevention, corrosion fatigue, hydrogen embrittlement (in detail). etc.

Uhlig's Corrosion Handbook, Part 1 (Edited by R. Winston Revie) third edition (2011) contains very nice schematic views (Fig. 25) of five intrinsic modes of corrosion penetration: general (including wear, erosion, fretting), intergranular; pitting, stress corrosion cracking and fatigue cracking [15, 16]. Fig. 25B illustrates a beautiful schematic view of pitting corrosion [22].

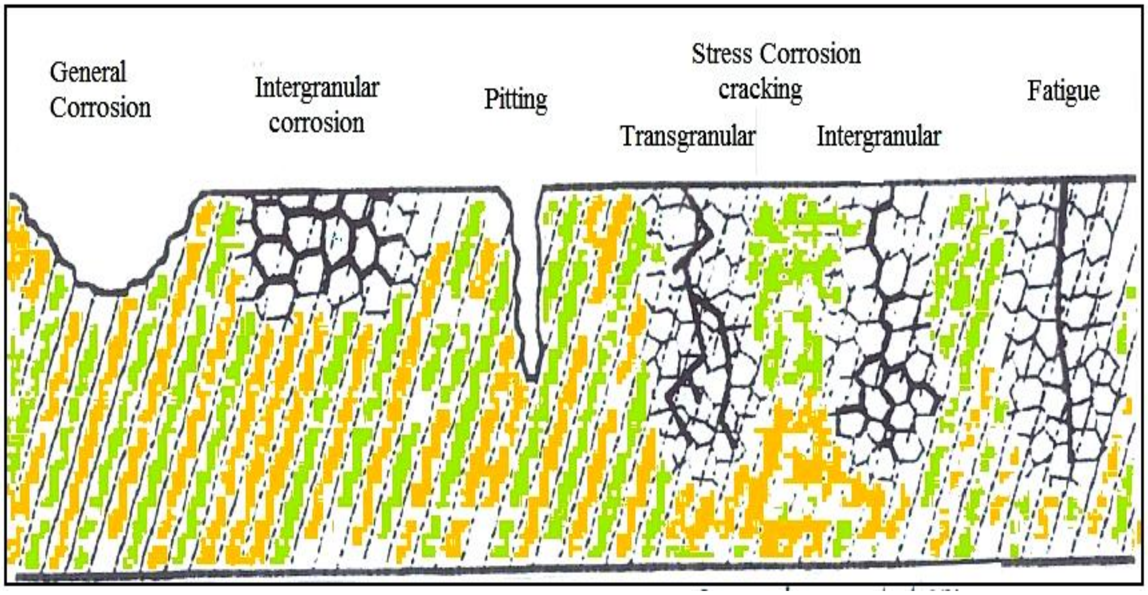

Fig. 25A: Schematic views of five intrinsic modes of corrosion penetration: general (including wear, erosion, and fretting), intergranular, pitting, SCC, and fatigue cracking [16].

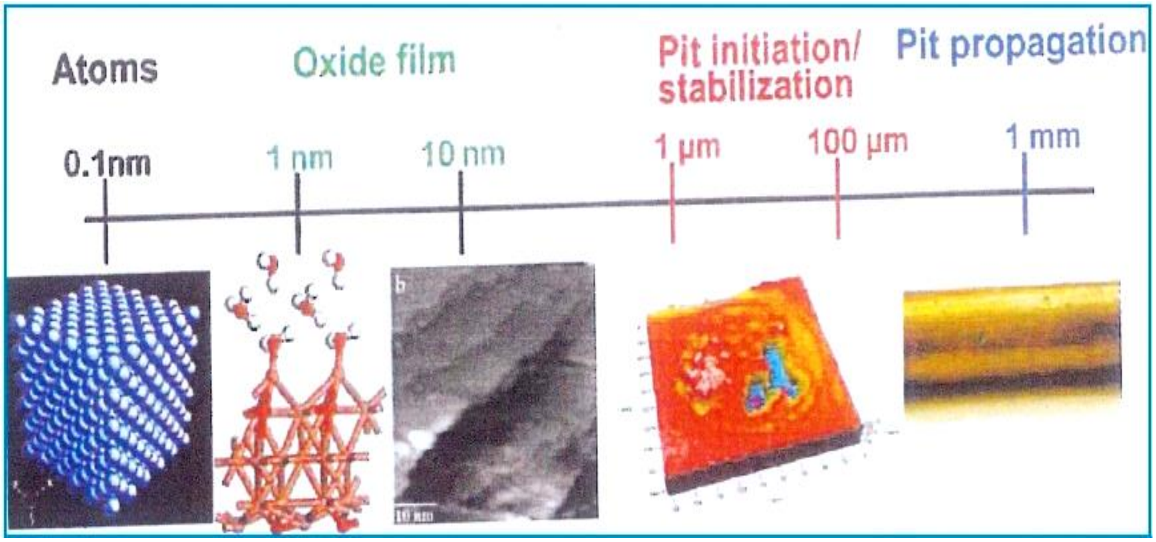

Fig. 25B: The length scales that must be considering to fully understand pitting corrosion [22].

Hydrogen cracking/embrittlement/stress corrosion

“Since hydrogen the rich elements and is always obtainable during production processing and service of metals, hydrogen damage can develop in many ways. The interaction between hydrogen and metals can result in the formation of solid solutions of hydrogen in metals. Depending upon the type of hydrogen/metal interaction, hydrogen damages metals in many ways, viz. hydrogen embrittlement, hydrogen-induced blistering, hydrogen-induced cracking, hydrogen attack, hydride formation, etc.” [23]

“The mechanisms based on slip interference by dissolved hydrogen. Hydrogen embrittlement is generally renowned from stress corrosion cracking by the interaction with applied currents. When the current makes the specimen more anodic and accelerates cracking, it is considered being stress-corrosion cracking. Conversely, where cracking accentuated by current in the opposed direction, which accelerates the hydrogen evolution reaction, consider being hydrogen embrittlement.” [11]

When high strength steel containing hydrogen is stressed in tension, even if the applied stress is less than the yield strength, it may fail prematurely in a brittle manner. High strength steels can be embrittled by hydrogen present in a few parts per million. It should be noted that hydrogen embrittlement decreases significantly with increasing temperature.

The mechanism of hydrogen embrittlement is rather complex. For detailed descriptions one may consult Fontana [11] and Davis [23].

Thermodynamic Principles of Corrosion

According to Fontana [11], “thermodynamics, the science of energy changes, is widely applied to corrosion studies”. Since corrosion involves chemical change, the corrosion scientists and engineers must have good knowledge of thermodynamics chemistry, electro chemistry, structure and composition of metals and alloys (physical metallurgy). All this makes it compulsory to have a thorough knowledge of thermodynamics of corrosion process.

We have clearly briefly discussed electro-chemical mechanism, definition of anode and cathode, and different kinds of cells. That brings us to the electromotive force or electrode potentials of a cell, what it is and how it is measured and what role it plays in corrosion process.

We know that corrosion is the depletion of material by the chemical action of its environment. It doesn’t incorporate mechanism such as erosion or wear, which are mechanical. Aqueous corrosion is the oxidation of a metal via an electrochemical reaction in water and its dissolved compounds. It’s dependent in presence of water to act as an ion conducting electrolyte.

It’s also essential for all industries. The lifetime and safety of chemical plants, offshore platforms and ships are all dependent on controlling and predicting corrosion rates and products.

We are dealing with the concepts of electrochemical equilibrium reactions, electrode potentials, and construction of Pourbaix diagrams by using the Nernst equation and their interpretation. A Pourbaix diagram is a plot of the equilibrium potential of electrochemical reactions against pH. It shows how corrosion mechanisms can be examined as a function of factors such as pH, temperature and concentrations of reacting species.

Electrode potentials – Electromotive Force EMF – Standard Electrode Potential E^o.

The electrode potential, E, of a metal as the potential difference calculated (in volts) involving a metal electrode and a reference electrode. E_e is the equilibrium potential (or reversible potential), describes the equilibrium between two different oxidation states with same element at whatever concentration (or pressure) they occur. E_e vary with conditions. It describea the electrode potential when the components of the reaction are in equilibrium. This doesn’t mean that they are in equilibrium with the standard hydrogen electrode. It means that the reaction components are in equilibrium with each other. In the reaction

$A^{z+} + ze^- = A$,

a concentration, $C^{AZ+'}$ of A^{Z+} is in equilibrium with solid A. the reaction move away from equilibrium only if there is a source of sink for electrons. If this were the case, then the potential would move away from E_e.

E^o, the standard equilibrium potential (or standard electrode potential), is defined as the equilibrium potential of an electrode reaction when all components are in their standard states, measured against the standard hydrogen electrode (SHE). It describes the equilibrium between two different oxidation states of the same element. E^o is a constant for a given reaction, defined at 298 K. Values of E^o for various electrochemical reactions can be found in data books.

Electromechanical mechanism of corrosion, the proneness of a metal/alloy to corrode is also expressed in terms of the electromotive force; emf, of the corrosion cells that are integral part of the corrosion process.

Balancing electrochemical equations

The scope of this method is to balance electrochemical equations in terms of electronic charge and moles of components, given the main reaction product and reactant. By convention, electrochemical reactions are written as the REDUCTION of the species concerned, proceeding to the right. The species with the lesser oxidation state is written on the right hand side.

(I removed 4 papragraphs)

Half-cell Electrochemical reactions – Half cell Potential

The emf of a cell is the algebraic summation of two electrode potential, it is rather easy to calculate both electrode potentials or of two half-cell potentials separately, .e.g.

$Zn^{2+} + 2e^- \rightarrow Zn$

$$\phi Zn = \phi^o zn - \frac{\mathbf{RT}}{\mathbf{2F}} \ln \frac{(\mathbf{Zn})}{(Zn^{2+})}$$

where (Zn^{2+}) is the activity of the zinc ions, (Zn) is activity of metallic zinc (solid) therefore for unity, ϕZn is the standard potential of Zn (equilibrium potential of Zn in contact with Zn^{2+} at unit activity.

A half-cell reaction is a type of electrochemical reaction which resulting a net surplus of electrons. It is the smallest complete reaction step from one species to another. This reaction may proceed as a sequence of more simple reactions, these intermediate stages are not stable. A half-cell reaction can also be a reduction, where electrons are gaining, or an oxidation, where electrons are losing. The following mnemonic is often helpful:

OILRIG: Oxidation Is loss, Reduction Is Gain (of electrons)

The anode is the site of oxidation –where electrons are lost.
The cathode is the site of oxidation –where electrons are gained.
Anions, such as O^{2-}, are negatively charged ions, attracted to the anode.
Cations, such as Fe^{2+}, are positively charged ions, attracted to the cathode.

Reduction half-cell reactions

Reduction reactions held at the cathode and involve the consumption of electrons. In corrosion these normally correspond to reduction of oxygen or evolution of hydrogen, such as:

$O_2 + H_2O + 4e^- = 4OH^-$
$O_2 + 4H^+ + 4e^- = 2H_2O$
$2H_2O + 2e^- = H_2 + 2OH^-$
$2H+ + 2e^- = H_2$

Oxidation half-cell reactions

Oxidation reactions held at the anode and involve the formation of electrons. For the corrosion of metals, these reactions normally correspond to the various metal dissolution or oxide formation reactions, such as:

$Fe = Fe^{2+} + 2e^-$
$Fe^{2+} = Fe^{3+} + e^-$
$Fe + 2OH^- = Fe(OH)_2 + 2e^-$
$2Fe + 3H_2O = Fe_2O_3 + 6H^+ + 6e^-$

In addition to causing corrosion, oxidation may result in the formation of a *passive oxide*. The passive oxide formed may shelter the metal from further corrosion –considerably slow further corrosion. A case of such passivation is that of aluminum in water, where aluminum is oxidized to from a layer of Al_2O_3 that protects the metal beneath from further oxidation. Since only differences in potential can be measured, a benchmark electrode is needed, against which all other electrode potentials can be compare. The particular reference electrode used must be stated as part of the units [4].

"Absolute potentials of electrodes are not well known it is easy to suppose arbitrarily that the standard potential for the reaction $2H^+ + 2e^- \rightarrow H_2$ is equal to zero at all temperatures. Thus, the half-cell potential for any electrode expressed on this basis is said to be on the normal hydrogen scale [4].

The Standard Hydrogen Electrode (SHE)

The electrode reaction

$2H^+ + 2e^- = H_2$

It is defined as: an electrode potential, E_{H+}/H_2 of zero volts, when all the reactants and products are in the standard state. The standard chemical potential of H^+ at 1 molar (M) concentration is by definition equal to zero. The standard state is defined as 298 K, 1 bar pressure for gases and a concentration 1 molar (1 mol dm^{-3}) for ions in aqueous solution.

https://www.doitpoms.ac.uk/tlplib/pourbaix/printall.php

The result is the standard hydrogen electrode (SHE) is usually used as a reference electrode. When coupled with an electrode, the potential difference measured is the electrode potential of that electrode, as the SHE establishes by definition the zero point on the electrochemical scale. The standard hydrogen electrode consists of a platinum electrode suspended in a sulphuric acid solution with a one molar concentration of H^+. Purified hydrogen is bubbled through to equilibrate the $2H^+ + 2e^- = H_2$ electrode reaction.

[Prop-up for other reference electrodes]

The diagram above shows how the standard potential, E^0 of nickel can be determined. The nickel electrode contains Ni^{2+} ions in equilibrium with nickel metal. Thy hydrogen electrode is connected via a salt bridge to the deaerated solution in which the nickel electrode is absorbed. This permit charge transfer and potential measurement but not mass transfer of the acid solution in the electrode. When E_e or E^0 are measured relative to the SHE (or some other reference electrode), a voltmeter is used. The voltmeter is required to have a high impedance to resist any current flowing between the electrode and the SHE. If a current were allowed to flow, the electrodes would become polarized and would no longer be at equilibrium. In practice, it is often difficult or impossible to determine experimentally the standard electrode potential for electrochemical systems. Many systems lie outside the water stability zone or are passive. For example, zinc will immediately start to oxidize when immersed in water. It is very easy to determine the standard equilibrium potential from the equation linking chemical driving force with the electrical driving force,

$$\Delta G^0 = -zFE^0$$

Now ΔG^0, the standard free energy of formation can be expressed as

$$\Delta G^0 = \mu^0(\text{products}) - \mu^0(\text{reactants})$$

where μ^0 is the standard chemical potential. By combining these equations,

$$E^0 = \frac{\Delta G^0}{zF} = \frac{\mu^0(\textbf{products}) - \mu^0(\textbf{reactants})}{zF}$$

To obtain a standard equilibrium potential, E^0, for an electrochemical reaction, all that is required is to look up relevant values of standard chemical potential.

Other reference electrodes

It is often impractical to use the standard hydrogen electrode owing to the clumsy nature of using hydrogen gas. In practice, a variety of alternative, secondary electrodes are used. The potentials of these electrodes are exactly known with respect to the SHE, so a measured potential can be simply converted to an equivalent relative to the SHE. Three of the most common secondary electrodes are:

- The saturated calomel electrode (SCE)
- The silver/silver chloride electrode
- The copper-copper(II) sulphate electrode.

The Saturated calomel electrode (SCE)

The reaction is base on the reaction between this elemental mercury (Hg) and mercury (l) chloride (Hg_2Cl_2, "calomel").,

$$Hg_2Cl_2 + 2e^- \Leftrightarrow 2Hg + 2Cl^-$$

A one molar solution of potassium chloride in water forms the aqueous phase in contact with the mercury and the mercury (l) chloride. The Nernst for this electrode can be expressed as

$$E_e = E^0 - \frac{2.303RT}{2\mathbf{F}} \log [Cl^-]^2 = E^0 - 0.0591 \log[Cl^-]$$

In cell notation the electrode is written as:
$Cl^-_{\text{(saturated)}} | Hg_2Cl_{2(s)} | Hg_{(l)} | Pt$

The silver/silver chloride electrode

This is based on the reaction is between the silver metal (Ag) and silver(l) chloride (AgCl). The half-cell reaction is

$AgCl + e^- = Ag + Cl^-$

which gives a Nernst equation of

$$E_e = E^0 - \frac{2.303RT}{F} \log [Cl^-]^2 = E^0 - 0.0591 \log[Cl^-]$$

Changing the electrolyte concentration with this electrode changes the equilibrium electrode potential, so fixed values of chloride concentration are required. In cell notation, this is written as Ag | AgCl |$KCl_{(1M)+}$

The measured potential, *E* = *+0.235* (SHE) at 298 K.

The copper-copper(II) sulphate electrode

The copper-copper(II) sulphate electrode is base on the redox reaction between copper metal and its salt – copper (II) sulphate. The corresponding equation can be presented as follows:

$Cu^{2+} + 2e^- = Cu$

The Nernst equation below shows the dependence of the potential of the copper-copper(II) sulphate electrode on the concentration copper-ions:

$$E_e = E^0 - \frac{2.303RT}{2F} \log [Cu^{2+-}] = E^0 - 0.295 \log[Cu^{2+}]$$

The equilibrium potential of a copper-copper sulphate is -0.318 V with respect to the standard hydrogen electrode for a saturation concentration of copper ions at 298 K.

Example

Find the electrochemical reaction for an equilibrium between Zn and $Zn(OH)_4^{2-}$

1. Write reduced species on right
   $Zn(OH)_4^{2-} \rightarrow Zn$
2. Balance zinc atoms
   $Zn(OH)_4^{2-} \rightarrow Zn$
3. Balance oxygen atoms with water
   $Zn(OH)_4^{2-} \rightarrow Zn$
4. Balance hydrogen atoms with hydrogen ions
   $Zn(OH)_4^{2-} + \rightarrow Zn + 4H_2O$
5. Balance charge with electrons
   $Zn(OH)_4^{2-} + 4H^+ \rightarrow Zn + 4H_2O$

Check: Each side of the equation has: 1 Zn, 4 O, 4 H and 0 residual charge – so it is balanced.

Galvanic Series

According to Fontana [11] in actual corrosion problems, galvanic compiling between metals in equilibrium with their own ions rarely occurs. Most galvanic corrosion effects result from the electrical connection of two correcting metals.

Table-3: Standard emf series of metals.

	Metal-metal ion Equilibrium (unit activity)	**Electrode potential vs. normal hydrogen electrode at 25°C, volts**
↑ Noble or cathodic	**$Au\text{-}Au^{+3}$**	**+1.498**
	$Pt\text{-}Pt^{+2}$	**+1.2**
	$Pd\text{-}Pd^{+2}$	**+0.987**
	$Ag\text{-}Ag^{+}$	**+0.799**
	$Hg\text{-}Hg_2^{+2}$	**+0.788**
	$Cu\text{-}Cu^{+2}$	**+0.377**
	$H2\text{-}H^+$	**0.000**
	$Pb\text{-}Pb^{+2}$	**-0.126**
	$Sn\text{-}Sn^{+2}$	**-0.136**
	$Ni\text{-}Ni^{+2}$	**-0.250**
	$Co\text{-}Co^{+2}$	**-0.277**
	$Cd\text{-}Cd^{+2}$	**-0.403**
	$Fe\text{-}Fe^{+2}$	**-0.440**
	$Cr\text{-}Cr^{+3}$	**-0.744**
	$Zn\text{-}Zn^{+2}$	**-0.763**
Active or Anodic ↓	**$Al\text{-}Al^{+3}$**	**-1.662**
	$Mg\text{-}Mg^{+2}$	**-2.363**
	$Na\text{-}Na^{+}$	**-2.714**
	$K\text{-}K^{+}$	**-2.925**

Source: A. J. de Bethune and N. A. S. Loud, "Standard Aqueous Electrode Potentials and Temperature Coefficients at 25°C," Clifford A. Hampel, Skokie, III., 1964. These potentials are listed in accordance with the Stockholm Convention. See J. O'M. Bockris and A. K. N. Reddy, Modern Electro-chemistry, Plenum Press, New York, 1970

Table-3 shows such tabulation, after term the electromotive force emf (EMF) series. All potentials are referred against the hydrogen electrode ($H_2\backslash H^+$) which is arbitrarily defined as Zero. Potentials between metals are found out by taking the absolute differences between their standard emf potentials. For example, there is a potential of 0.462 volts between reversible copper and silver electrodes and 1.1 volt between copper and zinc. It is not possible to establish a reversible potential for alloys containing two or more reactive components, so only pure metals are listed in Table-3. [11]. For the most part general materials are alloys; galvanic couples usually include one or two metallic alloys. Under these conditions, the galvanic series listed in Table-4 yields a more accurate prediction of galvanic relationships than the emf series. Table-4 [11] is base on potential measurement and galvanic corrosion tests in unpolluted seawater conducted by the International Nickle Company at Harbour Island, N.C. In general, the position of metals and alloys in the galvanic series agrees closely with their constituent elements in the emf series. Passivity influences galvanic corrosion behavior. In Table-4, the more noble position assumed by the stainless steels in the passive state as compared with the lower position of these materials when in the active condition. Similar behavior is shown by Inconel. Table-4 shows that the alloys grouped in brackets are somewhat similar in bare composition and they have little danger of galvanic corrosion if these metals are coupled with each other. The reason is that these materials are close together in the series and the potential generated by these couples is not great. The more distance, the greater the potential generated.

Table-4: Galvanic series of some commercial metals and alloys in seawater.

	Platinum
	Gold
Noble or	**Graphite**
cathodic	**Titanium**
	Silver
	Chlorimet 3(62 Ni, 18 Cr, 18 Mo)
	Hastelloy C (62 Ni, 17 Cr, 15 Mo)
	18-8 Mo stainless steel (passive)
	18-8 stainless steel (passive)
	Chromium stainless steel 11-30% Cr (passive)
	Inconel (passive) (80 Ni, 13 Cr, 7 Fe)
	Nickel (passive)
	Silver solder
	Monel (70 Ni, 30 Cu)
	Cupronickels (60-90 Cu, 40-10 Ni)
	Bronzes (Cu-Sn)
	Copper
	Brasses (cu-Zn)
	Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)
	Hastelloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)
	Inconel (active)
	Nickel (active)
	Tin
	Lead
	Lead-tin solders
	18-8 Mo stainless steel (active)
	18-8 stainless steel (active)
	Ni-resist (high Ni cast iron)
	Chromium stainless steel, 13% Cr (active)
	Cast iron
	Steel or iron
	2024 aluminum (45.5 Cu, 1.5 Mg, 0.6 Mn)
Active or	**Cadmium**
Anodic	**Commercially pure aluminum (1100)**
↓	**Zinc**
	Magnesium and magnesium alloys

Measurement of EMF of a cell

Since we just discussed the importance of emf in corrosion technology, we find it necessary to discuss, for the convenience of students, how the emf of a cell is measured.

Revie and Uhlig [4] have described this method in these words:

"The emf of a cell, can be measured using a voltmeter of high impedance, >$10^{12}\Omega$(ohms) or by using a potentiometer, the emf of the cell can be opposed with a known emf until no current flows through a galvanometer in series with the cell. At exact balance (i.e., when the emf of the cell is exactly balanced by the known emf), no current flows through the cell, and the reading of the known emf indicates the exact emf of the cell. In making these measurements, it is essential that any current that flows in the circuit is sufficiently small that the cell is not polarized – that is, that the emf of the cell is not changed because of the current flow. For this reason, sensitive galvanometers of high input impedance, at least $10^{12}\Omega$, must be used, so that, if the potentiometer and cell are unbalanced to the extent of 1V, a current of only 10^{-12}A flows. Such a current is not sufficient to polarize (temporarily alter the emf of) the cell."

The electromotive force, emf, is also known as standard potential, E^o.

In order to measure the EMF, a standard hydrogen electrode (SHE) is used is the reference electrode to do the measurements. This reference electrode must be reversible, since classical thermodynamics applies to all reversible process. The SHE cell diagram for potential E^o_M measurement is given in Fig. 26 and the reversible cell is shown in Fig. 27. By convention the SHE potential is Zero, E^o_M= 0.

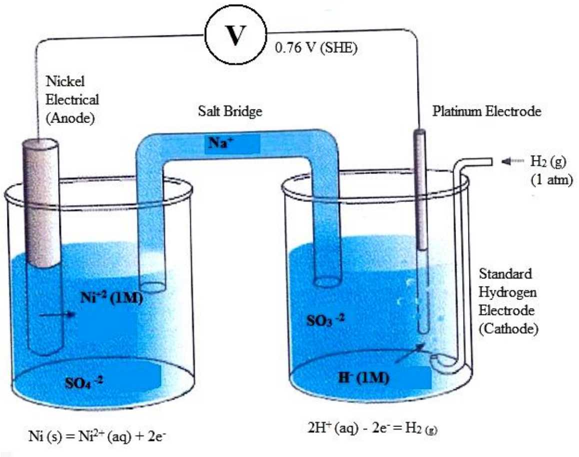

Fig. 26: Standard hydrogen electrode [17].

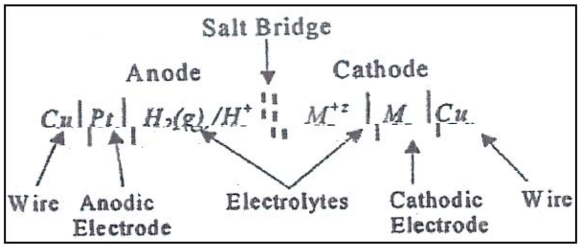

Fig. 27: Metal/SHE standard cell diagram [7].

In short, the cell potential is the difference between the electrode potentials (reduction potential) of the cathode and anode. It is called the cell EMF when no current is drawn through the cell. And the EMF = potential difference between two electrodes when no current is flowing in the circuit.

Free energy

"The tendency for any chemical reaction, including the reaction of a metal with its environment, is measured by the change in Gibbs energy, ΔG. The more negative the value of ΔG, the greater is the proneness for the reaction to take place. For example, ΔGº, for Mg and water reaction ($Mg+H_2O+\frac{1}{2}O_2(g)$

$\rightarrow Mg(OH)_2(s)$ = -596,600 J (at 25ºC) shows pronounced tendency for Mg to react with H_2O. On the other hand, ΔGº for $Cu+H_2O(l)+\frac{1}{2}O_2(g) \rightarrow Cu(OH)_2(s)$ = -119,700 J (1 cal = 4.18 abs. J) shows less tendency. And finally, ΔGº for $Au\frac{3}{2}H_2O(l) + \frac{3}{4}O_2(g) \rightarrow Au(OH)_3(s)$ = +65700 J shows proneness to reaction [4].

It must be noted that the greater the value of E (ΔG = ~nFE, F, being Faraday constant= 96500 c/eq, n is the number of electrons or chemical equivalents taking part in the reaction) for any cell, the greater the tendency for the overall reaction of all types of cells. [4].

"Table-5 [15] lists some conversion of potentials verses Standard Hydrogen and half-cell reactions for secondary reference electrodes used for measuring corrosion potentials of metals and alloys in specific applications [7]."

Table-5: Secondary reference electrode potentials.

Name	**Half-cell reaction**	***E*(*V*) vs. *SHE***
Mercury Sulfate	$HgSO_4 + 2e^- = 2Hg + SO_4^{-2}$	**0.615**
Copper Sulfate	$CuSO_4 + 2e^- = 2Cu + SO_4^{-2}$	**0.318**
Saturated Calomel	$Hg_2Cl_2 + 2e^- = 2Hg + 2Cl^-$	**0.241**
Silver Chloride	$AgCl + e^- = Ag + Cl^-$	**0.222**
Standard Hydrogen	$2H+ + 2e^- = H2$	**0.000**

pH

We are moving towards consideration of the Pourbaix Diagrams which are extremely useful for studying corrosion and related problems. They are based on Potential – pH diagrams. We must first discuss the pH. First what is pH?

A hydrogen ion is just the nucleus of a hydrogen atom, which is a proton (Fig. 28). Since an acid gives H^+ ions to a base, we can say that an acid is a proton donor and a base is a proton acceptor. There is a scale for showing the strength if an acid or alkali; known as pH which is an abbreviation for power or fugacity of the Hydrogen and has values from 0 to 14. Values below 7 are acidic and above 7 are alkaline. The value of 7 is neutral. The term pH was originally introduced by the Danish biochemist Sorensen (1865-1939). He used the term when investigating methods of improving the quality of beer. The concentration of hydrogen ions in aqueous solutions commonly ranges from about 2 mol dm^{-3} to about 1 x 10^{-14}. The pH value is given as pH = $\log_{10}[H^+(aq)]$. An indicator can tell whether a substance is acid, alkaline or neutral, but a universal indicator is convenient and move accurate way of measuring pH is by using an electrode connected to a scale meter. A pH meter is often used to measure the pH of soils, river waters, and aqueous solutions.

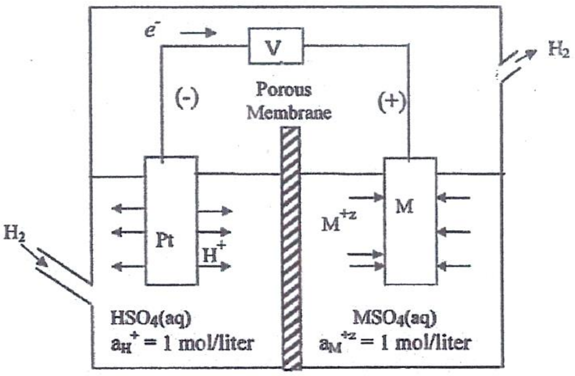

Fig. 28: Schematic metal/SHE cell [7].

We have discussed so far general corrosion phenomenon, principle of corrosion, various kinds of corrosion, electrochemical reaction, cells, electrodes, types of cells, thermodynamic principles, electrode potential, measurement of EMF of a cell, Half-cell potential, standard hydrogen cell, reference electrodes, free, energy, pH (Power or fugacity of hydrogen) etc. We will now discuss Nernst Equation which plays a very important role in corrosion service.

Nernst Equation

Walther Nernst was a German scientist. He helped establish the modern field of Physical Chemistry and contributed to Electrochemistry Thermodynamics and Solid State Physics. He is famous for developing the Nernst Equation in 1887.

In electrochemistry, the Nernst equation is an equation that relates the reduction potential of an electrochemical reaction (half-cell or full cell reaction) to the standard electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing reduction and oxidation. It is the most important equation in the field of electrochemistry.

The Nernst equation links the equilibrium of an electrode, E_e, to its standard potential, E^0, and the concentrations or pressures of the reacting components at a given temperature. It describes the value of E_e for a given reaction as a function of the concentrations (or pressures) of all participating chemical species.

In its most fundamental forms, the Nernst equation for an electrode is written as:

$$E_e = E^0 - \frac{2.303\mathbf{RT}}{zF} \log \frac{[\mathbf{reduced}]}{[\mathbf{oxidized}]}$$

This equation can be applied both to the potentials of individual electrodes and the potential differences across a pair of half-cells. However, it is generally more convenient to apply the Nernst equation to one electrode at a time.

General expression of the Nernst Equation

Taking the general equation for a half-cell reaction as,

$aA + mH^+ + ze^- = bB + H_2O$

the Nernst equation becomes

$$E_e = E^0 + \frac{0.0591}{z} \log \frac{[A\}^a}{[B]^b} - \frac{m}{z}\, 0.0591pH$$

Application of the Nernst equation

The Nernst equation links the equilibrium potential of an electrode, E_e, to its standard potential. E^0, and the concentrations or pressures of the reaction components at a given temperature, it describes the value of E_e for a given reaction as a function of the concentration (or pressures) of all participating chemical species.

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R is the universal gas constant (8.3145 J K^{-1} mol^{-1})
T is the absolute temperature
Z is the number of moles of electrons involved in the reaction as written
F is the Faraday constant (96 485 C per mole of electrons)

The notation [*reduced*] represents the product of the concentrations (or pressures where gases are involved) of all the species that appear on the reduced side of the electrode reaction, raised to the power of their stoichiometric coefficients. The notation [*oxidized*] represents the same for the oxidized side of the electrode reaction.

Example 1

In the reaction $O_2 + 4H^+ + 4e^- = 2H_2O$

Water is the reduced species and the oxygen gas is the oxidized species. By convention, electrochemical half-equations are written as

Oxidized State + ne ⇆ Reduced State

Taking into account the stoichiometric coefficients of the species, the log term of the Nernst equation for this reaction appears as

$$\text{Log} \frac{[[H]_2\mathbf{O}]^2}{po_2[[H]^+]^4}$$

At 298.15 K (25 ^{0}C), the numeric values of the constants can be combined to give a simpler form of the Nernst equation for an electrode under standard conditions:

Example 2

The reaction al = Al^{3+} + $3e^-$ has a Nernst equation of

$$E_e = E^0{}_{Al:Al}{}^{3+} - \frac{2.303RT}{zF} \log \frac{[Al]}{[[Al]^{3+}]}$$

$$= -1.66 + 0.0197 \log[Al^{3+}]$$

At 298 K, as E^0 is -1.66 V(SHE) and the activity of pure aluminum is 1. In this simple reaction, the resulting equilibrium potential is independent of *pH*.

Example 3

$Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O$ E^0 = 1.060 V(SHE), the Nernst equation is

$$E_e = E^0 - \frac{2.303RT}{zF} \log \frac{[\mathbf{Fe}^{2+}][\mathbf{H}]_2[\mathbf{O}]^3}{[Fe(OH)_3][H^+]^3}$$

$= 1.060 - 0.0591 \log[Fe^2] / H^+]^3$
$= 1.060 - 0.0591 \log[Fe^{2+}] + (3 \times 0.0591) \log[H^+]$
at 298 K.

Since the *pH* scale is defined as $pH = -\log[H^+]$

- ✓ $E_e = 1.060 - 0.0591 \log[Fe^{2+}] + 0.177 \log[H^+]$
- ✓ DolTPoMS – TLP Library The Nernst Equation and Pourbaix Diagrams
- ✓ Academic consultant: G. Tim Burstein (University of Cambridge)
- ✓ Content development: Andy Bennett, Andy Collier, Carol Newby
- ✓ Photography and video: Brian Barber and Carol Best
- ✓ Web development: Lianne Sallows and David Brook
- ✓ DolTPoMS – is funded by the UK Centre for Materials Education.

Detailed derivation of the Nernst equation

Consider the following reaction at equilibrium: $A^{z+} + z/2H_2 \Leftrightarrow A + zH^+$

This can be expressed as two half equations:

$A^{z+} + ze^- = A$ and $z/2H_2 = zH^+ + ze^-$

The left hand reaction represents the equilibrium between atoms of *A* on a metal surface and A^{z+} ions in solution. The term 'equilibrium' refers to the fact that the rate of reaction in one direction equals the rate of the reverse reaction.

For the above reaction, the free energy change Δ*G*, is given by

$$\Delta G = \Delta G^0 + RT \ln \frac{\frac{X_A}{X_A^0}}{\frac{C_{A^{z+}}}{C_{A^{z+}}^0}}$$

where X_A is the mole fraction of A in the metal and C_A is the concentration of A^{z+} in solution. When the metal, *A*, is pure $X_A = 1$. Also, the standard states X^0_A and C^0_{AZ+} can be omitted, as the standard state for the metal phase is unit mole fraction, and for the dissolved ions is 1 mol dm^{-3}. Thus, the free energy change can be expressed as

$$\Delta G = \Delta G^0 + RT \ln \frac{1}{C_{A^{z+}}} \quad (1)$$

At equilibrium, the chemical driving force, Δ*G* is always equal to the electrical driving force, E_{e-}. As discussed previously, this can be expressed as

$\Delta G^0 = -zFE_e$

where z is the number of moles of electrons exchanged in the reaction and *F* is Faraday's constant, 96 485 coulombs per mole of electrons. Under standard conditions,

$\Delta G^0 = -zFE$

From the fundamental thermodynamic equation
$\Delta G^0 = -RT \ln K$
E^0 can therefore be expressed as

$$E^0 = \frac{RT}{zF} \ln K$$

where *K* is the equilibrium constant for the reaction.

However, only the standard equilibrium potential, E^0, is related to *K*. The non-standard potential, E_e is not.

Equation (1) can now be expressed in terms of electrode potential by substituting for Δ*G* and Δ*G*^{0}

$$-zFEe = -zFE^0 + RT \ln \frac{1}{C_{A^{z+}}}$$

Water is expressed by the electrochemical reaction $Fe \rightarrow Fe^{2+} + 2e^-$. The equilibrium potential for the Fe^{2+}/Fe couple can be calculated using the Nernst equation:

$$E_{Fe^{2+}/Fe} = E^0_{Fe^{2+}} + \frac{RT}{2F} \ln a_{Fe2+}$$

where $E^0_{Fe^{2+}}$ is the standard potential value for the couple, R is the gas constant, T is the absolute temperature, F is the Faraday constant, and $a_{Fe^{+2}}$ is activity for the ferrous ion in solution. For a given temperature and Fe^{2+} concentration (activity a_{Fe2+}), the equilibrium potential is constant and is represented as a horizontal line in E-pH diagram (Fig. 30). This line indicates the potential at which Fe and Fe^{2+} at a given concentration are in equilibrium and can co-exist with no net tendency for one to transfer into the other. At potentials above the line, iron metal is not stable and tends to dissolve as Fe^{2+}, hence the Fe^{2+} concentration increases metal a new equilibrium is reached – this is a domain of stability for Fe^{2+}. At potentials below the equilibrium line, the stability of the metallic iron increases, Fe^{2+} tends to be reduced, and thus its concentration decreases, this is the domain of stability for the metal, iron (Fig. 30).

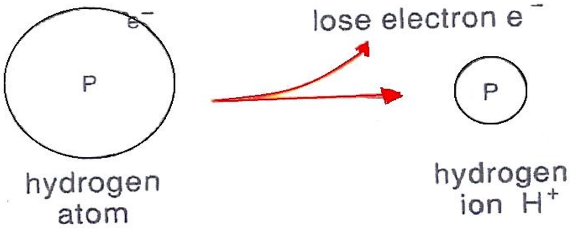

Fig. 29: Formation of hydrogen ions [15A].

[15A] Prescott, C. N., Chemistry – A course for 'O' level, Publishers Marketing Associates, Karachi, Pakistan (2006)

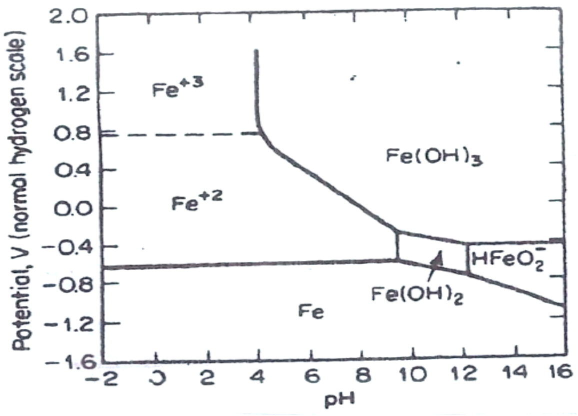

Fig. 30: Simplified potential-pH diagram for the Fe-H2O system. (M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, pp. 307-321, Pergamon Press, New York, 1966) [11].

"The diagrams or all metal-water systems have the same common features; the lower *E*-pH lines give the limit between the domain of stability of the metal and the domain of stability of either the first metallic ion or the first metallic oxide.

For *E*-pH conditions below these lines, the metal is stable, and corrosion cannot take place. This is the immunity region (Fig. 30).

For *E*-pH conditions above the line for the equilibrium between the metal and the first metallic ion, the metal is not stable, and it tends to be oxidized and dissolved into ions. The system is then in the corrosion or activity region of the diagram. Besides the main corrosion region in the stability domains of the metallic ions at low pH (acid corrosion), there is generally also a smaller domain of stability of oxygenated metallic ions at high pHs, leading to alkaline corrosion (Fig. 30).

When the reaction of the metal with water produces an oxide (or hydroxide) that forms a protective layer, the metal is said to be passivated. For *E*-pH conditions above the lines for the metal-oxide and ion-oxide equilibria, the system is in the passivation region (Fig. 30).

Diagrams such as Fig. 30 [3, 18-21] have proved to be useful in corrosion as well as in many other fields, such as industrial electrolysis, plating, electrowinning and electrorefining of metals, primary and secondary electric cells, water treatment, and hydrometallurgy. It is important to emphasize that these diagrams are based on thermodynamic calculations for a number of selected chemical species and the possible equilibria between them. It is possible to predict from a *E*-pH diagram if a metal will tend to corrode or not. It is not possible, however, to determine from these diagrams alone how long a metal will resist corrosion. Pourbaix diagrams offer a framework for kinetic interpretation, but they do not provide information on corrosion rates (Ref 20). They are not a substitute for kinetic studies. Each *E*-pH diagram is computed for selected chemical species corresponding to the possible forms of the element considered in the solution under study. The addition of one of more elements, for example, carbon, sulfur, or chlorine, to a system will introduce new equilibria. Their representation in the *E*-pH diagram will produce a new diagram more complex than the previous one". [3]

It must be noted that Nernst calculations are a must before making any prediction about spontaneous direction at concentrations other than unit activity [11].

Pourbaix Diagrams [3]

"The application of thermodynamics to corrosion phenomena has been nicely generalized by means of Potential-pH diagrams. These are known as Pourbaix Diagrams" [11].

The Principle of Potential-pH diagrams was established in the 1940s in Brussels, Belgium by Prof. Dr. Maral Pourbaix [3, 18-21]. A potential-pH diagram is a graphical representation of the relations, derived from the Nernst Equation, between the pH and the equilibrium potentials (E) of the most probable equilibrium potentials are computed from thermodynamic data (standard chemical potentials, or Gibbs force energies of formation). The equilibrium relations are drawn for a given concentration of the element or for a given ratio of activities of two dissolved species of the element give E-ph lines. The representation of the equilibrium pHs domains of stability for the various species of the element, metal, ions, oxides and hydroxides. Potential-pH diagrams synthesize many important types of information that are useful in corrosion and in other fields. They make it possible to discern at a glance the stable species for specific conditions of potential and ph [3, 18-21].

The principle of E-pH diagrams may be simply understood with the case of iron in water. Corrosion in de-aerated water is expressed by the electrochemical reaction Fe → Fe^{2+} + $2e^-$. The equilibrium potential for the Fe^+/Fe couple can be calculated using the Nernst equation:

$$E_{\mathbf{Fe}^{2+}\mathbf{Fe}} = E^{0}_{\frac{\mathbf{Fe}^{2+}}{\mathbf{Fe}}} + \frac{RT}{2F}\ln a_{\mathbf{Fe}^{2+}}$$

where $E^{0}_{\frac{\mathbf{Fe}^{2+}}{\mathbf{Fe}}}$ is the standard potential value for the couple, R is the gas constant, T is the absolute temperature, F is the Faraday constant, and $a_{\mathbf{Fe}^{2+}}$ is activity for the ferrous ion in solution.

For a given temperature and Fe^{2+} concentration (activity $a_{\mathbf{Fe}^{2+}}$), the equilibrium potential is constant and is represented as a horizontal line in a E-pH diagram. This line indicates the potential at which Fe and Fe^{2+} at a given concentration are in equilibrium and can coexist with no net tendency for one to transform into the other. At potentials above the line, iron metal is not stable and tends to dissolve as Fe^{2+} concentration increases until a new equilibrium is reached; this is a domain of stability for Fe^{2+}. At potentials below the equilibrium line, the stability of the metallic iron increases, Fe^{2+} tends to be reduced, and thus its concentration decreases; this is the domain of stability for the metal (Fig. 20)". [3].

Construction of Pourbaix diagrams

"The potential-pH diagrams (Pourbaix diagrams are based on thermodynamic calculations. The equilibrium lines that set the limits between the various stability domains are calculated for the various electrochemical or chemical equilibria between the chemical species considered. There are three types of reaction to be considered:

(a) Electrochemical reactions of pure charge (electron)
(b) Electrochemical reactions involving both transfer electron and solvated proton (H^+) transfer
(c) Acid-base reactions of pure H^+ transfer (no electrons involved)

These points have been thoroughly discussed in ASM Handbook, Volume 13A, Part 1 [3].

"It must be noted that a vast amount of data may be presented simply and concisely in Pourbaix diagrams. One must try to understand first the advantages and limitations of such diagrams and only then valuable inferences may be made regarding corrosion process. The selection of conditions for cathodic and anodic protection is simplified to draw these diagrams. They also help select inhibitors with greater efficiency.

Corrosion processes involve both chemical and electrochemical phenomena. It is therefore a must to consider not only chemical thermodynamics but also electrochemical thermodynamics when dealing with corrosion problems. Chemical equilibrium are defined as those that do not involve oxidation-reduction processes but do involve the law of mass action and law of solubility product (involving partial pressure or fugacities and concentrations or activities). By contrast, electrochemical reactions are defined as those in which free electric charges, or electrons, participate." [16].

Pourbaix diagram plots the equilibrium potential (E_e) between a metal and its various oxidized species as a function of pH. The extent of half-cell reactions that describe the dissolution of metal depend on various factors, including the potential, E, pH and the concentration of the oxidized species, Mz+. The Pourbaix diagram can be thought of as analogous to a phase diagram of an alloy, which plots the lines of equilibrium between different phases as temperature and composition are varied. To plot a Pourbaix diagram the relevant Nernst equations are used. As the Nernst equation is derived entirely from thermodynamics, the Pourbaix diagram can be used to determine which species is *thermodynamically* stable at a given E and pH. It gives no information about the kinetics of the corrosion process.

M = Mz+ + ze

A Pourbaix Diagram does not have to be limited to two dimensions. Three (or higher) dimension diagrams can be constructed by varying other parameters such as concentration or temperature.

The following animation illustrates how a Pourbaix diagram is constructed from first principles, using the example of Zinc, gold and aluminum (Fig. 31).

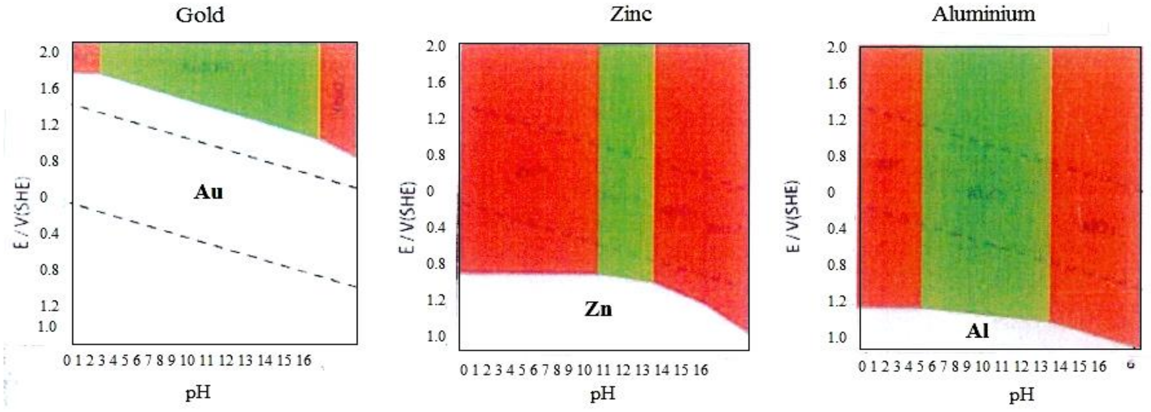

Fig. 31: The animation illustrates how a Pourbaix diagram is constructed from First principles, using the example of zinc, gold & aluminum [17].

Gold's Pourbaix diagram explains why it is the most immune substance known. It is immune in all regions in which cathodic reactions can take place. Solid gold never* corrodes in an aqueous environment.

Immunity of aluminum only occurs at lower potentials. Therefore, unless under conditions that cause it to passivate, it is much more susceptible to corrosion than gold or zinc.

*provided that the water is pure: that no ion complexes are present to provide a cathodic half cell reaction that occurs at a potential higher than +1.5. E/V (SHE)

Some common Pourbaix diagrams (Fig. 32 – 48) are reproduced here:

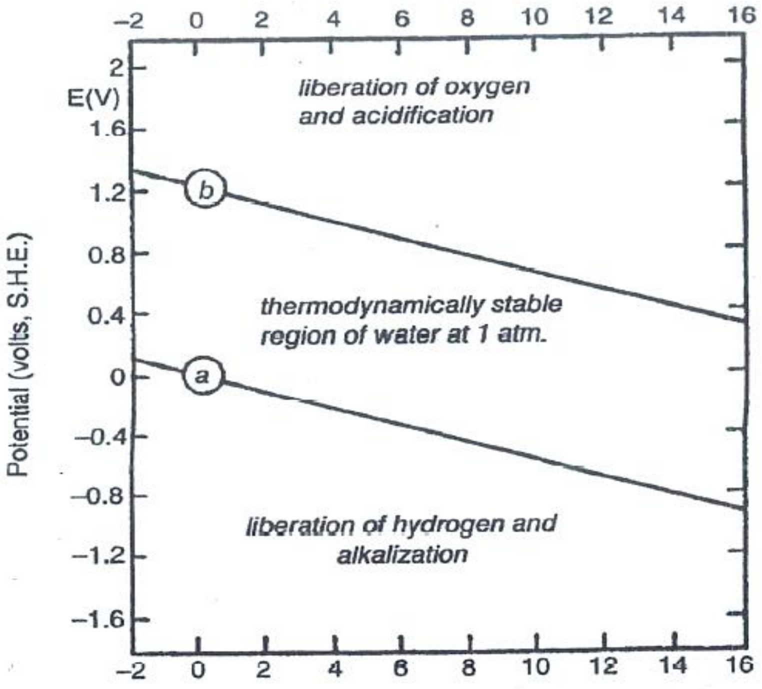

Fig. 32: Pourbaix diagram for water at 25ºC, showing the oxygen line, b, above which oxygen is evolved, and the hydrogen line, a, below which hydrogen is evolved, from the surface of an immersed electrode. Between these two lines, water is stable. (M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd English edition, p. 100, copyright NACE International 1974 and CEBELCOR.) [21].

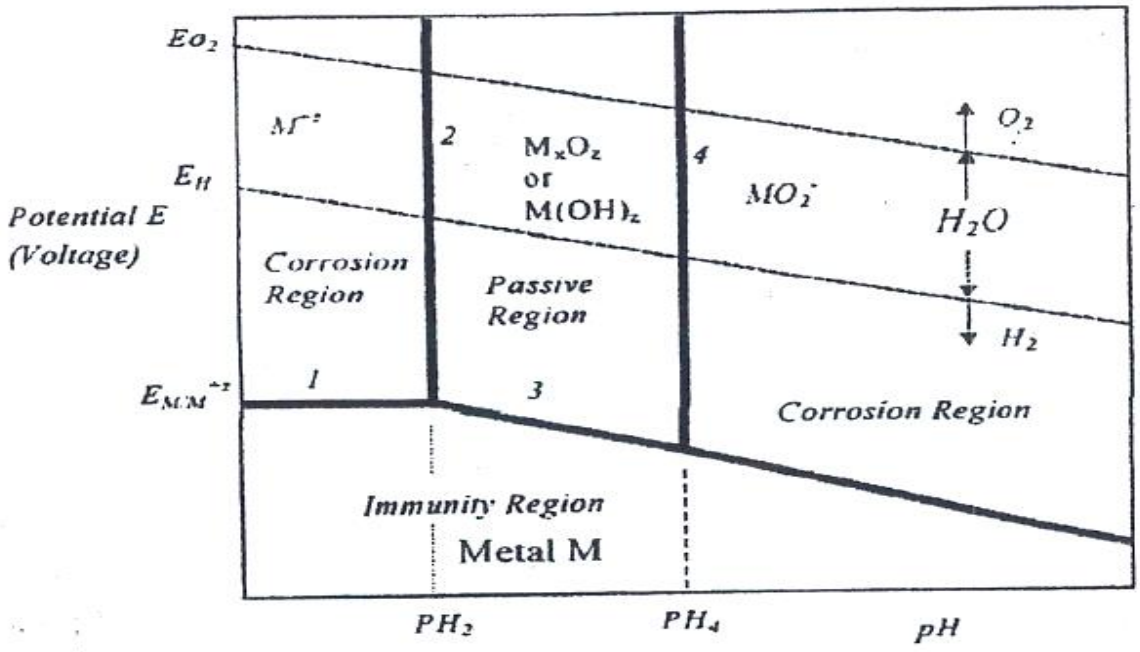

Fig. 33: Schematic Pourbaix diagram for a metal M, water and oxygen [21].

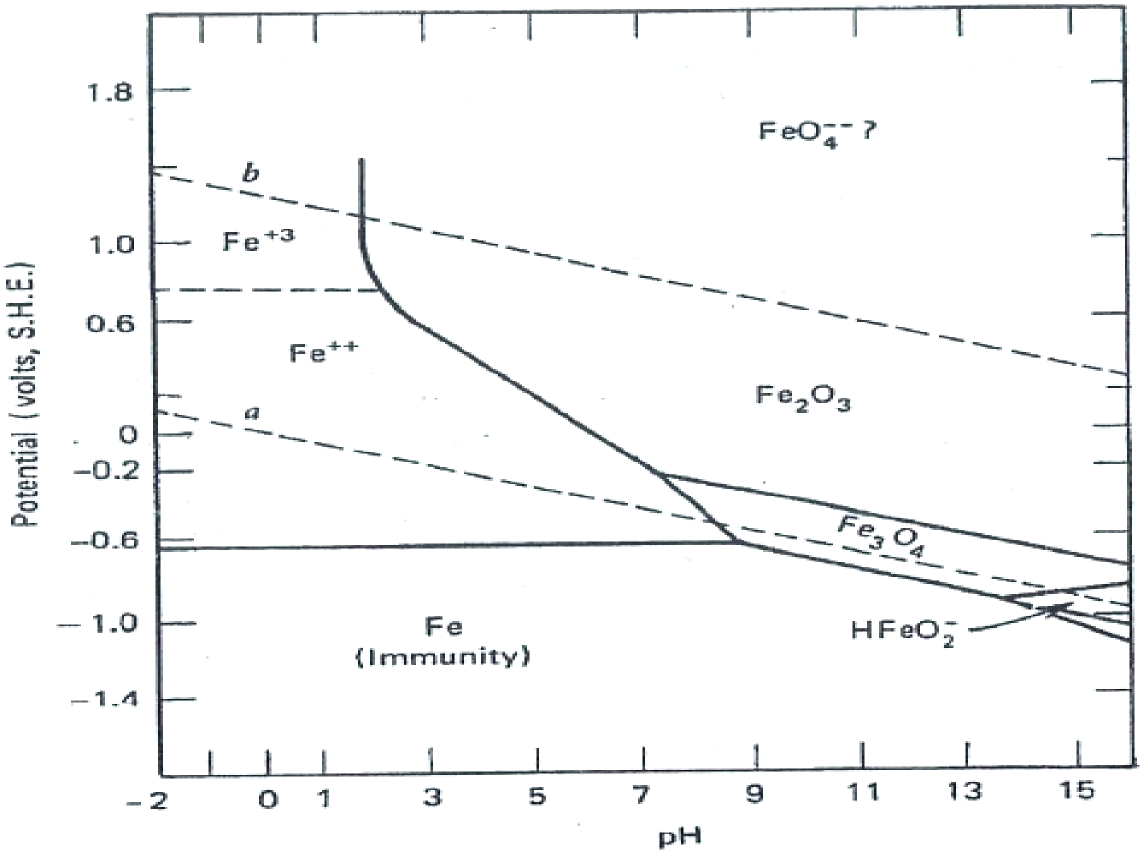

Fig. 34: Pourbaix diagram for the iron-water system at 25ºC, considering Fe, Fe3O4, and Fe2O3 as the only solid substances [21].

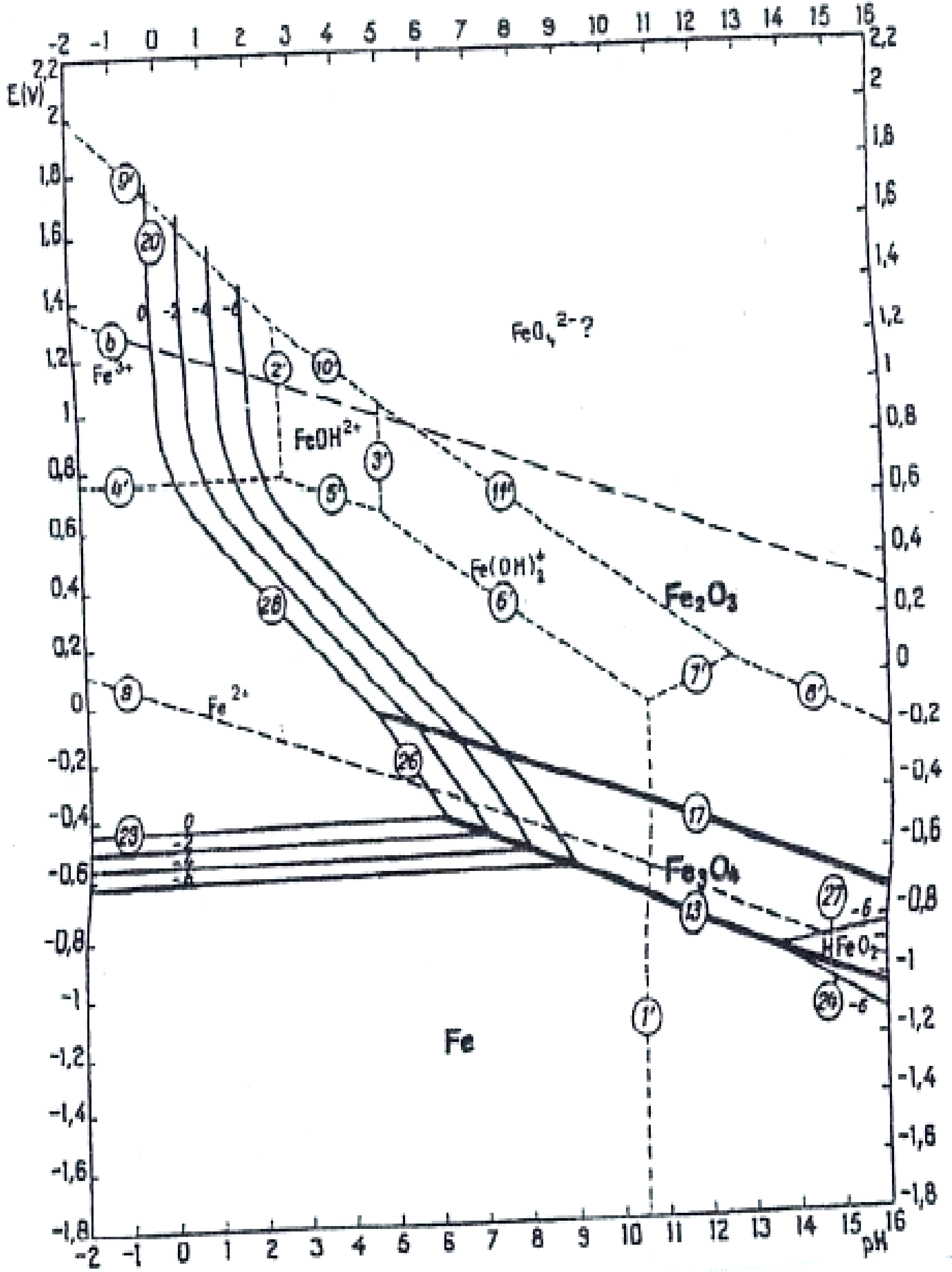

Fig. 35: Potential-pH equilibrium diagram for the system iron-water at 25ºC (considering as solid substances only Fe, Fe3O4 and Fe2O3) [1], Reproduced with permission from [1]. Copyright © Marcel Pourbaix [21].

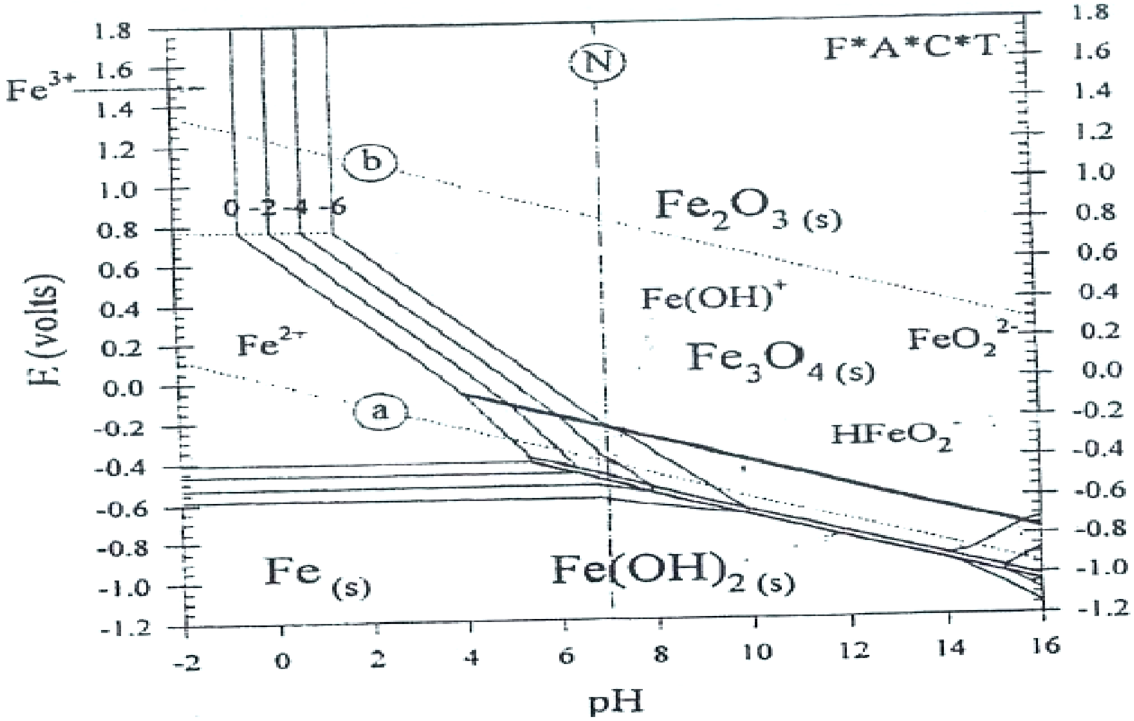

Fig. 36: The Fe Pourbaix diagram at 298 K (25ºC). Concen-trations of aqueous species range from 1 to 10−6m [21].

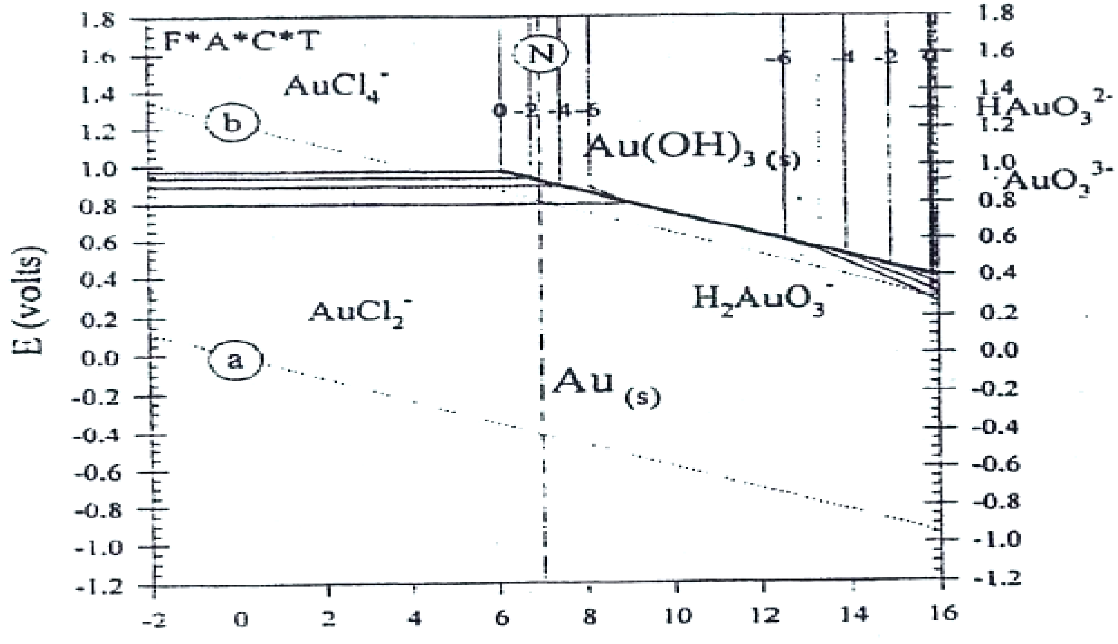

Fig. 37: The Au Pourbaix diagram at 298 K (25ºC) in chloride solution at 1 m Cl$^-$ concentration. The concentration of the Au-containing species is shown at 10 −6, 10 −4, 10 −2, and 1 m. The domain of gold immunity does not extend into strong acid solutions for oxygen saturated conditions (line (b)) because of the stability of AuCl4$^-$ [21].

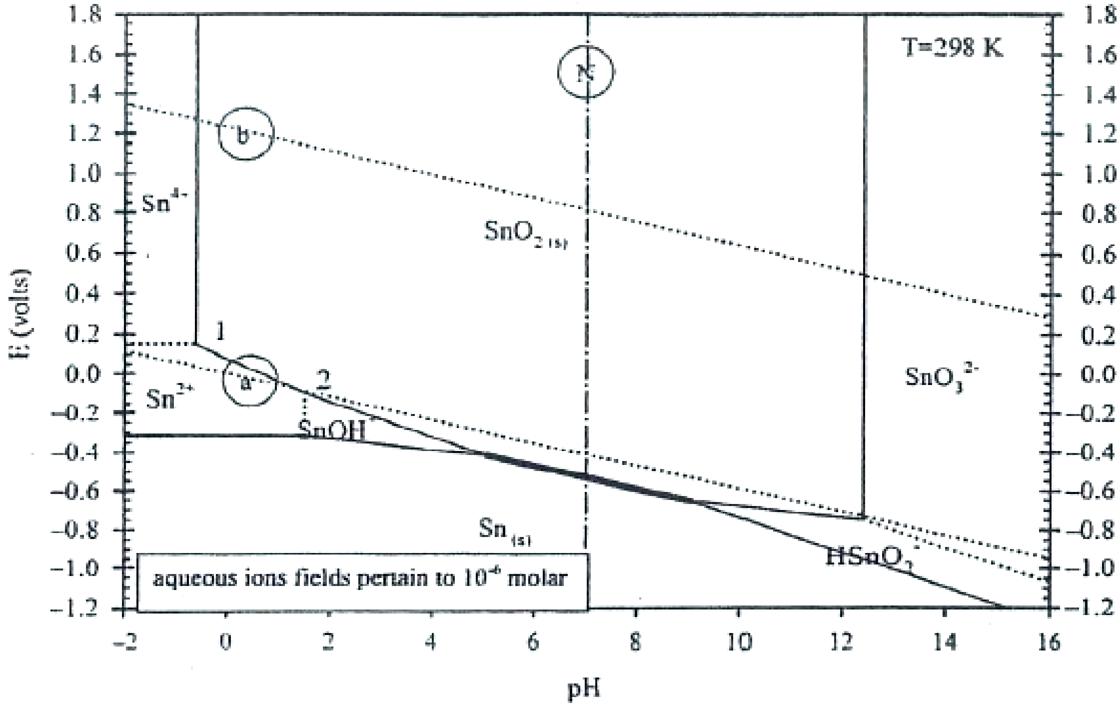

Fig. 38: Pourbaix diagram for Sn at 298K. The heaviest line represents the phase boundary between coexisting solid phases. The lighter solid lines represent conditions of a condensed phase coexisting with an aqueous solution of the adjacent ion at a concentration of 10 −6m. The broken lines represent conditions where the concentrations of ions flanking those lines are equal. The downward-sloping dotted lines [(a) and (b) correspond to H2 and O2 saturation at 1 atm partial pressure. The pH of neutrality is indicated with a vertical line labeled (N) [21].

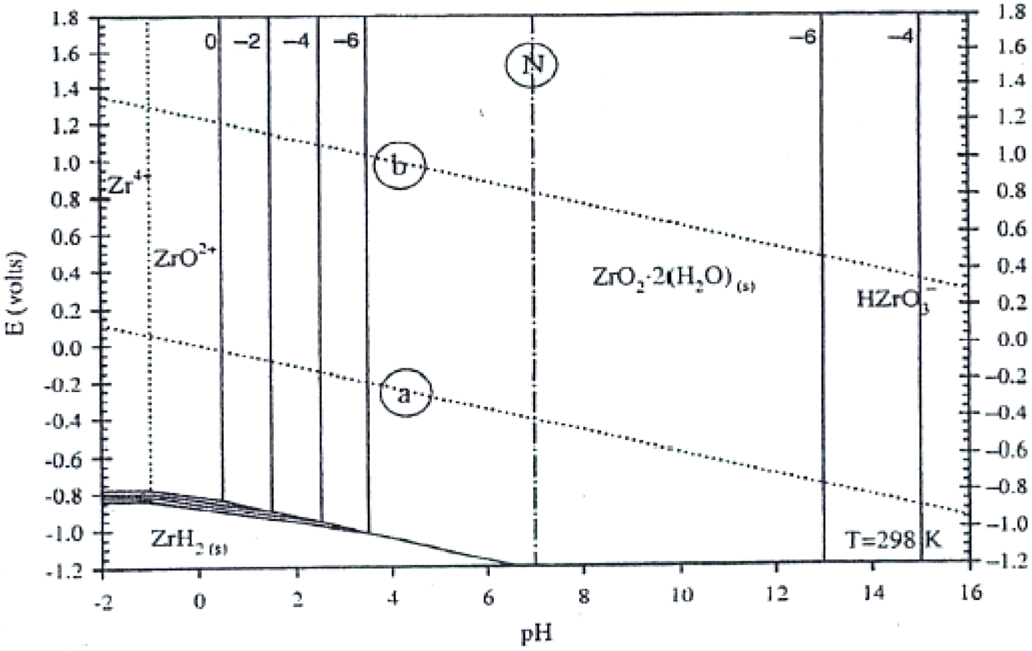

Fig. 39: Pourbaix diagram for Zr at 298K showing aqueous concentrations for the Zr species at 1, 10 −2, 10 −4, and 10 −6m. [21].

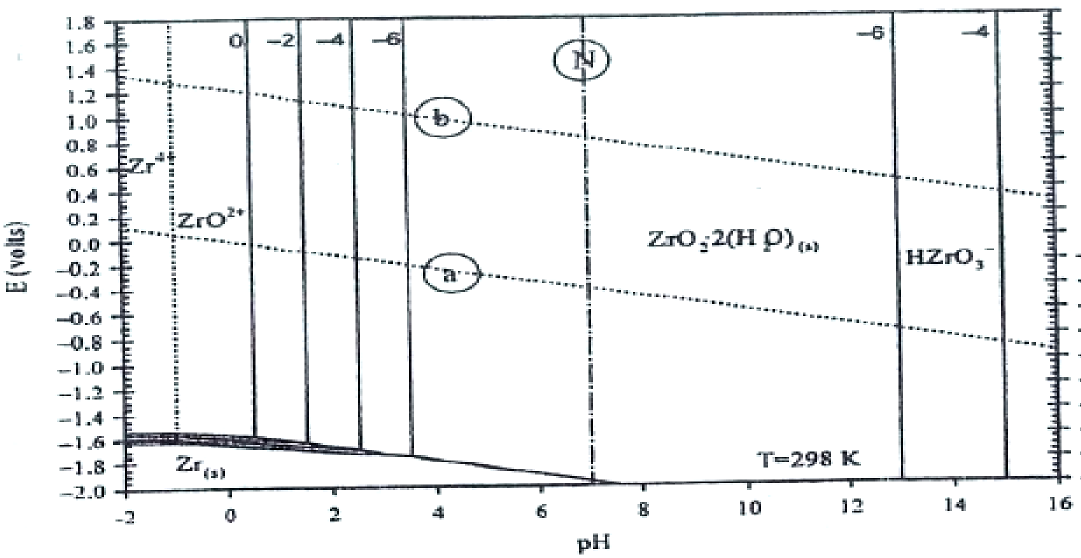

Fig. 40: Pourbaix diagram for Zr at 298K when ZrH2 is withdrawn from the calculation. Aqueous concentrations for the Zr species are at 1, 10 −2, 10 −4, and 10 −6m.[21].

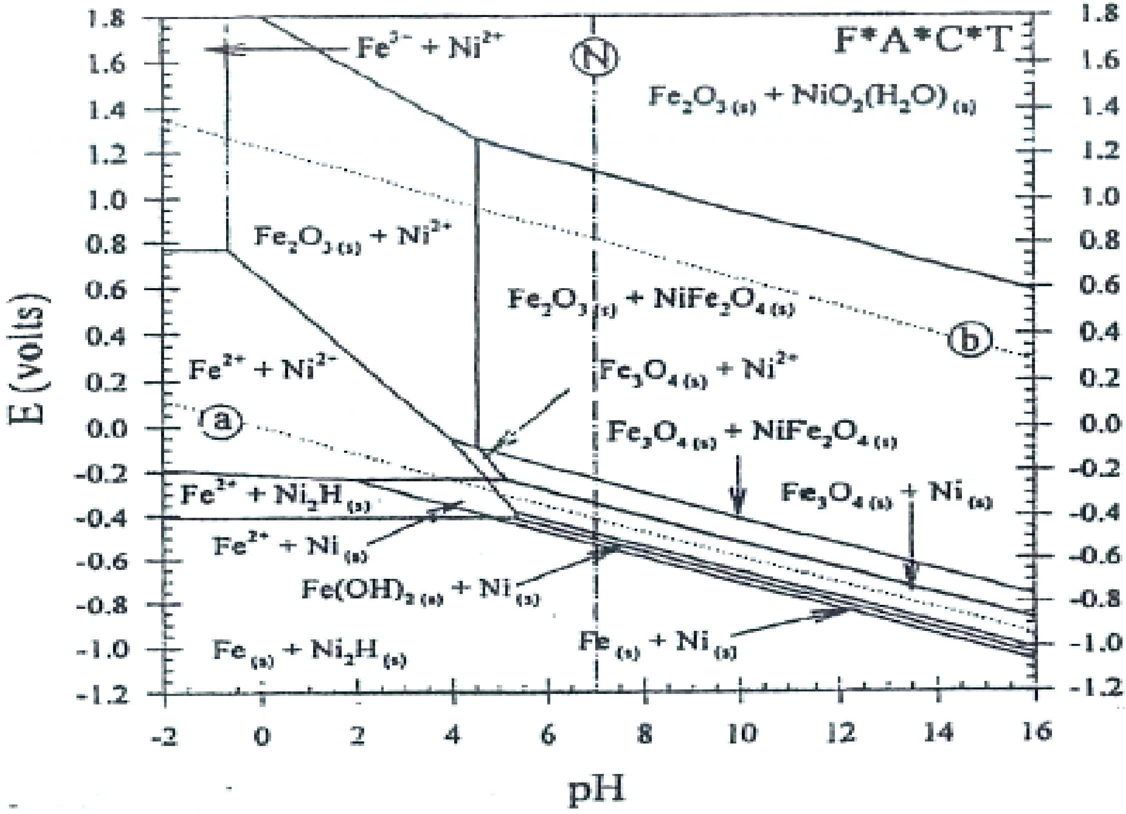

Fig. 41: The Fe-Ni composite Pourbaix diagram at 298 K (25° C). The concentration of all aqueous species is 1 m. The molar proportion of Fe to Ni is > 2:1. The specific proportion affects the phase proportions in each doubly labeled field but does not affect the topology until the ratio falls below 2:1 (when, e.g., NiFe2O4 could not coexist with Fe2O3 for mass balance reasons). Note the placement of NiFe2O4 solid spinel, which is outlined in bold [21].

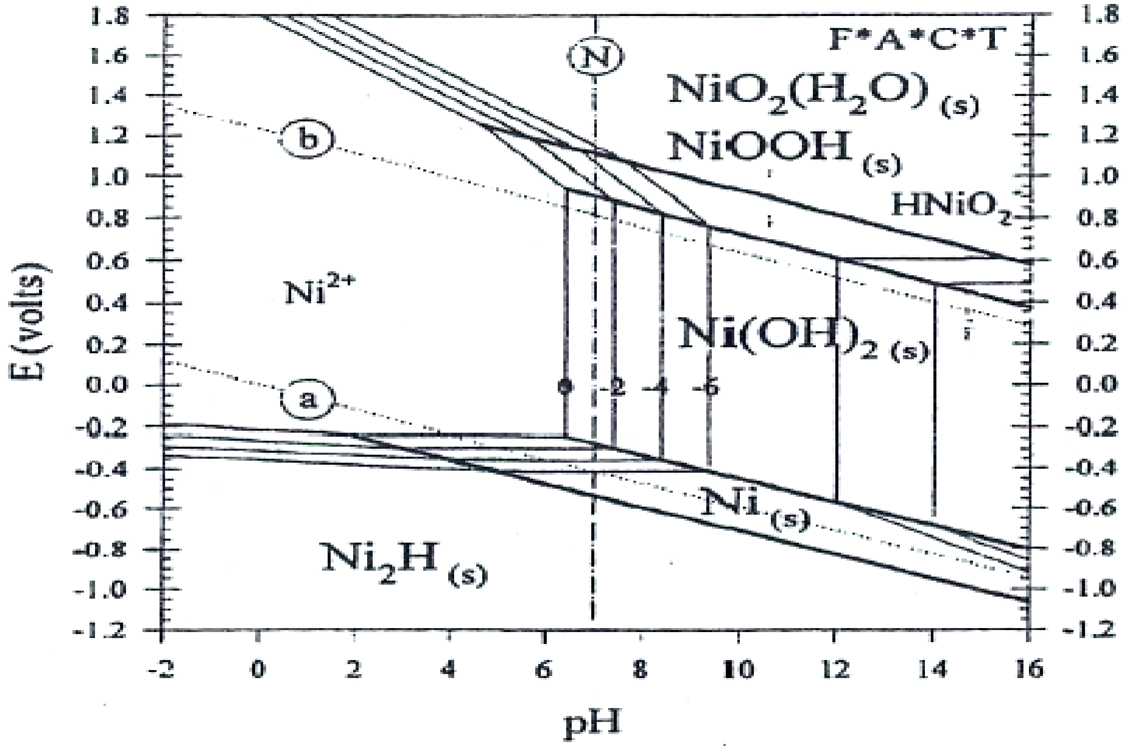

Fig. 42: The Ni Pourbaix diagram at 298 K (25º C). Concentrations of aqueous species range from 1 to 10 −6m. [21].

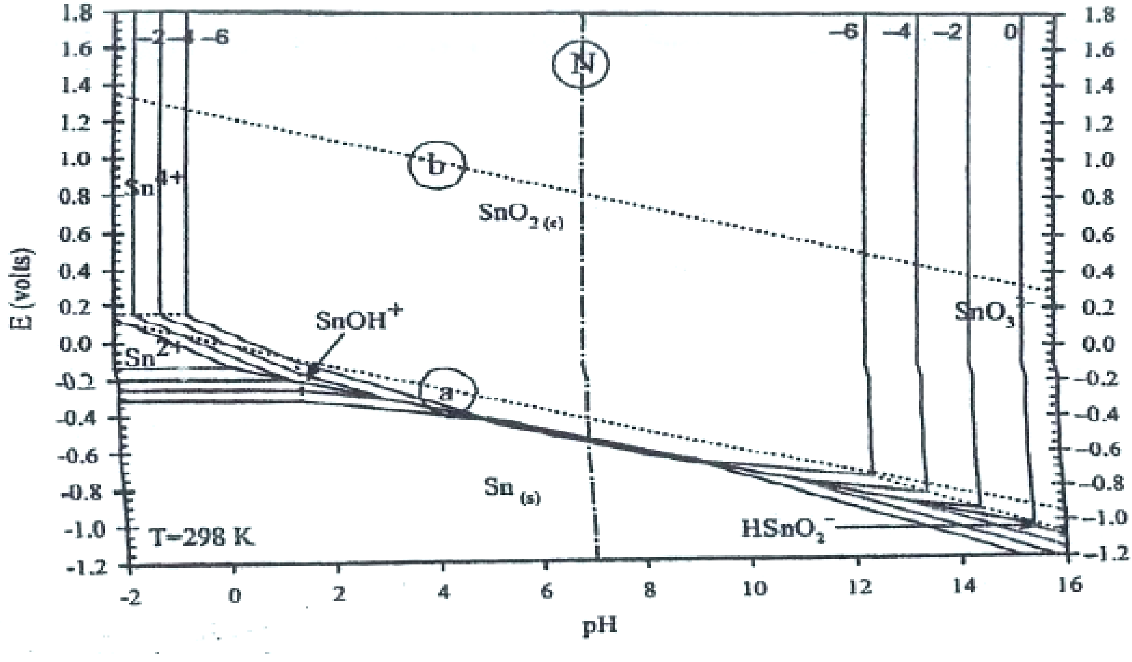

Fig. 43: Pourbaix diagram for Sn at 298K showing aqueous concentrations (activity) for the Sn species at 1, 10 −2, 10 −4, and 10 −6m. [21].

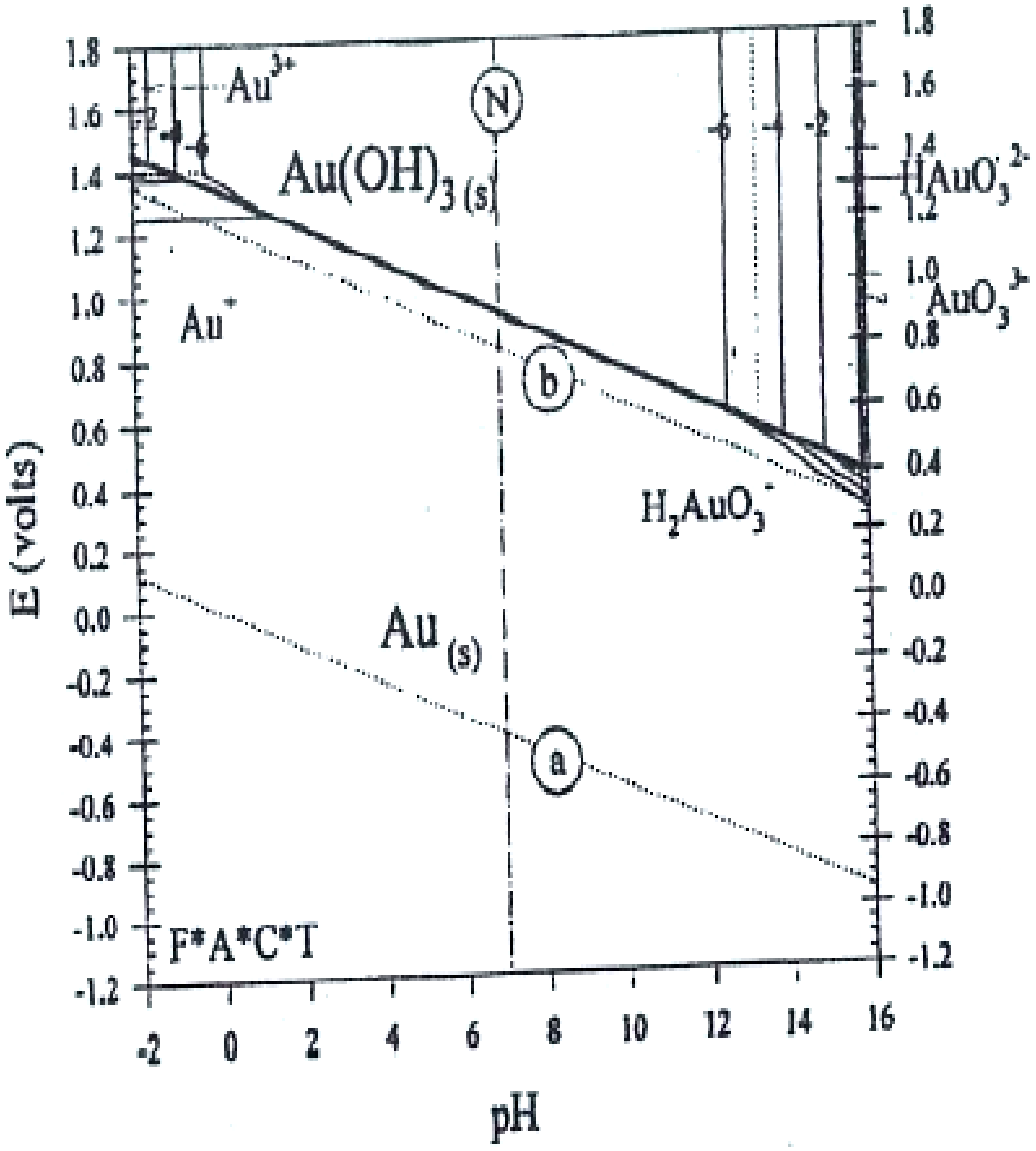

Fig. 44: The Au Pourbaix diagram at 298 K (25ºC). Concentration of aqueous species range from 1 to 10 ¯6m. Gold immunity extends into the strong acid region even under oxygen-saturated conditions (line b) [21].

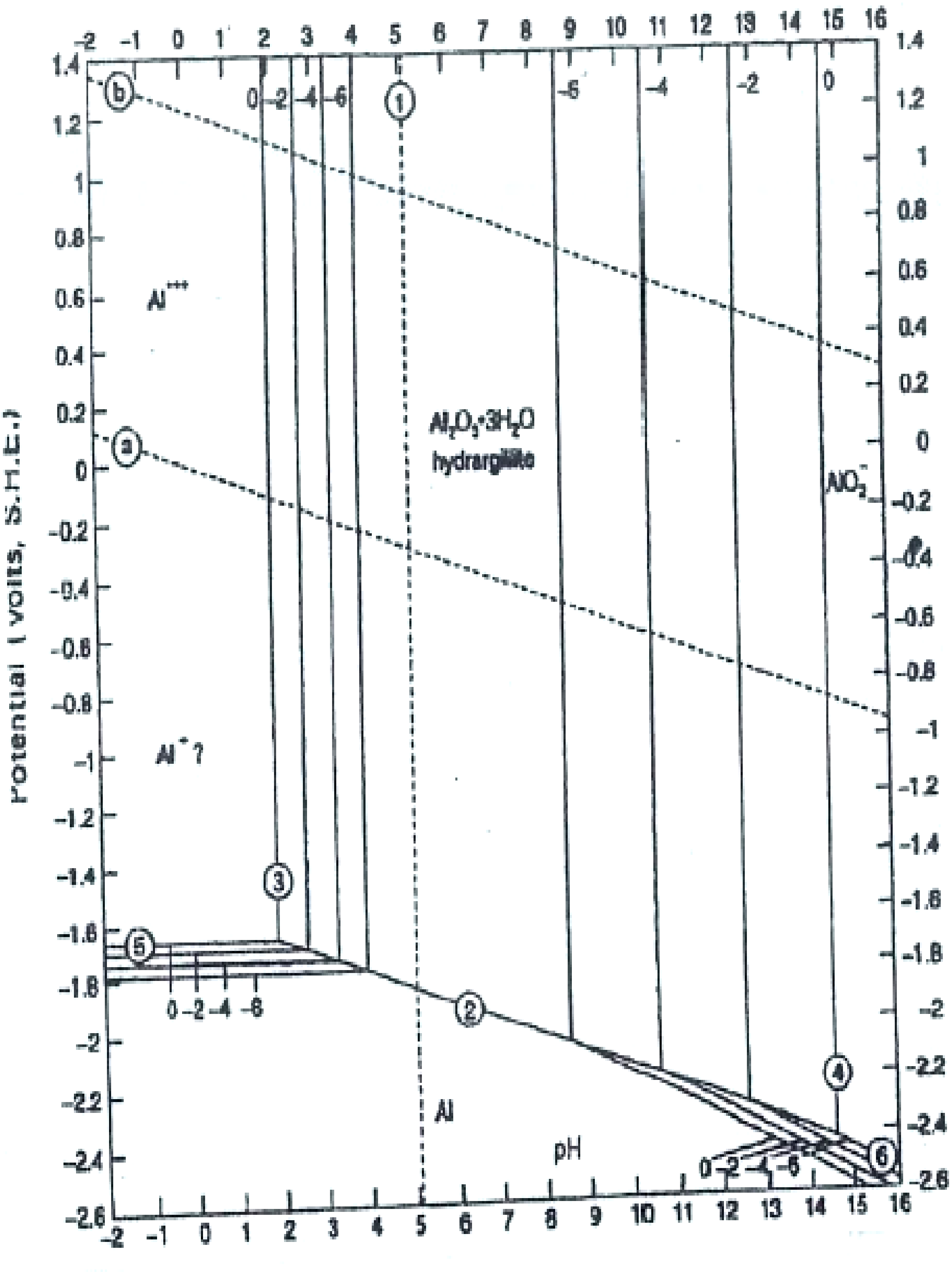

Fig. 45: Pourbaix diagram for the aluminum-water system at 25ºC [2]. (M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd English edition, p. 171, copyright NACE International 1974 and CEBELCOR.) [21].

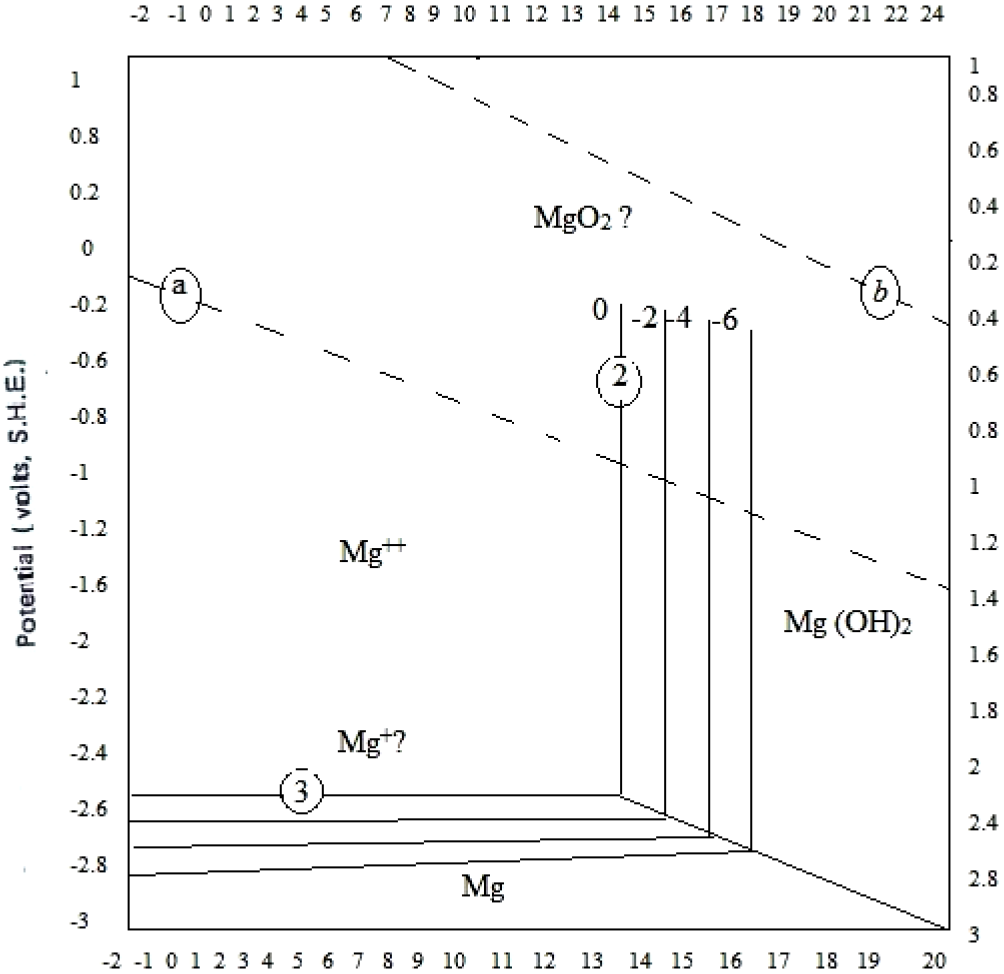

Fig. 46: Pourbaix diagram for the magnesium-water system at 25ºC [3]. (M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, 2nd English edition, p. 141, copyright NACE International 1974 and CEBELCOR.) [21].

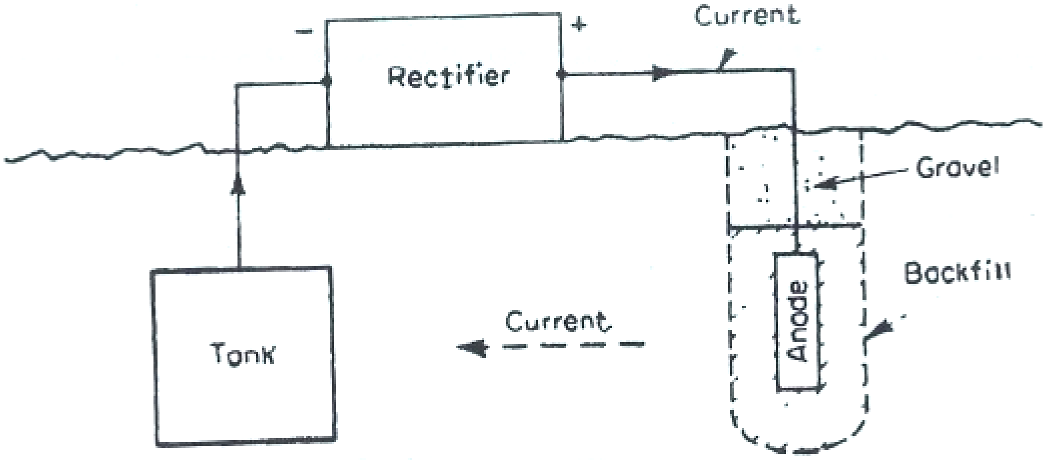

Fig. 47: Cathodic protection of an underground tank using impressed currents [11].

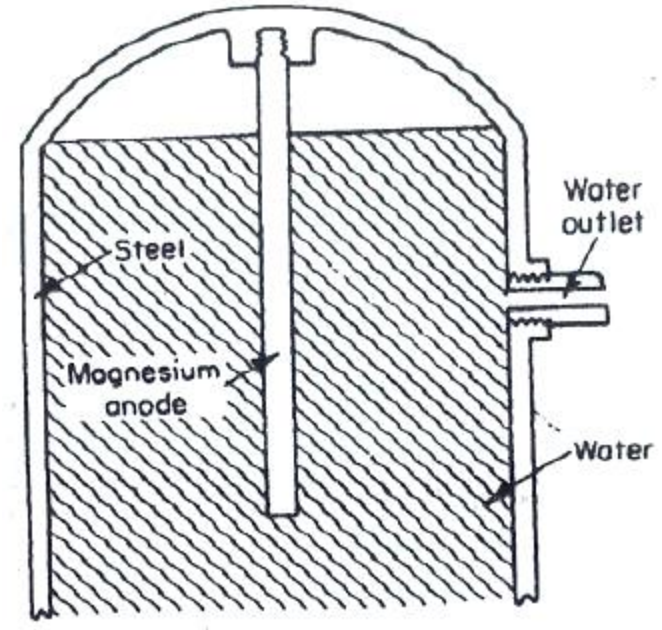

Fig. 48: Cathodic protection of a domestic hot-water tank using a sacrificial anode [11].

Control & Prevention of Corrosion

The more we learn about the causes and mechanism of corrosion, the easier it becomes to control its damaging effect. Several main possibilities offer themselves towards this solution.

"We know that corrosion has great impact on safety, reliability and the economy over a broad range of technological applications from national defence and infrastructure to health and welfare of population. Proper and successful corrosion protection engineering application can save huge amounts annually and avert big disasters." [22]

"There are five primary methods of corrosion control: (1) Material selection (2) Coatings (3) Inhibitors (4) Cathodic protection and (5) Design.

Material Selection

"The most common way of stopping corrosion is the selection of the proper material for a specific service. It is the most important method of protecting or reducing corrosion damage". [11].

"Each metal and alloy has specific inherent corrosion behavior (susceptible or resistant). Metals and Alloys can be classified as higher resistant (noble metals like gold, platinum) and low resistant (active metals such as sodium and magnesium). The corrosion resistance of a metal/alloy strongly depends on the environment to which it is exposed, i.e. the chemical composition, temperature, velocity of the fluid and so on so forth.

The general relation between the rate of corrosion, the corrosive property of environment and the corrosion resistance of a material is given by:

$$\frac{\textbf{Corrosion proneness of environment}}{\textbf{Corrosion resistance of the material}} = \text{rate of corrosion attack}$$

For a given corrosion resistance of the metal/alloy as the proneness of the corrosion of the environment increases, the rate of the corrosion increases. Similarly, for a given corrosivity of the environment, as the corrosion resistance increases, the rate of corrosion decreases. Then there is a challenge to fix an acceptable rate of corrosion and to metals the corrosion resistance of the material and the proneness to corrosion of the environment to be at or less than the desired (fixed) corrosion rate. One can find many reasonably good corrosion resistance materials and it is upto the corrosion engineer (expert) to find the most economical solution by selecting the right material. The corrosion engineer must realize that corrosion resistance and the mechanical properties go hand in hand and must be taken into account. A good, competent corrosion engineer changes the corroding material with one having better corrosion resistance and still economical. Nowadays, there is a treasure of information about materials, their properties, including corrosion resistivity in all kinds of environment. One can quite easily find that using the internet [22].

"There are some general, quite reliable, rules that can applied to the resistance of the materials. For reducing or non-oxidizing environments (air-free acids, aqueous solutions) nickel, copper and their alloys are usually suitable. For oxidizing conditions, chromium-containing alloys are used. For extremely powerful oxidizing conditions, titanium and its alloys are preferable". [11].

Coatings

"Thin coatings of metallic and inorganic and organic materials can provide a satisfactory protective barrier between metal and its environment. The main function is to provide an effective barrier." [11]. "Coatings for protection from corrosion can be divided into two broad categories – metallic and non-metallic (inorganic and organic). Either type is used to do the same job, i.e. to isolate (and protect) the underlying metal from the corrosive media" [11].

Metallic and inorganic coatings

"Metallic coatings are applied by electro deposition, flame spraying, cladding, hot dipping and vapour deposition."

"Inorganic coatings are applied by spraying, diffusion or chemical conversion. Spraying is usually followed by baking or firing at high temperatures. Contrary to metallic coatings (which are elastic), the inorganic coatings are brittle. In both the cases a complete, non-porous, barrier must be provided. Porosity or other defects will result in fast localized attack on the basic metal because of two metal effects." [11]. Details of electro deposition, flame spraying, cladding, hot dipping, vapour deposition, diffusion, chemical conversion, surface modification, ion implantation etc can be found in Fontana's excellent work [11].

Organic coatings

The main objective of the organic coatings in corrosion protection is to isolate and protect the metal from the corrosion environment. The coating not only forms a barrier to stop corrosion, the organic coating can contain corrosion inhibitors. Now a large number of organic coating formulations exist as well as many application processes to select from for a given product or service requirement.

Inorganic coatings

"These coatings include porcelain enamels, ceramic coatings, chemical-setting, silicate cement linings, glass coatings, inorganic coatings for corrosion prevention applications serve as barrier coatings. Ceramic coatings include carbides, suicides which work as wear-resistant coatings and heat-shields."]23].

Tables 6 and 7 give useful information about common coatings. [11].

Table-6: The resistance of common maintenance coatings to chemicals, weather, abrasion, and oxidation.

	Acids	**Alkalies**	**Salts**	**Solvents**	**Water**	**Weather**	**Oxidation**	**Abrasion**
Oil-base	**1**	**1**	**6**	**2**	**7**	**10**	**1**	**4**
Alkyd	**6**	**6**	**8**	**4**	**8**	**10**	**3**	**6**
Chlorinated rubber	**10**	**10**	**10**	**4**	**10**	**8**	**6**	**6**
Coal-tar epoxy	**8**	**8**	**10**	**7**	**10**	**4**	**5**	**4**
Catalyzed epoxy	**9**	**10**	**10**	**9**	**10**	**8**	**6**	**6**
Silicone aluminum	**4**	**3**	**6**	**2**	**8**	**9**	**4**	**4**
Vinyl	**10**	**10**	**10**	**5**	**10**	**10**	**10**	**7**
Urethane	**9**	**10**	**10**	**9**	**10**	**8**	**9**	**10**
Zinc(inorganic)	**1**	**1**	**5**	**10**	**5**	**10**	**10**	**10**

A value of 10 represents the best protection

**Paints and Protective Coatings* (Army TM5-618, Navfac MO-110, Air Force AFM (85-3), Superintendent of Documents, USGPO, Washington, D.C. 20402.

†Gary N. Kirby, What You Need to Know About Maintenance Painting-Part I, *Chem. Eng.*, 75-78 (July 26, 1982); Part II, 113-116 (Aug. 23, 1982).

‡See also S. P. Thompson, Managing a Maintenance Painting Program to Reduce Costs, *Materials Performance*, 48-51 (Oct. 1982). (Could save up to 50% of annual painting costs.)

Table-7: Important points to know about the various coatings you can select.

Coating	Advantages	Remember
Oil-base	**Good rust penetration. Good substrate wetting.**	**Poor acid, alkali, solvent and oxidation resistance. Slow-drying, embrittles and yellows with aging.**
Alkyd Short-oil	**Inexpensive, fast-drying, good adhesion, easy recoating.**	**Do not use over zinc-rich primers. Fair acid, alkali, solvent and oxidation resistance. Fair impact resistance.**
Long-oil Chlorinated rubber	**Good durability, good weathering, flexible, easy recoating.**	**Poor acid, alkali, solvent and oxidation resistance.**
Epoxy	**Good water, acid, alkali resistance. Easy recoating**	**Poor aromatic solvent resistance; "strings" when brushed. Moderate temperature resistance.**
Coal-tar Amine	**Versatile. Excellent resistance to water, seawater and soil immersion.**	**May surface-chalk in sunlight. Use light colors outdoors.**
Polyamide	**Good water, acid, alkali, solvent resistance. Hard, good temperature resistance.**	**Check touch-up and recoating limits. Check flexibility and abrasion resistance. Dark colors only.**
Ketimine	**Good water, alkali resistance. Tough, good temperature resistance.**	**Skin sensitizer. Check recoating limits. Check recoating limits.**
Urethane (2-component, aliphatic)	**Indefinite recoating time. Wide range of chemical and solvent resistance.**	**Ketone fumes while drying.**
Vinyl	**Good water, acid, alkali, solvent resistance. Good abrasion resistance. Good gloss and color retention. Low-temperature application.**	**Check temperature resistance. Check solvent fumes. Expensive. Check recoatability.**
Zinc-rich primers (untop-coated) Inorganic	**Good water, acid, alkali resistance. Tough, good recoatability, rapid drying. Low-temperature (5°F) application. The best organic-solvent resistant. Good abrasion resistance. Temperature resistance to 1,000°F.**	**Low temperature resistance (150°F). Poor aromatic ketone solvent-resistance. Low percent solids. Needs good surface. Mostly sprayed. Ketone fumes. Requires good surface preparation. Limited (untop-coated), to pH of 5 to 10. Generally sprayed (conventional). Film thickness limited.**

Inhibitors

"We know that chemicals (like salt, acids) promote corrosion, other chemical stop corrosion. Chromates, silicates and organic amines are common inhibitors. The mechanism or science of inhibition is rather complex. In the case of organic amines, the inhibitor is adsorbed on anodized cathodic sites and restricts the corrosion current. Other inhibitors specifically affect either the anodic or cathodic process. But there are other inhibitors which promote the formation of protective film on the substance (metal) surface.

Cathodic and anodic protection

Cathodic protection

"Since corrosion is largely associated with the generation of small currents, it is sometimes possible to reduce corrosion by creating conditions under which an electric current, opposite in direction to the small current, is formed in the corroding metal. This process is known as cathodic protection. The zinc corrodes in preference to the steel. Hence steel is galvanized or zinc plating of mild steel. The positive current flows from the steel to the zinc. The zinc coating slowly slowly disappears but it delays the resting of steel. This process is usually described as the "sacrificial protection". A somewhat similar system is used for the protection of underground steel mains. These are usually wrapped with impregnated cloth or bitumen coating. Additional protection is provided by burying magnesium anodes in the soil closed to the steel pipes and connecting them to it by an insulated wire. The steel becomes cathodic to the magnesium, which corrodes instead of the steel and is thus replaced periodically. Another form of cathodic protection is applied, particularly to steel structures in seawater. In this case a direct electric current, to counterbalance the potential and current of the corrosive effect, is deliberately applied. A cathodic direct current, closely controlled as to potential and amperage, is passed through the seawater on to the steel structure. The current (shielded wire) is put into the seawater through graphite, lead, silicone-iron alloy or a titanium rod or plate coated with platinum. Many of the piers and jetties used by oil-tankers are protected in this way [1], (Figs. 49 - 52) illustrate some cathodic protection examples [11]. Table-9 shows the typical current requirements for cathodic protection of steel [11].

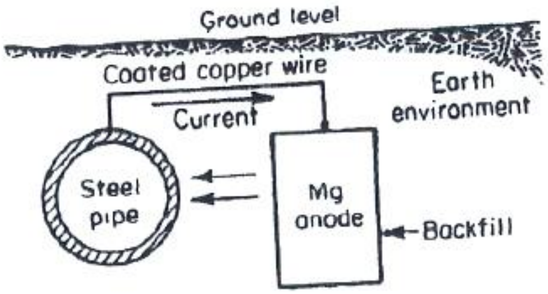

Fig. 49: Protection of an underground pipe-line with a magnesium anode [11].

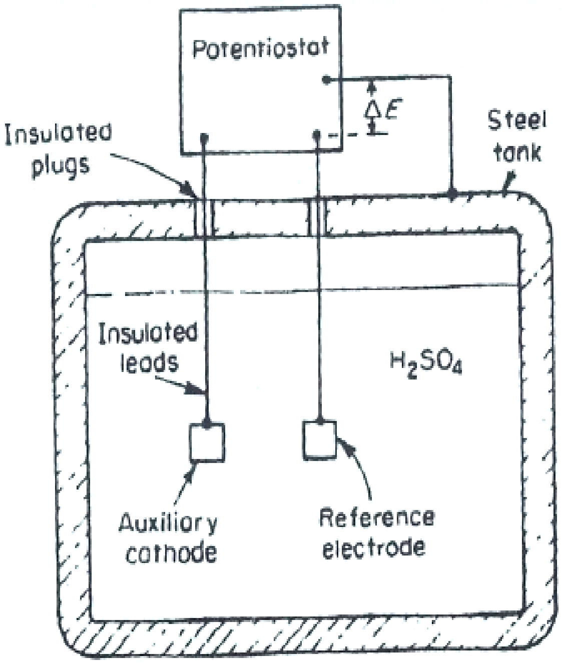

Fig. 50: Anodic protection of a steel storage tank containing sulfuric acid [11].

Table-9: Typical current requirements for cathodic protection of steel.

Structure	Environment	Conditions	Current density, mA/ft^2
Tank	Hot H_2SO_4	Static	50,000
Pipelines and storage tanks	Underground (soil)	Static	1-3
Pipelines	Fresh water	Flowing	5-10
Water heaters	Hot, fresh water	Slow flow	1-3
Pilings	Seawater	Tidal motion	6-8
Reinforcing rods	Concrete	Static	0.1-05

Source: Some data taken from M. Stern, Principles of Cathodic Protection, *Symposium on Corrosion Fundamentals*, p. 84, University of Tennessee Press, 1956.[11]

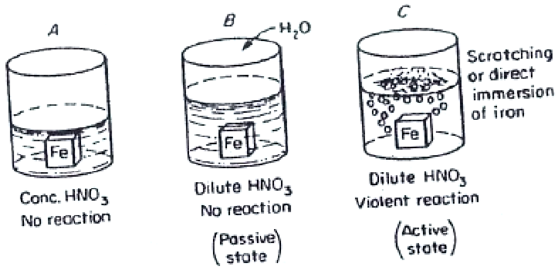

Fig. 51: Schematic illustration of Faraday's passivity experiments with iron [11].

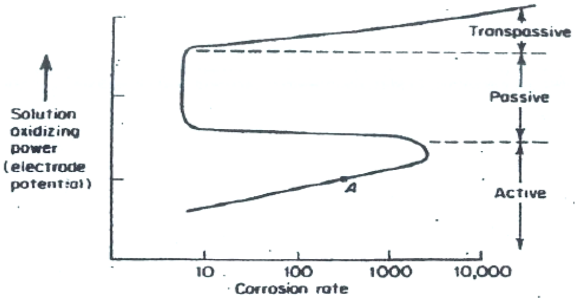

Fig. 52: Corrosion characteristic of an active-passive metal as a function of solution oxidizing power (electrode potential) [11].

Anodic Protection

"Some metals and alloys, such as titanium and stainless steel have a protective film naturally formed. They can be reinforced in corrosive solutions by passing positive current through it at closely controlled potentials. The metal thus becomes the anode of the corrosion cell but it does not corrode in depth because the first corrosion product formed is a tightly adherent protective film which insulates, and protects, the metal both physically and electrically from the corrodent." [1]

"Anodic protection can decrease corrosion rate substantially, Table-10 for austenitic stainless steel at 30ºC. And Table-11 shows the current requirements for anodic protection.[11]

Table-10: Anodic protection of austenitic stainless steel at 30ºC. Protected at 0.500 volt vs. saturated calomel electrode

Alloy type	Environment (air exposed)	Corrosion rate, mpy	
		Unprotected	Anodically protected
304 (19Cr-9Ni)	*N* H_2SO_4 + 10^{-5} *M* NaCl	14	0.025
	N H_2SO_4 + 10^{-3} *M* NaCl	2.9	0.045
	N H_2SO_4 + 10^{-1} *M* NaCl	3.2	0.20
	10*N* H_2SO_4 + 10^{-5} *M* NaCl	1930	0.016
	10*N* H_2SO_4 + 10^{-3} *M* NaCl	1125	0.04
	10*N* H_2SO_4 + 10^{-1} *M* NaCl	77	0.21

Source: S. J. Acello and N. D. Greene, *Corrosion*, 18:286*t* (1962). [11]

Table-11: Current requirements for anodic protection.

Fluid and concentration	Temperature, ºF	Metal	Current density, mA/ft^2	
			To passive	To maintain
H_2SO_4	75	316SS	2100	11
1 molar	75	304	390	67
15%	75	304	500	22
30%	150	304	165,000	830
45%	75	304	4700	3.6
67%	75	316	470	0.09
67%	75	Carpenter	400	0.8
67%	75	20	260	21
93%	75	Mild steel	4400	11
Oleum		Mild steel		
H_3PO_4	75		38,000	19,000
75%	180	Mild steel	0.03	0.00014
115%		304SS		
NaOH				
20%	75	304SS	4400	9.4

Source: C.E. Locke et al., *Chem. Eng. Progr.*, 56:50 (1960). [11]

Cathodic vs anodic protection

Fontana [11] has listed the comparison between cathodic and anodic protection (Table-12).

Table-12: Comparison of anodic and cathodic protection.

	Anodic protection	Cathodic protection
Applicability Metals	Active-passive metals only Weak to aggressive	All metals
Corrosives	High	Weak to moderate
Relative cost Installation Operation	Very low	Low Mediums to high
Throwing power Significance of applied current	Very high Often a direct measure of protected corrosion rate	Low Complex – does not indicate corrosion rate
Operating conditions	Can be accurately and rapidly determined by electrochemical measurements	Must usually be determined by empirical testing

According to Fontana [11] "each method has advantages and disadvantages, and anodic and cathodic protection tend to complement one another. Anodic protection can be used in corrosive materials ranging from weak to very aggressive, while cathodic protection is restricted to moderately corrosive conditions because of its high current requirement which increases as the corrosivity of the environment increases. Compared to cathodic protection system, the anodic protection system is complex and expensive. Anodic protection possesses two important advantages, viz. (1) The applied current is usually equal to the corrosion rate of the protected system. Thus, anodic protection not only protects but offers a means for monitoring instantaneous corrosion rate. (2) The operating conditions for anodic protection can be precisely established by laboratory polarization measurements. Contrary to it, the operating limits for cathodic protection are usually established by empirical trial-and-error tests.

The concept of anodic protection is based on sound scientific principles and has been successfully applied to industrial corrosion problems. Anodic protection can be classed as one of the most significant advances in the entire history of corrosion science" [11]

Design Principles

"The choice and detailed specification of a material known to be chemically resistant to a given environ is the first important step in the selection of the correct material. The choice of correct design of the equipment and principles to let the material perform in the desired manner, Professor Verink Jr. [16] has listed the following design-related reasons of corrosion in metallic systems: (1) Dissilimar metals (2) Improper drainage (3) Joints between metals and non-metals (4) Crevices (5) Stray Currents (6) Complex cells (7) Relative motion between two interacting parts or between a part and its environment (8) Selective loss of one or more ingredients of the alloy (9) Inability to clean the surface properly". According to Prof. Verink, [16] people usually, unfortunately, don't give adequate attention to careful inspection and verification of the design.

Verink [11] has further listed detailed methods by which corrosion may be avoided/ restricted:

a. Where dissilimar metals are involved, select materials that have a minimum difference in electrode potential under the conditions of temperature and electrolyte composition encountered.
b. Where feasible, design structure so that butt joints

rather than lap joints are employed, use drip skirts to avoid moisture collecting under structures.

c. Support tanks on stanchions rather than pads if possible. If pads are required for tanks, provide sufficient "crown" on the pads to assure drainage and to avoid "oil can" effects. For large field-erected tanks use domed, compacted, oiled sand where appropriate as a support for tank bottoms.
d. Employ resilient sealants to exclude moisture from potential crevices.
e. Employ cathodic protection where appropriate. This includes the use of galvanized steel or alclad aluminum products or sprayed metals to provide cathodic protection in crevices.
f. Equalize the electrode between electrically interfering structures that are exposed in the same electrolyte (e.g., underground or in large tanks). Cross-bonding, use of cathodic protection, and careful grounding are important methods for accomplishing this.
g. Use special care to avoid turbulence. This involves study of flow patterns, avoidable of constrictions, or sharp changes in direction and attention to the relationship between pressure and amplitude of motion between parts.
h. Select materials known to be compatible with the environment and with each other. For important structures this implies pretesting.
i. Provide redundant systems for critical applications. This includes spare heat exchanger bundles, replaceable spools in pipe systems, or scavengers for removal of dissolved heavy metals.
j. Use nonmetallic materials when required.

For detailed information on each factor, please refer to [16]. In short, "The application of rational design principles can eliminate many corrosion problems and greatly reduce the time and cost associated with corrosion maintenance and repair. Corrosion usually takes place in dead ends and crevices where the corrosive medium becomes more active. These areas can be eliminated or reduced in the design of the equipment. At places where stress corrosion cracking is possible, the components must be designed to function at stress levels below the threshold stress for cracking. Where corrosion is expected to take place, design can provide for maximum interchangeability of critical components and standardization of components. Part standardization and interchangeability reduce the inventory of the essential parts required. Maintenance and repair is a normal practice and can easily be handled. For large essential items, standby units are installed to print maintenance and repair without stopping the operation. The longing factors help in proper corrosion and damage control. [23]

Passivity

According to Fontana [11] the phenomenon of metallic passivity has fascinated scientists and engineers for more than 100 years since the days of Faraday. "In simple words, passivity is a condition in which a piece of a metal in the active state. Similarly, a positive direction of electrode potential and the state of the metal surface characterized by low corrosion rates in a potential region that is strongly oxidizing for the metal." [23]. "Passivity or passive behavior, the metal corrodes but a state of passive behavior is observed. When a metal is immersed in the solution, there is a reaction and the metal does corrode, however, an in soluble protective corrosion-product film is formed. This then protective layer (about 25-30 Angstrom), also known as a passive film, allows the corrosion rate to very low levels. The corrosion behavior, when in the passive state, depends on the integrity of the protective film. If the protective film is changed, then the metal reverts to the active behavior and rapid dissolution occurs. An example is that of iron sample immersed in dilute or concentrated nitric acid shows passive behavior, Fig. 51 shows such a behavior, immunity means no reaction whatsoever, like that with noble metals. Iron, chromium, titanium, nickel and alloys containing these metals show passivation. Passivation is generally associated with oxidizing media" [23] but under extremely strong oxidizing conditions these metals lose their corrosion-resistance.

The subject passivity is complex and rather extensive. In short two definitions are there to express the phenomena in simple terms [4].

(1) "A metal is passive if it substantially resists corrosion in a given environment resulting from marked anodic polarization.
(2) A metal is passive if it substantially resists corrosion in a given environment despite a marked thermodynamic tendency to react. For details see [4]". For illustration of this phenomenon some diagrams (Figs. 53 - 61) are presented.

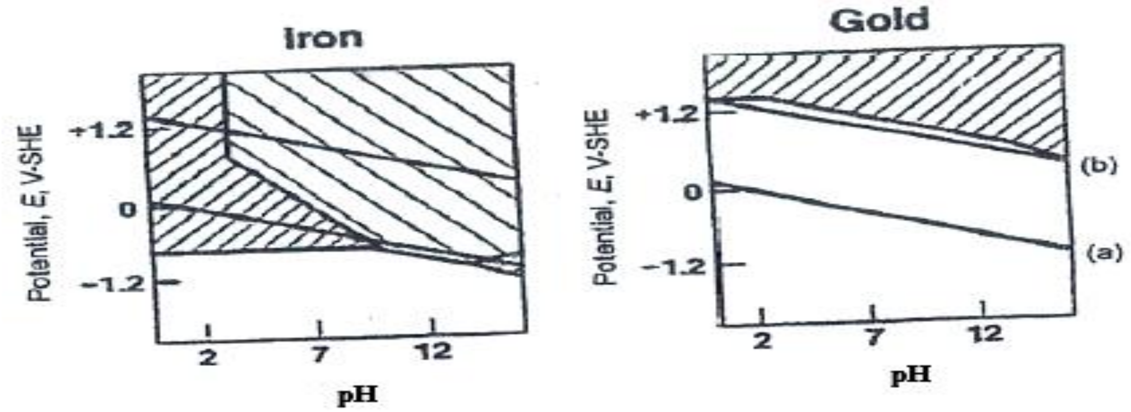

Fig. 53: Potential-pH diagrams for iron and gold. The broad-banded, cross hatched area in the iron E-pH diagram represents a region of passivity. The narrow-banded cross-hatched areas represent where iron and gold will corrode [23].

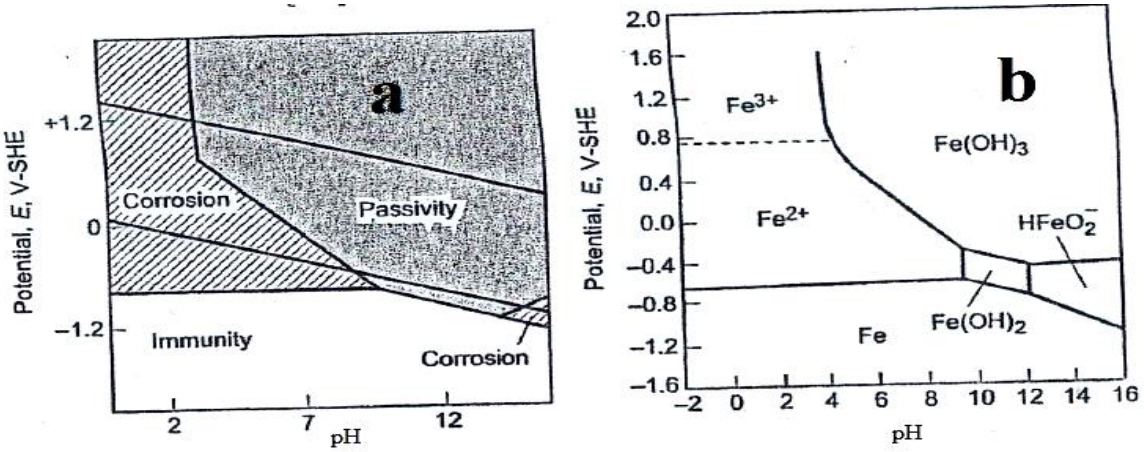

Fig. 54: Simplified potential-pH diagrams for iron at 25 ºC (75 ºF) show (a) areas of immunity no corrosion), passivity, and corrosion, (b) reaction/corrosion products produced [23].

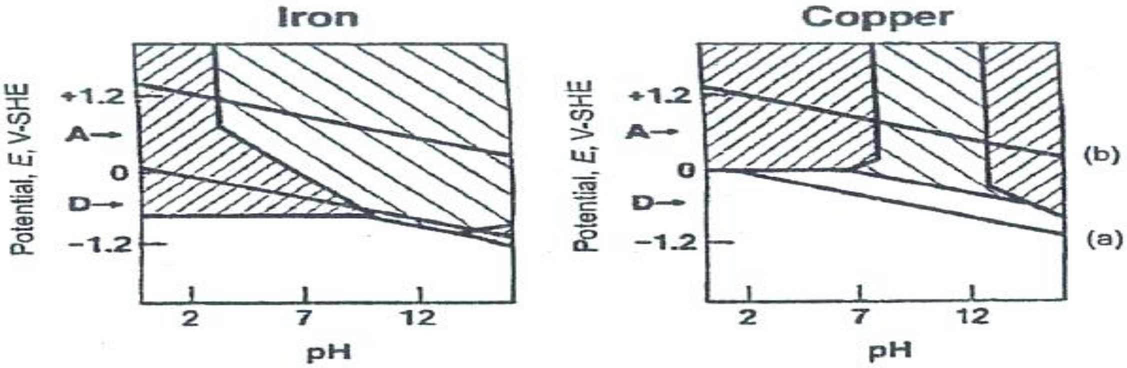

Fig. 55: Potential-pH diagrams for iron and copper. A, aerated; D, deaerated [23].

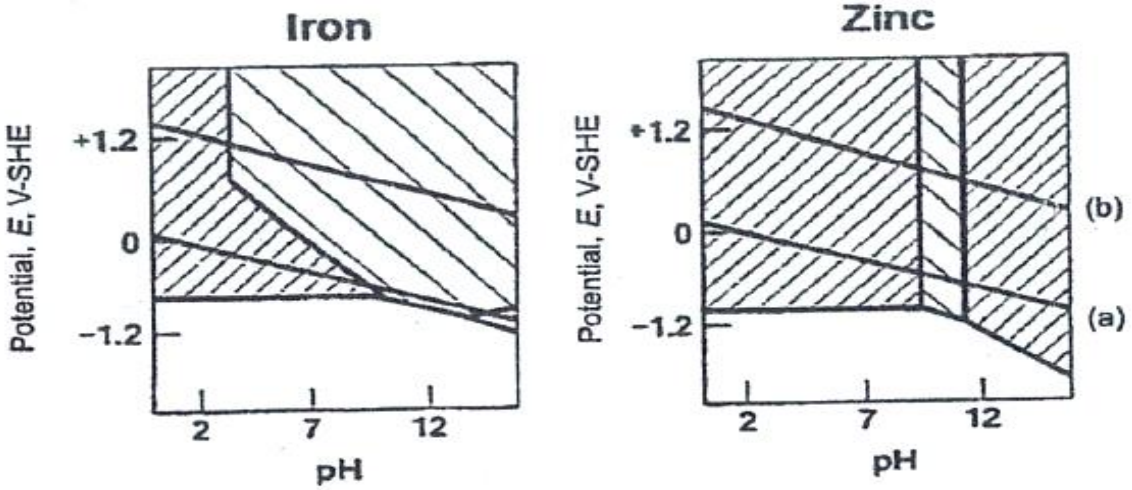

Fig. 56: Potential-pH diagrams for iron and zinc [23].

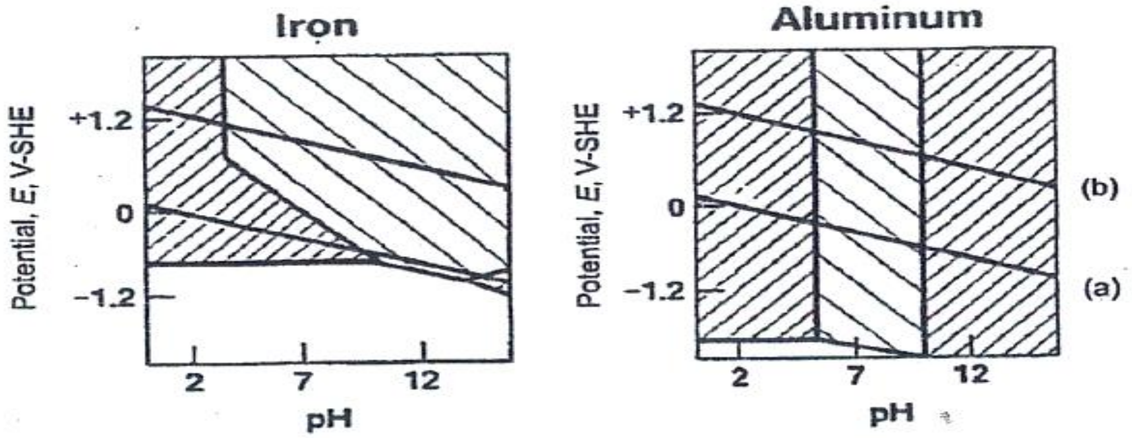

Fig. 57: Potential-pH diagrams for iron and aluminum [23].

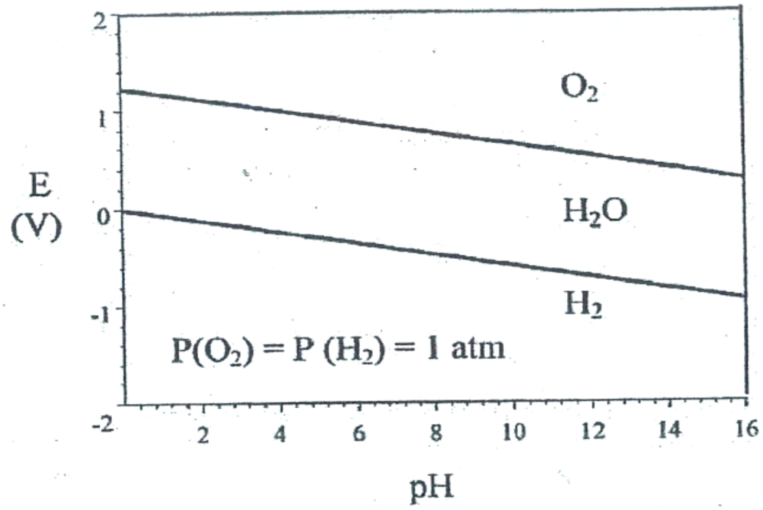

Fig. 58: Pourbaix diagram for water and oxygen [14].

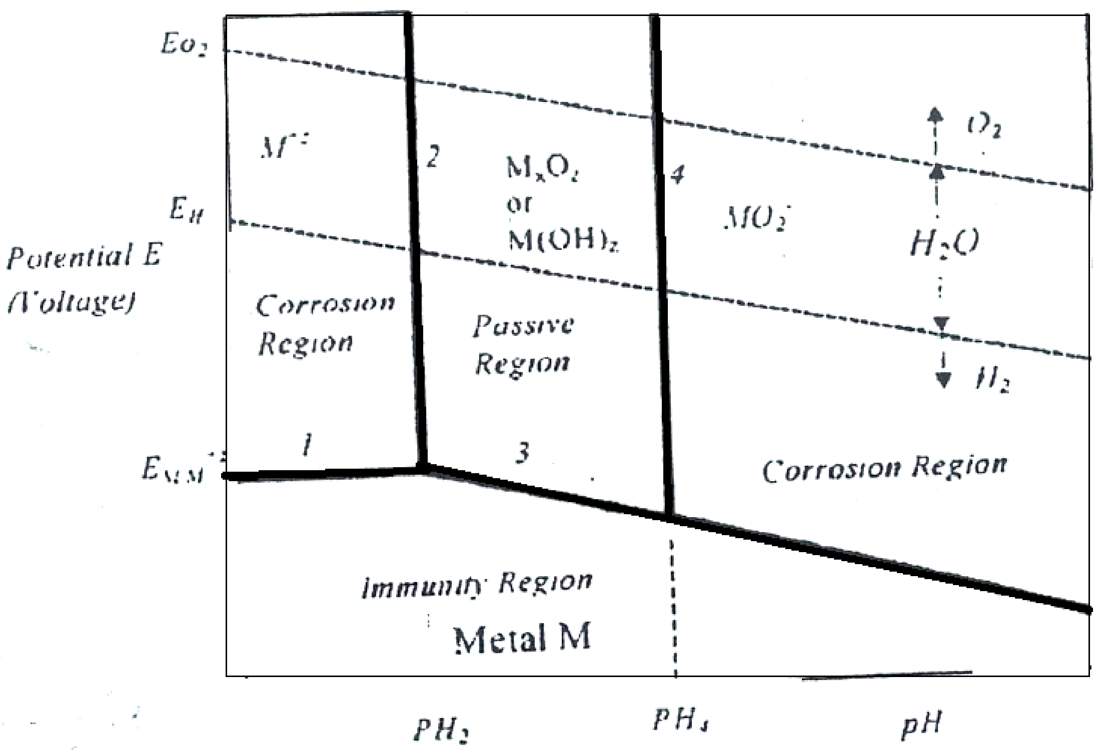

Fig. 59: Schematic Pourbaix diagram for a metal M, water and oxygen [14].

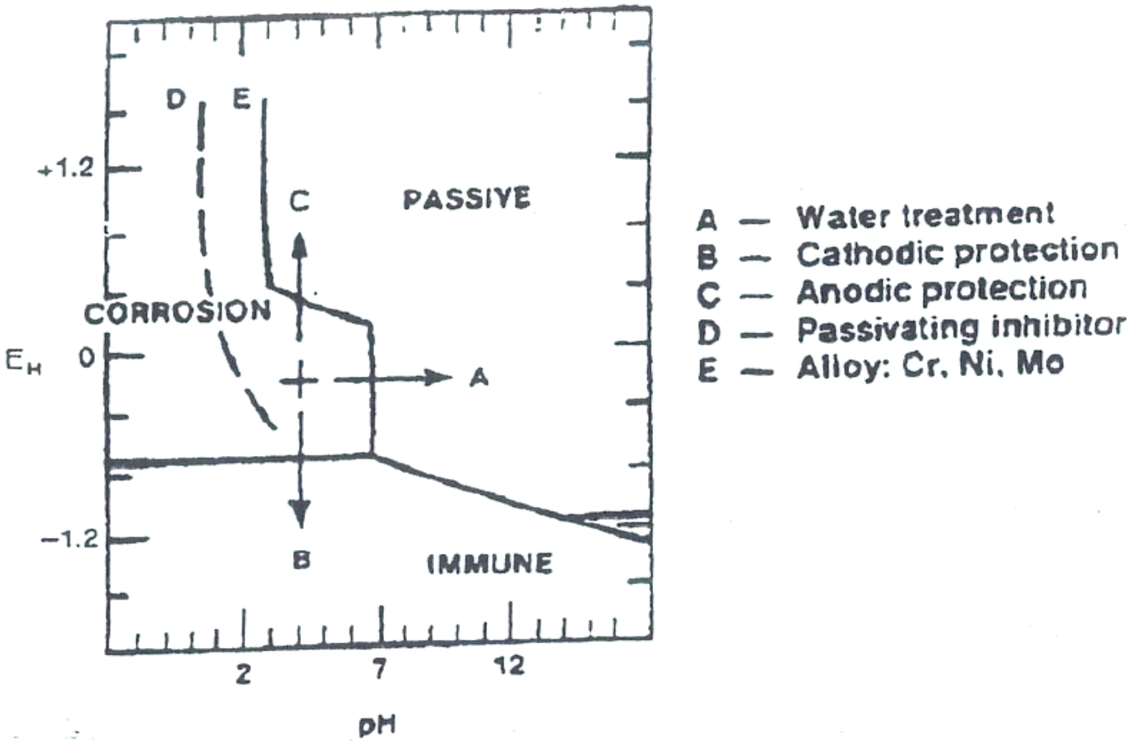

Fig. 60: Methods of corrosion control for iron related to the potential-pH diagram [23].

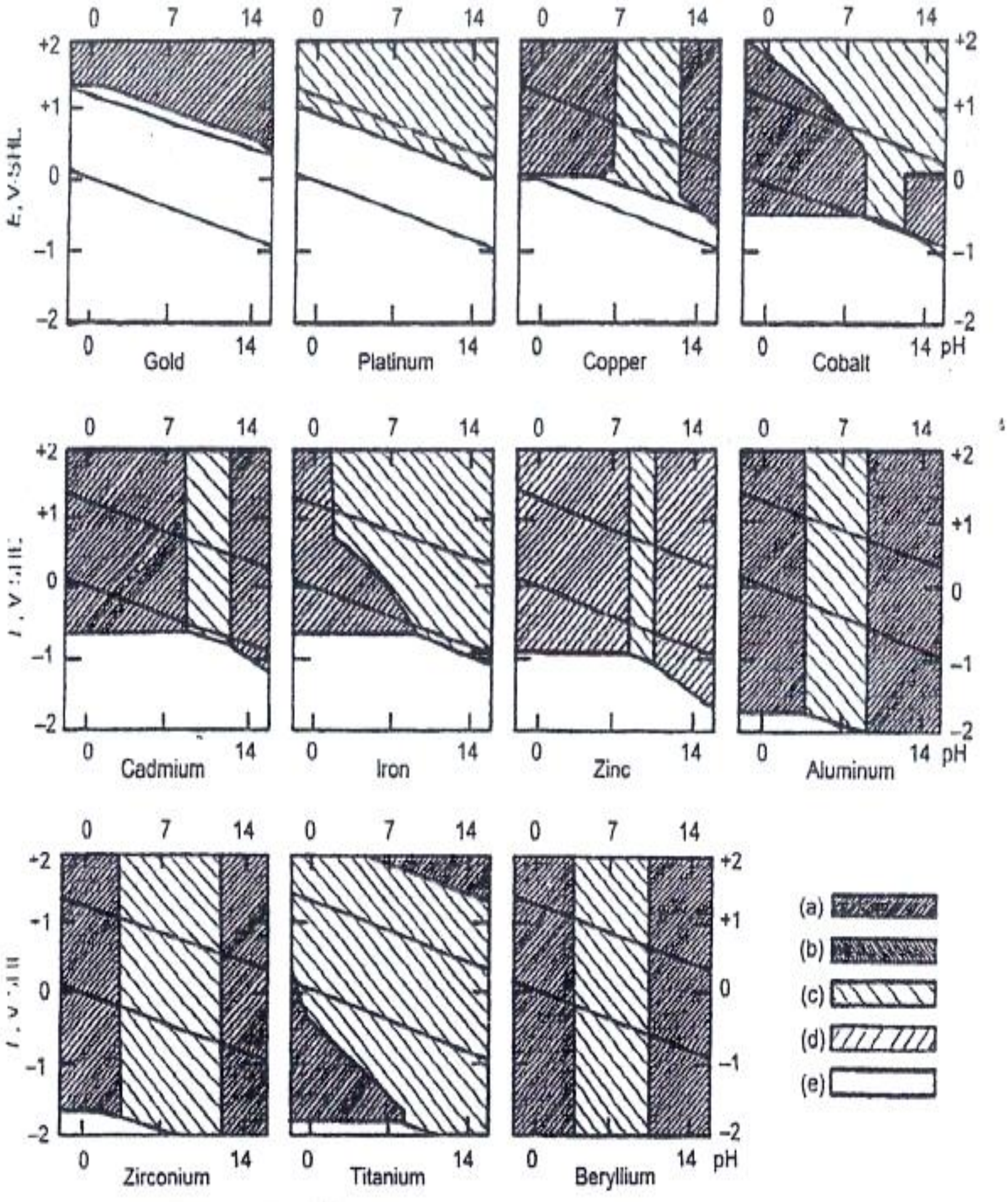

Fig. 61: Potential-pH diagrams for several metals in water at 25 ºC(75ºF). (a) Corrosion by dissolution. (b) Corrosion by gasification. (c) Passivation by oxide or hydroxide layer. (d) Passivation by hydroxide layer. (e) Immunity [23].

Some illustrations of the corrosion attack

The following figures (62 - 75) show how corrosion attacks metals and alloys.

Fig. 62: Coating damage in tidal zone [27].

Fig. 63: Galvanic corrosion resulting from placing a bronze sea strainer on an aluminum hose barb [28].

Fig. 64: Oil and gas pipeline under crevice corrosion [28].

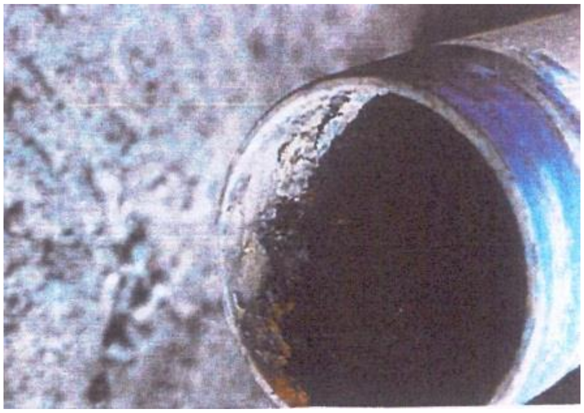

Fig. 65: Oxygen corrosion [28].

Fig. 66: Oil and gas pipeline after being attacked by stress corrosion cracking [28].

Fig. 67: Pipeline affected by micro-bilogically-induced corrosion MIC [28].

Fig. 68: Pitting corrosion [28].

Fig. 69: Oil and gas pipeline under sour (under hydrogen sulphide and moisture) corrosion [28].

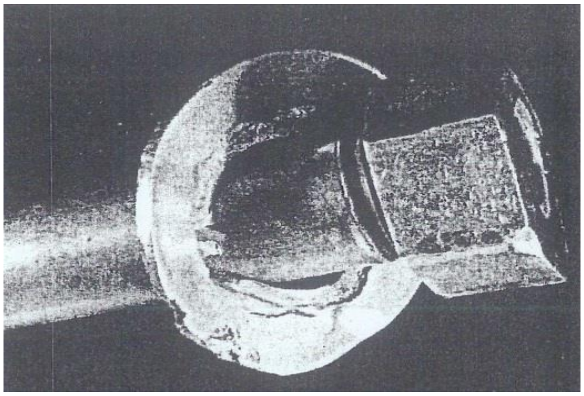

Fig. 70: Crevice corrosion at a metal-to-metal crevice site formed between components of type 304 stainless steel fastener in seawater [23].

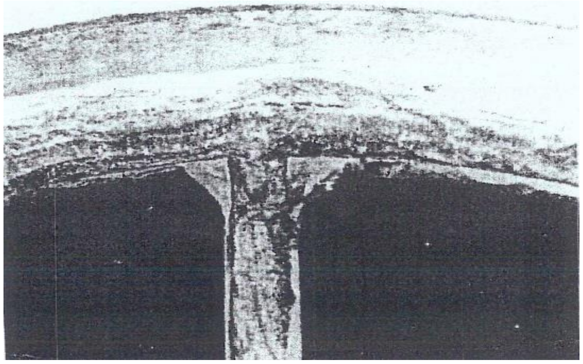

Fig. 71: Crevice corrosion at normal gasket site on an alloy 825 seawater heat exchanger [23].

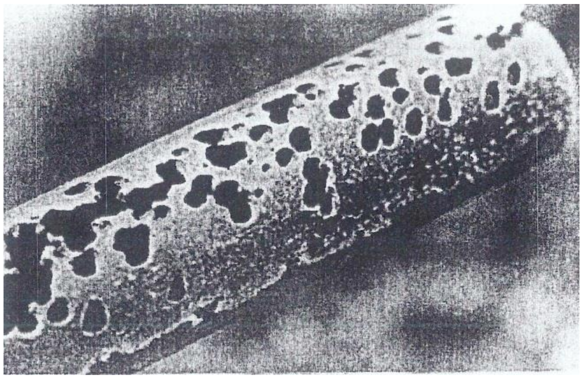

Fig. 72: Severely pitted aluminum heat exchanger tube. Pits were caused by sulfate-reducing bacteria beneath a slime layer. The edge of the slime layer is just visible as a ragged border between the light-colored aluminum and the darker, uncoated metal below. Source: Nalco Chemical Company [23].

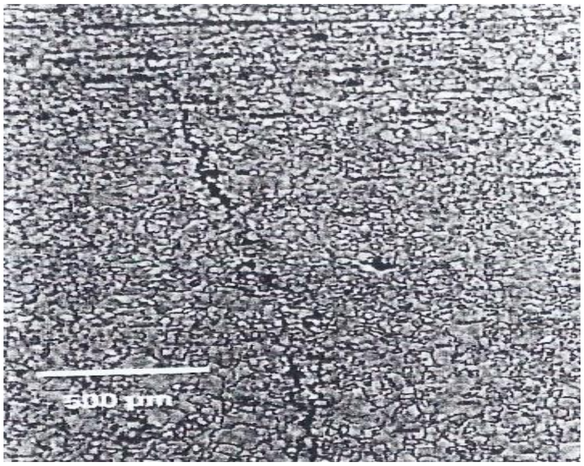

Fig. 73: Light photomicrograph showing circumferential, internal stress corrosion cracks in API 5L Grade B piping used in ethanol service (axial cross section, 4% Nital etchant) [16].

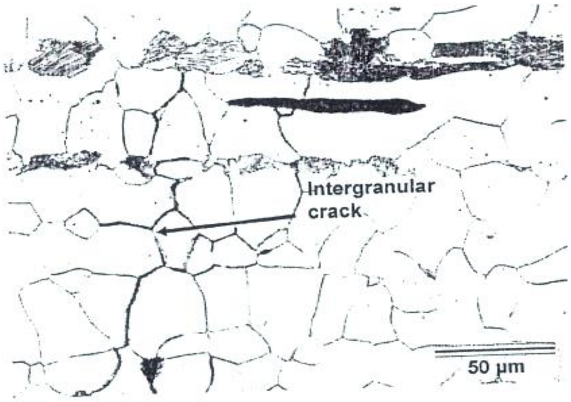

Fig. 74: Light photomicrograph of tip of crack shown in
Fig. 73 [16].

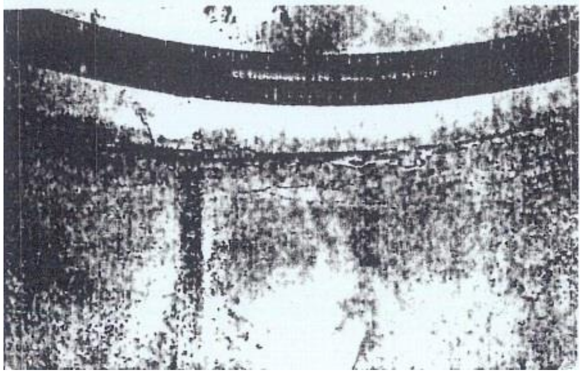

Fig. 75: Photograph of the internal surface of API 5L Grade B piping used in ethanol service following magnetic particle inspection to reveal stress corrosion cracks [16].

Corrosion monitoring is a very important aspect of corrosion technology. It generally refers to corrosion measurement methods performed under industrial or practical operating conditions. Outside and field conditions pose difficulties and need special techniques and procedures. P. R. Roberge [24, 25] has summarized the various techniques used in corrosion monitoring. They are reproduced below:

Physical techniques

- Mass loss coupons
- Electrical resistance (ER)
- Visual inspection

Electrochemical DC techniques

- Linear polarization resistance (LPR)
- Zero-resistance ammeter (ZRA) between dissimilar alloy electrodes—galvanic
- Zero-resistance ammeter (ZRA) between the same alloy electrodes
- Potentiondynamic/galvanodynamic polarization
- Electrochemical noise (ECN)

Electrochemical AC techniques

- Electrochemical impedance spectroscopy (EIS)
- Harmonic distortion analysis

Nonintrusive Techniques

Physical techniques for metal loss

- Ultrasonics
- Magnetic flux leakage (MFL)
- Electromagnetic—eddy current
- Electromagnetic—remote field technique (RFT)
- Radiography
- Surface activation and gamma radiometry
- Electrical field mapping

Physical techniques for crack detection and propagation

- Acoustic emission
- Ultrasonics (flaw detection)
- Ultrasonics (flaw sizing)

Corrosion products

- Hydrogen monitoring

Electrochemical techniques

- Corrosion potential (E_{COTT})

Water chemistry parameters

- pH
- Conductivity
- Dissolved oxygen
- Oxidation reduction (Redox) potential

Fluid detection

- Flow regime
- Flow velocity

Process parameters

- Pressure
- Temperature
- Dewpoint

Deposition monitoring

- Fouling

External monitoring

- Thermography

Offline Techniques

Water chemistry parameters

- Alkalinity
- Metal ion analysis (iron, copper, nickel, zinc, manganese)
- Concentration of dissolved solids
- Gas analysis (hydrogen, H2S, other dissolved gases)

Corrosion Monitoring

- Residual oxidant (halogen, halides, and redox potential)
- Microbiological analysis (sulfide ion analysis)

Residual inhibitor

- Filming corrosion inhibitors
- Reactant corrosion inhibitors

Chemical analysis of process samples

- Total acid number
- Sulfur content
- Nitrogen content
- Salt content in crude oil

For details please consult [25]

Diagnosis of corrosion failures

Davis [23] has summarized the following techniques for diagnosis of corrosion failures:

(1) Visual and microscopic examinations of corroded surfaces and microstructure.
(2) Chemical analysis of the metal, corrosion products and bulk environment
(3) Non-destructive evaluation methods
(4) Corrosion testing techniques
(5) Mechanical testing methods

These techniques have been described by Davis [23] in details. Table-13 gives investigative techniques used in corrosion failure analysis given by the Davis [23].

Table-13: Investigative techniques for diagnosing corrosion failures.

Technique
Metallography and Fractography
A.1 Macroexamination **Examination of bulk failure or sample by eye or low-power optical device**
A.2 Optical (light) microscopy **Examination of small region or area of either unprepared or polished and normally etched surface at magnification of 25 to 1000x. Normally examination is of a sample cut from the bulk, but on-site examination and replication techniques are possible.**
A.3 Electron microscopy
A.3.1 Transmission (TEM) **Examination of very thin section (foil) or surface replica through which electrons are transmitted. Magnification 2,000 to 40,000x**
A.3.2 Scanning (SEM) **Examination of unprepared (e.g., fracture) or prepared (e.g., polished and etched) surface or surface replica. Surfaces must be**

electrically conductive, which may be achieved by coating with, for example, Au-Pd by evaporation. Magnification 100 to 29,000x

Nondestructive evaluation

B.1 Magnetic susceptibility
Application (contact or close proximity) of a permanent magnet to a material/sample/structure

B.2 Electrical resistance
Application of known DC or high-frequency AC current and measurement of resulting potential(s) or of relative change of potential(s)

B-3 Dye-penetrant inspection
Enhancement of detail of cracks or defects by application and subsequent “development” of a penetrating dye

B-4 Magnetic particle inspection
Similar to B.3 above but with use of magnetic particles in a carrier fluid attracted to cracks or defects causing perturbations in an applied magnetic field

B-5 Eddy-current inspection
Detection of cracks or defects and thickness of coatings, which cause variation in eddy currents induced by an applied alternating magnetic field

B-6 Ultrasonic inspection

B.6.1 Longitudinal waves.
Application and detection of reflection of pulsed (typically 1000 s^{-1}) high-frequency wave (typically 5 to 10 MHz), normal to surface

B.6.2 Shear waves.
As B.6.1, but with wave angled to surface

B-7 Radiography
Penetration of sample/structure (and subsequent photographic recording) by x-rays or γ-rays. Extent of penetration depends on thickness and on material and its contained cracks and defects

B-8 Acoustic emission
Detection by multiple transducers of acoustic signals emitted by growing cracks

B.9 Temperature measurement

B.91 Temperature indicators
(crayons/paints/lacquers), which undergo color change or soften over specific temperature range, applied to surface

B.9.2 Radiation pyrometry
Matching by color a heated electrical filament and the target using emitted visible radiation (optical pyrometry). Detection of both infrared and visible radiation emitted by the target (total radiation pyrometry). Detection by scanning of infrared radiation emitted by the target (Thermography).

B.10 Pressure measurement
Pressure transducer “plumbed” in or temporarily attached to a pressure line or vessel

Chemical Analysis

C.1 Spot test(s)
Application of selected reagent(s) to surface and detection, by eye or with aid of a microscope, of subsequent reaction

C.2 Classical wet analytical chemistry
Gravimetric/volumetric/colorimetric/electrochemical/atomic absorption techniques

C.3 Emission spectrography
Recording on a photographic plate of the visual and ultraviolet spectrum produced by sparking a solid sample or by introduction of a solution into a plasma. Spectral line densities compared, subsequently, with a standard

C.4 Mass spectrography
Recording on a photographic plate of the spectrum produced after ionizing a solid sample and accelerating the ions through a magnetic field. Spectral line densities compared, subsequently, with a standard

C.5 Emission/mass spectrometry
As C.3 and C.4, but the output is converted using photomultipliers to direct reading of elemental concentrations

C.6 Electron probe microanalysis

Analysis by crystal spectrometry or energy dispersion of x-rays emitted as a result of applying a focused (1μm diam) electron beam to a surface

C.7 Electron spectroscopy
Analysis of either photoelectrons or Auger electrons emitted from a surface excited by an x-ray beam or an electron beam. (Techniques known as x-ray photoelectron spectroscopy, XPS, or Auger electron spectroscopy, AES

C.8 electron diffraction
Scattering of electrons, transmitted through a thin film or reflected from a solid surface (from depths up to 50Å) by crystal lattice in a 1 μm diam sampled area

C.9 X-ray diffraction
Scattering of x-rays transmitted through or reflected from a solid sample

Mechanical Testing

D.1 Tensile test
Load specimen in tension at known loading or deflection rate. Normally test carried out at low strain rate and ambient pressure and temperature

D.2 Impact test
Specimen (usually prenotched) loaded at high strain rate. Tests may be carried out at range of temperatures (low). Energy absorbed in impact failure recorded

D.3 Hardness test

D.3.1 Bulk (macro) indentation of specimen surface by standard indenter (pyramid, ball, or cone) under known load, normally in range 1 to 3000 kgf

D.3.2 Micro. Similar to D.3.1 but with pyramid diamond indenters only under load in range 0.001 to 3.5 kgf

D.4 Static load

D.4.1 Creeep. Maintain load on specimen subjected to high temperature (relative) for periods of up to 100,000 h

D.4.2 Stress corrosion. Maintain load on specimen, often notched or precracked, subjected to specific environment. Load applied normally up to 0.9 yield strength and exposure often limited to 1000 h. (Note for some techniques load is allowed to fall during the test.)

D.5 Cyclic load
Application of cyclic load to smooth or prenotched or precracked specimens sometimes subjected to specific environment. Normally a range of loads is applied.

D.6 Fracture toughness
Application of tensile load to prenotched and/or cracked specimen of known crack dimensions. Maximum load and/or crack opening displacement (COD) recorded.

Davis [23] has described the type of information provided, advantages and limitations of these methods. To know about this information, please consult him [23].

Analysis of corrosion failures

Davis [23] has described in detail the various methods of analyzing corrosion failures, viz., collection of background data, on-site examination, on-site sampling, preliminary laboratory examination, microscopic examination, chemical analysis, surface chemical analysis, bulk material analysis, non-destructive evaluation etc.

Corrode testing

Davis [23] has also described the various methods of corrosion testing, viz., accelerated tests, simulated-use-tests, mechanical tests etc.

Analyzing the evidence, formulating conclusions and writing the report

A series of questions, has been proposed by Davis [23] as an aid in analyzing the evidence derived from examinations and tests and in formulating conclusions (Ref 5). The questions are also helpful in calling attention to details of the overall investigation that may have been overlooked. The questions are as follows:

- Has failure sequence been established?
- If failure involved cracking or fracture, have the initiation sites been determined?
- Did cracks initiate at the surface or below the surface?

- Was cracking associated with a stress concentrator?
- How long was the crack present?
- What was the type of loading—static, cyclic, or intermittent?
- How were the stresses oriented?
- What was the failure mechanism?
- What was the approximate service temperature at the time of failure?
- Did temperature contribute to failure?
- Did wear contribute to failure?
- Did corrosion contribute to failure? What type of corrosion?
- Did the crack surface corrode during the failure or subsequent to the failure?
- Was the proper material used? Is a better material required?
- Was the cross section adequate for the class of service?
- Was the quality of the material acceptable in accordance with specification?
- Were the mechanical properties of the material acceptable in accordance with specification?
- Was the component that failed properly heat treated?
- Was the component that failed properly fabricated?
- Was the component properly assembled or installed?
- Was the component properly protected (pint thickness, kind of surface protection and so on)?
- Was the component repaired during service? If so, was the repair performed correctly?
- Was the component properly run in?
- Was the component properly maintained?
- Was the component properly lubricated?
- Was failure related to abuse in service?
- Can the design of the component be improved to prevent similar failures?
- Are failures likely to occur in similar components now in service? What can be done to prevent their failure?

A proper handling and analysis of the answers to these questions will help the scientist/engineer to enable him to formulate the report.

Writing the report

Davis [23] advises that the report must be written legibly, concisely and logically. He has quoted Vander Vort [26] to divide the report into the following main sections:

- Description of the failed component
- Service conditions at the time of failure
- Prior service history
- Manufacturing and processing history of the component
- Mechanical and metallurgical study of failure
- Metallurgical evaluation of quality
- Summary of the mechanisms that caused failure
- Recommendations for prevention of similar failure or for correction of similar components in service.

If a corrosion scientist/engineer follows this procedure, a good investigative report can be prepared.

Photograph of some pioneers in corrosion science and technology

Conclusions

This short brief illustrates the vastness of the subject. In short, the subject of corrosion is a very hard nut to crack. To handle it, the corrosion scientist/engineer must have thorough knowledge of physical metallurgy, mechanical metallurgy, chemistry (inorganic solid state and organic), electrochemistry, physics, thermodynamics and kinetics, hydrodynamics mechanical engineering, etc.

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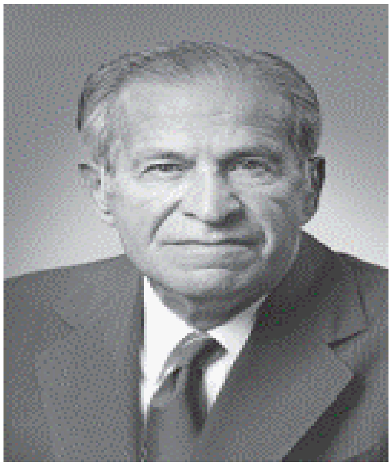
Photographs of some Pioneers in Corrosion Science and Technology

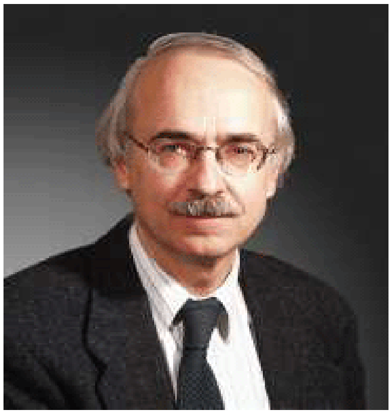
Prof. Dr. Herbert H. Uhlig

Prof. Dr. Marcel Pourbaix



Professor Mars G Fontana

Prof. Philippe Marcus



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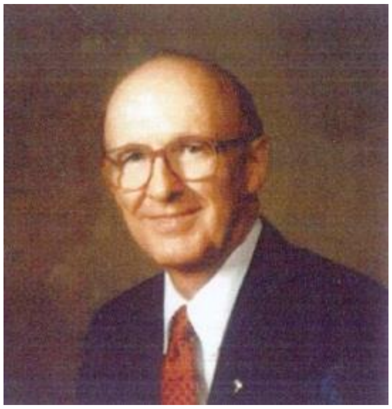

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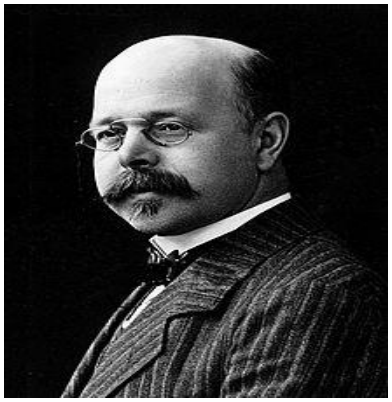
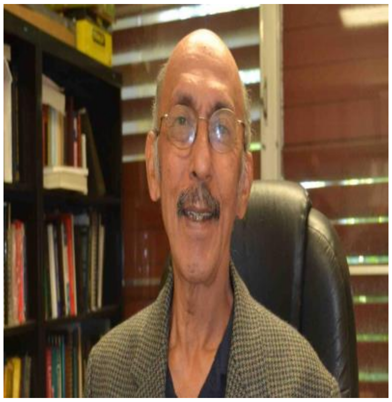
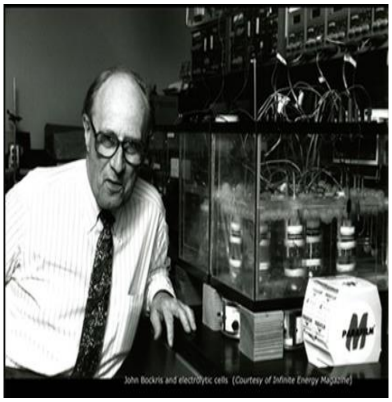


Prof. Dr. Walther Nernst



Prof. Dr. Nestor Perez



Prof. Dr. J. O' M. Bockris

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