

7 CHAPTER

METALLURGY

Objectives

- * Occurrence of Metals
- * Metallurgy of Iron
- * Principles of Metallurgy
- * Extraction of Some Metals

OCURRENCE OF METALS

7.1.1 Minerals and ores

Metallurgy deals with the different methods of extracting metal from its natural sources and then converting them into useful materials to the mankind. The elements which have very low reactivity and have little or no affinity for oxygen, moisture and carbon dioxide occur in the free state also called native state. For example, some non-metals like nitrogen, oxygen, noble gases, carbon, sulphur, etc. and metals like gold, platinum, copper, silver, mercury, palladium, etc., occur in the native state.

Majority of metals are available in the combined state in the earth's crust. Abundance of various elements in the earth's crust is in the order : oxygen > silicon > aluminium > iron > calcium > sodium > potassium > magnesium.

Among metals, aluminium is the most abundant. It is the third most abundant element in the earth's crust. Many gem stones are impure forms of alumina and the impurities are chromium in ruby and cobalt in sapphire.

The natural substances in which metals occur either in native state or in combined state are called minerals. Generally every metal possesses more than one mineral. All the minerals of a metal may not be suitable to get the metal. Whether a mineral is suitable or not to extract a metal depends on the factors like percentage of metal in the mineral, nature and magnitude of impurities associated with the mineral, expenditure involved in the extraction and the industrial utility of the by-products in the extraction.

The mineral, from which the metal can be economically and conveniently extracted, is called an ore. For example, aluminium occurs in the earth's crust in the form of minerals like bauxite and clay. Out of these two, aluminium can be conveniently and economically extracted from bauxite, while it has been not possible to extract aluminium from clay by some easy and cheap method. Hence, bauxite is an ore of aluminium. All the ores are minerals but all the minerals are not ores.

Metals occur mostly as their oxide, carbonate, sulphide, halide, silicate, sulphate and phosphate minerals. Important types of minerals, their composition and the constituent metals are given in the Table 7.1.

Ore is the mineral from which metal is economically and conveniently extracted



P.7.1

In moist air copper corrodes to produce a green layer on the surface. What is that layer?

Solution

Copper, in the presence of moisture, oxygen and carbon dioxide of atmosphere, is converted into a basic carbonate, called malachite of composition, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. This basic carbonate is deposited as green layer on its surface.

Table 7.1 Classification and examples of important minerals

Type of mineral	Name of the mineral	Composition of mineral	Important constituent metal
Oxide minerals	Cuprite	Cu_2O	Cu
	Haematite	Fe_2O_3	Fe
	Magnetite	Fe_3O_4	Fe
	Zincite	ZnO	Zn
	Bauxite	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	Al
	Cassiterite (or) tin stone	SnO_2	Sn
	Pyrolusite	MnO_2	Mn
Carbonate minerals	Calamine	ZnCO_3	Zn
	Siderite	FeCO_3	Fe
	Lime stone (or) marble	CaCO_3	Ca
	Magnesite	MgCO_3	Mg
	Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	Cu
	Azurite	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	Cu
Sulphide minerals	Iron pyrites	FeS_2	Fe
	Copper pyrites	$\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ (or) CuFeS_2	Cu
	Copper glance	Cu_2S	Cu
	Zinc blende (or) sphalerite	ZnS	Zn
	Galena	PbS	Pb
	Argentite (or) silver glance	Ag_2S	Ag
Halide minerals	Cryolite	Na_3AlF_6 (or) $3\text{NaF} \cdot \text{AlF}_3$	Al
	Common salt (or) rock salt	NaCl	Na
	Carnallite	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Mg
	Horn silver	AgCl	Ag
Sulphate minerals	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Ca
	Barytes	BaSO_4	Ba
Phosphate	Monazite	Phosphates of Ln and Th	Th
	Phosphorite	$\text{Ca}_3(\text{PO}_4)_2$	Ca
Silicate minerals	Kaolinite (a form of clay)	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	Al
	Asbestos	$3\text{MgSiO}_3 \cdot \text{CaSiO}_3$	Mg/Ca

EXERCISE - 7.1.1

1. How do metals occur in nature? Give some examples for any two types of minerals.
2. What is an ore? On what basis a mineral is chosen as an ore?
3. Write the names and composition of some sulphide, oxide, carbonate and halide minerals.

PRINCIPLES OF METALLURGY

Extraction of metals from ores involves the following major steps:
Concentration of ore, isolation of metal from its concentrated ore and refining of the crude metal.

7.2.1

Concentration of ore

Flux combines with gangue to form slag

Leaching is a chemical method of ore dressing

Wilfley table is used for washing the ore

Wolframite is separated from tin stone by electromagnetic method

The ores are usually associated with impurities like sand, limestone, rocky impurities, etc. These unwanted impurities are called gangue or matrix and have to be removed before extracting the metals. The impurities of certain type can be eliminated from the ore in the molten state only. Most of the impurities in the ores do not melt easily at the temperatures of the normal industrial furnaces.

Substance added to ore to lower the melting point of the impurities is known as flux. Flux combines with the gangue chemically and forms easily fusible product, called slag. If the ore associated with basic impurities, then acidic fluxes like SiO_2 and P_2O_5 are used. If the ore associated with acidic impurities, then basic fluxes like CaO , MgO , etc., are used.

The partial purification of ore by removing gangue from it is known as ore dressing or concentration of ore or benefaction. Depending on the nature of the gangue and the manner in which they are bounded to the mineral, different types of ore dressing methods are adopted. Leaching is a chemical method. Except leaching, remaining methods are physical methods.

Hand Picking : Lumps of the ore are broken to small pieces. The sand and mud adhering to the ore are washed away by a stream of water. Then the pieces of the ore are dropped on a rotating roller belt and the stones are picked out by hand. For example, sand and stones are removed from the hematite ore by hand.

Hydraulic washing : This method is also called gravity separation or levigation. It is based on the difference in specific gravities of the ore and gangue particles. The ore is crushed to powder in ball mills. The powdered ore is washed in a stream of water. The lighter impurities are washed away leaving behind the heavier ore particles. Wilfley tables are specially made tables used for washing the ore. Galena (PbS), cassiterite (SnO_2) and alluvial sand are concentrated by this method.

Electro-magnetic separation: This method is used if the gangue or the ore particles are magnetic in nature. The finely powdered ore is dropped on a belt moving on two rollers in which one is magnetic. As the mass passes over the electromagnetic roller, the non magnetic particles fall away directly while the magnetic particles are held a little longer to the belt. When the belt moves a little further the magnetic force of attraction disappears and the magnetic particles fall into a separate heap as shown in the Fig 7.1.

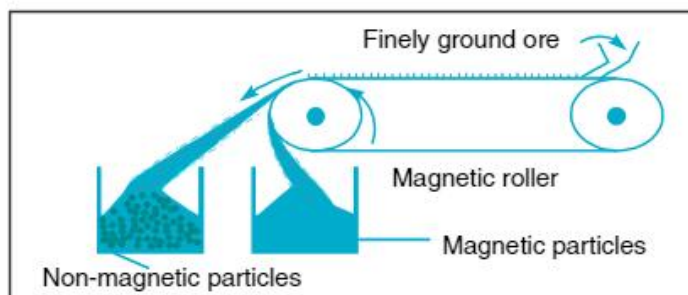


Fig 7.1 Magnetic separation

For example, tin stone (SnO_2), a non magnetic ore is separated from the magnetic impurity wolframite, FeWO_4 and haematite having the magnetic ore particles are separated from non magnetic gangue by this method.

Froth floatation process : This method is used for the concentration of sulphide ores like galena, zinc blende, cinnabar, copper pyrites, iron pyrites, etc. The process

Sulphide ores are concentrated by froth floatation process

is based on different wetting properties of gangue and the ore with water and oil. In this process the ore is finely powdered. It is suspended in water taken in a tank. To it, collectors like pine oil or olive oil or sodium ethyl xanthate and froth stabilizers like cresol or aniline are added. Collectors enhance non-wettability of the mineral particles and froth stabilisers stabilise the froth. A suitable pH is maintained in the solution by adding conditioners like lime or sodium carbonate. This makes the ore particles to float on water.

The mineral particles become wet by oils while the gangue particles by water. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles. The froth is light and is skimmed off as shown in Fig 7.2. It is then dried for recovery of the ore particles.

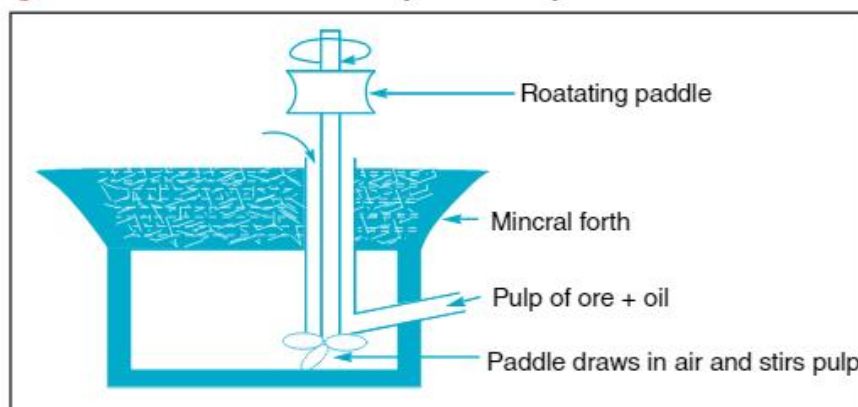
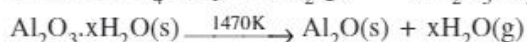
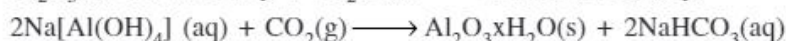
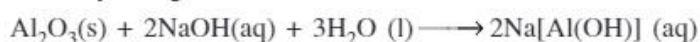


Fig 7.2 Froth floatation process

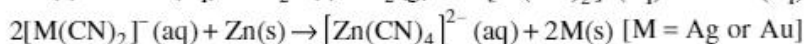
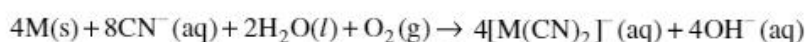
Sometimes, two sulphide ores are separated by adjusting proportions of oil to water or by using depressants. For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS from coming to the froth but allows PbS to come with the froth.

Liquation : This method is useful for such ores which contain easily fusible mineral particles and high melting gangue. The powdered ore is heated on a sloping floor of the furnace. The temperature is raised to just above the melting point of the ore. The ore melts and flows down the floor while the infusible impurities are left behind. For example stibnite, an antimony mineral, is concentrated by this method.

Leaching: In this method, the powdered ore is treated with certain reagents in which the ore is soluble but the impurities are not soluble. The impurities left undissolved are removed by filtration. For example, in Baeyer's process, red bauxite is purified by using concentrated caustic soda solution as leaching agent.



In the case of silver and gold ores, dilute solution of sodium or potassium cyanide in the presence of atmospheric oxygen is used.



Soluble ore is leached in to a solvent, leaving the insoluble impurities

7.2.2

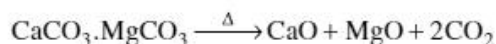
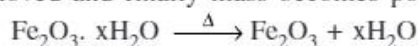
Extraction of crude metal

Metals are extracted from concentrated ore, generally by pyrometallurgy, hydro metallurgy and electrometallurgy.

In pyrometallurgy first the concentrated ore must be converted into a form which is suitable for reduction. Usually the sulphide ore is converted to oxide before reduction. Thus in pyrometallurgy isolation of metals from concentrated ore involves two major steps.

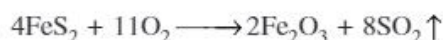
Conversion of concentrated ore to its oxide form: The concentrated ore can be converted into its oxide form by calcination and roasting.

Calcination is the process of strong heating of ore either in a limited supply of air or in the absence of air, but below its melting point. This is carried out in case of carbonate and hydrated oxide ores. During calcination, water from hydrated oxides is removed, carbonates decompose to oxides, moisture and volatile impurities are removed and finally mass becomes porous.



Roasting is the process of strong heating of ore in a free supply of air, but below its melting point. It is used in case of sulphide ores. Roasting is mainly three types: oxidising roasting, sulphatizing roasting and chloridizing roasting.

In oxidizing roasting method, sulphide ores when heated to high temperature, they change to oxides.



Sulphatizing roasting takes place under controlled conditions. Sulphides are converted to sulphates. For example, when zinc blende is heated to 650°C in air, in a furnace (Fig 7.3) a mixture of zinc oxide and zinc sulphate is formed.

Calcination is the process of strong heating of ore in the absence of air

Roasting is the process of strong heating of ore in air

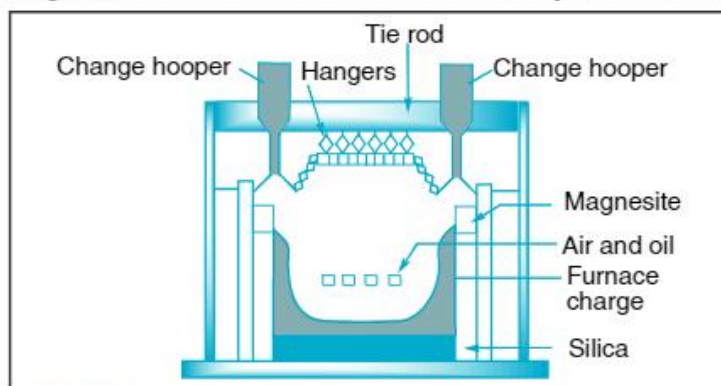
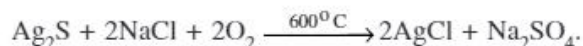


Fig 7.3 A section of modern reverborator furnace



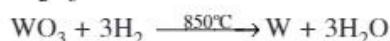
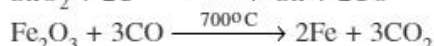
In chloridizing roasting, the sulphide ore is converted into a chloride. For example, argentite is mixed with sodium chloride and heated to 600°C . Then silver chloride is formed.



Metal oxides are reduced with coke, CO, H₂, water gas, Al, Ca, Mg, etc.

Reduction of oxides to metal : Some oxide and halide ores are reduced to obtain metals. Commonly used reducing agents are hydrogen gas, carbon monoxide, water gas, coke and metals like Mg, Ca and Al. The selection of the reductant depends on the chemical activity of metal.

Zinc oxide and tin oxide are reduced with coke. Haematite ore is reduced with carbon monoxide. Molybdenum oxide and tungsten oxide are reduced with hydrogen.



Some metal oxides cannot be reduced easily with coke, hydrogen and carbon monoxide. Such metal oxides can be reduced with the metals like Mg, Ca or Al. When aluminium is used as reducing agent, the process is referred as Goldschmidt aluminothermic process. Since the reaction is highly exothermic, metals are obtained in molten state. Metals like iron, chromium and manganese are obtained by thermite process.



Smelting is a process of melting ore with a flux or with a reductant

Smelting is a thermochemical process in which the ore is melted with a flux and often with a reducing agent. This is used for extracting a metal or a sulphide mixture from the ore in the fused state. For example, in the extraction of iron, haematite ore is smelted with coke and limestone. Iron is obtained in molten state and gangue is converted into slag, calcium silicate.

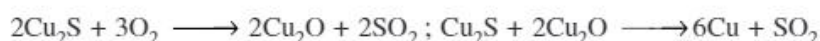
In the extraction of copper, the roasted copper pyrites is mixed with sand and coke and smelted. A mixture of sulphides of copper and iron is obtained in molten state. This matter mass is called matte.



Auto-reduction : Reduction can also be carried out by auto-reduction in which the anions associated with the metal help in the reduction. This is used for the reduction of sulphide ores of mercury, copper and lead. In this case no reducing agent is required. The metal is obtained either by simple roasting or by the reduction of its partly oxidized form. Mercury is directly obtained by the roasting of its ore cinnabar in air.

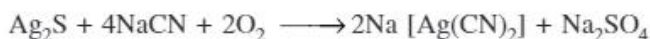


Copper is also obtained by reducing the oxide formed in partial oxidation of sulphide, with the remaining sulphide.



Hg and Cu can be obtained by self reduction of their sulphides

Hydrometallurgy : The process of extraction of metals by dissolving the ore in a suitable chemical reagent and then precipitation of the metal by more electropositive metal is called hydrometallurgy. Metals like silver, gold, etc. are extracted by this method. For example, concentrated argentite is leached with a dilute cyanide solution in the presence of air to form the soluble complex, sodium argentocyanide. Silver is precipitated from this by adding metal like aluminium or zinc.



Copper is extracted from low grade ores by hydrometallurgy. Copper is leached by using acid or bacteria. The solution containing cupric ions is treated with scrap iron or hydrogen.



Electrolytic reduction : Reduction of a molten metal salt may be based on electrochemical principle, given by the equation.

$$\Delta G^0 = -nFE^0$$

Here E^0 is the electromotive force of the redox couple formed by the system and n is the number of electrons transferred. More the positive E^0 values, more negative is the standard Gibbs Energy change (ΔG^0) and more is the feasibility of reduction leading to get metal as product. Metal cations (M^{n+}) are discharged and deposited at cathodes, during electrolysis precautions are taken considering the reactivity of metal produced. Suitable electrodes are selected and sometimes a flux is added for making the mass better conducting.

Highly electropositive metals like alkali and alkaline earth metals, aluminium, etc., are commonly extracted by the electrolysis of their fused salts. For example, in Hall Heroult's process, aluminium is extracted by the electrolysis of mixture of alumina and cryolite. The process of extraction of metals by electrolysis process is called electrometallurgy.

Highly electropositive metals are extracted by electrolysis

7.2.3

Thermodynamic principles

Gibbs energy
 $\Delta G = \Delta H - T\Delta S$

To understand the variation in the temperature requirements for thermal reductions (pyrometallurgy) and to predict which element will suit as the reducing agent for a given metal oxide, Gibbs energy interpretations are useful.

The relation between change in Gibbs energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) is, $\Delta G = \Delta H - T\Delta S$. When the value of ΔG is negative, then the reaction will be spontaneous. Ellingham diagram (Fig 7.4) consists of plots of ΔG^0 vs T .

$$\text{For any reaction, } \Delta G^0 = RT \ln K$$

Here K is the equilibrium constant of the reactant product system at temperature T

Ellingham diagram consists of plots of ΔG° vs T

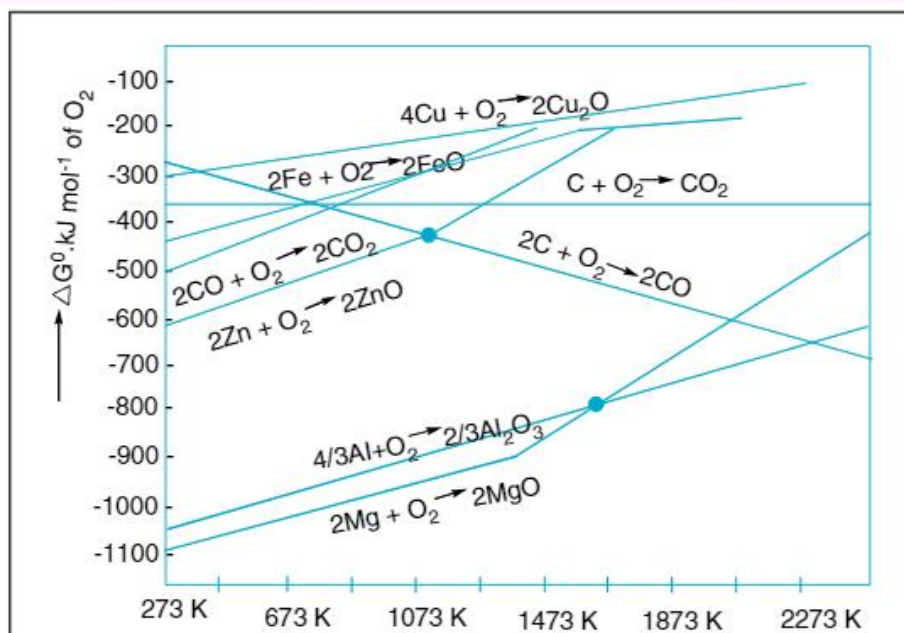


Fig 7.4 Ellingham diagram

These plots are useful to know the temperature where the phase transformation occurs, to know the decomposition temperature of metals and to select suitable reductant for reduction of metal oxides. For oxidation of metals ($2xM_{(s)} + O_{2(g)} \longrightarrow 2xM_xO_{(s)}$), ΔH is negative and ΔS is also negative due to decrease in gaseous molecules. Generally for the oxidation of metals, ΔG° is negative and increases with increasing the temperature. Thus for oxidation of metals, ΔG° vs T plot is a straight line with positive slope.

ΔG° is negative for the oxidation of metals

For oxidation of carbon to carbon dioxide, ΔS is almost zero due to no change in number of gas molecules. As a result, ΔG is almost equal to ΔH . Since ΔH does not change considerably with temperature, it almost remains the same with increasing the temperature. Hence for oxidation of carbon to carbon dioxide, ΔG° vs T graph is straight line and parallel to X-axis. For oxidation of carbon to carbon monoxide, ΔH is negative and ΔS is positive due to increase in number of gas molecules. As result, for oxidation of carbon to carbon monoxide, ΔG decreases with increasing temperature. Hence ΔG° vs T plot is a straight line with negative slope for the oxidation of carbon to carbon monoxide.

Each plot in Ellingham diagram is a straight line except when some change in phase (solid \rightarrow liquid or liquid \rightarrow gas) takes place. Increase in the slope of the line on positive side indicates the temperature of phase transformation. For example, in the Zn, ZnO plot around 800°C, the change in slope of the line indicates the melting of ZnO. There is a point in a curve below which ΔG is negative and metal oxide is stable. Above this point, metal oxide will decompose on its own.

During the reduction of a metal oxide with a reductant, metal oxide undergoes reduction and reductant undergoes oxidation. If the sum of ΔG° values for oxidation of reductant and reduction of metal oxide is negative, then that reductant is suitable for reduction of the metal oxide.

Possibility of reducing a metal oxide can be predicted by Ellingham diagram

In Ellingham diagram, the point of intersection of the two lines for oxidation of metal and oxidation of reductant is important. At a value greater than the temperature corresponding to the intersection of two lines, the element corresponding to the lower line can reduce the metal oxide corresponding to the upper line. The $\Delta G^\circ(\text{Zn, ZnO})$ and $\Delta G^\circ(\text{C, CO})$ lines, intersect at the temperature around 800°C . Thus carbon can reduce ZnO at the temperature greater than 800°C .

Ellingham diagram gives the information about the possibility of reduction of metal oxide with the reductant only, it does not give any information about the kinetics of the reduction process.



P.7.2 Why is the reduction of a metal oxide easier if the metal formed is in liquid state at the temperature of reduction?

Solution The entropy is higher if the metal is in liquid state than when it is in solid state. The value of ΔS of the reduction process becomes more positive, as a result the ΔG becomes more negative when metal formed is in the molten state than in solid state. Thus reduction becomes easier.



P.7.3 The value of ΔG_f° for formation of Cr_2O_3 is -540 kJ mol^{-1} and that of Al_2O_3 is -827 kJ mol^{-1} . Is the reduction of Cr_2O_3 possible with Al?

Solution $\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Cr}$; $\Delta G^\circ = -827 - (-540) = -287 \text{ kJ}$.
For the reduction of Cr_2O_3 with Al, ΔG° is negative and hence is possible.



P.7.4 Reduction of metal sulphides directly with carbon is not possible. Why?

Solution In the reduction of metal sulphides with carbon, carbon disulphide (CS_2) is supposed to be formed. CS_2 is thermodynamically less stable than metal sulphides. Thus reduction of metal sulphides directly with carbon is not possible.



P.7.5 Eventhough reduction of magnesia with aluminium is thermodynamically feasible, in practice aluminium is not used in the metallurgy of magnesium. Why?

Solution For the reduction of magnesia with aluminium, the temperature required is very high ($> 1400^\circ\text{C}$). Thus the process is uneconomic and technologically difficult.

7.2.4

Refining of crude metals

A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the differences in properties of metal and the impurity. Some important methods of refining the metals are: distillation, liquation, poling, cupellation, electrolysis, zone refining, vapour phase refining and chromatography.

Distillation is useful for the refining of low boiling metals like zinc, cadmium and mercury when they possess non-volatile impurity. The impure metal is evaporated to obtain the pure metal as distillate.

Liquation is useful for the refining of metals with low melting point like tin. The impure metal is heated on a slopping hearth, the metal runs down the slope and the impurities with high melting point are left behind.

Poling is useful for refining of the metals having its metal oxides as impurity. The impure metal is melted. It is covered by carbon powder and is stirred with green wood poles. The hydrocarbons produced from the green wood and carbon, reduce the oxides to the metal. Copper and tin are purified by this method.

Silver metal containing lead as impurity is purified by cupellation

Cupellation is useful when the metal possesses easily oxidisable impurities. Silver metal containing lead as impurity can be purified by this method. The impure silver is taken in cupel made of bone ash and air is blown into it. Lead is oxidized to volatile lead oxide (litharge) and gets separated. Pure silver is left behind.

Electrolytic refining is very convenient method for refining impure metals. Blocks of impure metal form the anode and thin sheets of pure metal form the cathode. A solution of a salt of the metal is taken as electrolyte. On passing electric current, the pure metal is deposited on cathode from the electrolyte. At the same time same amount of metal in anode enters into electrolyte by the oxidation. The impurities collect as anode mud, as shown in Fig 7.5.

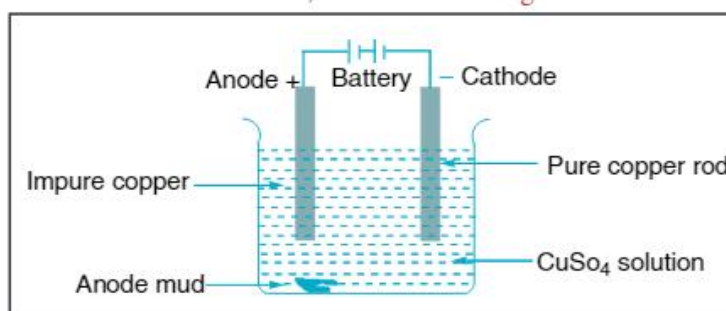


Fig 7.5 Electrolytic refining

In the electrolytic refining of copper, impurities like iron, zinc dissolve in the electrolyte while gold, platinum and silver are left behind as anode mud. Metals like copper, silver, zinc and aluminium are purified by electrolysis.

Zone refining is the method based on the principle that impurities are more soluble in the melt than in the solid state of the metal. A circular mobile heater is fixed at one end of a rod of the impure metal as shown in Fig 7.6.

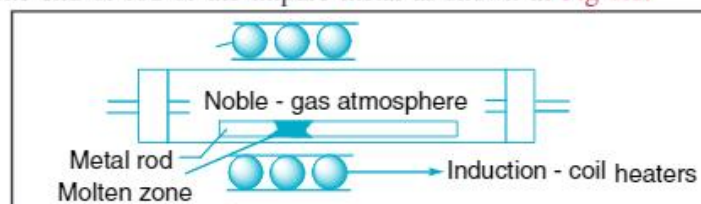


Fig 7.6 Zone refining

The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone. The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated. This end is cut off. Zone refining is very useful for producing semiconductors and other metals of very high purity. eg: silicon, germanium, boron, gallium and indium.

Vapour phase refining of metal involves conversion of the metal first into its volatile compound and then decomposing it to get pure metal. This method is used for the metals which form easily decomposable volatile compounds with an available reagent. Mond process and van Arkel method are examples for vapour phase refining.

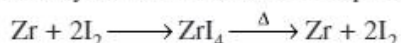
In **Mond's process**, impure nickel is heated in a stream of carbon monoxide forming a volatile compound, tetracarbonylnickel(0). This compound decomposes on heating to a high temperature and gives pure nickel.

Metal of highest purity is obtained in zone refining

Mond's process and van Arkel method are examples for vapour phase refining



van Arkel method very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like zirconium and titanium. The crude metal is heated in an evacuated vessel with iodine. Then volatile metal iodide is formed. The metal iodide is decomposed on a tungsten filament by heating electrically to about 1800K. The pure metal is thus deposited on the filament.



The simplest chromatographic technique is using columns

Chromatographic method is based on the principle that different components of a mixture have different extent of adsorption on the adsorbent. The mixture is put in a liquid or gaseous medium which is moved through the adsorbent. Different components are adsorbed at different levels on the column. Later the adsorbed components are removed (eluted) by using a suitable solvent (eluent). There are many types of chromatographic techniques, the simplest one among them is column chromatography Fig 7.7. This is very useful for purification of the elements which are available in minute quantities and the impurities are not very much different in chemical properties from the element to be purified.

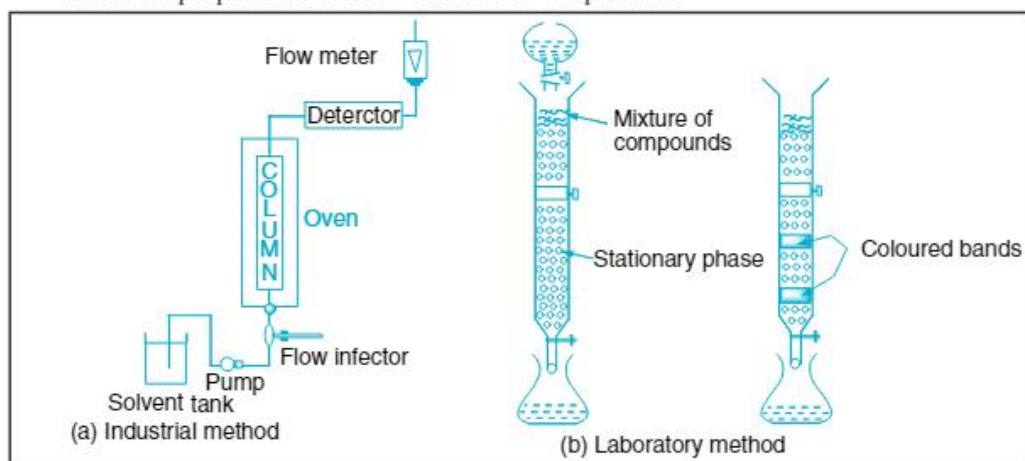


Fig 7.7 Diagrams showing columns in chromatography



P.7.6 Aluminium containing alumina as impurity can be refined by poling or not. Why?

Solution Aluminium containing alumina cannot be refined by poling. Aluminium is more electropositive, thus hydrocarbons released from green wood poles and carbon cannot reduce alumina.



P.7.7 The choice of a reducing agent in the extraction of a particular case depends on thermodynamic factor. Explain.

Solution Thermodynamic considerations are very important in deciding the temperature and reductant in the extraction of a metal.

Fe_2O_3 is reduced to metal using CO as reagent at 823 K. SnO_2 is reduced using coke at 1473 K.



P.7.8 Hydrogen is a common reductant of organic chemicals, but it is not widely used in metallurgy. Substantiate.

Solution Metallurgical reductions are usually high temperature processes. At elevated temperatures, hydrogen may form hydrides with metals. Metallurgical operations in open vessels lead to be combination of hydrogen with oxygen leading to the formation of water.

Ellingham curve has a positive slope and is parallel to the curves of several metal oxides.

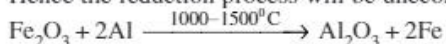


P.7.9 Although thermodynamically feasible, in practice alumina is not reduced using magnesium. Why?

Solution

Temperature above the point of intersection of Al_2O_3 and MgO curves, Mg can reduce Al_2O_3 . But the temperature required (1600 K) is very high.

Hence the reduction process will be uneconomic and difficult.



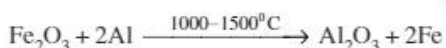
The ignition helps to overcome the energy of activation and hence the reaction is fast.



P.7.10 Reduction of metal oxides by thermit process becomes faster just after ignition. Why?

Solution

Aluminium is used as reductant in thermit process and the process is highly exothermic.



The ignition helps to overcome the energy of activation and hence the reaction is fast.

EXERCISE - 7.1.2

1. Write a note on ore dressing methods in metallurgy.
2. Describe different furnaces used in metallurgy.
3. What are the common methods used in the extraction of metals?
4. Define flux and slag, give examples.
5. Draw a neat diagram of a reverberatory furnace and label it.
6. Write short note on froth floatation process.
7. Write short notes on : roasting and calcination.
8. Write in brief about the refining of metals.
9. Comment on vapour phase refining.
10. Mention any four reducing agents used to reduce oxide and halide ores. Give equations.
11. What do you mean by self reduction?
12. What are (a) poling and (b) cupellation?

METALLURGY OF IRON

Elemental iron is present in meteorites. But iron occurs mostly in the combined state. Iron is the second most abundant metal in the earth's crust.

Important minerals of iron are: Haematite, Magnetite, Limonite and Siderite

Commercial varieties of iron are : cast iron, wrought iron and steel.

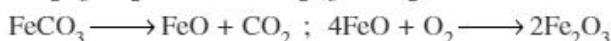
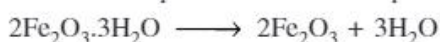
7.3.1 Manufacture of cast iron

*Cast iron is
manufactured from
haematite*

Cast iron is manufactured from its oxide ore, haematite and the following steps are involved.

Concentration : Haematite ore needs no concentration in most of the occasions. Only in few cases ore is concentrated by gravity separation process in which ore is washed with water to remove clay, sand, etc.

Calcination : The concentrated ore is heated strongly in the presence of limited supply of air in a reverberatory furnace. During calcination moisture is removed, impurities such as sulphur, phosphorus and arsenic are converted to their gaseous volatile oxides and iron carbonate is decomposed to oxide. If any ferrous oxide is present in the mineral it is oxidised to ferric oxide. This prevents the loss of iron due to the formation of ferrous silicate slag during smelting. The entire mass becomes porous which helps in the reduction process in latter stage.



Smelting is carried out in blast furnace

Smelting : The calcined ore, coke free from sulphur and lime stone are mixed in the mass ratio, 8:4:1. The charge is fed into the blast furnace Fig 7.8. A blast of hot air is sent into the furnace through the tuyers. Lime acts as a flux and coke serves as fuel and reducing agent. At the top part of the furnace, the reducing agent is carbon monoxide but at the bottom reducing agent is carbon itself. Various reactions that take place in the blast furnace are given in the Table 7.2.

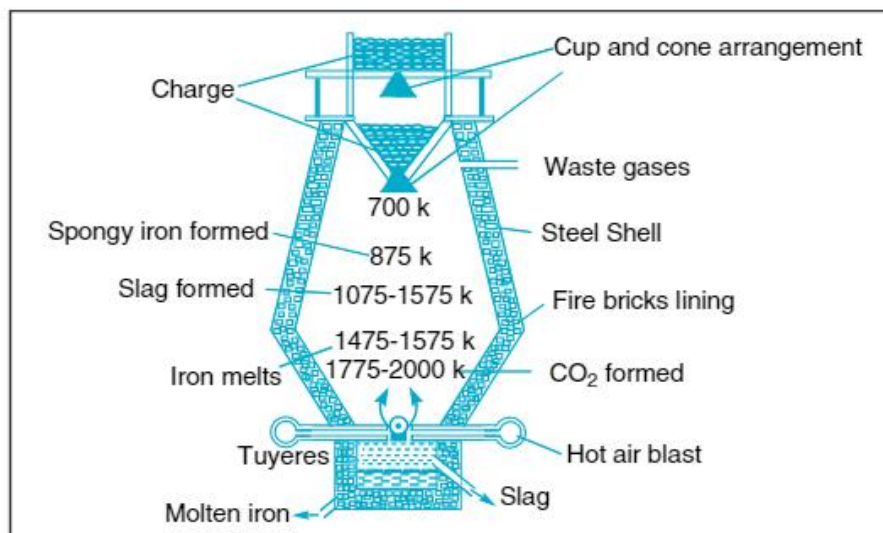


Fig 7.8 Blast furnace

Table 7.2 Various reactions that take place in the blast furnace

S.No.	Temperature range and name of the zone	Changes occurring	Chemical equations
1	400°C – 700°C Zone of reduction	Iron oxide is reduced and spongy iron is formed.	$\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{FeO} + \text{CO}_2$ $2\text{FeO} + 2\text{CO} \rightarrow 2\text{Fe} + 2\text{CO}_2$
2	800°C – 1000°C Zone of heat absorption or zone of slag formation	CO_2 is reduced to CO, limestone decomposes to lime and CO_2 and lime combines with SiO_2 to form the slag, CaSiO_3 .	$\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ $\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$ $\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$
3	1100° – 1300°C Zone of fusion	Coke burns to CO_2 , porous iron melts. Any iron oxide remaining is completely reduced to Fe.	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ $\text{FeO} + \text{C} \rightarrow \text{Fe} + \text{CO}$
4	Above 1300°C Near the hearth	Molten iron collects at hearth and slag floats on iron liquid.	---

The waste gases, known as blast furnace gases, escape from the outlet at the top. Iron obtained from blast furnace contains about 4% carbon and many impurities (Si, P, S, Mn) in smaller amount. This is known as pig iron and it can be cast into variety of shapes in moulds. Pig iron is the most impure form of iron.

Cast iron is different from pig iron. Cast iron is made by melting pig iron with scrap iron and coke using a blast of hot air. Cast iron has slightly lower carbon content (about 3%) and is extremely hard and brittle.

*Wrought iron is
purest form of iron*

Wrought iron or malleable iron is the purest form of commercial iron. It is prepared from cast iron by oxidising the impurities in a reverberatory furnace lined with haematite. This haematite oxidises carbon in the cast iron to carbon monoxide. It escapes through chimney and burns with a blue flame. The flames are known as 'puddlers candles' and the method is known as puddling process.



7.3.2

Manufacture of steel

*Pig iron contains
carbon as Fe_3C*

Steel contains lower percentage of carbon and other impurities than in pig iron. Steel can be prepared by purification of pig iron. The purification can be carried out in Bessemer converter process and open-hearth furnace process.

Pig iron possesses carbon as Fe_3C . Carbon in the pig iron is oxidised to carbon monoxide and it burns with blue flame. When blue flame puts off, Bessemer converter is tilted to remove steel and some more pig iron taken into it.

*Open-hearth
process is more
advantageous
than Bessemer
converter process
in preparing steel*

To avoid the wastage of iron, a calculated amount of carbon is added to the pig iron in the form of spiegeleisen. It is an alloy of iron with 15–20% manganese and 60% carbon. Manganese reduces the loss of iron and also the ferromanganese combines with oxygen caught in the steel after Bessemerization process.

Open-hearth process is the technique currently in use for the production of steel of high quality. Mixture of pig iron, iron ore (raw Fe_2O_3), scrap iron, scrap steel and lime stone is taken in shallow saucer like hearth of open hearth furnace. Chemical reactions take place slowly upon heating and steel will be formed. The quality of steel is analysed at different time intervals.

Iron ore is added till the carbon content comes to the desired level. To prepare the alloys of iron, requisite quantity of ferro-manganese is added.



P.7.11 Out of coke and carbonmonoxide, which is a better reducing agent for iron oxide?

Solution

Both coke and carbonmonoxide are reductants for iron oxide. At low temperature coke and at high temperature carbonmonoxide are good reducing agents.



P.7.12 Both coke and lime stone are used in smelting of iron ore. Why ?

Solution

Coke acts as a fuel and reducing agent, by forming carbon monoxide. Lime stone decomposes to give quick lime. Lime acts as a flux and removes acidic impurities as slag.



EXERCISE - 7.1.3

1. What are the different commercial forms of iron?
2. Write chemical reactions of four zones in blast furnace.
3. Describe a method for the manufacture of cast iron and wrought iron.
4. Discuss a process for the preparation of steel.

EXTRACTION OF OTHER METALS

7.4.1

Copper

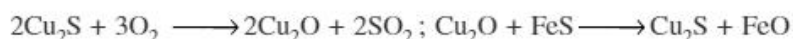
Copper is mainly extracted from its sulphide ore copper pyrites, by self reduction process.

Smelting : The roasted ore is mixed with some powdered coke and sand. It is heated strongly in a blast furnace. A blast of hot air, necessary for the combustion of

coke, is blown through the tuyers present at the base of the furnace. Most of the ferrous sulphide gets oxidised to ferrous oxide which combines with silica to form ferrous silicate slag.



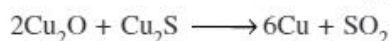
During roasting if any oxide of copper is formed, it combines with ferrous sulphide and is changed back into its sulphide.



Ferrous oxide thus formed again combines with silica to form more slag. As a result of smelting, two separate layers are formed at the bottom of the furnace. The upper layer consists of slag and is removed as a waste. The lower layer of molten mass contains mostly cuprous sulphide and a little amount of ferrous sulphide. It is called matte.

98% pure copper
is known as
blister copper

Bessemerisation : The molten matte from the blast furnace is transferred into a Bessemer converter. A blast of hot air mixed with sand is blown into the molten matte. During this process, traces of ferrous sulphide present in the matte is oxidised to FeO which combines with silica to form slag. Copper sulphide is partially oxidised which further reacts with remaining copper sulphide to form copper.



After the reaction has been completed, the converter is tilted and the molten copper is poured into sand moulds. The copper thus, obtained is about 98% pure and is known as blister copper. Copper is extracted from low grade ores by hydrometallurgy. The metal is leached using acid or bacteria



7.4.2

Zinc

Zinc can be
extracted by
carbon reduction
process

Zinc can be extracted from zinc blende and calamine. ZnO is obtained by roasting of zinc blende or by calcination of calamine. ZnO obtained in the calcination or roasting processes is reduced to zinc by carbon reduction process, heating with coke at 1100–1200°C.

The most commonly used method for the reduction is Belgian process. Zinc oxide is mixed with coke and is taken in bottle shaped retorts and heated to 1100°C by burning producer gas. Coke reduces zinc oxide to zinc.



Zinc distills over and collects in the condenser in molten conditions.

Crude zinc metal can be purified by liquation and distillation. Very pure form of zinc can be obtained by electrolytic process.

7.4.3

Aluminium

Bauxite is
dissolved in
cryolite and is
electrolysed in
Hall-Heroult's
process

Aluminium is mainly isolated from bauxite, which is generally contaminated with ferric oxide and silica. If the main impurity is ferric oxide, it is called red bauxite and if it is silica, it is white bauxite. The removal of ferric oxide and silica from bauxite ore is essential before it is subjected to electrolysis. Red bauxite is purified by Baeyer's process and white bauxite is purified by Serpeck's process.

Reduction of alumina: Pure alumina is a bad conductor of electricity. The fusion temperature of alumina is about 2000°C, hence it cannot be electrolysed. To increase the conductivity, cryolite is added and is in Hall-Heroult's process (Fig 7.9) to reduce

the fusion temperature. By adding these two, the fusion temperature is reduced to 900°C and it becomes a good conductor of electricity.

Electrolysis is carried out in an iron tank lined inside with carbon which acts as cathode. Anode consists of a number of carbon rods suspended in the electrolyte from the top of the cell.

The overall reaction may be written as : $2\text{Al}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Al} + 3\text{CO}_2$

During electrolysis aluminium is liberated at cathode : $\text{Al}^{3+}_{(\text{melt})} + 3\text{e}^- \rightarrow \text{Al}_{(\text{l})}$

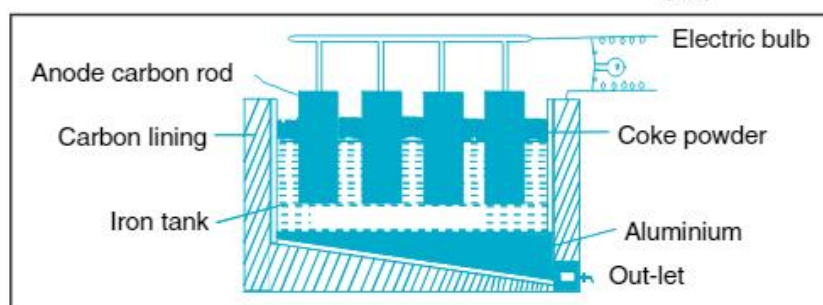
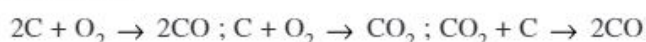
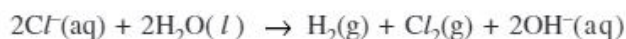


Fig 7.9 Hall-Heroult's process of electrolysis of fused alumina

The oxygen liberated at anode attacks carbon anode producing carbonmonoxide and carbondioxide.



While active metals are obtained by the reduction at cathode, some non metals are obtained based on oxidation. Extraction of chlorine from brine solution solution is a common example based on oxidation of chloride electrolytically.



A summary of occurrence and method of extraction of some metals along with remarks is listed in Table 7.3.

Table 7.3 Summary of extraction of some metals

Metal	Occurrence	Common method of extraction	Remarks
Aluminium	1. Bauxite, $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ 2. Cryolite, Na_3AlF_6	Electrolysis of Al_2O_3 dissolved in molten Na_3AlF_6	For the extraction a good source of electricity is required
Iron	1. Haematite, Fe_2O_3 2. Magnetite, Fe_3O_4	Reduction of the oxide with CO and coke in Blast furnace	Temperature approaching 2170 K is required
Copper	1. Copper pyrites, CuFeS_2 2. Copper glance, Cu_2S 3. Malachite, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ 4. Cuprite, Cu_2O	Roasting of sulphide partially and reduction	It is self reduction in a specially designed converter. The reduction takes place easily.
Zinc	1. Zinc blende or Sphalerite, ZnS 2. Calamine, ZnCO_3 3. Zincite, ZnO	Roasting followed by reduction with coke	The metal may be purified by fractional distillation.

7.4.4

Uses of metals

Aluminium foils are used as wrappers for chocolates. The fine dust of the metal is used in paints and lacquers. Aluminium, being highly reactive, is also used in the extraction of chromium and manganese from their oxides. Wires of aluminium are used as electricity conductors.

Aluminium is used for making household utensils, trays, frames, etc. It is used for making alloys which are used in making parts of air crafts, automobiles and speed boats. It is used as a deoxidiser for removing blow holes in metallurgy. Aluminium containers are used for transporting nitric acid. It is also used for painting iron surface.

Copper is used for making wires used in electrical industry and for water and steam pipes. It is also used in several alloys that are rather tougher than the metal itself, e.g., brass (with zinc), bronze (with tin) and coinage alloy (with nickel).

Zinc is used for galvanising iron. It is also used in large quantities in batteries, as a constituent of many alloys, e.g., brass, (Cu 60-80%, Zn 20-40%) and German silver (Cu 25-30%, Zn 25-30%, Ni 40-50%). Zinc dust is used as a reducing agent in the manufacture of dye- stuffs, paints, etc.

Cast iron, which is the most important form of iron, is used for casting stoves, railway sleepers, gutter pipes, toys, etc. It is used in the manufacture of wrought iron and steel. Wrought iron is used in making anchors, wires, bolts, chains and agricultural implements. Steel finds a number of uses. Alloy steel is obtained when other metals are added to it. Nickel steel is used for making cables, automobiles and aeroplane parts. Pendulum, measuring tapes, chrome steel for cutting tools and crushing machines, and stainless steel for cycles, automobiles, utensils, pens, etc.

Steel is an alloy of iron. It finds number of uses



P.7.13 In the auto-reduction taking place in Bessemer converter during the extraction of copper, what is the reductant?

Solution Reaction in the Bessemer converter is $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$.
In the auto-reduction reaction, sulphide ion is reductant and cuprous ion is oxidant.



P.7.14 During the smelting of roasted copper pyrites in blast furnace, why Cu_2S formed but not FeS ?

Solution Copper has greater affinity to sulphur than oxygen and iron has greater affinity to oxygen than to sulphur. Hence Cu_2S and FeO are formed in blast furnace.



P.7.15 Out of C and CO, which is a better reducing agent for ZnO ? Why?

Solution Carbon is the better reducing agent for reduction of ZnO. This is because the temperature required for reduction of ZnO with CO is very high when compared with the temperature required for reduction of ZnO with carbon. Reduction temperatures can be supported from Ellingham diagram.



P.7.16 How is a mixture of oxides of Al and Fe separated ?

Solution Fe_2O_3 is basic and Al_2O_3 is amphoteric. Hence aqueous solution of caustic soda or soda ash is used to dissolve Al_2O_3 , which forms soluble meta aluminate.
 Fe_2O_3 remains as a residue and is separated by filtration.



P.7.17 Aluminium vessels should not be cleaned by washing soda. Why ?

Solution Washing soda undergoes hydrolysis to give alkali, which reacts with aluminium vessels.
$$\text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O} \longrightarrow \text{H}_2\text{CO}_3 + 2\text{NaOH}.$$



P.7.18 Graphite rods are frequently replaced in Hall-Heroult's process of extracting aluminium metal. Why?

Solution Fluoride ions move towards graphite anode and are discharged to give active fluorine. This fluorine displaces oxygen of alumina. Oxygen reacts with graphite. Thus graphite gets corroded and is to be replaced frequently.



P.7.19 Write the composition of brass and german silver ?

Solution Brass is an alloy of copper and zinc (60% Cu and 40% Zn) German silver is an alloy of copper, zinc and nickel 30% Cu, 30% Zn, 40% Ni

EXERCISE - 7.1.4

1. Write the names and formulae of any two minerals of Cu. How is the Cu extracted?
2. Mention the ores of zinc. How is zinc dust obtained from zinc blende?
3. Write any two minerals of Cu.
4. What is the primary product of Bessemerization of matte?
5. Write the names of the minerals of zinc
6. Calamine is not directly reduced with carbon? Why?
7. Write an equation for the reaction between silver glance and NaCN solution.
8. Why cryolite is added to during electrolysis?
9. What is steel? Write its uses.



1. Some metals like gold, platinum, copper, silver, iron, etc., occur in the native state.
2. A non magnetic ore tin stone is separated from the magnetic impurity wolframite by electro-magnetic separation.
3. Sulphide ores are concentrated by froth flotation process.
4. Strong heating of ore in the absence of air or limited supply of air, below its melting point is called calcination.
5. Strong heating of ore in free supply of air below its melting point is called roasting.
6. A thermochemical process in which ore is melted with a flux and often with a reducing agent is called smelting.
7. Calcination and roasting are conducted in reverberatory furnace. Smelting is conducted in blast furnace.
8. Metal having its oxide as impurity is refined by poling.
9. Silver containing lead as impurity is refined by cupellation.
10. In electrolytic refining of metals, impure metal rod taken as anode, pure metal rod taken as cathode and salt solution of the metal to be taken as electrolyte.

11. Zone refining is useful for producing semiconductor quality pure substances.
12. Slag formed in the manufacture of cast iron is calcium silicate, but slag in the extraction copper is ferrous silicate.
13. Pig iron is the most impure form of iron. Wrought iron is the purest form of commercial iron and is prepared from cast iron by oxidising the impurities.
14. Steel is prepared by purification of pig iron. Cu, Cr, Mo, Ni, etc., are the alloying elements with iron in steel.
15. During the extraction of copper, auto reduction reaction takes place in Bessemer converter

$$2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu} + \text{SO}_2$$
16. About 98% pure copper extracted in bessemerisation is called blister copper.
17. In Belgian process of reduction of zinc oxide, coke is used as reductant.
18. Zinc is a volatile metal and is refined usually by liquation, distillation or electrolysis.
19. Aluminium is extracted by the electrolysis of fused bauxite dissolved in cryolite in Hall-Heroult's process.

EXERCISE - 7.2

1. Natural abundance of iron in the earth's crust is very high. Why?
2. Metal sulphides occur mainly in rocks, but metal halides occur in lakes and sea. Explain.
3. Explain the selection of suitable reducing agent for the reduction of metal oxide by using Ellingham's diagram.
4. Roasting of the sulphide ore is partially done in the metallurgical operation of copper. Explain.
5. Egg shells on treating with dilute mineral acids give brisk effervescences. Why?
6. Why a charge of coke and flux is used in smelting?
7. What criteria is followed for the selection of the stationary phase in chromatography?
8. Why iron is extracted from oxide minerals but not from sulphide minerals?
9. Which metals are extracted by auto-reduction process? (Ans: Cu and Hg)
10. Carbon can reduce copper oxide, but not calcium oxide. Explain.
11. Why copper pyrites roasted partially during the extraction of copper?
12. Ag and Cu are below hydrogen in activity series, yet they are found in combined state. Why?
13. CO is more effective reducing agent than coke below 983 K, but above 983 K the reverse is true. Why?
14. How the following metals are refined:
 - (a) Copper with cuprous oxide as impurity, (b) Copper with zinc, silver and gold as impurities and (c) Silver with lead impurity (Ans : (a) poling, (b) electrolysis and (c) cupellation)

15. Metals of high purity are obtained by zone refining. Mention the principle and process.
16. When hematite is burnt in air with coke and lime at 2000°C , steel is produced along with a bi-product 'X'. 'X' is useful as building material. Discuss. (Hint : X is CaSiO_3)
17. Why limestone is added in the metallurgy of iron?
18. Differentiate between cast iron, pig iron and wrought iron.
19. Extraction of copper from pyrites is more difficult than that from oxide through reduction. Why?
20. How is leaching carried out in case of low grade copper ores?
21. Hydrogen is good reductant, but not widely used in metallurgy. Why?
22. Copper can be extracted by hydrometallurgy but not zinc. Explain.
23. Alkali metals are extracted only by electrolysis of their fused salts. Justify.
24. Is it true that under certain conditions, magnesium can reduce alumina and aluminium can reduce magnesia? What are those conditions?
25. a) $4\text{M} + 8\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4[\text{M}(\text{CN})_2]^- + 4\text{OH}^-$. What is M ?
 b) $2[\text{M}(\text{CN})_2]^- + \text{Zn} \longrightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{M}$. What is M ? (Ans : Ag and Au)
26. In the extraction of Fe, what is the advantage of difference in temperatures of blast furnace ?
27. Metal oxide is easily reduced if the metal is in molten state at the temperature of reduction. Explain.
28. What are the compositions of gem stones, ruby and sapphire?
29. Active metals are not extracted by the electrolysis or aqueous electrolytes. Explain.
30. ΔG_f° values for the formation of CuO , CO and H_2O are respectively -129.7 , -137.2 and $-237.2 \text{ kJ mol}^{-1}$ respectively. In between carbon and hydrogen, which is good reductant for reduction of the metal oxide. Why? (Ans : Hydrogen)
31. Anhydrous pure alumina can not be electrolysed. Give reasons.

