

IRON AND STEELS

“Chemistry is the integrated study of the preparation, Properties, structure and reactions of the elements and their compounds and of the systems which they form.”

INTERNATIONAL CONFERENCE OF EDUCATION IN
CHEMISTRY, COLORADO, USA JULY 1970

CHEMISTRY OF IRON

Name	:	Iron (Prehistoric, from the Anglo- Saxon iren or isern).
Symbol	:	Fe (From the Latin ferrum = iron).
At. No.	:	Z = 26.
At. Mass	:	55. 85.
Ele. Conf.	:	2, 8, 14, 2, ; or $3d^6 4s^2$.
Valence	:	2 and 3 .

Iron is the main transition element, belongs to 3d series, and present in the Gr. 8th (VIII_B) and the 4th period of the periodic table.

A WORD ON IRON

Iron is most widely used popular metal from a pre-historical period. Its commercial and industrial importance is rather greater than any other metals. Number of advanced materials : such as synthetic rubber, plastic, etc. have been developed, but iron has maintained its supreme position in the industrial decorum.

Steel making is of immense importance throughout the world now and then. Today it is rather difficult to find out any side of modern living without involving iron or steels. Aeroplanes, boats, buildings, bridges, cookers, cars, railways, refrigerators, watches, utensils, etc. all contain iron and steels. Thus iron has occupied the most important place in our daily life. As a transitional element, iron is also the most important metal in plants and animals. Biologically it is important as an electron carrier in plants and animals (cytochromes and ferredoxins); as haemoglobin, the oxygen carrier in the blood of mammals, as myoglobin for oxygen

storage, in nitrogenase (the enzyme in nitrogen fixing bacteria) and for iron scavenging and storage (ferretin and transferrin). It forms several unusual complexes, including ferrocene, etc.

The very importance of iron lies in its extra ordinary features such as :

- (i) It is the fourth most abundant element in the earth's crust. After O, Si and Al.
- (ii) It is very widely distributed in the earth's crust; and makes up 62,000 ppm or 6.2% by mass of the earth's crust ; commonly associated with several hundred minerals.
- (iii) It is very easily isolated from its natural sources, simply by reducing the minerals with carbon.
- (iv) It has several desirable properties even in its impure form such as steels.

It is the most cheapest, strongest, most magnetic and the most indispensable material from the constructional point of view.

Now-a-days iron and steel makings are regarded as the measures of technological developments of any country . Greatest stress has been laid by Government of India on the production of iron and steel , so that the country can industrialize quickly and extensively. At Jamshedpur, Bhilai, Durgapur, Rourkela, Bokaro and other place enormous quantities of cast iron and steel are being produced to meet the industrial and defence needs of India.

7.1 OCCURRENCE

Iron is wide spread in its occurrence. Its extent in earth's crust is 62,000 ppm or 6.2% by mass. It is 4th most abundant element on the earth, next to oxygen, silicon and aluminium. In meteorites, it occurs in free state while in nature, it is found in combined state such as oxides, sulphides, silicates etc. Its compounds occur in soli, rocks, minerals, green plants and in haemoglobin, the red colouring matter of blood.

The important minerals of iron are as follows :

(a) Oxides :

- (i) **Magnetite (Black) :** Ferrosferric oxide, Magnetic iron ore : Fe_3O_4 or $\text{FeO} \cdot \text{Fe}_2\text{O}_3$. It is magnetic and black in colour . It is exceedingly pure having high content (72.4%) of Iron. It gives iron of high quality.

It is found in large amounts in Canada, Sweden, USA and India. (In India it is found at A.P., Bihar, Chennai and Orissa).

(The reserves estimated in India are 314 core tones of magnetite).

- (ii) **Haematite (Red) : Ferric Oxide :** Fe_2O_3 . It has red colour and high percentage (~ 70%) of Iron. It is found in Brazil, China, USA and India ; (Bihar, Orissa, Maharashtra, (Chanda and Ratnagiri), Goa, Karnataka, M. P. and Tamilnadu. Estimated amount of Haematite is 960 crore tones in India)

- (iii) **Limonite (Brown Haematite) :** Hydrated ferric Oxide $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ or $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. It is found in Belgium, Germany, France, USA and India. It contains ~ 60% Iron.

(b) Carbonate :

Siderite or Spathic Iron ore : Ferrous Carbonate : FeCO_3 . It

Contains about 40 – 45% Iron. It occurs in England and at West Bengal in India.

(c) Sulphides

- (i) **Iron Pyrites :** FeS_2 (Fool's Gold) (It is yellow metallic).
(ii) **Copper Pyrites :** CuFeS_2
(iii) **Arsenical Pyrites :** FeAsS .

Sulphur is an objectionable impurity as it causes iron to be hard and brittle and thus useless for technological purposes. The sulphides cannot be used for extraction of iron though they are plentiful.

The World production of iron ores was 970 million tones in 1988.

The largest sources are Russia 26%, China 17%, Brazil 15%, Australia 10% , the USA 6% , India 5%, Canada 4%, From these the yield of pig iron was found to be 538 million tones in 1988.

Indian Seen :

The Indian iron ores contain 60 to 68% iron and are best in the world. The estimated total iron reserves of India are about 21000 million tonnes. This is regarded to be the largest deposit of high quality mineral source of iron in the whole world. The large deposits of iron ore are at Bengal, Bihar, Goa, Karnataka, Madhya Pradesh, Maharashtra and Tamilnadu.

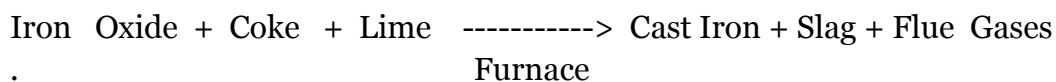
Different Forms of Iron :

Iron is produced in three different commercial forms depending upon the amount of impurities present, especially carbon. They are :

Cast Iron (Pig Iron)	Steel	Wrought Iron (Pure form)
2.5 to 5% C	0.2 to 1.5% C	0.1 to 0.2% C

Iron is generally isolated as cast or pig iron by extracting it from oxide ore by simple reduction method using carbon as the reducing agent and lime as the flux in a blast furnace.

Blast



In general, any alloy of iron containing more than 2% carbon is called as Pig Iron (where varying amounts of other impurities are also present.) Pig iron is the direct metallic product of the blast furnace. It cannot be shaped into articles by forging or hammering. It is, therefore, melted and then cast into the castings or the moulds of the desired shape. It is then called Cast Iron. Thus, chemically, there is no much difference between cast iron and pig iron. Wrought iron also known as malleable iron is very pure form of iron containing not more than 0.5% carbon and useful for articles to be subjected to sudden stresses such as chains, wires, anchors, bolts, nails, etc.

The different forms of iron have different specific properties and hence they have different commercial and industrial applications.

7.2 EXTRACTION OF IRON

The extraction of iron has played a very significant role in the development of modern civilization. Iron is produced in following steps :

Step I: Preliminary Treatment :

- (i) Crushing and Grinding
- (ii) Concentration
- (iii) Calcination or Roasting

Step II : Secondary treatment : Reduction or Smelting :

Preliminary Treatment :

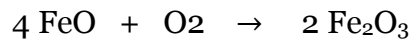
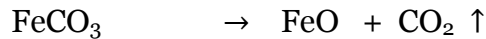
Concentration : Iron ore is first crushed and ground to suitable fineness. and then washed by using a powerful current of water (Gravity Separation). The mass free from clay sand and other earthy impurities is then dried and subjected to magnetic separation (Fig 1). Thus the ore is concentrated to 90-95%.

Fig 1 Magnetic separation

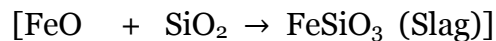
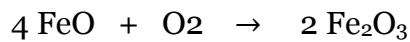
Roasting :

The concentrated ore is roasted or calcined in a reverberatory furnace(Fig 2) at a low temperature, with a little coke ; in free supply of air. By roasting following changes are brought about.

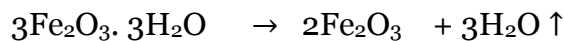
- (a) Carbonate ore is converted to oxide :



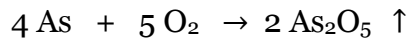
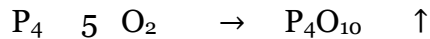
- (b) Ferrous oxide is oxidized to ferric oxide and thus its conversion to ferrous silicate (slag) is avoided.



- (c) The mass is dried up by removing moisture



- (d) The lighter non-metallic impurities such as sulphur, arsenic, phosphorus etc. are all removed, as volatile substances.



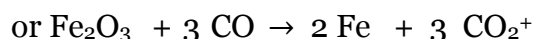
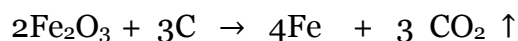
- (e) Ore becomes porous and hence easy to reduce.

Fig-2 : Reverberatory furnace

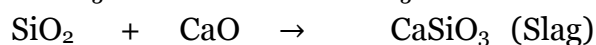
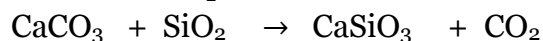
Smelting : Reduction :

The process of reduction of iron ore under molten condition is called smelting. Smelting is carried out in a blast furnaces (designed in 1350 in Germany.) It has two functions to perform.

- (i) To reduce the ore to metallic iron :



- (ii) To remove impurities in the form of slag.



Blast Furnace : Blast furnace is a huge chimney - like tower constructed by steel plates. It is about 20 to 30 meters in height and 4 to 8 meters in width at the central part . It is lined with fireclay bricks, from inside. The furnace is

narrow near the mouth.(Fig 3) Such shape of the furnace facilitates wide spread of the charge inside the furnace and helps easy escape of the flue gases. This also makes proper heat flow . At the top, it is provided with double “ bell ” or “ cup and cone ” arrangement to permit charging of furnace without escape of waste gases. The flue gases are forced to escape only through the outlet, provided near the top of the furnace. The upper part of the furnace is called the throat, the middle part is known as the body and the bottom portion of the furnace is called the hearth. The furnace increases in diameter from the throat downwards until it attains a maximum diameter at the bosh.From the bosh downwards, furnace contractsore rapidly upto twyers and then it becomes nearly cylindrical. It retains this form even up to the bottom.

Fig. 3: **Blast Furnace**

The lower part of the hearth called well of the furnace collects molten slag and molten iron. It is provided with two outlets. These are called tap holes. Molten slag is taken out from upper tap hole while molten iron is taken out from the lower tap hole.(Fig.3)

A little above the base, the furnace is provided with series of water jacketed pipes called bustles or twyers.

The hot blast of air, at temperature of about 800° C (1073 K) is blown into the furnace through the twyers at the rate of about 20,000 cu. Meter per minute and at a pressure of 1 kg/sq. cm. If the hot blast of air contains water vapour , a considerable absorption of heat (on account of the following endothermic reaction) may take place in the lower part of the furnace.



Hence air blast should not contain more than two per cent moisture . A nine to ten per saving of fuel is reported by drying the blast.

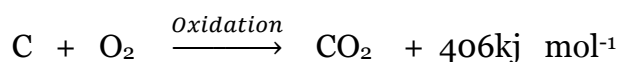
Working : The charge consisting of 8 parts of calcined ore, 4 parts of desulphurised coke and 1 part of limestone is carried to the top of the furnace and fed to it calculated amount periodically. Series of reactions occur in the furnace at different temperatures, 250° C (525 K) (near throat) to 1500°C (1773 K) (near hearth).(Fig 4)

Fig. 4: Blast furnace showing working conditions for chemical reactions during smelting

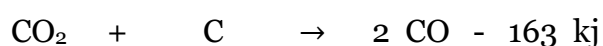
Reactions in the Blast Furnace :

1. $3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$
2. $\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2$
3. $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$
4. $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
5. $\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$
6. $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$ (slag)
7. $\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$
8. $\text{MnO}_3 + 3\text{C} \rightarrow 2\text{Mn} + 3\text{CO}$
9. $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$

The hot blast of air passing through bustle, oxidises coke to carbon dioxide. The reaction is exothermic and temperature rises to about 1500°C (1773 K) near the hearth.



Carbon dioxide rises up in the furnace where it meets with incoming coke. Here CO_2 reacts with coke and gets reduced to carbon monoxide.

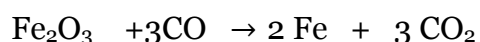


This reaction being endothermic, with ascending CO_2 the temperature goes on decreasing from 1500°C to 250°C (1773 to 523 K) towards the neck of the furnace. Complicated reactions are found to occur at different temperatures as discussed.

1. Zone of Reduction : [Top of the Furnace] :

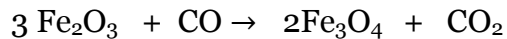
($573 - 1073\text{ K}$) ($300^\circ - 800^\circ\text{C}$) [Dull Red Heat]

The main reaction that occurs near the top of the furnace is reduction of the iron oxide to metallic iron by carbon monoxide.



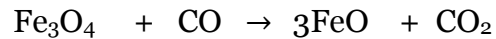
The process of reduction continues as the charge descends down. The reaction is not so simple but it is a series of reactions, taking place at different stages at different temperatures.

- (i) At the top of the furnace, where the charge is heated between 300°C to 500°C (573 – 773 K), Fe_2O_3 is converted to Fe_3O_4 .



This Fe_3O_4 is stable upto 650° C (923 K), in presence of CO, CO_2 and free coke.

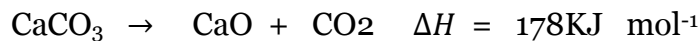
- (II) At temperature between 650°C to 700°C, (923 - 973 K), Fe_3O_4 is converted to FeO



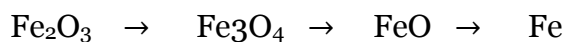
- (III) At temperature between 700°C to 800°C (973 to 1073 K), FeO is reduced to metallic iron



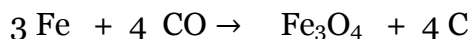
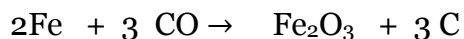
Simultaneously the limestone, present in the charge, is also decomposed to produce lime.



In short, iron oxide gets reduced in stages as follows,



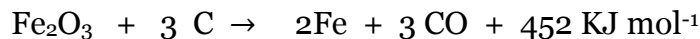
The metal produced at first is spongy. Therefore, simultaneously with the process of reduction, a part of metallic iron reacts with carbon monoxide to form ferric oxide or ferrous-ferric oxide.



2. **Zone of Heat Absorption : (Body of furnace) :**

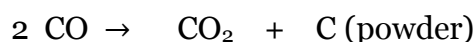
(800° – 1200° C) (1073 – 1473 K) [Bright Red Heat]

- (i) Unreacted iron oxide gets reduced to iron by red hot coke.



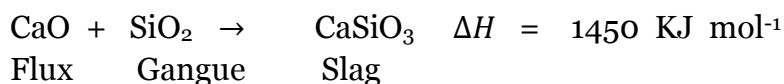
The hot spongy iron meets the ascending carbon monoxide.

- (ii) Carbon monoxide gets disproportionated to CO_2 and carbon :

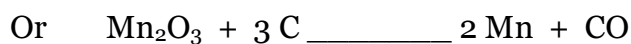


This finely divided carbon powder gets mixed with iron in the finished product.

- (iii) Lime obtained at the end of first zone combines with sand to produce slag.



(iv) Other impurities get reduced to the elementary substances and are mixed with finished iron :



Sulphur freed from iron sulphide also mixes with iron. Thus mixing of C, P, S, Si, Mn etc. Makes iron impure.

3. Zone of Fusion : (Base of Furnace) : (1474 – 1773 K)

(1200° – 1500°C) ; (Bright White Heat)

Due to the presence of impurities iron melts at 1200° to 1300°C (1473 – 1573 K) though its M.P. is (1808K) 1535°C . Molten iron then gets collected at the base called the well of the furnace. Slag also melts at the lower temperature (1200°-1250°C) (1473 – 1523 K) and being lighter than iron, it floats over molten iron and protects it from oxidation. Slag is removed from the upper tap-hole while iron is removed from the lower tap hole, from time to time. The metal is drawn out, led to sand moulds and cast into “pigs” or led to steel furnace and converted into different types of steels.

The extraction of iron by blast furnace is a continuous process where charge is fed from the top while metal is removed from the base periodically. The process runs day and night for years together. Everyday round about 1000 tonnes of cast iron and 500 tonnes of slag are removed at four different intervals.

The modern blast furnace may be of 40 × 15 m in dimensions and can produce 10,000 tonnes of cast or pig iron per day.

Products of the Blast Furnace

Cast iron, slag and flue gases are the products of the blast furnace.

(a) Cast or Pig Iron : The average composition of the cast or pig iron is as follows :

Iron	92 to 95%	Phosphorus	0.5 to 1%
Carbon	2.5 to 4.5%	Manganese	0.2 to 1%
Silicon	0.7 to 3%	Sulphur	0.1 to 0.3%

Cast iron is brittle and has low tensile strength . It melts at 1150°C - 1250°C ($1423 - 1523$ K). It can be forged, rolled and welded. It is therefore suitable only for casting not subject to sudden strain and shock. It is used for casting metal objects such as fire gates, pipes, railings, stoves, etc. where low cast is more important than strength. When molten iron from the blast furnace is cooled suddenly, white crystalline cast iron is obtained. It is known as white cast iron and it contains iron carbide Fe_3C . On the other hand, if molten iron is slowly cooled, most of the carbon separates out as graphite, giving gray colour to the iron. It is softer variety and is called gray cast iron. Carbon, present in the pig iron thus exists partly as free carbon in the form of graphite and partly in the combined state as iron carbide, Fe_3C .

(b) Slag : Slag consists mostly calcium and aluminium silicates. It contains approximately 55% SiO_2 . 30% CaO and 15% Al_2O_3

The slag is used as a ballast (filler) for rail roads. It is also used in cement manufacture, as a cement for road building, and as a fertilizer.

(c) Flue Gases : Flue gases have average composition 25% carbon monoxide, 10% CO_2 , 58 to 60% N_2 , 4 to 5% H_2 and 1 to 2% hydrocarbons. It consists about $\frac{1}{4}$ of combustible part, hence used as hot blast of air, to give (973 K) 700°C temperature, to the furnace.

7.3 STEELS

Introduction : Iron is the workhorse of the metals. It has many useful mechanical properties especially when it is alloyed with other elements.

Pure iron (called wrought iron has had all the carbon removed) is highly malleable and ductile but not especially strong. With increase in its carbon content, strength of iron increases but at the same time, its malleability and ductility decreases.

Cast iron containing about 5% C and other impurities is very hard and brittle . The impure iron is converted into steel by removing practically all the impurities and then adjusting the carbon content between 0.1 to 1.5%. In other words, steel making is nothing but purification of cast iron, to specific extent.

Steel, one of the most useful construction materials, is essentially iron which contains a small percentage of carbon and some other elements. Several steel making techniques have been developed so far.

In old processes such as open hearth, electrolytic or Bessemer, hot air is blown through molten pig iron to remove carbon and other impurities as volatile oxides. In more modern processes such as Kaldo process or L.D process pure oxygen is used rather than air when conversion becomes very fast and allows larger quantities to be handled and gives purer product, free from nitrides. After this a precise quantity of carbon is added to the molten iron whereby steel of desired

strength and malleability is obtained. Frequently, traces of transitional elements such as V, Cr, Mn, Co, Ni, W, etc are also added to modify the properties of the metal. For example when 18% chromium and 8% nickel are added, we get a stainless steel.

Definition :

“ Alloys of iron containing upto 1.5% carbon, either in combined state (Fe_3C) or as solid solution, are called steels. “Hence steels are essentially “carbon steels ” or “plain carbon steels .”

Types / Classification of Steels :

According to the presence of alloying elements steels are broadly classified into three categories :

- (a) (Plain) Carbon Steels, (b) Alloy Steels, and
- (c) Brittle Steels.

(a) Plain Carbon Steels :

Based on the percentage of carbon, steels are classified into following types :

- (1) **Mild Steels: Low Carbon Steel :** Steel containing 0.05 to 0.3% carbon.
- (2) **Structural Steel : Medium Carbon Steel :** Steel containing 0.3 to 0.6% carbon.
- (3) **High Carbon Steel :** Steel containing 0.6 to 0.9% carbon.
- (4) **Tool Steel : (Higher Carbon Steel):** Steel containing 0.9 to 1.5% carbon.

Mild steel is very soft, tough, malleable and ductile. It is used for thin soft wires, wires for rope, nails, chains, tubes, rivets, bolts, gears, fans blades, girders, etc.

Medium carbon steel has high tensile strength. It is shock resistant and has a good heat response. It is mainly used in railway engineering say for rail roads, wheels, railway axles and fish plates, crane hooks, crank shafts, rotors, etc. It is also used for machine parts, springs, etc.

High carbon steel is hard, tough, resistant to wear and characterized by higher tensile strength. It is used for making tools, drills, knives, punches, hammers, etc.

Tool steels are higher quality high-carbon steels. These can produce keen cutting edges. Hence these are specifically used for preparing cutting tools, lathe tools, wood working tools, blades, razors, cutters, saws, knives, etc.

(b) Alloy Steels : Special Steels : Steel containing small quantities of transition elements, viz. nickel, cobalt, chromium vanadium, molybdenum, tungsten, etc. are called alloy steels or special steels. Such steels have wide range of special properties and thus find wide spread applications for number of purposes.

Alloy steels may be classified on the basis such as :

- (a) Chemical composition,
- (b) Structure, and
- (c) Purpose of application.

Some important alloy steels have been listed in table 7.1 for brief information :

(c) **Brittle Steels** : Steel or iron containing excessive amounts of (i.e. more than 0.06%) of phosphorus and sulphur become brittle. Sulphur causes brittleness in hot while phosphorus makes it brittle in cold, (i.e. red short and cold short respectively).

Conclusion : Presence of different elements and their different extents alter the properties of steel radically. Steel is mainly the alloy of iron and carbon. Its properties mainly depend on extent of carbon. Along with carbon other elements such as Si, P, Mn, S and various transition elements etc. if present, wide varieties of steels with varying properties are formed.

	Name	Composition	Properties	Uses
1	Molybdenum steel	0.3 to 3% Mo	Resistant to corrosion even at high temperature	Axles and cutting tools
2	Nickel steel Platinite	46% Ni	Hard tough, elastic and rustless coefficient of expansion equal to that of glass	Axles and cutting tools
3	Chrome steel	2 to 4% Cr	High tensile strength, hard	Ball bearings, Cutting Tools, etc.
4	Manganese steels	6 to 15% Mn	Very tough and hard and resistant to water	Crushing machine, Helments, Railroad, Railway points, etc.
5	Stainless steel	12 to 20% Cr, 8% Ni	Resistant to corrosion non-magnetic, bright shining, stainless	Ornamental units, Cutlery, Utensils, Surgical appliances, Chemical plants, etc.
6	Nickel Steel	2.5-5% Ni	Very hard, resists corrosion and wear, very high magnetism	High speed tools and permanent magnets
7	Cobalt steel	Upto 35% Co	Very hard, resists corrosion and wear, very high magnetism	High speed tools and permanent magnets
8	Silicon steel	Upto 15% Si	Extremely hard, resistant to acids	Pumps, pipes carrying acids, electromagnets

				and transformers
9	Tungston steel	15-20% W, ~ 5% Cr a little V	Retains hardness even at high temperature s	High speed machine and drilling tools, cutting tools, etc,
10	Invar	~ 35% Ni with ~ Mn	Hard, resists corrosion and very very low coefficient of expansion	Pendulum rods, balance wheels,etc

7.4 STEEL MAKING

(Manufacture of Steel) : (Conversion of Cast into Steel)

In general, steel is manufactured by blowing hot air or oxygen through molten cast iron whereby impurities are oxidized and removed as volatile gases or subsequent slags. The process is then followed by adding precise small quantities of carbon to the pure molten iron; steel of the required strength and malleability is obtained. At present, steel-making is done by several different methods.

- | | | |
|--|---|--|
| (A)1. Electric Process,
2. Bessemer Process,
3. Open- Hearth Process,
4. Duplex Process, etc. | } | Old processes (Hot Air is blown) |
| (B)1. Kaldo Process
2. Linz – Donawitz process | } | (Modern Processes : Oxygen is
blown) (Basic oxygen process)
(BOP) |

1. Bessemer Process

This process is invented in 1855 by Henry Bessemer (a Frenchman, Resident of England.) In this method ,a furnace called Bessemer converter is used. It is a pear or egg shaped vessel constructed by using steel plates. It is supported on side arms called trunnions, whereby it can be oriented in different angles:

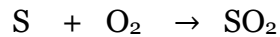
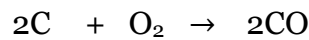
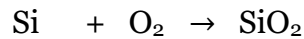
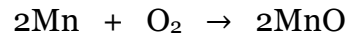
- (i) It is tilted to horizontal position for charging,
- (ii) It is inverted to pour out the finished product, and
- (iii) It is kept vertical to run the process of oxidation.

It is provided with twyers or nozzles at the bottom to blow hot air. Hence it is called bottom-blown converter.

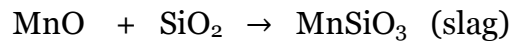
It is lined with refractory lime bricks or silica bricks. When acidic impurities are to be removed (such as SiO_2 , P_4O_{10}), a basic lining such as dolomite (CaCO_3 , MgCO_3) is used. This process is called Basic Bessemer Process. When basic impurities are to be removed, acidic lining of silica bricks (SiO_2) is used and the process is called Acid Bessemer Process.

Working : (a) Acid Bessemer Process : In this process the converter is lined with silicious refractory material which is acidic in nature. To start with,

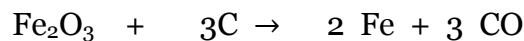
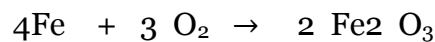
the converter is turned into the horizontal position, and charged with about 60 tonnes of molten cast iron, at about (1200°C). It is turned to vertical position and a blast of air is blown from the bottom. Impurities get oxidized and temperature raises to 2173 K (1900°C). The various reactions take place in the converter.



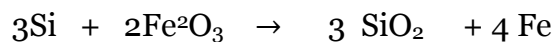
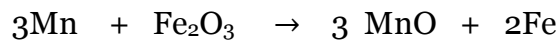
The oxides of silicon and manganese combine to form a slag of manganese silicate.



A little amount of iron is also oxidized to ferric oxide but it gets readily reduced by carbon present in the cast iron



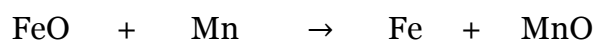
Ferric oxide formed above also oxidises manganese and silicon to their respective oxides.



The course of the reaction in the plant is followed from the burning of waste gases and observing the colour of the flame produced. The carbon monoxide produced in the above reactions burns at the mouth of the converter with a blue flame and orange-red tinge, throwing out showers of sparks. When the whole of carbon is oxidized, the blue flame suddenly dies down.

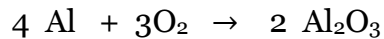
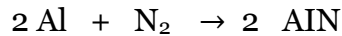
When blue flame at the top dies, a calculated quantity of Spiegeleisen (alloy of Fe, Mn and C) is added followed by the addition of scavenger such as ferrosilicon or aluminium. Blast of air is passed, mass is mixed well, slag is tapped off, the converter is tilted down and molten steel is taken out.

Role of Spiegeleisen : Carbon and Mn present in it reduce FeO from the molten iron.



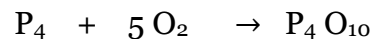
It contains 20 to 33% Mn and about 6% carbon. Here carbon regulates the desired quality of steel.

Role of Scavenger : The molten iron contains dissolved gases such as O₂, N₂, CO₂ etc. which create blow holes or gas bubbles in castings and defects are created. When aluminium is added, it reacts with these gases and removes them as slag.

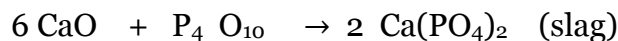


Thus spiegeleisen acts as a deoxidizer while Al acts as a scavenger.

(b) Basic Bessemer (Thomas-Gilchrist Process) : This process is used to treat cast iron containing phosphorus. In this process, the converter is lined with magnesia and lime prepared by calcinations of dolomite (CaCO₃.MgCO₃). Some limestone is added into the converter. Molten cast iron from blast furnace is then run into the converter and the blast continued. Carbon, sulphur and manganese are oxidized first as usual, but if the blast is continued even after the flame sinks down, then the phosphorus forms phosphorus pentoxide.



The phosphorus pentoxide thus formed, combines with lime to form a basic slag, containing calcium phosphate.



The slag, also known as Thomas slag, is used as a valuable fertilizer. As in Acid Bessemer Process, after complete removal of carbon and other impurities, requisite amount of carbon in the form of spiegeleisen is added and the product thoroughly mixed by air-blow.

In recent plants instead of air, oxygen diluted either with steam or carbon dioxide is used.. It is found that nitrogen from air is retained in steel and makes it brittle. Pure oxygen is avoided as it burns the nozzles very quickly and further a large volume of iron oxide fumes are formed. Further CO₂ is preferred to steam, since hydrogen in the later, tends to make the steel brittle.

Merits and demerits Of Bessemer Process :

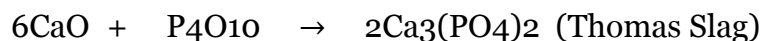
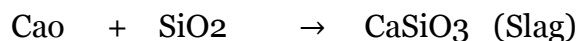
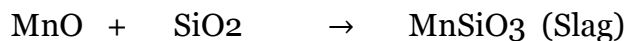
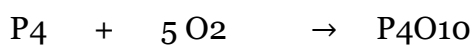
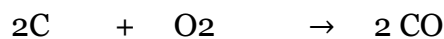
- (1) The process is Useful for rapid production of steel.
- (2) Since the molten cast iron obtained from blast furnace, is directly taken in the converter, no extra fuel is required for melting of cast iron.
- (3) Hence, the cost of operating the process is low.
- (4) But it should be noted that the process is not continuous and charging is rather tedious.

- (5) Comparatively small quantities (about 5 to 8 tonnes) of iron can be converted into steel, in 20 minutes, in conventional Bessemer converters.
- (6) This steel produced is of inferior quality.
- (7) The loss of iron in the slag is comparatively more (about 15%).

2. L.D. Process : Linz Donawitz Process :

This is the most recent process due to Linzer and Dusen Verfahren. It was first operated in 1953 in Austria at Linz-Donawitz and therefore carries the name L.D. Process. The furnace is an egg shaped steel vessel, sealed from bottom and supported on the side arms called trunnions. It is lined from inside with basic lining of magnesite or lime or limestone (CaCO_3). At the top, it is provided with water-cooled copper lance, Pure and dry oxygen is passed under pressure of atm, ($10 \times 10^5 \text{ Pa}$) through this lance into the furnace. It is commonly known as L.D. converter and may be termed as a top-blown converter.

Working : The converter is charged with cast iron (80%), scrap steel (18%) and limestone (2%) . Pure and dry oxygen say (99.5 to 99.7%) is injected into the molten mass through copper lance as shown in the Oxygen jumps on the molten mass from the copper lance at 40 to 50 cm. The impurities like S,P, Mn, Si etc. are oxidized by oxygen and removed as slag by combining with lime. Very much heat is given out and temperature reaches to about (2773K) 2500°C . Thus a hot spot is creted at the top of charge. When metal is purified, it becomes dense and sinks to the bottom of the converter while the lighter and impure mass moves towards the hot spot. Thus convection currents are set in and entire metal gets purified.



Flux Impurity

When purification is complete, convection currents are stopped and process is regarded to be completed . This takes about 45 minutes for one complete cycle and steel produced is about 30 to 60 tonnes. Now-a-days even larger quantities can be handled in a shorter time, say 300 tonnes in 40 minutes. LD. Process for Basic Oxygen process (BOP) is much suitable to produce

low carbon/mild steels. Hindustan Steel Ltd., Rourkela produces (75%) Steel by this method.

Advantages :

1. L.D. process is very rapid. It requires about 45 minutes for one batch.
2. Its productivity is comparatively high; 30 to 60 tonnes in about 45 minutes, or even higher say 300 tonnes in 40 minutes in recent plants.
3. On unit cost basis, its capital expenditure is less.
4. The manufacturing cost is low.
5. Energy needed is comparatively low.
6. Steel is of superior quality.
7. Molten cast iron and scrap steel can be used directly.
8. Both carbon and phosphorus are removed simultaneously due to intense heat.
9. The process gives a purer product is the most superior to all the processes known.

7.5 HEAT TREATMENT ON STEELS

Introduction : When metals and alloys are heated and cooled under specific conditions, their crystalline structures are changed and in turn their mechanical and physical properties like hardness, tensile strength, elasticity, etc. are appreciably changed.

Definition : “Heat treatment causes change in structure, hardness, magnetic properties, surface hardness, resistance to heat and corrosion, strength and workmanship, etc.

Types : Type important processes of heat treatments are : Annealing, Hardening, Tempering and Normalising.

1. **Annealing :** The process of heating steel to bright red heat (850°C) (1123 K) and cooling it very slowly is known as annealing. By annealing steel becomes rather soft and pliable and it wears better than wrought iron.
2. **Hardening :** The process of heating steel to bright red heat (850°C) (1123 K) and cooling it suddenly by plunging it into oil or cold water is called quenching or quench hardening or simply hardening. Due to rapid cooling, carbon does not form (Fe₃C) cementite and instead it gets separated and deposited as carbon atoms. Thus it causes steel to become hard but brittle.
3. **Tempering :** The process of heating the hardened steel to the temperature much below redness (230° to 300°C) (503 to 573 K) and cooling it very slowly is called tempering. Due to this process, steel retains much of its hardness but its brittleness disappears. On tempering, a very thin film of oxide is formed on the surface of the steel and that

imparts from yellow to blue colour to steel depending on temperature (230° to 3000°C) (503 to 573 K).

4. **Case Hardening** :The process of heating strong flexible mild steel, in contact with charcoal and then quenching it in oil, is called case hardening. Due to this process, a very thin coating of hardened steel is imparted on mild steel. Such steel can withstand wear and tear due to hardened surface. This steel is used for locomotive axles.
5. **Nitriding** : The process of heating steel, in the atmosphere of ammonia is called nitriding. This process converts the surface of steel into the hard nitride that can withstand wear and tear.
6. **Normalising** : It is similar to annealing process. The process of heating steel to a definite temperature (i.e. about 50°C)(323 K) above the critical temperature of iron i.e 725°C(998 K), and then cooling it freely in air, at the rate 5°C(5K) per second, is called normalising. By normalising steel becomes homogeneous and more soft, where the ultimate structure of steel consists of fine grains. In normalising, the steel is heated to slightly higher temperature than annealing. Since steel is cooled in air, in normalising, the rate of cooling is faster as compared to annealing. In general, normalising is similar to annealing, the consumption of fuel or electric power is greater than normalising process. The time required for normalising is less than annealing. In normalising, the mechanical properties of steel are significantly modified.

Heat treatments are usually performed on finished goods.

Distinction between Normalising and Annealing

	Normalising	Annealing
1	The time required for normalising	The time required for annealing is more than normalising.
2	Due to normalising, steel becomes homogeneous and more soft. The mechanical properties of steel are more improved.	Due to annealing, steel becomes more soft, pliable malleable and ductile.
3	The consumption of fuel or electricity is 'less for heating.	The consumption of fuel or electric power is 'greater' for heating.
4	It is the process of heating the steel at a temperature of 50°C (50 K) above the critical temperature (998 K) (725°C) and cooling it freely in air at a rate 5°C (K) sec ⁻¹	It is the process of heating the steel at a temperature of 850°C (1123 K) and cooling it in the furnace.

Comparison between Cast Iron and Steel

	Cast Iron	Steel
1	Cast iron contains 2.5-5% carbon.	Steel contains 0.2-1% carbon.
2	Crystalline structure is seen.	Structure for steel varies according to the

		nature and the percentage of constituents present.
3	M.P. is (1373-1523 K) 1100 to 1250°C.	M.P. is (1573-1673 K) 1300 to 1500°C.
4	It is hard, brittle and possesses high tensile strength.	Both types-hard and mild, are somewhat hard and brittle. Both steels possess high tensile strength.
5	Cast iron is neither malleable nor ductile.	Steel is malleable and ductile, if carbon content is low.
6	It cannot be magnetised permanently	It can be magnetised permanently .
7	It cannot be tempered.	It can be tempered.
8	It cannot be welded.	It can be welded.

Comparison of Bessemer Process and L.D. Process (BOP)

	Bessemer Process	BOP(L.D. Process (BOP))
1	High grade cast-iron is required.	Low grade cast iron, scrap iron and limestone can be used directly.
2	No external heating is required, hence no fuel is used. Only air blast is supplied.	Oxygen gas is burnt to supply heat. No air blast is used.
3	This process is very fast and is completed within half an hour. Yield is less.	This process takes about 40 minutes. Yield is relatively very high
4	No control over the chemical composition of the product..	Sample product of desired composition can be obtained
5	Steel obtained is of a low grade and heterogeneous in composition	Steel obtained is a high grade steel and homogeneous in composition
6	A large amount of slag is formed . some iron is also wasted as slag.	Very small amount of slag is formed , Very little iron is wasted as slag.
7	The process is costly and the operation is more difficult to be performed .	This process is costly too, but higher yield of better quality, compensates the high cpst.
8	Acid and Basic Bessemer process are carried out to oxidize S and P	All impurities are oxidised in single pass.

Iron and Steel Industry in India.

Manufacture of iron and steel was initiated in 1854 in India. Bengal Iron Works (1854) and Tata Iron and Steel Co. Ltd., (TISCO) Jamshedpur (1874) are the first two concerns in this field. Indian Iron and Steel Company (IISCO) Burnpur started its manufacture in 1919. Hindustan Steel Private Ltd. (1954) at Rourkela, Bhilai and Durgapur ; Mysore Iron and Steel Works, Bhadravati are all producing cast iron and steel in enormous quantities. At Salem (Tamil Nadu) Vijaynagar (Karnataka) and Vishakhapattanam (A.P.) new steel plants have been irrected. The Salem Steel Plant produces special steels while the other two are producing mild steel. Our country has six major steel plants with a total capacity of production of 6.79 million tones of saleable steel and 8.9 million tonnes of iron and steel are manufactured per year in India.

Table 7.5 shows the plant – wise production of pig iron, ingot steel and saleable steel of different plants under SAIL (Steel Authority of India Ltd.) respectively for 1991-92 and 1992-93

7.5 : Actual production (in ‘ 000 tonnes) for 1991-92 and 1992-93 respectively

Plant	Pig Iron (for sale)	Ingot	Steel	Saleable Steel
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Bhilai	175	134.7	3744	3941.8	3104	3118.2
Durgapur	69	17.1	871	675.5	632	640.5
Rourkela	41	29.5	1234	1257.4	1125	1179.3
IISCO	389	429.6	364	369.3	387	398.3
Bokaro	171	153.3	3417	3589.4	2730	2998.5
Total	845	764.2	9630	9827.4	7978	8334.8

[* Ingot : The castings obtained when melted metal is poured into a mould].

It is happy to state that the future of steel industry in India is very promising. India has a great advantage of having the raw materials nearby, making steel production easier and cheaper. Hence, in near future, India will not only be able to meet her entire requirement of steel but be able to have a fairly good export trade in steel. So, let us hope for Brighter Future !

Please, bear in mind, and forget Not :

“ STEEL loses much of its Value when it loses its Temper ”

ANONYMOUS

QUESTIONS

(A) Objective Type Question

1. Choose the most appropriate alternative from the following :
 - (i) The most important ore of iron is
 - (a) Siderite
 - (b) Limonite
 - (c) Copper pyrites
 - (d) Haematite
 - (ii) Ferrosferric oxide called magnetic ore of iron has the chemical composition
 - (a) $\text{Fe}_2\text{O}_3 \cdot x \text{H}_2\text{O}$
 - (b) $2 \text{Fe}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$
 - (c) FeCO_3
 - (d) Fe_3O_4
 - (iii) Extent of iron in earth's crust is
 - (a) 60.000 ppm
 - (b) 4.5%
 - (c) 72.4%
 - (d) 62000 pmm

- (iv) The process of reduction called smelting is done in the furnace called.....
- (a) Reverberatory furnace
 (b) L.D. converter
 (c) Open hearth furnace
 (d) Blast furnace
- (v) The chief product of blast furnace is ...
- (a) slag (b) flue gases
 (c) cementite (d) pig iron
- (vi) The principal change in blast furnace is.....
- (a) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$
 (b) $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$ (slag)
 (c) $\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO}$
 (d) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2 \uparrow$
- (vii) Iron containing 2.5 to 5.0% carbon is known as.....
- (a) Mild steel (b) wrought iron
 (c) alloy steel (d) cast iron
- (viii) The process of heating steel to bright red heat and then cooling it very slowly in Air is known as
- (a) Nitriding (b) Hardening
 (c) Tempering (d) Annealing
- (ix) The most modern method of steel making is
- (a) Electric process (b) Kaldo process
 (c) Bessemer process (d) L.D. process
- (x) Nickel steel containing ~ 35% Ni with little Mn is known as
- (a) stainless steel (b) nichrome steel
 (c) special steel (d) invar

(B) Short Answer Questions

2. Distinguish between :

- (i) Annealing and Normalising,
 (ii) Bessemer Process and L.D. Process,

(iii) Steel and Cast iron.

(C) Long Answer Questions

3. Explain the function of carbon monoxide in the manufacture of cast iron.
4. Draw a neat sketch of a modern blast furnace and indicate, by means of equations, the chemical reactions taking place in its different zones.
5. How does iron occur in nature?
6. What are the sources of iron in India?
7. What is cast iron and what is its composition? What is the difference between white and grey cast iron?
8. In what ways Acid Bessemer process differ from Basic Bessemer Process?
10. Write notes on :
 - (a) Blast furnace,
 - (b) Commercial forms of iron,
 - (c) Different varieties of iron,
 - (d) Action of carbon monoxide on iron oxide,
 - (e) The by-products of cast iron industry,
11. (a) Discuss the L.D. process for the manufacture of steel.
(b) How are the impurities of pig iron removed in Acid Bessemer process?
12. (a) Steel-making processes are mainly divided into acid and Basic process - Why?
(b) Describe Basic Bessemer process for manufacture of steel giving chemical reactions.
13. Describe a modern blast furnace of the manufacture of pig iron. Give a sketch of the furnace and label its various parts.
14. Describe fully the manufacture of cast iron from iron ore (red haematite), discussing the chemical reactions occurring in the blast furnace.
15. (a) Write notes on (any two):
 - (i) Special steels, (ii) Tempering, (iii) Hardening.
 - (b) Differentiate between cast iron and steel.
16. (a) Point out the properties of steel which are modified by

(i) varying carbon content, (ii) heat treatment.

(b) Comment on the advantages of L.D. process. Sketch out the L.D converter and label it.

17. Give brief answers to the following (any four) :

(i) Before smelting iron ore is roasted in free supply of air. Why ?

(ii) L.D. process is far superior to Bessemer process. Why ?

(iii) Iron does not occur in free state . Why ?

(iv) Now-a-days steel is manufactured by L.D. Process Why ?

(v) Alloy steels are called special steels. Why ?

(vi) Steel articles are given suitable 'heat treatment' . Why ?

(vii) Iron ores of India are regarded to be the best quality ores in the world .
Why ?

18. (a) How does iron occur in nature ?

(b) Discuss the manufacture of cast iron from haematite.

(c) Define the term steel. How do you classify the steels ?

(d) Discuss one important method of conversion of cast iron into steel.

(Answer any two)