2)IRON Occurrence:

(Iron is the fourth most abundant element and the second most abundant metal in nature. Itoccurs in combined state. The main ores of iron are:

1. Oxide ores:

Magnetite, fe3O4. It is usually black in colour. It is richest ore of iron and contains upto 70'% of the metal.

Hematite, Fe203. t is usually red in colour.

Limonite or hydrated ferric oxide, Fe203.3H20. t has yellow, brown or red colour

2. Carbonate ore:

Siderite or spathic iron, FeC03. t is also called clay- iron stone due to the presence of excess of clay in it.

Sulphide ores:

Iron pyrites, FeS2.

Pig or Cast Iron ::::) most impure form ::::) 2.5 - 5 .carbon and other impurities like Mn, Si, S and p ::::) It is hard and Brittle and hence cannot be ferged or moulded by hammering	Will'Ought Iron Purest form of iron 0.2 - 0.5% carbon Its is ductile, soft malleable.	and	Steel It is in between pig iron and wrought iron. => 0.1to 1.5% carbon

Extraction of iron:

- Iron is extracted from its oxide ores especial from the magnetite, hematite and limonite ores. The extraction involves the following steps:
- Concentration of ore: The concentration of ore is done by gravity process. The ore is crushed to small pieces and washed with water to remove siliceous impurities. The washed ore is then subjected to electromagnetic separation.

- Calcination and roasting: The concentrated ore are heated in excess of air.
 This treatment produces the following results
- Moisture and carbon dioxide are removed.
- 2 Fe203.3H20----- 2Fe203 + 3H20

Iron carbonate if present decompose to FeO which is further converted to fe2O3

Sulphur, arsenic, etc., are oxidized to their oxides and are, thus, removed as volatile gases.

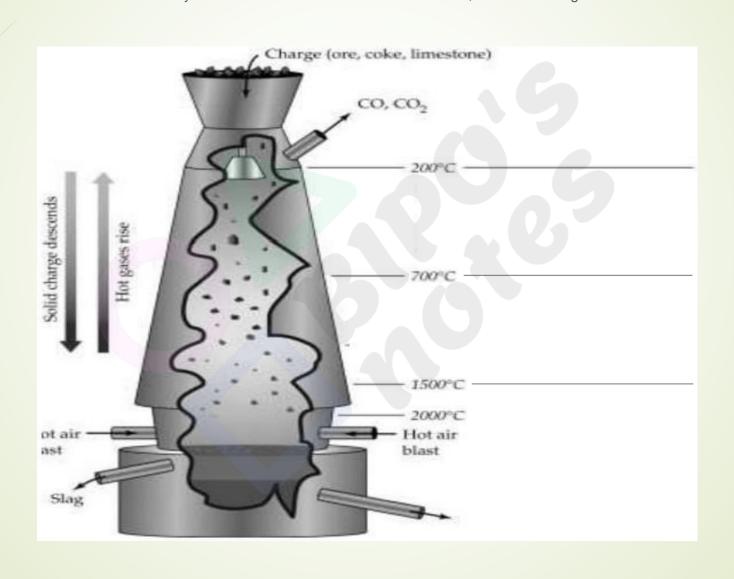
S+ 02--7 S02

The entire mass becomes porous

Smelting: The calcined ore is mixed With limestone (CaC03) and coke in the ratio of 8:1:4 and introduced in a blast furnace for smelting in Blast furnace.

8:1:4 ratio of ore. limestone and coke is called as charge.

Blast furnace is a chimney like tall steel structure lined with fire bricks, 25-60 metre high and 8-10 metre in diameter at its widest part.



The charge is introduced in the furnace by lowering the cup and cone arrangement and at the same time the furnace is lit and a blast of hot air is sent upwards through the tuyeres. The temperature varies from 1600°C to 250°C in the furnace from bottom to top. On the basis of variation in temperature, there are four zones where different chemical changes occur. The four zones are.

1. Combustion zone: This is the lowest part of the furnace above hearth where the

temperature is about 1500° - 1600° C. n this zone carbon burns in presence of hot air producing carbon dioxide and a lot of heat.

$$C + 02 -+ C02 + 97.0 kcals$$

The process is exothermic and raises the temperature to about 1500 ° c

Carbon dioxide rises upwards and meets with red hot coke. It is reduced to carbon monoxide.

This reaction is endothermic and hence the temperature suddenly falls to about 1200°C.

2.Reduction zone: This is the uppermost part of the furnace. The temperature varies from 250°C to 700°c. The oxide ore is reduced to iron in this zone. The reduction takes place through the following stages:

- 3Fe203 + 3CO → 2Fe3O4 + CO2
- ► Fe3O4 + CO → FeO + CO2
- FeO + CO → Fe + CO2

Iron formed is called spongy iron. In the reduction reactions, heat is also evolved which decomposes part of carbon monoxide into carbon.

■ 2CO--→ C02 + C

3.Slag formation zone: This is the central zone where the temperature varies from 800 -IOOOC. The limestone present in the charge decomposes into calcium oxide and carbon dioxide

CaC03 → CaO + CO2

The calcium oxide acts as a flux as it combines with silica present as an impurity (gangue) to form a fusible slag of CaSiO3.

CaO + SiO2 → CaSiO3

Silicates, phosphates and manganates present as impurities in ore, are reduced to Si, P and Mn, respectively.

P4010 + 10C → 4P + 10CO

 $SiO2 + 2C \rightarrow Si + 2CO$

 $Mn02 + 2C \rightarrow Mn + 2CO$

These are partly absorbed by iron (spongy) and partly by slag.

4.Zone of fusion: This zone just above the zone of combustion. The temperature ranges between 1200 - 1500°C. The spongy iron which has absorbed already C, Si,P,Mn, etc.,melts at 1300°C and collects at the bottom of the hearth.

- The slag which being lighter floats over the molten iron and prevents the oxidation of molten metal. The slag and molten metal are removed from their respective holes. The molten metal is run into moulds and is allowed to solidify. (Fe = 93 % I C = 5'% and impurities of Mn, P, Si etc.= 2'%)
- There are three commercial varieties of iron depending on their carbon content.
- The iron obtained from a blast furnace is called **Pig ron**. (Contains 95% Fe, 4% C and varying quantities of other impurities).

Cast ron can be obtained by pouring pig iron directly into the moulds of desired shape. Cast ron is very hard and brittle and can be used where it will not be subjected to mechanical or thermal shock.

Wrought Iron is prepared by Pudding process in which cast iron is fused in a reverberatory furnace, the hearth of which is lined with haemetite. Cast iron takes in puddling furnance and metled by hot blast of air. The chemical reactions which occur are

- S + 02 ---- > S02;
- 3S + 2Fe203----→4Fe + 3S02
- 3Si + 2Fe203 -- → 4Fe + 3Si02
- Mn + Fe203 \rightarrow 2Fe + 3Mn0
- \longrightarrow MnO + Si02 -- \rightarrow MnSi03 (slag)
- 3C + Fe203 --→ 2Fe + 3CO
- → 4P + 502 --→ 2P205;
- Fe203 + P205 → 2FeP04 (slag)
- The impurities are removed from iron, the melting point of the metal rises and it becomes a semi solid mass. Metal taken out from the furnace in the form of balls with the help of the rabbles. The balls are then beaten under hammer to separate out the slag. The product thus formed is called wrought iron.

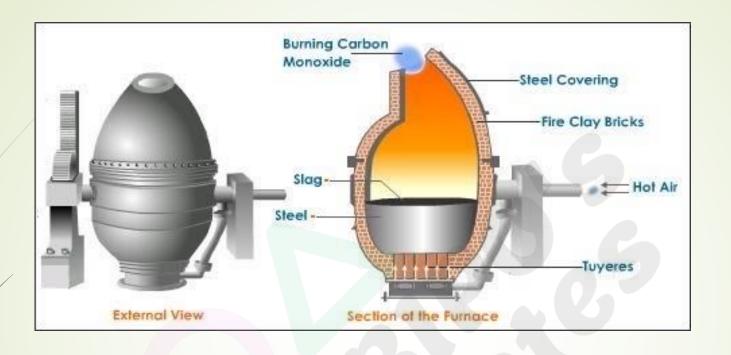
Manufacture of Steel

By Bessemerisation Process:-Principle:-

In bessemerisation process, the impurities present in cast iron are removed by air oxidation and calculated amount of carbon is added in the form of spigelesien (Fe + Mn +C) is added to obtain Steel. The lining of Bessemer converter depends upon presence or absence of phosphorous.

If phosphorous is present, then basic lining of CaO or MgO is used and **if phosphorous is absent**, then acidic lining of SiO₂ is used. The reactions occurring during manufacture of steel are.

$$\begin{array}{cccc} 2C + O_2 & \rightarrow & 2CO \\ S + O_2 & \rightarrow & SO_2 \\ Si + O_2 & \rightarrow & SiO_2 \\ 2Mn + O_2 & \rightarrow & 2Mno \\ MnO + SiO_2 & \rightarrow & MnSiO_3 \\ & & & & Manganous silicate (slag) \end{array}$$



- If phosphorous is present,
- $P2O_5 + 3CaO$ \rightarrow $Ca_3(PO_4)_2$

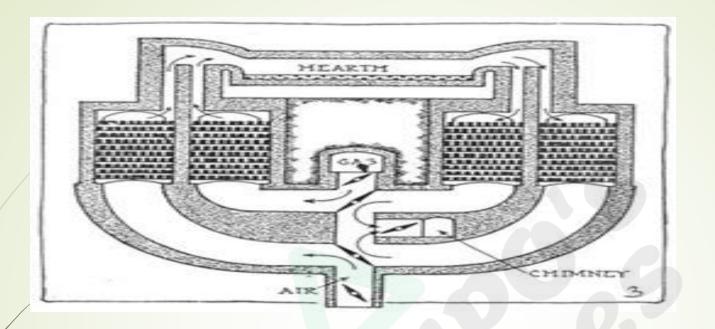
Calcium phosphate (thomas slag)

Process:

Molten cast iron is kept in Bessemer converter lined internally by basic lining (if phosphorous is present) or acidic lining (if Phosphour is absent) and blast of air is passed into the mixture. At first impurities other than carbon are oxidized. Then carbon is oxidized to carbon monoxide which burns with light blue fame at the mouth of bessemer converter. When the flame dies out, calculated amount of spigelesin is added and mixed by passing air for some time. Then steel is manufactured. The process is completed in 15-20 minutes and the batch size is 500-600Kgs. The quality of steel obtained by Bessernerization process is not uniform. During the process some amount of Iron is lost as slag

2. By Siemen Martin's process or open hearth process:Principle:-

In open hearth process, the impurities present in cast iron are removed by oxidation by haematite. The percentage of carbon is decreased by adding scrap iron. The heat required for the process is obtained by burning perheated producer gas (Co+N₂) by regeneration of heat economy. Depending upon the impurities the lining of hearth is acidic (If phosphorous is absent) or basic lining (if phosphorous is present). The percentage of carbon is maintained by adding required amount of splgelesien. The reactions during manufacture of steel are



$$3C + 2Fe_2O_3 \rightarrow 4Fe + 3CO_2$$

$$\rightarrow$$
 SiO₂ + Cao \rightarrow CaSiO₃ (slag)

- If phosphorous is present,
- $\bullet \quad \mathsf{6P} + \mathsf{5Fe}_2\mathsf{O}_3 \rightarrow \quad \mathsf{10Fe} + \mathsf{3P}_2\mathsf{O}_5$

Mixture of cast iron, scrap iron, haematite and small amount of lime is kept on hearth of open hearth furnace & mixture is heated by burning producer gas by regenerative system. The outgoing hearth gas pre. Heats the incoming producer gas which an combustion can generate higher temperature. The slag formed is removed and a small amount of steel is withdrawn from the hearth and is analyzed. The percentage of carbon in steel can be increased by adding spigelicien and can be decreased by adding scrap iron. The process is slow and takes about 8-10 hours and quality steel is better as sample can be analyzed.

The advantages of open hearth process over bessemerization process are as flows:-

- The quality of steel is uniform.
- Substance like Haematite, scrap iron is converted to valuable steel.
- The loss of iron is very small.
- The batch size in open hearth process is very large compared to bessernerisation process.

Heat Treatment of Steel

Steel can be given desire property by heat treatment there are three different heat treatment.

1. Annealing:-

■ This method is done to obtain soft steel. When steel is heated to red hot (about 1100°c) and then cooled & lowly, steel becomes soft and the process is called annealing. In annealed steel, carbon is present in free state.

2. Quenching or Hardening:-

■ This process is done to obtain hard steel and brittle steel. When steel is heated to red not and then cooled rapidly by plunging into water or oil, gives hard and brittle steel and the process is called Quenching. In quenched steel, carbon is present in combined form as iron carbide (Fe₃C) or Cementite

. Tempering:-

This process is done to obtain hard and malleable steel Quenched steel is heated below red hot (about 700°c) and then cooled slowly to obtain mild steel and the process is called tempering. In tempered

steel, carbon is present in both combined and free state.

	Steel Stainless Steel	Composition Fe=75% Cr=18% Ni=8% C=1%	Properties Have very high chemical resistance.	Uses in using ornamental pieces, cutleries, utensils, etc.
	Manganese Steel	Fe=86% Mn=135 C=1%	Very hard and resistant to wear and tear.	Railway tracks, safes, safety helmets.
/	Tungsten Steel	Fe=94% W=5% C=1%	Very hard.	Many high speed cutting tools.
	Invar	Fe=64% Ni=36%	Have very small coefficient of linear expansively.	in making clock hands, pendulum rods, meter scales, etc.
	Nickel Steel	Fe=96-98% Ni=2-4%	Resistant to corrosion and is elastic.	wire cables, gears, drive shafts, etc.
	Perm alley	Fe=21% Ni=78% C=1%	Strongly magnetized by electric field and gets demagnetized when current is switched off.	used in making electromagnet

Rusting

■ The chemical corrosion of iron by oxidation with moist air to give hydrated ferric oxide is called rusting and the produce is rust. The nesting process is accelerated by acidic oxide like CO₂, SO₂, NO₂, etc.

2Fe +
$$O_2$$
 + xH_2O \rightarrow Fe $_2O_3$. xH_2O Rust

- There are many theories to explain the rusting of iron is any which most reliable theory is electrochemical theory.
- Acc. to this theory, rusting of iron occurs due to formation of galvanic cell in the iron. At anode, iron atom oxides to Fe⁺⁺ ion by losing 2 electrons.
- At anode, Fe \rightarrow Fe⁺⁺ + 2e The electon moves to cathode where oxygen reduces to OH by gaining electron. At cathode, $12O_2 + H_2O + 2e$ \rightarrow 2OH

of Fe⁺³ stages.

Fe⁺⁺ and OH⁻ ion combines forming Fe(OH)2. Fe⁺² +2OH \rightarrow Fe (OH)₂ Ferrous compound are unstable, so Fe(OH)₂ is oxided by air in presence of water to Fe (OH)₃. Which then decompose forming Ferric oxide which is rust. $2\text{Fe}(OH)_2 + \text{H}_2O + 12O_2 \rightarrow 2\text{Fe}(OH)_3$ $2\text{Fe}(OH)_3 \rightarrow \text{Fe}_2O_3 + 3\text{H}_2O$. This theory is supported by fact that analysis of rust shows presence

Prevention of Rusting:-

This phenomenon can be prevented by:

- By applying layer of enamel, grease oil etc.
- By galvanising iron by zinc.
- By making passive by dipping in conc HNO₃ or by passing steam over red hot iron.
- By cathodic protection, this process is generally used in ships. Iron is kept in contact with more electropositive metals like Zn, Al, Mg, etc. which acts as anode where iron is protected as cathode. The metal used as anode is called sacrificial anode.

Ferrous Sulphate or Green vitriol (FeSO4 7H2O)

Preparation:-

It is obtained by dissolving Fe, FeO or FeCO₃ in dil. H_2SO_4 the FeSO₄ solution on crystallization gives light green crystals of FeSO₄. $7H_2O$.

Fe +
$$H_2SO_4$$
 \rightarrow Fe SO_4 + H_2
FeO + H_2SO_4 \rightarrow Fe SO_4 + H_2O
FeCO $_3$ + H_2SO_4 \rightarrow Fe SO_4 + H_2O + CO_3
FeSO $_4$ (aq) crystallization \rightarrow Fe SO_4 7 H_2O
Green vitriol

Properties

- 1. It is light Green colored crystalline solid highly soluble in water.
- 2. It is an efflorescent compound and when exposed in air for long time is oxidized to give brown color of ferric salt.

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4FeSO_4 + O_2 + 2H_2O \rightarrow 4Fe(OH)SO_4
Basic Ferric Sulphate
(Brown in water)
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3. Action of Heat :-

On heating, it gives anhydrous FeSO₄ which is white in color.

FeSO₄. $7H_2O \rightarrow FeSO_4$ Green White.

Anhydrous FeSO4 on Further heating decompose forming Fe₂O₃ Ferric oxide (brown)

 $\begin{array}{ccc} \text{2FeSO}_4 & \rightarrow & \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3 \\ \text{White} & \text{Brown.} \end{array}$

- 5. Action of potassium Ferrec cyanide:With potassium fericyanide, it gives a deep blue coloured ppt of ferro ferricyanide commonly known as turn-bull's ppt which is used for making blue coloured ink as blue pigment.

 FeSO₄ + K₃ [Fe (CN)₆] → Fe₃ [Fe(CN)₆]₂ + K₂SO₄

 Ferroferricyanide

 (Turn-bull's ppt)

- 6. Hydrolysis: It is soluble in water and gets hydrolyzed to give acidic salt solution as it is salt of strong acid and weak base.
 FesSO₄ + 2H₂O → Fe (OH)₂ +H₂SO₄
 Weak base strong acid.
- 7. Reaction with $K_2Cr_2O_7$ and $KMno_4$ in acidic medium:FeSO $_4$ is a reducing agent and in acidic medium if reduce $KMNo_4$ and $K_2Cr_2O_7$ $10 FeSO_4 + 8H_2SO_4 + 2KMNO_4$ $2MNSO_4 + K_2SO_4 + 8H_2O$ Pink

 Colorless
- 6 FeSO₄ + 7H₂SO₄ + 2K₂Cr₂O₇ \rightarrow 3Fe₂ (SO₄)₃ + Cr2 (SO₄)₃+ K2SO4+7H₂O green

Uses:-

- It is used as reducing agent.
- It is used in medicine.
- It is used as modant in dye.
- It is used in mfg of ink.

Ferric chloride (FeCl3)

- 1. It is used in medicine as antiseptic.
- 2. It is used as mordant in dying.
- 3. It is used as a catalyst in friedal craft's reaction.

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Mohr's salt or ferrous ammonium sulphate FeSO4(NH4)2 SO4.6H2O)

■ It is used in laboratory as primary standard reagent in redox titration.