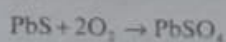**Note:** The chief reducing agent for carbon reduction process is $CO(g)$ and not $C(s)$ because the interaction between solid oxide ore and gaseous CO is much higher as compared to that between the solid oxide ore and solid C.

Self reduction

This method is applicable to some of the sulphides, e.g. PbS, Cu_2S and HgS. It does not involve use of reducing agent from an external source. Here the sulphide ore is partially roasted into its oxide, which in turn reacts with unreacted sulphide to produce molten metal. For example,
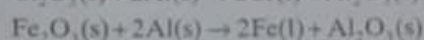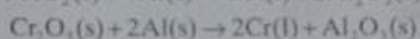
$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$
$$PbS + 2PbO \rightarrow 3Pb + SO_2 \uparrow$$
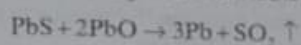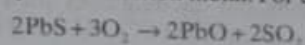
Another side reaction takes place, which is as follows

$$PbS + 2O_2 \rightarrow PbSO_4$$
$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2 \uparrow$$

Thermite reduction (or Goldschmidt-Thermite process)

The metal oxides having very high melting points, e.g. the oxides of Cr, Mn, Ti, Mo, Fe, etc., are very difficult to reduce by carbon reduction method. These can be reduced by thermite reduction method using Al powder as reducing agent. For example,

$$3Mn_3O_4(s) + 8Al(s) \rightarrow 9Mn(l) + 4Al_2O_3(s)$$
$$3TiO_2(s) + 4Al(s) \rightarrow 3Ti(l) + 2Al_2O_3(s)$$
$$Cr_2O_3(s) + 2Al(s) \rightarrow 2Cr(l) + Al_2O_3(s)$$
$$Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(l) + Al_2O_3(s)$$

All these reactions are highly exothermic in nature. Here Al is chosen as reducing agent due to its very high oxygen affinity. Since the formation of Al_2O_3 is exothermic in nature, it helps keep the temperature very high and thus the metal produced comes out in molten state.

The reaction of Fe_2O_3 is not used for commercial production of Fe. Primarily it is used in thermite welding for rail road joining all over the world due to flexibility of its use anywhere. In this process, magnesium ribbon/tape is ignited and it carries the fire up to the ignition mixture, which burns together to provide
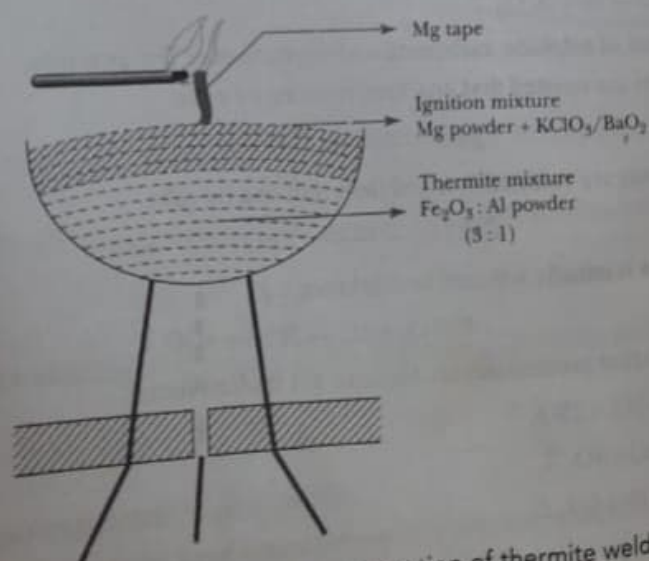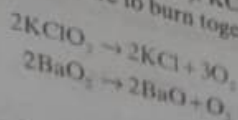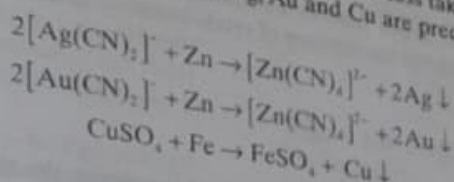

Figure 6.6 Diagrammatic representation of thermite welding.

Labels in figure:
- Mg tape
- Ignition mixture — Mg powder + $KClO_3/BaO_2$
- Thermite mixture — Fe_2O_3 : Al powder (3 : 1)

the activation energy required for the reaction (Figure 6.6). $KClO_3$ or BaO_2 provides O_2 from each and every part of mixture and helps the ignition mixture to burn together.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$
$$2BaO_2 \rightarrow 2BaO + O_2$$

Metal replacement method (Hydrometallurgy)

In this process, the desired metal is extracted from its solution by the addition of a more electropositive metal. The fuel cost is nil in this process because the reduction process takes place at room temperature or slightly higher temperature. Using this process, Ag, Au and Cu are precipitated from their respective solutions as follows:

$$2[Ag(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Ag \downarrow$$
$$2[Au(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2Au \downarrow$$
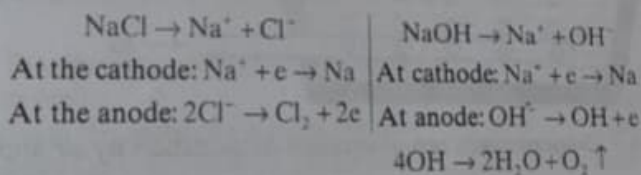$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu \downarrow$$

Electrolytic reduction

The oxides of strong electropositive metals such as K, Ca, Na, Al and Mg are very stable. It is difficult to reduce them into metallic state by carbon reduction process because of the following reasons.

1. The temperature requirement is very high so the fuel cost is high.
2. The collection of metals is to be done very carefully under inert environment, otherwise the metals react with air to form their respective oxides again.
3. At high temperatures, the metals being extracted may also form carbides in the presence of excess carbon taken for carbon reduction.

Such metals are extracted by passing electricity through their fused chlorides or oxides or hydroxides. For example,

1. Na is extracted from molten NaCl or molten NaOH.

$NaCl \rightarrow Na^+ + Cl^-$	$NaOH \rightarrow Na^+ + OH^-$
At the cathode: $Na^+ + e \rightarrow Na$	At cathode: $Na^+ + e \rightarrow Na$
At the anode: $2Cl^- \rightarrow Cl_2 + 2e$	At anode: $OH^- \rightarrow OH + e$
	$4OH \rightarrow 2H_2O + O_2 \uparrow$

2. Al is extracted from molten Al_2O_3 (details will be discussed in the individual extraction).

Note: Aqueous solution cannot be used as electrolyte here because then these electropositive metals will react again with H_2O to liberate H_2 at the cathode.

3. The metals which come below Al in the electrochemical series can be extracted by the electrolysis of the aqueous solutions of their salts. This process is applicable for Cu, Zn, Sn, Pb, etc. For example, $ZnSO_4$ solution can be used to get Zn

$$ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-}$$
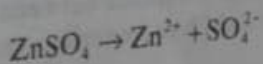
The electrode used is Zn or Al (as cathode) and the reaction at the cathode is

$$Zn^{2+} + 2e \rightarrow Zn$$
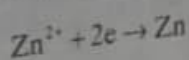
Similarly, $CuSO_4$ and $SnSO_4$ solutions are used to get Cu and Sn respectively.

Thermal decomposition method

Some of the metal oxides are thermally unstable and thermal decomposition is utilized to get metals from these oxides. For example,

$$HgO \xrightarrow{400^\circ C} Hg + \tfrac{1}{2}O_2$$

$$Ag_2O \xrightarrow{300^\circ C} 2Ag + \tfrac{1}{2}O_2$$
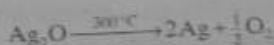
6.6 | PURIFICATION OR REFINING OF METAL

Metals obtained by any of the above mentioned reduction processes are not pure and require further refining. There are two methods for the refining of crude metals – thermal refining and electrorefining.

Thermal refining

Oxidation by air and poling

This process is applicable for refining of Cu and Sn. In this process, the crude metal is melted and air is blasted through the melt. After air is blown, the melt is stirred with a raw wooden pole and its unburnt condition produces sufficient amount of carbon and CO to reduce the metallic oxide formed and yield refined metal. A coke powder layer is maintained at the top of the surface to prevent reoxidation of the metal formed (Figure 6.7). A small amount of metal to be refined, however, may get oxidized in this process.
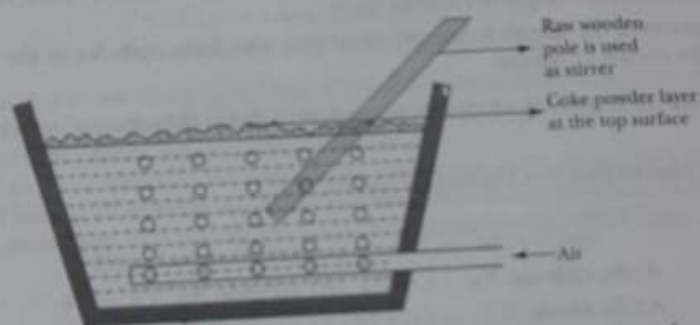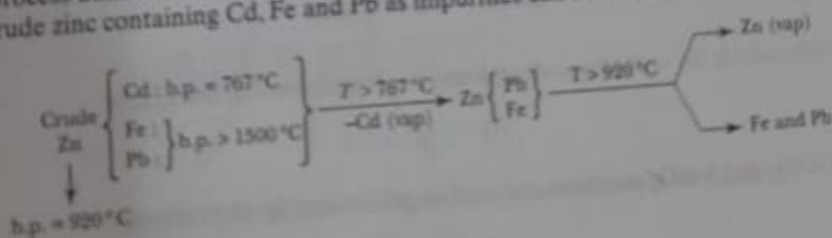

Figure 6.7 Diagrammatic representation of oxidation by air and poling.

The more basic metallic impurities are preferably oxidized by oxygen of air forming volatile or nonvolatile oxides (i.e. scum). The less basic impurities (if any) are not removed by oxidation, because under this situation metal to be refined will be oxidized in preference.
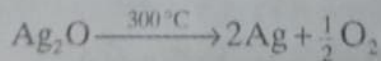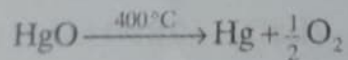
Fractional distillation

This refining process utilizes the boiling point difference between the metal and that of the impurity. Using this process, crude zinc containing Cd, Fe and Pb as impurities can be refined as follows:

Thermal decomposition method

Some of the metal oxides are thermally unstable and thermal decomposition is utilized to get metals from these oxides. For example,

$$HgO \xrightarrow{400\,^{\circ}C} Hg + \frac{1}{2}O_2$$

$$Ag_2O \xrightarrow{300\,^{\circ}C} 2Ag + \frac{1}{2}O_2$$

6.6 | PURIFICATION OR REFINING OF METAL

Metals obtained by any of the ab...

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At temperature >767 °C, Cd separates as vapours; and at temperature >920 °C, pure Zn separates as vapours leaving behind Fe and Pb impurities in the melt.

Liquation

This method is applicable for metals, such as Sn, Pb and Bi, which have low melting points as compared to their impurities. In this method, the block of crude metal is kept at the top of the sloping furnace and heated just above the melting point of the metal to be refined. The pure metal melts and flows down the sloping hearth and gets collected in a receiver at the bottom of the slope (Figure 6.8). The perforated block of impurity is thrown later.

The impurity content has to be high enough in the crude metal, otherwise the impurities also flow down with the molten metal.

Zone refining

Metals like Si, Ge and Ga of high purity (which are used in semiconductors) are purified by this method. This process is known as ultrapurification because it results in impurity level decreasing to ppm level.

Zone refining is based upon fractional crystallization as the impurity prefers to stay in the melt and on solidification only the pure metal solidifies on the top surface of the melt. In this process, a ring furnace is heated to a suitable temperature for melting the metal rod (Figure 6.9) and producing a thin zone throughout the cross-sectional area as shown in Figure 6.10.

It is desirable that the diameter of the rod, d is small enough to give a uniform melt.

When the melted zone in the metal rod is ready, the furnace is allowed to move downwards very slowly together with the melted zone (Figure 6.11). The furnace is then switched off, cooled down and taken to the top again for repetition of the process. Almost all impurity sweeps out to the bottom after several repetitions of the process.

Vapour phase refining

The two essential criteria for the zone refining process are listed as follows:

1. The intermediate compound formed has to be volatile.
2. The intermediate compound formed has to be relatively unstable, i.e. it should decompose on heating at practically achievable temperature.

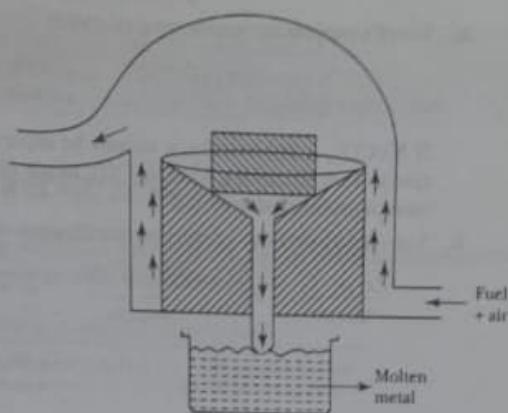This refining technique is used in the following purification processes.

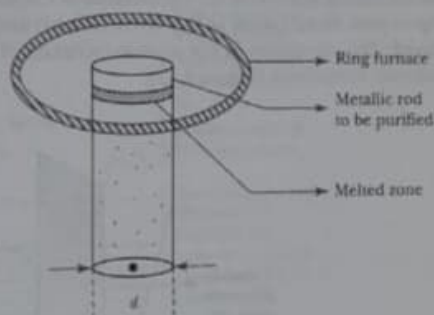Figure 6.8 Diagrammatic representation for liquation.

Figure 6.9 Metal rod heated by ring furnace.

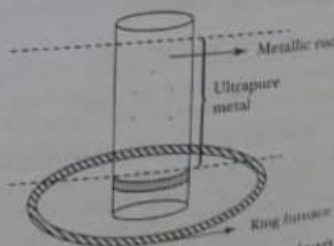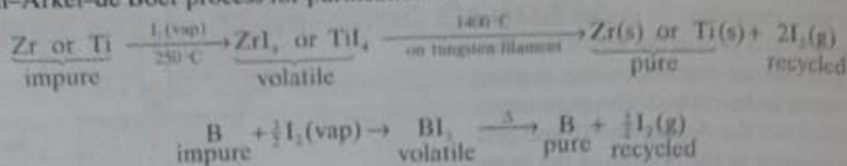Figure 6.10 Cross-sectional view of the metal rod.

Figure 6.11 Ring furnace moving down the metal rod.

a. Mond's process for purification of nickel

$$Ni(s) + 4CO(g) \xrightarrow{50-60\ C} Ni(CO)_4(g) \xrightarrow{150-180\ ^\circ C} Ni(s) + 4CO(g)$$
$$\underset{\text{impure}}{} \qquad \underset{\text{volatile}}{} \qquad \underset{\text{pure \quad recycled}}{}$$

If $Ni(CO)_4$ is not volatile, it cannot be separated from impurities, so its volatile nature helps to free it from impurities. Also $Ni(CO)_4$ needs to undergo thermal decomposition easily, otherwise it cannot produce pure metal.

b. Van–Arkel–de Boer process for purification of zirconium, boron and titanium

$$\underset{\text{impure}}{Zr \text{ or } Ti} \xrightarrow[250\ C]{I_2 (vap)} \underset{\text{volatile}}{ZrI_4 \text{ or } TiI_4} \xrightarrow[\text{on tungsten filament}]{1400\ C} \underset{\text{pure}}{Zr(s) \text{ or } Ti(s)} + \underset{\text{recycled}}{2I_2(g)}$$

$$\underset{\text{impure}}{B} + \tfrac{3}{2}I_2(vap) \rightarrow \underset{\text{volatile}}{BI_3} \xrightarrow{\Delta} \underset{\text{pure}}{B} + \underset{\text{recycled}}{\tfrac{3}{2}I_2(g)}$$

Electrorefining

This method is applicable for purification of Cu, Zn, Sn, Ag, Au, Ni, Pb and Al. The cathode is made of thin strip of pure metal (same as that to be refined) and the anode is made of large slab of impure metal (to be refined). The electrolyte is the aqueous solution of suitable salt of the metal (to be refined) or the melt of oxide/salt sometimes (Figure 6.12).
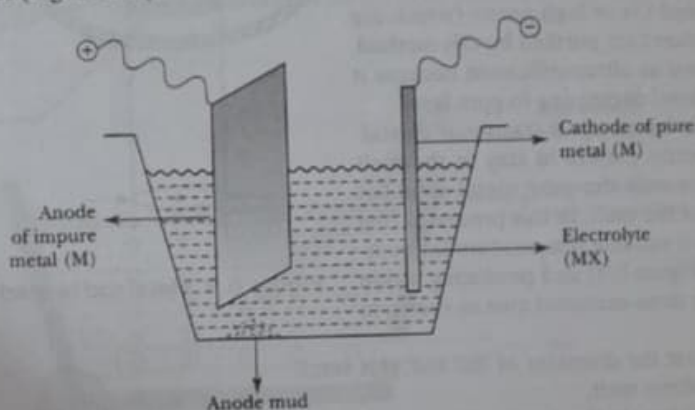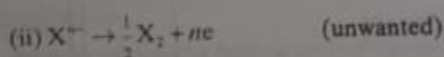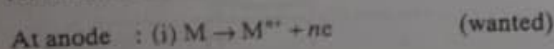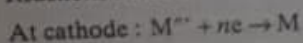

Figure 6.12 Diagrammatic representation of electrorefining.

The metal gets corroded from the anode. Pure metal gets deposited at the cathode and is purified in this way.

Reactions at the electrodes:

At cathode : $M^{n+} + ne \rightarrow M$

At anode : (i) $M \rightarrow M^{n+} + ne$ (wanted)

(ii) $X^- \rightarrow \tfrac{1}{2}X_2 + ne$ (unwanted)

There are two reactions competing at the anode. So the anionic part of the electrolyte is to be chosen in such way that the reaction (ii) does not take place at the anode.

Hence at a particular moment, the number of moles of metal dissolved in the electrolyte is equal to the number of moles of metal ions deposited at the cathode. The concentration of metal ion in the electrolyte remains the same at a particular time.

The metallic impurities having lower oxidation potential than that of the metal to be refined are separated in the form of anode mud at the bottom.

At 600–900°C:

At 900–1000°C:

$$\underset{\text{(Partially reduced)}}{Fe_3O_4} + 3CO \rightarrow 2Fe + 3CO_2 \uparrow$$

At 1000–1300°C:

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow$$
$$CO_2 + C \rightarrow 2CO \uparrow$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \uparrow$$
$$CaO + SiO_2 \rightarrow CaSiO_3 (slag)$$

At 1500°C (i.e. at the hearth): The coke powder crossing the line of tuyers does not have the scope of burning any more and reacts with MnO_2 and SiO_2 to produce impurities like Mn and Si as follows:

$$MnO_2 + 2C \rightarrow Mn + 2CO$$
$$SiO_2 + 2C \rightarrow Si + 2CO$$

$Ca_3(PO_4)_2$ present in the limestone reacts with SiO_2 to produce slag and P_2O_5 is reduced by coke to produce P, as impurity.

$$Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + 2P_2O_5$$
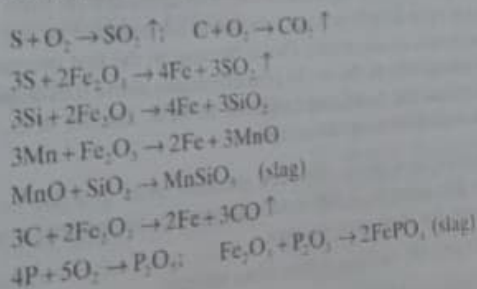$$2P_2O_5 + 10C \rightarrow P_4 + 10CO \uparrow$$

Finally the cast iron produced consists of impurities like Mn, Si, P, C and S.

Purification of iron or preparation of wrought iron

Wrought iron is the purest form of iron which contains the total impurity less than 0.5%. The carbon content is 0.1 – 0.15% and other impurities (Mn, P, S, Si) are less than 0.3%. The steps involved in preparation of wrought iron are shown in the flow diagram given in Figure 6.38.

The haematite lining has a special significance as it removes the impurity as well as produces iron at that place.

The various reactions taking place in the process are:

$$S + O_2 \rightarrow SO_2 \uparrow \quad C + O_2 \rightarrow CO_2 \uparrow$$
$$3S + 2Fe_2O_3 \rightarrow 4Fe + 3SO_2 \uparrow$$
$$3Si + 2Fe_2O_3 \rightarrow 4Fe + 3SiO_2$$
$$3Mn + Fe_2O_3 \rightarrow 2Fe + 3MnO$$
$$MnO + SiO_2 \rightarrow MnSiO_3 \ (slag)$$
$$3C + 2Fe_2O_3 \rightarrow 2Fe + 3CO \uparrow$$
$$4P + 5O_2 \rightarrow P_2O_5 \quad Fe_2O_3 + P_2O_5 \rightarrow 2FePO_4 \ (slag)$$

| Cast iron Mn, P, Si, C, S taken in puddling furnace which is lined with haematite | Puddling process Hot air is blamed and carried well Removes CO_2, SO_2 and slag | Wrought iron |

Figure 6.38 Flow chart for preparation of wrought iron from cast iron.

Byproducts of iron extraction

1. **Slag:** It consists of huge amount of $CaSiO_3$ and little $Al_2(SiO_3)_3$. These days it is used for making cement and now is known as slag cement.

2. **Blast furnace gas:** The composition of the blast furnace gas is 58% N_2, 25% CO, 10.5% CO_2 and 6.5% H_2 and the rest are hydrocarbons. It contains a very large quantity of CO and the H_2 which constitutes a good fuel. It is used for preheating the air used and for cooking purpose also.
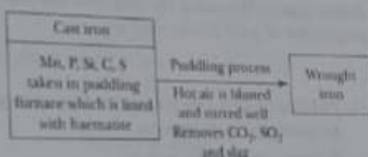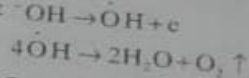
$$4\dot{O}H \rightarrow 2H_2O + O_2 \uparrow$$

Note: The H_2SO_4 is added in the electrolyte together with $ZnSO_4$ to increase the over voltage of It This helps in the deposition of only Zn^{2+} at the cathode, otherwise H_2 will be evolved at the cathode

6.18 | EXTRACTION OF IRON

The various ores of iron are:

1. Haematite   : Fe_2O_3
2. Magnetite   : Fe_3O_4
3. Brown haematite or limonite : $Fe_2O_3 \cdot 3H_2O$
4. Siderite or spathic iron ore : $FeCO_3$
5. Iron pyrite   : FeS_2

The chief ore used for extraction of iron is haematite, while FeS_2 is never used because iron obtained from this ore contains a lot of sulphur which makes it brittle and of no use. The flow diagram for extraction of iron from different ores is depicted in Figure 6.36
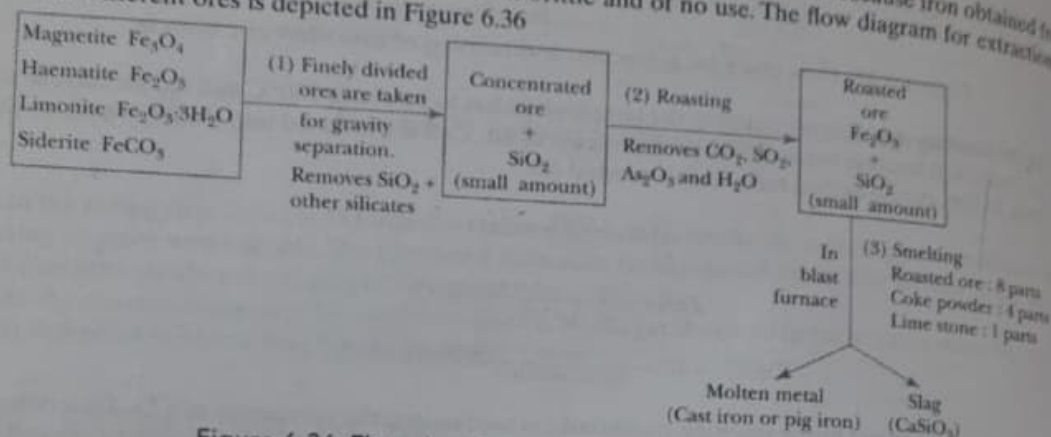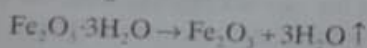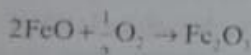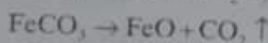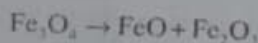

Figure 6.36 Flow chart for extraction of iron from haematite.

The reactions at various steps of the iron extraction process are :

1. **In the roasting step:**

$$Fe_3O_4 \rightarrow FeO + Fe_2O_3$$

$$FeCO_3 \rightarrow FeO + CO_2 \uparrow$$

$$2FeO + \tfrac{1}{2}O_2 \rightarrow Fe_2O_3$$

$$Fe_2O_3 \cdot 3H_2O \rightarrow Fe_2O_3 + 3H_2O \uparrow$$

Hence the final product of roasting is Fe_2O_3.

Though there is no sulphide ore yet roasting is adopted here to convert all FeO present into Fe_2O_3. As Fe_2O_3 does not form slag, this prevents the loss of FeO as slag $(FeSiO_3)$.

2. **In the smelting step:** The various changes taking place during smelting in the blast furnace are shown in Figure 6.37 The reactions involved are:
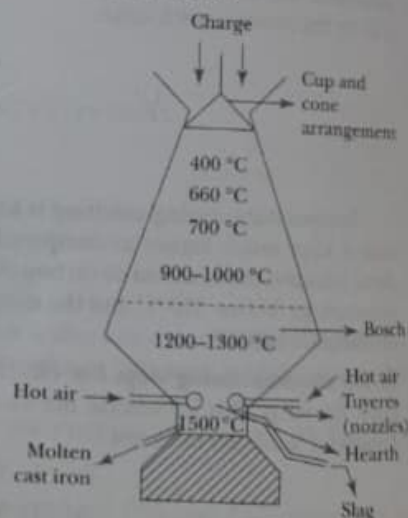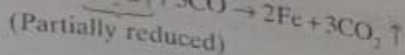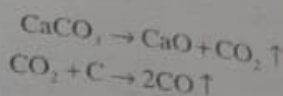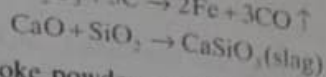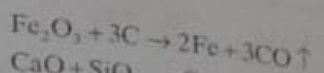

Figure 6.37 Smelting in the blast furnace.

$$\text{(Partially reduced)} \quad \overline{} \to 2Fe + 3CO_2 \uparrow$$

At 900–1000 °C:

$$CaCO_3 \to CaO + CO_2 \uparrow$$
$$CO_2 + C \to 2CO \uparrow$$

At 1000–1300 °C:
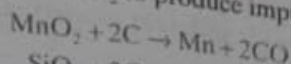
$$Fe_2O_3 + 3C \to 2Fe + 3CO \uparrow$$
$$CaO + SiO_2 \to CaSiO_3 \text{ (slag)}$$

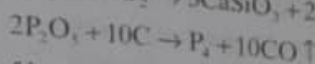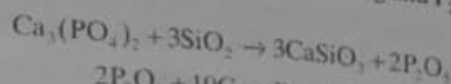**At 1500 °C (i.e. at the hearth):** The coke powder crossing the line of tuyers does not have the scope of burning any more and reacts with MnO_2 and SiO_2 to produce impurities like Mn and Si as follows:

$$MnO_2 + 2C \to Mn + 2CO$$
$$SiO_2 + 2C \to Si + 2CO$$
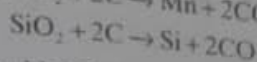
$Ca_3(PO_4)_2$ present in the limestone reacts with SiO_2 to produce slag and P_2O_5 is reduced by coke to produce P_4 as impurity.

$$Ca_3(PO_4)_2 + 3SiO_2 \to 3CaSiO_3 + 2P_2O_5$$
$$2P_2O_5 + 10C \to P_4 + 10CO \uparrow$$

Finally the cast iron produced consists of impurities like Mn, Si, P, C and S.

Purification of iron or preparation of wrought iron

Wrought iron is the purest form of iron which contains the total impurity less than 0.5%. The carbon content is 0.1 – 0.15% and other impurities (Mn, P, S, Si) are less than 0.3%. The steps involved in preparation of wrought iron are shown in the flow diagram given in Figure 6.38.

The haematite lining has a special significance as it removes the impurity as well as produces iron at that place.
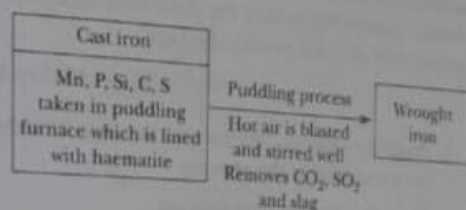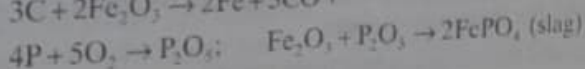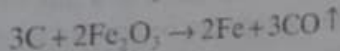
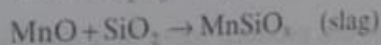The various reactions taking place in the process are:

Cast iron
Mn, P, Si, C, S taken in puddling furnace which is lined with haematite

Puddling process
Hot air is blasted and stirred well. Removes CO_2, SO_2 and slag

| Wrought iron |

Figure 6.38 Flow chart for preparation of wrought iron from cast iron.

$$S + O_2 \to SO_2 \uparrow; \quad C + O_2 \to CO_2 \uparrow$$
$$3S + 2Fe_2O_3 \to 4Fe + 3SO_2 \uparrow$$
$$3Si + 2Fe_2O_3 \to 4Fe + 3SiO_2$$
$$3Mn + Fe_2O_3 \to 2Fe + 3MnO$$
$$MnO + SiO_2 \to MnSiO_3 \text{ (slag)}$$
$$3C + 2Fe_2O_3 \to 2Fe + 3CO \uparrow$$
$$4P + 5O_2 \to P_2O_5; \quad Fe_2O_3 + P_2O_5 \to 2FePO_4 \text{ (slag)}$$

Byproducts of iron extraction

1. **Slag:** It consists of huge amount of $CaSiO_3$ and little $Al_2(SiO_3)_3$. These days it is used for making cement and now is known as slag cement.

2. **Blast furnace gas:** The composition of the blast furnace gas is 58% N_2, 25% CO, 10.5% CO_2 and 6.5% H_2 and the rest are hydrocarbons. It contains a very large quantity of CO and the H_2 which constitutes a good fuel. It is used for preheating the air used and for cooking purpose also.

Some heat treatment processes related to steel

1. **Annealing:** The hard steel is heated to bright redness (700–800 °C) and then allowed to cool to the room temperature very slowly by which the hard steel becomes soft. This process is known as annealing.

2. **Quenching or hardening:** The soft steel is heated to bright redness and then cooled suddenly to the room temperature immersing it into water or oil by which the steel becomes hard and brittle. This process is known as quenching.

3. **Tempering:** The hard and brittle steel is heated to 200–300 °C temperature range and cooled very slowly to the room temperature by which the brittleness of the steel disappears while the hardness remains same. This process is called as tempering.

4. **Case-hardening:** For this process the mild steel or wrought iron is heated to bright redness in the presence of hydrocarbons or $K_4[Fe(CN)_6]$ or heated to bright redness followed by dipping into NaCN/KCN solution. This makes the surface layer hard due to the formation of carbide of Fe (called cement-ite). This kind of steel is used for making armour plates, cutting tools and machinery parts which are in constant wear and tear.

5. **Nitriding:** The mild steel containing 1% Al is heated to 550 °C in the presence of NH_3. This makes the surface layer hard due to formation of the nitrides of Fe and Al. This kind of steel is used for making borewell drilling equipment.

## SINGLE CORRECT CHOICE TYPE QUESTIONS

Steel making

Steel is made by removing most of the carbon and other impurities from pig iron. Composition of various steels depending upon percentage of carbon is given as follows

% C	Type of steel
0.15 – 0.3	Mild steel
0.3 – 0.6	Medium steel
0.6 – 0.8	High carbon steel
0.8 – 1.4	Tool steel

The steel making process involves melting and oxidizing C, Si, Mn, S and P present in the pig iron so that these impurities are removed as gases or converted into slag. This is followed by addition of requisite additives (i.e. different elements) to iron to impart desired properties to steel.

Different elements present in steel provide different properties as described below

Element	Properties imparted
P above 0.05%	Imparts low tensile strength and cold brittleness
Mn	Imparts high hardness and increases tensile strength, e.g. rail road contains 13% Mn
Cr and Ni	Imparts stainless characteristic by producing impervious coating of their oxides on the surface
N (above 0.01%)	Makes steel brittle as well as difficult to weld
C	Improves hardness and strength

The addition of mixture of C and Mn into produced steel is known as 'spiegeleisen'. C and Mn act as deoxidizers, remove any dissolved O_2 and reduce FeO (if any). The excess carbon (if any) supplies the desired quality. Mn makes the steel hard and improves its tensile strength also. Various processes used for preparation of good quality steel are:

$$FeO + Mn \rightarrow MnO + Fe; \quad FeO + C \rightarrow Fe + CO \uparrow$$
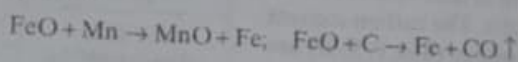
1. **Puddling process:** This process involves stirring of molten iron in reverberatory furnace by rods which are consumed in the process.
2. **Bessemer and Thomas process**
3. **Siemens open hearth process**
4. **Basic oxygen process** (also called Linz-Donawitz (L.D.) process).

All these processes are developed to economize the production of steel from iron. In the Bessemer and Thomas process or Siemens open hearth process, impurities are oxidized by air; while in the L.D. process pure O_2 is used for the oxidation of impurities. This is because in the first two processes the molten metal takes up small amount of nitrogen from the air. In concentrations above 0.01%, nitrogen makes steel brittle and nitriding the surface makes the metal more difficult to weld. The use of O_2 not only helps overcome these problems but also has the following advantages:

1. There is faster conversion, so a given plant can produce more in a day i.e. larger quantities can be handled in lesser time. For example, a 300 tonnes charge can be converted in 40 minutes compared to 6 tonnes in 20 minutes by the Bessemer process.
2. It gives a purer product and the surface is free from nitrides.

The lining of the furnace is designed based on the impurities present in the cast iron:

1. If the cast iron contains Mn, but not P, S, Si, then the lining used is silica brick and the process is known as acid Bessemer process.
2. If the cast iron contains acidic impurities such as Si, S, P, a lining of calcined dolomite ($CaO \cdot MgO$) or magnesia (MgO) is used and the process is called basic Bessemer process. In this process, the P_2O_5 formed from P combines with lime and forms basic slag [$Ca_3(PO_4)_2 \cdot CaO$] which is known as Thomas slag. It is a valuable byproduct and sold as phosphate fertilizer.