Syllabus: Metals and Metallurgy: Role of metals in our life with special reference of ironl recovery of iron from its ores, stainless steel, rusting of iron and its prevention

From being a crucial building block of steel to nourishing plants and helping carry oxygen in your blood — iron is always busy helping sustain life on Earth. Iron is a brittle, hard substance, classified as a metal in Group 8 on the Periodic Table of the Elements. The most abundant of all metals, its pure form rapidly corrodes from exposure to moist air and high temperatures. Iron is also the fourth most common element in Earth's crust by weight and much of Earth's core is thought to be composed of iron. Besides being commonly found on Earth, it is abundant in the sun and stars.

It is used to make steel. Its atomic number is 26, atomic weight (average mass of the atom) 55.845, density 7.874 g/cc, solid under ambient conditions, melting point 1,538^o C, boiling point 2,861^o C and Number of isotopes are 33, but stable isotopes are 4 and most common isotopes are Iron-56 (natural abundance: 91.75 %).

People have been using iron for more than 5,000 years. Iron is mostly obtained from minerals hematite and magnetite, it can also be obtained from the minerals taconite, limonite and siderite. Iron has four different allotropic forms, which means that it has four different structural forms in which atoms bond in different patterns. Those forms are called ferrites, known as alpha (which is magnetic), beta, gamma and omega.

Iron is an important nutrient in our diet. Iron deficiency, the most common nutritional deficiency, can cause anaemia and fatigue that affects the ability to perform physical work in adults. There are two types of dietary iron: heme iron and non-heme iron. Heme iron — which is the more readily absorbed type of iron — is found in meat, fish and poultry, whereas non-heme iron — which is also absorbed but to a lesser extent than heme iron — is found in both plant foods (such as spinach, kale and broccoli) and meat.

The metal : Finely divided Fe is pyrophoric in air, but the bulk metal oxidizes in dry air only when heated. In moist air, Fe rusts, forming a hydrated oxide $Fe_2O_3.xH_2O$. Rusting is an electrochemical process (equation 1) and occurs only in the presence of O_2, H_2O and an electrolyte. The latter may be water, but is more effective if it contains dissolved SO_2 (e.g. from industrial pollution) or NaCl (e.g. from seaspray or salt-treated roads). Diffusion of the ions formed in reaction (1) deposits $Fe(OH)_2$ at places between the points of attack and this is further oxidized to hydrated iron(III) oxide:

$$2Fe \rightarrow 2Fe^{2+} + 4e^-$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4\,[OH]^- \qquad (1)$$

Iron reacts with halogens at 470–570K to give FeF_3, $FeCl_3$, $FeBr_3$ and FeI_2, respectively. The metal dissolves in dilute mineral acids to yield Fe(II) salts, but concentrated HNO_3 and other powerful oxidizing agents make it passive; it is unaffected by alkalis. When powdered iron and sulfur are heated together, FeS is produced. The formation of iron carbides and alloys is crucial to the steel industry. Most of the chemistry of Fe involves Fe(II) or Fe(III), with Fe(IV) and Fe(VI) known in a small number of compounds; Fe(V) is rare.

Iron(III): The old name for iron (III) is ferric. Iron (III) fluoride, chloride and bromide are made by heating Fe with the halogen. The fluoride is a white, involatile solid isostructural with ScF_3. In the solid state, $FeCl_3$ adopts the BiI_3 lattice but the gas phase (bp 588K) contains discrete molecules, dimers below 970K and monomers above 1020 K. Anhydrous $FeCl_3$ forms hygroscopic dark green or black crystals. It dissolves in water to give strongly acidic solutions from which the orange-brown hydrate $FeCl_3.6H_2O$ (properly formulated as trans-$[FeCl_2(H_2O)_4]Cl.2H_2O$) can be crystallized. The trichloride is a useful precursor in Fe(III) chemistry, and both anhydrous $FeCl_3$ and $FeBr_3$ are used as Lewis acid catalysts in organic synthesis. Anhydrous $FeBr_3$ forms deliquescent, red-brown, watersoluble crystals; the solid adopts a BiI3 structure, but in the gas phase, molecular dimers are present. Iron (III) iodide readily decomposes (equation 2) but, under inert conditions, it can be isolated from reaction 3.

$$2\ FeI_3 \rightarrow 2\ FeI_2 + I_2 \qquad (2)$$

$$2Fe(CO)_4I_2 + I_2 \qquad (3)$$

Iron (III) oxide exists in a number of forms. The paramagnetic α-form (a red-brown solid or grey-black crystals) occurs as the mineral haematite and adopts a corundum structure with octahedrally sited Fe (III) centres. The β-form is produced by hydrolysing $FeCl_3.6H_2O$, or by chemical vapour deposition (CVD, at 570K from iron(III) trifluoroacetylacetonate. On annealing at 770 K, a β→α phase change occurs. The γ-form is obtained by careful oxidation of Fe_3O_4 and crystallizes with an extended structure in which the O^{2-} ions adopt a ccp array and the Fe^{3+} ions randomly occupy octahedral and tetrahedral holes. γ-Fe_2O_3 is ferromagnetic and is used in magnetic recording tapes. Iron (III) oxide is insoluble in water but can be dissolved with difficulty in acids. Several hydrates of Fe_2O_3 exist, and when Fe (III) salts are dissolved in alkali, the red-brown gelatinous precipitate that forms is not $Fe(OH)_3$ but $Fe_2O_3.H_2O$ (also written as Fe(O)OH). The precipitate is soluble in acids giving $[Fe(H_2O)_6]^{3+}$, and in concentrated aqueous alkalis, $[Fe(OH)_6]^{3-}$ is present.

Several forms of Fe(O)OH exist and consist of chain structures with edge-sharing FeO_6 octahedra. The minerals goethite and lepidocrocite are α- and γ-Fe(O)OH respectively.

Mixed metal oxides derived from Fe_2O_3 and of general formula $M^{II}Fe^{III}_2O_4$ or $M^{I}Fe^{III}O_2$ are commonly known as ferrites despite the absence of discrete oxoanions. They include compounds of commercial importance by virtue of their magnetic properties, e.g. electromagnetic devices for information storage; for discussion of the magnetic properties of mixed metal oxides. Some oxides of the $M^{I}Fe^{III}O_2$ type adopt structures that are related to NaCl (*e.g.* $LiFeO_2$, in which the Li^+ and Fe^{3+} ions occupy Na^+ sites and O^{2-} ions occupy Cl^- sites). Among the $M^{I}Fe^{III}O_2$ group of compounds, $CuFeO_2$ and $AgFeO_2$ are noteworthy in being semiconductors. Other ferrites exist with more complex structures: permanent magnets are made using $BaFe_{12}O_{19}$, and the iron garnet family includes $Y_3Fe_5O_{12}$ (yttrium iron garnet, YIG) which is used as a microwave filter in radar equipment. When Fe_2O_3 is heated at 1670 K, it converts to black Fe_3O_4 ($Fe^{II}Fe^{III}_2O_4$) which also occurs as the mineral magnetite, and possesses an inverse spinel structure. Its ferrimagnetic behaviour makes Fe_3O_4 commercially important, *e.g.* it is used in magnetic toner in photocopiers. Mixtures of Fe_3O_4 and γ-Fe_2O_3 are used in magnetic recording tape, and this market competes with that of CrO_2.

Iron(II): The old name for iron(II) is ferrous. Anhydrous FeF_2, $FeCl_2$ and $FeBr_2$ can be prepared by reaction 4, while FeI_2 is made by direct combination of the elements.

$$Fe + 2HX \rightarrow FeX_2 + H_2 \qquad (X = F, Cl; Br) \qquad (4)$$

Iron (II) fluoride is a sparingly soluble, white solid with a distorted rutile structure; the environment around the high-spin Fe (II) centre (d^6) is surprisingly irregular with 4F at 212 pm and 2F at 198 pm. In the gas phase, FeF_2 is monomeric. Iron(II) chloride forms white, hygroscopic, water-soluble crystals and adopts a $CdCl_2$ lattice. In the gas phase of $FeCl_2$, monomers and dimers are present. The pale green hydrate $FeCl_2.4H_2O$, properly formulated as octahedral $[FeCl_2(H_2O)_4]$, is a convenient precursor in Fe(II) chemistry. The hexahydrate (which loses water readily) can be obtained by recrystallizing $FeCl_2$ from water below 285 K. Iron (II) bromide is a deliquescent, yellow or brown solid and adopts a CdI_2 structure. It is very soluble in water and forms hydrates $FeBr_2.xH_2O$ where x = 4, 6 or 9 depending on crystallization conditions. Dark violet FeI_2 has a CdI_2 layer structure, and is hygroscopic and light-sensitive; it forms a green tetrahydrate. All the halides or their hydrates are commercially available, as are salts such as the perchlorate, sulfate and $[NH_4]2Fe[SO_4]_2.6H_2O$. Iron(II) sulfate is a common source of Fe(II) and is available as the blue-green $FeSO_4.7H_2O$, an old name for which is green vitriol. Like most hydrated Fe(II) salts, it dissolves in water to give $[Fe(H_2O)_6]^{2+}$, the electronic spectrum and magnetic moment of which are consistent with high spin d^6. The salt $[NH_4]_2Fe[SO_4]_2.6H_2O$ is an important source of Fe^{2+} since in the solid state, it is kinetically more stable towards oxidation than most Fe (II) salts. Iron (II) oxide is a black, insoluble solid with an NaCl lattice above its Curie temperature (200 K); the lattice suffers defects because it is always deficient in Fe. Below 200 K, FeO undergoes a phase change and becomes antiferromagnetic. It can be made *in vacuo* by thermal decomposition of iron(II) oxalate but the product must be cooled rapidly to prevent disproportionation

$$4FeO \rightarrow Fe_3O_4 + Fe \qquad (5)$$

While $Fe(OH)_2$ is precipitated by adding alkali to solutions of Fe(II) salts but it rapidly absorbs O_2, turning dark green, then brown. The products are a mixed $Fe^{(II)}Fe^{(III)}$hydroxide and $Fe_2O_3.H_2O$. Iron (II) hydroxide dissolves in acids, and from concentrated NaOH solutions, the bluegreen $Na_4[Fe(OH)_6]$ can be crystallized.

Anaemia, in which the body suffers from a deficiency of iron, leads to a general state of lethargy and weakness. Iron is usually administered orally to a patient as iron supplement tablets containing an Fe(II) or Fe(III) salt. Iron(II) salts are more typical because they exhibit better solubilities than Fe(III) salts at physiological pH, but Fe(III) has the advantage that, unlike Fe(II), it is not susceptible to oxidation in aqueous solution. Among compounds which are in common use are iron(III) chloride, iron(II) sulfate, iron(II) fumarate, iron(II) succinate and iron(II) gluconate.

Extraction of iron from its oxide ores

Oxide ores of iron, after concentration through calcinations/roasting (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with limestone and coke and fed into a blast furnace from its top. Here, the oxide is reduced to metal. Thermodynamics will tell us how coke reduces the oxide and why this furnace is chosen. One of the main reduction steps in this process is:

$$FeO\ (s) + C\ (s) \rightarrow Fe\ (s/l) + CO\ (g) \qquad (1)$$

It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidised to CO:

$$FeO\ (s) \rightarrow Fe\ (s) + 1/2O_2\ (g) \qquad [\Delta G_{(FeO/Fe)}] \qquad (2)$$

$$C\ (s) + ½\ O_2 \rightarrow CO\ (g) \qquad [\Delta G_{(C/CO)}] \qquad (3)$$

When both the reactions take place to yield the equation (1), the net Gibbs energy change becomes $\Delta G_{(C/CO)} + \Delta G_{(FeO/Fe)} = \Delta_r G$

Naturally, the resultant reaction will take place when the right hand side in equation (4) is negative. In ΔG^o *vs* T plot representing reaction (2), the plot goes upward and that representing the change C → CO (C, CO) goes downward. At temperatures above 1073 K (approx), the C,CO line comes below the Fe, FeO line [$\Delta G_{(C/CO)} < \Delta G_{(FeO/Fe)}$]. So in this range, coke will be reducing the FeO and will itself be oxidised to CO. In a similar way, reduction of Fe_3O_4 and Fe_2O_3 at relatively lower temperaturesby CO can be explained on the basis of lower lying points of intersection of their curves with the CO, CO_2 curve as shown in figure.

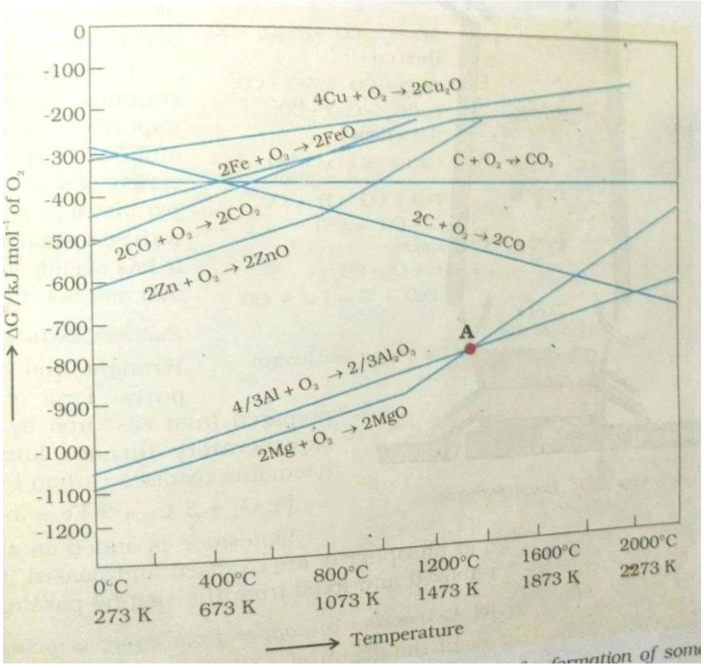

Figure: Gibbs energy (ΔG^o) *vs* T plots (schematic) plots for formation of some oxides) Ellingham diagram)

In the blast furnace, reduction of iron oxides takes place in different temperature ranges. Hot air is blown from the bottom of the surface and coke is burnt to give temperature upto about 2200K in the lower portion itself. Burning of coke therefore supplies most of the heat required in the process. CO and heat moves to upper part of the furnace. In upper part, temperature is lower and iron oxides, [Fe_2O_3 and Fe_3O_4] coming from the top are reduced in steps to FeO. Thus the reduction reactions taking place in lower temperature range and in the higher temperature range, depend on the points of corresponding intersections in the ΔG^o *vs* T plots. These reactions are as follows:

$3Fe_2O_3 + CO \rightarrow 2 Fe_3O_4 + CO_2$

$Fe_3O_4 + 4 CO \rightarrow 3Fe + 4 CO_2$

$Fe_2O_3 + CO \rightarrow 2 FeO + CO_2$

At 900-1500 K (higher temperature range in the blast furnace):

$CO_2 + C \rightarrow 2 CO$

$FeO + CO \rightarrow Fe + CO_2$

Limestone is also decomposed to CaO which removes silicate impurity of the ore as slag. Slag is in molten state and separates out from iron.

Blast Furnace

Another set of presentation of iron from oxide ores bu blast furnace are again explained below:

Common ores of iron are iron oxides, which can be reduced to iron by heating them with carbon in the form of coke. Coke is produced by heating coal in the absence of air. Coke is cheap and provides both the reducing agent for the reaction and also the heating source. Most commonly used iron ore are **hematite**, Fe_2O_3 and magnetite Fe_3O_4.

Blast Furnace

Various steps and reactions occurring in the blast furnace:

At 500^{o}C $3Fe_2O_3 + CO \rightarrow 2\,Fe_3O_4 + CO_2$
$Fe_2O_3 + CO \rightarrow 2\,FeO + CO_2$
At 850^{O}C $Fe_3O_4 + CO \rightarrow 3FeO + CO_2$
At 1000^{O}C $FeO + CO \rightarrow Fe + CO_2$
At 1300^{O}C $CO2 + C \rightarrow 2CO$
At 1900^{O}C $C + O_2 \rightarrow CO_2$
$FeO + C \rightarrow Fe + CO$

Air blown into the bottom of the furnace is heated using the hot waste gases from the top. The coke (essentially impure carbon) burns in the blast of hot air to form CO_2 – a strongly exothermic reaction. This reaction is the main source of heat in the furnace:

$$C + O_2 \rightarrow CO_2$$

Reduction of Ore: at high temperature, at the bottom of the furnace, carbon dioxide reacts with carbon to produce carbon monoxide:

$$C + CO_2 \rightarrow 2CO$$

Carbon monoxide is the main reducing agent in furnace

$$Fe_2O_3 + 3CO \rightarrow 2\,Fe + 3\,CO_2$$

In the hotter parts of the furnace, the carbon itself also acts as a reducing agent. It is to be noted that at these temperatures, the other product of the reaction is carbon monoxide, not carbon dioxide.

$$Fe_2O_3 + 3C \rightarrow 2\,Fe + 3CO$$

Temperature of the furnace is hot enough to melt the iron which trickles down to the bottom where it can be tapped off.

Function of the limestone: Iron ore is not pure iron oxide. It also contains a mixture of rocky material that would not melt at the temperature of the furnace, and would eventually clog it up. Limestone is added to convert this into slag which melts and runs to the bottom. Heat of the furnace decomposes limestone to give calcium oxide.

$$CaCO_3 \rightarrow CaO + CO_2$$

This is an endothermic reaction, absorbing heat from the furnace. It is therefore important not to add too much limestone as it would cool the furnace. Calcium oxide is a basic oxide and reacts with acidic oxides such as silicon dioxide present in the rock. Calcium oxide reacts with with silicon dioxide to give calcium silicate.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

Calcium silicate melts and runs down through the furnace to form a layer on top of the molten iron. It can be tapped off from time to time as **slag**. Slag is used on road making and as slag cement, a final ground slag which can be used in cement often mixed with Portland cement.

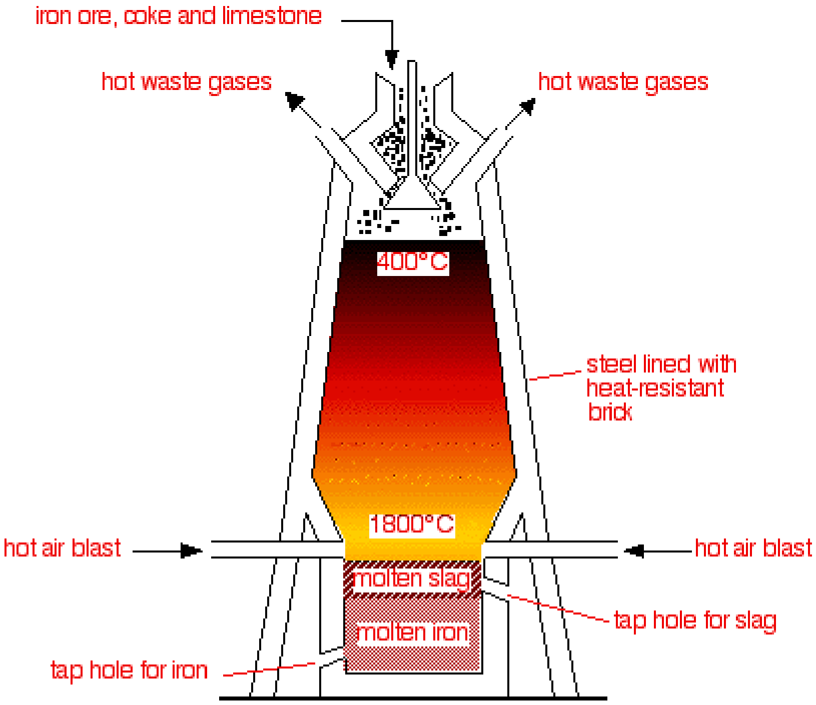

Figure: Schematic presentation of blast furnace with reactions at various temperatures inside furnace

Iron obtained from blast furnace contains about 4% carbon and many impurities in smaller amount such as S,P,Si, Mn. This is known as **Pig iron** and cast into various shapes. **Cast iron** is made by melting pig iron with scrap iron and coke using hot air blast. Molten iron from bottom of the surface can be used as cast iron. It is runny when molten and doesn't shrink much on solidifying. It is therefore ideal for castings, hence its name. However, it is impure containing approx 4% carbon. This carbon makes it very hard and brittle also. If hit hard, it tends to shatter rather than bend or dent. Cast iron is used for things like manhole covers, guttering and drainpipes, cylinder blocks in car engines, etc. More purer form is called **Wrought iron.** Following is the composition:

Pig iron	C content 4 %
Cast iron	C content 3 %
Wrought iron	C content 0.5 %
Steel	C content 0.5-1.5 %

Steel is an alloy of iron and carbon. Its grade and properties depend on C content.

Mild steel or low steel	C content 0.15-0.3 %
Medium steel	C content 0.3-0.6 %
High C steel	C content 0.6-0.8 %
Tool Steel	C content 0.8-1.6 %

Steel which contains various transition metals (V, Cr, Mn, Ni, W, etc) in small quantities are known as **special steel.** They are corrosion resistant and possess special properties.

Methods of making steel

Bessemer's method Impurities of pig iron are removed by oxidation.then Spiegel (a mixture of Fe, Mn, C) is mixed in the oxidized product to produce steel. This method uses SiO_2 lined Bessemer converter. It is filled with a perforated bottom to blow air. Impurities are removed by oxidation and Mn as $MnSiO_3$.

When pig iron contains P as major impurity, (MgO + CaO) mixture lined furnace is used. Phosphorus is removed as basic slag $Ca_3(PO_4)_2CaO$. Following are the involved reactions:

$Si + O_2 \rightarrow SiO_2$

$S + O_2 \rightarrow SO_2$

$2C + O_2 \rightarrow 2CO$

$2\,MnO + O_2 \rightarrow 2MnO$

$MnO + SiO_2 \rightarrow MnSiO_3$ (slag)

$2\,P + \frac{1}{2}\,O_2 \rightarrow P_2O_5$

$3\,CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$

Fe + spiegel → STEEL

Siemen's Martin open Hearth process

This process is carried out in a produced gas fired furnace. SiO_2 or (CaO + MgO) lined furnace is used in this method, the impurities are removed by oxidation with Fe_2O_3 and also as slag. The charge consists of pig iron, scrap iron, haematite ore. Although slow, this method produces steel of superior quality. Following are the involved reactions:

$2\,Fe_2O_3 + 3S \rightarrow 4\,Fe + 3\,SO_2$

$Fe_2O_3 + 3C \rightarrow 2\,Fe + 3\,CO$

$5\,Fe_2O_3 + 6P \rightarrow 10\,Fe + 3\,P_2O_5$

$P_2O_5 + 3\,CaO \rightarrow Ca_3(PO_4)_2$ (slag)

$3\,Si + 2\,Fe_2O_3 \rightarrow 4\,Fe + 3\,SiO_2$

$SiO_2 + CaO \rightarrow CaSiO_3$ (slag)

$3Mn + Fe_2O_3 \rightarrow 2\,Fe + 3\,MnO$

$MnO + SiO_2 \rightarrow MnSiO_3$ (slag)

Fe + Spiegel → Steel

The above processes have one major drawback, *i.e.* taking up of nitrogen by the molten iron. When it is simply above 0.01% N, makes steel brittle. In addition to that nitridying of the surface of iron makes it unfit for welding.

L-D Process

It is modern method of steel making. This method uses pure O_2 for removal of impurities. A jet of hot O_2 is held above molten iron surface. The impurities are removed quickly in 20-30 minutes. Subsequently:

Fe + Spiegel → Steel

L-D process produces better quality of steel compared to Bessemer and open Heaarth processes.

Electrical process

This method produces high grade steel. Steel from Bessemer method is used and silica with dolomite ($CaCO_3$ + $MgCO_3$) lined furnace is used. Graphite is used as electrode, low grade steel melts by heating effects of current; slag is produced and removed subsequently. Then alloying metal is mixed to produce Spiegel steel.

Steels constitute a wide range of iron-based alloys. General types include ***carbon steels*** (containing from 0.5 to 2.0% carbon) and only small amounts of other metals (generally less than 3% to 4%). Other metals in the alloys may include nickel, manganese, molybdenum, chromium, or vanadium in varying amounts. These ingredients are added to produce a steel having the desired characteristics. The properties of the steel are determined by the composition as well as the heat treatment methods employed. If the total amount of metals added to iron exceeds about 5%, the alloy is sometimes called a ***high alloy*** steel. Most stainless steels are in this category because the chromium content is between 10% and 25%, and some types also contain 4% to 20% nickel. Stainless steels, so called because of their resistance to corrosion, are of several types. The form of iron having the *fcc* structure is known as γ –Fe or ***austenite*** , and one type of stainless steel (which contains nickel) is known as ***austenitic stainless steel*** because it has the austenite (*bcc*) structure. ***Martensitic*** stainless steels have a structure that contains a body-centered tetragonal arrangement that results from rapidly quenching the austenite structure. In addition to these two types, ***ferritic*** stainless steel has a *bcc* structure and does not contain nickel. In addition to the stainless steels, a large number of alloys known as tool steels are important. As the name implies, these are special alloys that are used to make tools for cutting, drilling, and fabricating metal. These alloys commonly include some or all of the following in various amounts: Cr, Mn, Mo, Ni, W, V, Co, C, and Si. In many cases, the alloys are engineered to have the desired properties of resistance to impact, heat, abrasion, corrosion, or thermal stress. Heat treatment of a steel having the desired composition can alter the structure of the metal so that certain properties are optimized. Thus, there are a large number of variables in the manufacture of steel. The manufacture of special steels is an important area of metallurgy.

It is possible that when the galvanized steel is scratched, the air may oxidize some iron. The Fe^{2+} so produced is immediately reduced to iron by the zinc, and rusting does not occur.

$$Zn + Fe^{2+} \rightarrow Fe + Zn^{2+}$$

Similar applications in which one metal is sacrificed to protect another are the attaching of sacrificial blocks of magnesium to"underground steel pipelines and the hulls of ships to prevent the rusting of iron. Thus the coating of zinc serves two purposes - first it covers the iron and prevents its oxidation (rather like a coat of paint) and second it provides anodic protection.

All steels are alloys, or chemical combinations of many elements. The foundation of all steel is iron. Iron in its pure form is rarely used for industrial applications because it’s relatively soft and brittle and thus not suited for mechanical work. But iron is the most common element in the Earth’s crust so it’s abundant, easy to extract and not expensive. Somewhere in ancient history it was discovered that by adding up to 2% of carbon to iron you get steel, a relatively simple mixture we now call “mild steel.” This discovery really was a revolution, and we’ve been tinkering with the recipe for different kinds of steel ever since.

It’s important to remember that steel has excellent mechanical properties for which there are still no viable commercial substitutes, so steel will be with us for a long time. It’s stronger than aluminum, easily worked, inexpensive, tough and it doesn’t shatter or crack. But mild steel has limitations, especially when exposed to the environment.

Stainless steel is an alloy of iron with a minimum of 10.5% Chromium. Chromium produces a thin layer of oxide on the surface of the steel known as the 'passive layer'. This prevents any further corrosion of the surface. Increasing the amount of Chromium gives an increased resistance to corrosion. Stainless steel also contains varying amounts of Carbon, Silicon and Manganese. Other elements such as nickel and molybdenum may be added to impart other useful properties such as enhanced formability and increased corrosion resistance. It was experimented with different types of steel for weapons and noticed that a 13% Chromium steel had not corroded after several months. Stainless steels of various kinds are used in thousands of applications. The following gives a flavour of the full range:

Domestic – cutlery, sinks, saucepans, washing machine drums, microwave oven liners, razor blades

Architectural/Civil Engineering – cladding, handrails, door and window fittings, street furniture, structural sections, reinforcement bar, lighting columns, lintels, masonry supports

Transport – exhaust systems, car trim/grilles, road tankers, ship containers, ships chemical tankers, refuse vehicles.

Chemical/Pharmaceutical – pressure vessels, process piping.

Oil and Gas – platform accommodation, cable trays, subsea pipelines.

Medical – Surgical instruments, surgical implants, MRI scanners.

Food and Drink – Catering equipment, brewing, distilling, food processing.

Water – Water and sewage treatment, water tubing, hot water tanks.

General – springs, fasteners (bolts, nuts and washers), wire.

Although stainless steel is much more resistant to corrosion than ordinary carbon or alloy steels, in some circumstances it can corrode. It is 'stain-less' not 'stain-impossible'. In normal atmospheric or water based environments, stainless steel will not corrode as demonstrated by domestic sink units, cutlery, saucepans and work-surfaces. In more aggressive conditions, the basic types of stainless steel may corrode and a more highly alloyed stainless steel can be used.

Stainless steel is usually divided into 5 types:

a. Ferritic – These steels are based on chromium with small amounts of carbon usually less than 0.10%. These steels have a similar microstructure to carbon and low alloy steels. They are usually limited in use to relatively thin sections due to lack of toughness in welds. However, where welding is not required they offer a wide range of applications. They cannot be hardened by heat treatment. High chromium steels with additions of molybdenum can be used in quite aggressive conditions such as sea water. Ferritic steels are also chosen for their resistance to stress corrosion cracking. They are not as formable as austenitic stainless steels. They are magnetic.
b. Austenitic - These steels are the most common. Their microstructure is derived from the addition of nickel, manganese and nitrogen. It is the same structure as occurs in ordinary steels at much higher temperatures. This structure gives these steels their characteristic combination of weldability and formability. Corrosion resistance can be enhanced by adding chromium, molybdenum and nitrogen. They cannot be hardened by heat treatment but have the useful property of being able to be work hardened to high strength levels whilst retaining a useful level of ductility and toughness. Standard austenitic steels are vulnerable to stress corrosion cracking. Higher nickel austenitic steels have increased resistance to stress corrosion cracking. They are nominally non-magnetic but usually exhibit some magnetic response depending on the composition and the work hardening of the steel.
c. Martensitic - These steels are similar to ferritic steels in being based on chromium but have higher carbon levels up as high as 1%. This allows them to be hardened and tempered much like carbon and low-alloy steels. They are used where high strength and moderate corrosion resistance is required. They are more common in long products than in sheet and plate form. They have generally low weldability and formability. They are magnetic.
d. Duplex - These steels have a microstructure which is approximately 50% ferritic and 50% austenitic. This gives them a higher strength than either ferritic or austenitic steels. They are resistant to stress corrosion cracking. So called “lean duplex” steels are formulated to have comparable corrosion resistance to standard austenitic steels but with enhanced strength and resistance to stress corrosion cracking. “Superduplex” steels have enhanced strength and resistance to all forms of corrosion compared to standard austenitic steels. They are weldable but need care in selection of welding consumables and heat input. They have moderate formability. They are magnetic but not so much as the ferritic, martensitic and PH grades due to the 50% austenitic phase.

e. Precipitation hardening (PH) - These steels can develop very high strength by adding elements such as copper, niobium and aluminium to the steel. With a suitable “aging” heat treatment, very fine particles form in the matrix of the steel which imparts strength. These steels can be machined to quite intricate shapes requiring good tolerances before the final aging treatment as there is minimal distortion from the final treatment. This is in contrast to conventional hardening and tempering in martensitic steels where distortion is more of a problem. Corrosion resistance is comparable to standard austenitic steels like 1.4301 (304).

Magnetic properties of stainless steel:

It is commonly stated that “stainless steel is non-magnetic”. This is not strictly true and the real situation is rather more complicated. The degree of magnetic response or magnetic permeability is derived from the microstructure of the steel. A totally non-magnetic material has a relative magnetic permeability of 1. Austenitic structures are totally non-magnetic and so a 100% austenitic stainless steel would have a permeability of 1. In practice this is not achieved. There is always a small amount of ferrite and/or martensite in the steel and so permeability values are always above 1. Typical values for standard austenitic stainless steels can be in the order of 1.05 – 1.1. It is possible for the magnetic permeability of austenitic steels to be changed during processing. For example, cold work and welding are liable to increase the amount of martensite and ferrite respectively in the steel. A familiar example is in a stainless steel sink where the flat drainer has little magnetic response whereas the pressed bowl has a higher response due to the formation of martensite particularly in the corners. In practical terms, austenitic stainless steels are used for “non-magnetic” applications, for example magnetic resonance imaging (MRI). In these cases, it is often necessary to agree a maximum magnetic permeability between customer and supplier. It can be as low as 1.004. Martensitic, ferritic, duplex and precipitation hardening steels are magnetic.

What Is Rust?

One of the most chemically reactive of all elements is oxygen. It easily join with other elements to create new chemical compounds. When it joins with iron, it makes iron oxide, or rust. This will happen to mild steel very quickly unless the surface is protected with some treatment like painting, glavanizing or powder coating. Each of these surface treatments have their merits but eventually water will find its way in and cause rust. As we all know, rust is not just unsightly but causes the substrate to lose mechanical strength and eventually fail completely.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion.

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth’s moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminium cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both. In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($Fe_2O_3.xH_2O$), commonly known as rust, that does not provide a tight protective film. Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil saturated with oxygen will not rust because of the absence of water.

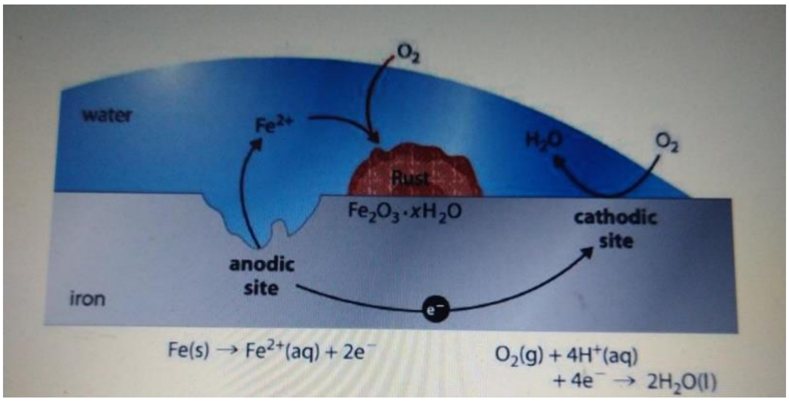

Figure: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to $Fe^{2+}(aq)$ at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($Fe_2O_3.xH_2O$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen.

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

  $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ E° = 1.23V

  $O_2(g) + 4H^+ (aq) + 4e^- \rightarrow 2H_2O (l)$ E°=1.23V

- at anode:

  $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ E° = − 0.45V

  $Fe(s) \rightarrow Fe(aq)^{2+} + 2e^-$ E° = − 0.45V

- overall:

  $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O (l)$ E° = 1.68V

  $2Fe(s) + O_2(g) + 4H(aq)^+ \rightarrow 2Fe(aq)^{2+} + 2H_2O(l)$ E° = 1.68V

The Fe^{2+} ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing Fe^{3+}, as represented in the following equation:

$$4Fe^{2+}(aq) + O_2(g) + (2+4x)\ H_2O \rightarrow 2\ Fe_2O_3 \cdot xH_2O + 4H^+(aq)$$

$$4Fe(aq)^{2+} + O_2(g) + (2+4x)\ H_2O \rightarrow 2Fe_2O_3 \cdot xH_2O + 4H^+\ (aq)$$

The sign and magnitude of E° for the corrosion process indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure.

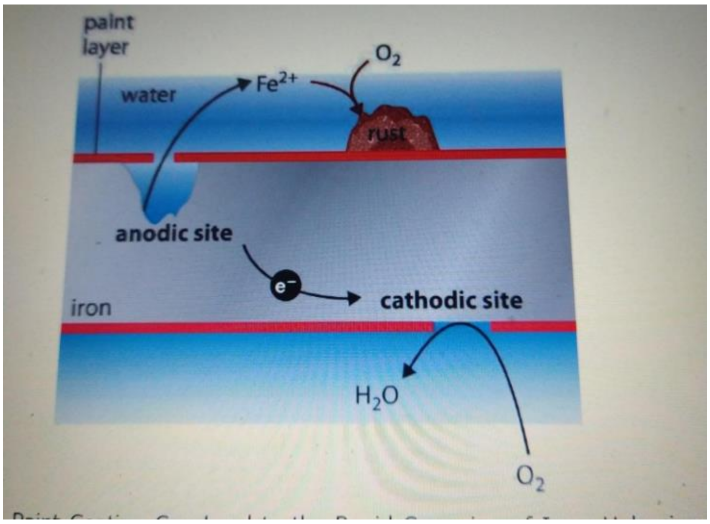

Figure: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). Rust is formed when Fe^{2+}(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually made of steel coated with a thin layer of tin. Neither chromium nor tin is intrinsically resistant to corrosion, but both form protective oxide coatings.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as Zn ($E° = -0.76$ V for $Zn^{2+} + 2e^{-} \rightarrow Zn$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$O_2(g) + 4e^{-} + 4H^{+}(aq) \rightarrow 2H_2O\ (l)$	reduction at cathode
$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^{-}$	oxidation at anode
$2\ Zn(s) + O_2\ (g) + 4H^{+}\ (aq) \rightarrow 2\ Zn^{2+}\ (aq) + 2\ H_2O\ (l)$	overall

The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes. Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

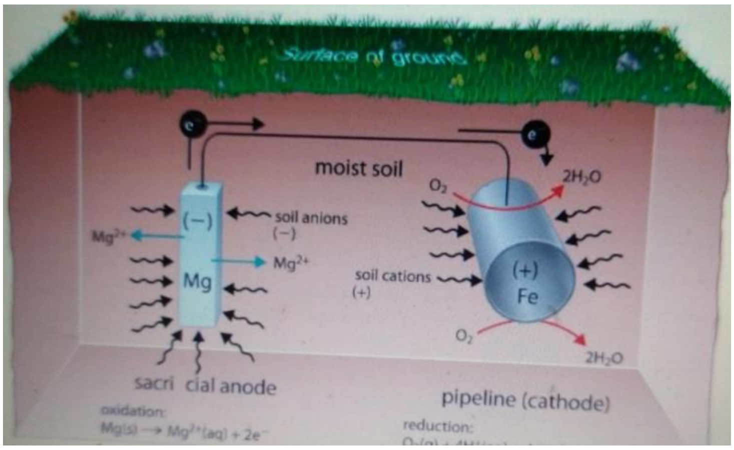

Figure : The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium ($E° = -2.37$ V) is much more easily oxidized than iron ($E° = -0.45$ V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^{+} or NH_4^{+}, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

The most common forms of corrosion in stainless steel are:

a. Pitting corrosion - The passive layer on stainless steel can be attacked by certain chemical species. The chloride ion Cl- is the most common of these and is found in everyday materials such as salt and bleach. Pitting corrosion is avoided by making sure that stainless steel does not come into prolonged contact with harmful chemicals or by choosing a grade of steel which is more resistant to attack. The pitting corrosion resistance can be assessed using the Pitting Resistance Equivalent Number calculated from the alloy content.
b. Crevice corrosion - Stainless steel requires a supply of oxygen to make sure that the passive layer can form on the surface. In very tight crevices, it is not always possible for the oxygen to gain access to the stainless steel surface thereby causing it to be vulnerable to attack. Crevice corrosion is avoided by sealing crevices with a flexible sealant or by using a more corrosion resistant grade.
c. General corrosion - Normally, stainless steel does not corrode uniformly as do ordinary carbon and alloy steels. However, with some chemicals, notably acids, the passive layer may be attacked uniformly depending on concentration and temperature and the metal loss is distributed over the entire surface of the steel. Hydrochloric acid and sulphuric acid at some concentrations are particular aggressive towards stainless steel.
d. Stress corrosion cracking (SCC) - This is a relatively rare form of corrosion which requires a very specific combination of tensile stress, temperature and corrosive species, often the chloride ion, for it to occur. Typical applications where SCC can occur are hot water tanks and swimming pools. Another form known as sulphide stress corrosion cracking (SSCC) is associated with hydrogen sulphide in oil and gas exploration and production.
e. Intergranular corrosion - This is now quite a rare form of corrosion. If the Carbon level in the steel is too high, Chromium can combine with Carbon to form Chromium Carbide. This occurs at temperatures between about 450-850 deg C. This process is also called sensitisation and typically occurs during welding. The Chromium available to form the passive layer is effectively reduced and corrosion can occur. It is avoided by choosing a low carbon grade the so-called 'L' grades or by using a steel with Titanium or Niobium which preferentially combines with Carbon.
f. Galvanic corrosion - If two dissimilar metals are in contact with each other and with an electrolyte e.g. water or other solution, it is possible for a galvanic cell to be set up.

This is rather like a battery and can accelerate corrosion of the less 'noble' metal. It can be avoided by separating the metals with a non-metallic insulator such as rubber.

The secret to stopping **rust** is to prevent oxygen from forming bonds with iron. The best way to do this is to get something else to bind with the iron first. After many experiments, it was discovered that by adding up to 10% of chromium to mild steel you get a new alloy that doesn’t rust – stainless. This innovation, by the way, took place in Sheffield, England in the 1930’s, giving that city its reputation for making some of the finest cutlery in the world. Stainless is not as tough as mild steel in many applications and it’s more expensive, but it also resists the corrosive effects of water and many other chemicals. Now, metallurgists play with different trace additives like manganese, copper and nickel to get stronger steels that are still rust-free.

Acknowledgements:

- Inorganic Chemistry by CE Housecroft and AG Sharpe, 2nd Ed, Prentice Hall.
- Texbook of Chemistry (Class XII), NCERT
- Website: https://chem.libretexts.org
- Many other webpages were also used.