# Metallurgy of Iron

**Occurrence**

Next to aluminium, iron is the most abundant metal in earth's crust. Iron is the fourth most abundant ( about 5 % ) **metallic element in the earth's crust . Because of its strong**

affinity to oxygen, it is not found in nature in the elemental state but only in combined forms such as oxide. Iron is easily attacked by humid atmosphere. It is generally found associated with other metals like copper, cobalt and nickel. Principally iron occurs as oxides, much less as sulphide and sometimes as the carbonate.

The chief sources of iron are –

(i) Red Haematite – $Fe_2O_3$, Brown Haematite or Limonite – 2 $Fe_2O_3$ . $H_2O$, Magnetite – $Fe_3O_4$

(ii) Siderite – or Spathic Iron ore - $FeCO_3$

(iii) Iron pyrites – $FeS_2$

(iv) Chalcopyrites – $CuFeS_2$

## Commercial forms of iron

There are three commercial forms of iron .

(i) Cast or Pig iron – It is the most impure form of iron. It contains about 1.5 % to 4.5 % carbon. Other impurities like Si, P, Mn and S are present up to about 1.5 %.

(ii) Wrought or Malleable iron – It is the purest form of iron. It contains about 0.2 % carbon.

(iii) Steel – It is an alloy of iron with carbon and other elements like manganese, silicon and phosphorus. It is midway between cast and wrought iron as far as impurities are concerned. It contains 0.1 to 1.5 % carbon.

The three varieties differ from each other mainly in their carbon content.

The first step in the extraction of iron is the production of pig or cast iron which is subsequently used in making wrought iron or steel.

# Extraction of iron

- The extraction of iron is **pyrometallurgy. It is the extractive metallurgy which consists** of the thermal treatment given to minerals or ores to recover the metal. The process involves chemical reactions at elevated temperature.
- The process of extraction of iron is fundamentally very simple as it consists essentially of the reduction of iron oxide by carbon. But as molten iron dissolves carbon and other impurities, iron obtained is impure and is known as pig iron or cast iron. The ore ( red haematite or hydrated oxide or carbonate ) is calcined in shallow kilns to remove moisture, carbon dioxide etc. The ore thereby becomes porous and is then more easily reduced in the blast furnace.
- Iron is normally extracted from its oxide ore called haematite and rarely extracted from carbonate ore called siderite. Iron pyrite is an important source of sulphur and therefore it is not used in the extraction of iron. The extraction of iron involves following steps.

# Manufacture of cast iron

- It is done in following steps.

(i) **Washing and concentration or dressing of the ore**

Haematite ore is washed with water. It is subjected to magnetic separation. The ore being magnetic in nature, falls apart as a separate heap. This way the ore becomes rich in oxide of iron. It is then broken into small pieces of 1" to 2" size, screened and shifted. This helps to remove gangue. Due to washing, silicious impurities are removed. The ore is thus concentrated.

(ii) **Preliminary roasting and calcinations**

The concentrated ore is roasted and calcined with a little coal in shallow kiln ( furnace ) in excess air. Following changes take place during roasting and calcinations.

(i) Moisture escapes as steam and organic matter present burns off to give $CO_2$ and sulphur and arsenic are oxidized to form their volatile oxides $SO_2$ and $As_2O_3$ respectively.

(ii) Ferrous oxide is converted to ferric oxide which avoids formation of ferrous silicate In the slag during smelting and (iii) The mass becomes porous and thus makes it more suitable for reduction to metallic iron. Following reactions take place.

$Fe_2O_3 . 3H_2O \rightarrow Fe_2O_3 + 3\,H_2O \uparrow$ ; $FeCO_3 \rightarrow FeO + CO_2 \uparrow$ ;

- $4\,FeO + O_2 \rightarrow 2\,Fe_2O_3$

# (iii) Reduction or smelting in a Blast Furnace

The roasted and calcined ore ( 8 parts ) is mixed with coke ( 4 parts ) which acts as a reducing agent and limestone ( 1 part ) which acts as a flux. The mixture is introduced in a tall **Blast Furnace. The blast furnace has two functions (i) to reduce the** ore to metallic iron and (ii) to remove the impurities in the form of slag.

**Description of Blast Furnace**

a) It consists of an outer shell which is made of steel plates riveted ( fastened ) together.

From inside it sis lined with fire bricks. ( Refer Figure )

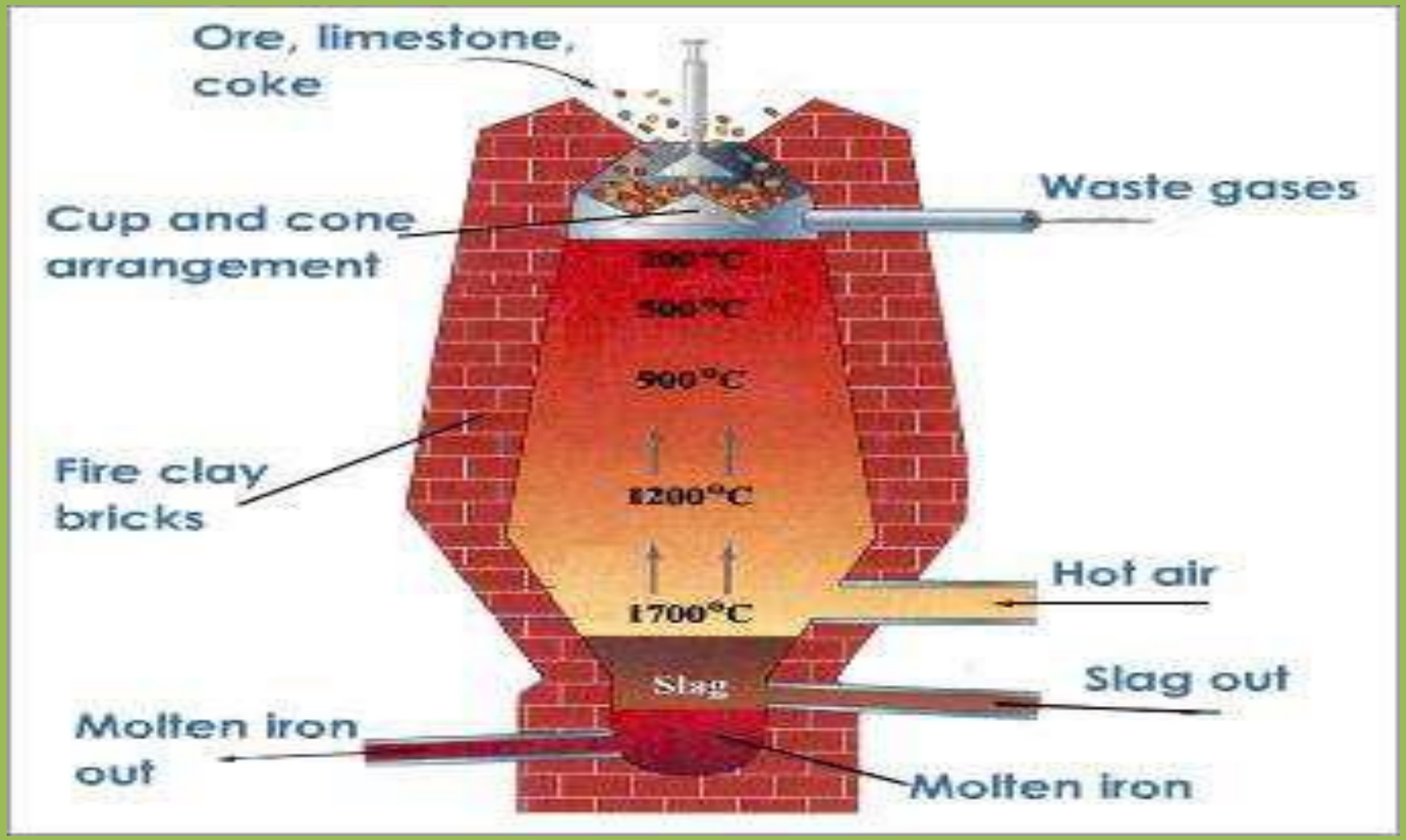
b) It is about 15’ to 120’ tall. ( The height varies from place to place. ) It is 15’ to 24’ in diameter at the wider end near the bottom. ( boshes, lower cone ) It is kept in a vertical position with the help of iron columns.

c) In its lower part, the furnace gradually narrows down below the boshes. The lower part of the furnace is called **hearth (floor ) or crucible where molten iron and slag is** collected.

d) The mouth of the furnace i.e. the top is closed by a **double cup and cone arrangement** through which the mixture ( called **charge ) of the calcined ore, limestone and coke is** fed from time to time. The hot gases escape through the flue. ( Refer diagram )

e) The cone is made of iron and is kept tight against the top of the furnace being counterpoised by weights

# Blast Furnace



- f) A blast of hot and dry air, obtained by hot gases, escaping from the blast furnace itself and freed from dust in a scrubber , is blown into the furnace , just above the **hearth** by a number of water-cooled pipes, called **tuyeres or twyers ( pipe rings).**
- g) Near the bottom of the furnace, there are two outlets on opposite sides, one for the removal of slag ( called slag hole ) and the other for taking out molten metal ( called metal hole or tap hole ).
- h) The temperature of the furnace is not constant in all the parts. It is maximum at the hearth ( about 17000C ) and decreases slowly towards the throat of the furnace ( about 3000C )

# The Process

- The charge ( roasted ore + coke + limestone in the proportion 8: 4:1 ) is introduced in the furnace from the top. Simultaneously, the furnace is lit and a hot blast of air is passed through the tuyeres. The different heat zones of the blast furnace are shown in the figure.
- **Reactions in the blast furnace**
- Following chemical reactions take place in different zones of the blast furnace.
- (i) **Zone of reduction – ( $300^0$C to $800^0$C - i.e. dull red heat )**

- This is the uppermost zone of the blast furnace. It is called the zone of reduction. Here the iron oxide from the charge is reduced by carbon monoxide to spongy iron.

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

  The reduction of $Fe_2O_3$ actually takes place in following three stages.

  a) Conversion of ferric oxide to ferroso - ferric oxide

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

  b) Conversion of ferroso – ferric oxide to ferrous oxide.

  $Fe_3O_4 + CO \rightarrow CO_2 + 3\ FeO$

  c) Conversion of ferrous oxide to metallic iron.

  $FeO + CO \rightarrow CO_2 + Fe$

- When the spongy iron falls in the middle region ( zone of heat absorption ), limestone, $CaCO_3$ decomposes to give CaO ( lime ) and $CO_2$. Lime thus obtained acts as a flux. It combines with silica to form a fusible ( meltable ) slag.
- $CaCO_3 \rightarrow CaO + CO_2$ ; $CaO + SiO_2 \rightarrow CASiO_3$ ( slag )
- (ii) **Zone of heat absorption – ( 8000C to 12000C – i.e. bright red heat )**

- This is the middle part or zone of the blast furnace. In this zone, the ascending $CO_2$ is reduced to carbon monoxide when it reacts with carbon ( coke ).

  $CO_2 + C \rightarrow 2\ CO - 39$ kcal
- As the reaction is endothermic, the temperature in this region falls and comes in the range $800^0C$ – $1000^0C$.

## (iii) **Zone of combustion – ( 1300$^0$C to 1500$^0$C – i.e. white heat )**

This is the zone near the tuyeres . Here the carbon burns to form $CO_2$ producing tremendous amount of heat.

$C + O_2 \rightarrow CO_2 \uparrow + 97$ kcal

The heat evolved raises the temperature to 1500$^0$C. As the hot gases go up and meet the descending charge, the temperature falls slowly to about 1300$^0$C.

# (iv) **Zone of fusion – (1500$^0$C to 1900$^0$C )**

- In this zone, the spongy iron melts and dissolves some carbon, phosphorus and silica.
- The molten iron collects at the bottom of the furnace while the fusible slag floats on it and protects the iron from oxidation. The layers of molten iron and slag are withdrawn through separate tapping holes from time to time.

- The process is economical as it is continuous one. The waste gases containing about 25% CO, 15% $CO_2$, 56% $N_2$ and 4% $H_2$ are let out through the outer pipe. These are burnt with air to produce heat which is used for preheating the air blast passed through the tuyeres. The blast furnace can work day and night for years together. Iron so obtained is known as **Pig Iron. It is remelted in a vertical furnace ( known as cupola )and**
- can be cast or poured into moulds. It is then called **cast iron. Thus cast iron is obtained** after remelting pig iron.

# Varieties of cast iron

- When pig iron in the blast furnace is suddenly cooled, crystalline cast iron is obtained. It is known as **white cast iron. In this form, carbon is present in the combined** state as iron carbide. It is very hard and white in colour. On the other hand, if molten iron is slowly cooled in sand moulds a graphite coloured iron is formed. It is known as **grey cast iron. In this type, a part of carbon separates out as graphite and gives grey colour to** the metal. It is softer and more coarse grained than the white form.

# Products of Blast Furnace

- The products of blast furnace are (i) Pig iron (ii) Slag (iii) Flue gases .

  (i) **Pig iron – Average composition of pig iron is : a) Iron – 92 to 95 % , b) Carbon – 2.5** to 4.5 % c) Silicon – 0.7 to 3% d) Phosphorus –0.5 to 1 % e) Manganese - 0.2 to 1 % f) Sulphur – 0.1 to 0.3 %

  (ii) **Slag - It is mostly calcium silicate containing some amount of aluminium silicate. It** Contains 55 % SiO2 , 30 % CaO and 15 % $CO_2$ and 15 % $Al_2O_3$. It is useful for road making and cement manufacture.

(iii) **Flue gases - The gases leaving the blast furnace through the flue are known as flue** gases. The average composition of the gaseous mixture is a) CO – 25 % b) $CO_2$ – 10 % c) $N_2$ – 58 to 60 % d) $H_2$ – 1 to 2 % Due to the appreciable proportion of carbon monoxide, the gaseous mixture has a fuel value and hence it is used for heating the air blast in Cowper's stoves.

Major part of cast iron is used to manufacture steel. It is also used for casting metal objects such as pipes, railings, weights and heavier parts of machinery.

# Physical and Chemical Properties of Cast Iron

- (i) Since cast iron is impure, it has melting point ( about $1200^0$C ) lower than that of pure iron ( about $1530^0$ C).
- (ii) On solidifying, it expands
- (iii) It is harder due to the presence of carbon and silicon.
- (iv) Due to sulphur, it is brittle when red hot ( red short ) and due to phosphorus, it is brittle when cold ( cold short ).
- (v) It can not be welded and can not be permanently magnetized.
- (vi) **Action of air - Pure iron is not affected by dry air. In presence of moist air and**
- carbon dioxide, it begins to rust readily forming reddish brown hydrated ferric oxide. When heated in air, it is oxidized and gets covered with thick bluish black scales of ferroso – ferric oxide $Fe_3O_4$.
- (vii) **Action of steam – When steam is passed over iron heated to $800^0$C to $1000^0$C, iron** is oxidized to $Fe_3O_4$.
- $3\ Fe + 4\ H_2O \rightarrow Fe_3O_4 + 4\ H_2 \uparrow$