UNIT 10

Principles and Processes of Extraction of Elements

SYLLABUS

Modes of occurrence

Chemical principles underlying—

Concentration of ores, reduction/ oxidation (electronation/de- electro- nation), refining of metals.

10.1. General Introduction

Elements are the basic units of all types of matter in this universe. How were these elements originally formed and how are they distributed on earth ? What are their modes of occurrence in the earth's crust and how are they obtained in the pure firm ? These are some of the interesting questions which come up in our minds and in this unit we shall try to find plausible answers for them. Since 80% of the elements known are metals, therefore, the major part of our study in this unit shall focus on their extraction/isolation and purification.

10.2. Origin of Elements

According to currently accepted views, within two hours of the formation of the universe, there was a great fall in the temperature and most of the matter at that time still consisted of hydrogen (89%) and helium (11%). The condensation of some of the clouds of H and He resulted in the formation of stars. These stars under the influence of gravity gave rise to high temperatures and densities within them. As the nuclei began to merge together, vigorous nuclear reactions occurred. The energy released during these nuclear reactions led to the formation of elements upto Fe (Z = 26) which constituted the interior of the stars. The elements with atomic numbers higher than iron (*i.e.* Z > 26) were produced by a variety of nuclear reactions* involving capture of neutrons emitted by lighter elements. For example,

$$^{23}_{10}\text{Ne} + ^{4}_{2}\text{He} \longrightarrow ^{26}_{12}\text{Mg} + ^{1}_{0}n$$

$$\begin{aligned} ^{98}_{42}\text{Mo} + ^{1}_{0}n \longrightarrow\ & ^{99}_{42}\text{Mo} + \gamma\text{-rays} + \text{neutrino} \\ & \ \ \downarrow \\ & ^{99}_{43}\text{Tc} + ^{0}_{-1}\beta \end{aligned}$$

The daughter nuclide such as $^{99}_{42}\text{Mo}$ and $^{99}_{43}\text{Tc}$ may capture more neutrons giving rise to elements with higher atomic numbers. Besides neutron capture, elements may also be produced by impact of cosmic rays present in the upper atmosphere. For example, ^{14}C is produced in this way.

$$^{14}_{7}\text{N} + ^{1}_{0}n \longrightarrow ^{14}_{6}\text{C} + ^{1}_{1}\text{H}$$

This reaction still continues and is responsible for a steady concentration of ^{14}C in the living world.

10.3. Distribution of Elements on Earth

It is believed that terrestrial (*i.e.* on the earth) distribution of elements depend upon their volatility. Thus, some elements may be volatile like noble gases or may form compounds which are volatile under conditions prevailing at the time of condensation of the earth while others may be non-volatile. For example,

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*In nuclear reactions, the number on the top left of the symbol of the element represents the mass number while the one at the bottom left denotes the atomic number.

Volatile elements : C, halogens, Hg, Pb, Zn

Non-volatile elements : Fe, Co, Ni, Si, Be, Ca

It is, therefore, reasonable to believe that terrestial distribution of non-volatile or less volatile elements would be somewhat similar to the overall cosmic (*i.e.* in the universe) distribution. On the other hand, volatile elements are greatly less abundant on earth due to their loss during the high temperature periods accompanying the formation of the earth.

Cosmic abundances of elements.* The cosmic abundances of elements are shown in Fig. 10.1. These data are only approximate because of the following reasons :

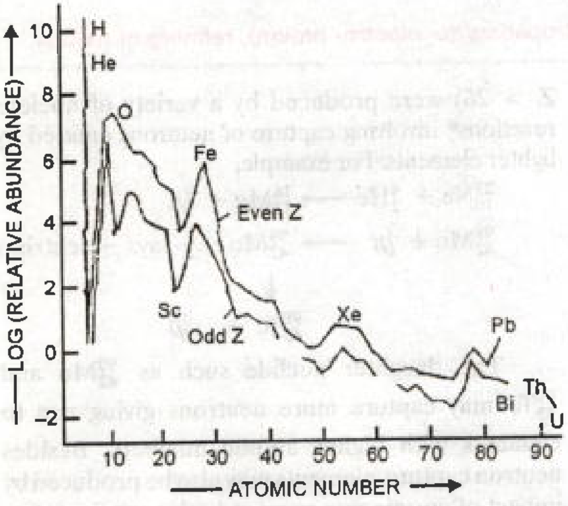

FIGURE 10.1. Cosmic abunances of elements relative to Si (taken as 10^6). Note that elements with even Z (atomic number) are more abundant their those with odd Z.

(i) Elements are not uniformly distributed, i.e. there are higher concentrations of certain elements in different regions of the earth.

(ii) Earth is not uniform from the core to the crust.

(iii) Composition of other planets is not the same as that of the earth.

In view of the above facts, terrestial abundances have little or no relation with cosmic abundances. However, there is a broad concensus on the following conclusions :

(i) Based upon the stabilities of the nuclei, elements with even atomic numbers are more abundant than those with odd atomic numbers.

(ii) The high abundance of iron is due to its high nuclear binding energy.

(iii) The low abundances of lighter elements such as Li, Be and B are due to their ability to react with more α- particles forming other elements. For example,

$${}^{8}_{4}\text{Be} + {}^{4}_{2}\text{He} \longrightarrow {}^{12}_{6}\text{C}$$

10.3.1. Condensation Processes

The non-volatile elements because of their high melting points underwent condensation without any loss at relatively high temperatures and thus appeared as minerals in high abundances. The moderately volatile elements such as Ag, Zn, Ge, Sn and F, however, condensed in lower abundances while volatile elements such as Cd, Hg, Pb and halogens (other than F) condensed in rather relatively low abundances. Thus, the early condensates include metallic iron (with 12·5% Ni) and *diopside* ($CaMgSi_2O_6$) and *anorthite* ($CaAl_2Si_2O_8$).

In this way, Fe, O, Mg and Si account for about 90% of the earth, the elements S, Ni, Al and Ca account for another 6 – 7% while all other elements account for 3 – 4% of the earth.

10.3.2. Zonal Distribution

The earth mainly consists of the following five zones :

1. The atmosphere
2. The hydrosphere
3. The crust or The lithosphere
4. The mantle
5. The core

A portion of the outermost three zones, viz. atmosphere, hydrosphere and lithosphere where living organisms interact with these parts and live together is called **biosphere.** For example, green plants during photosynthesis release oxygen into the atmosphere, the animals inhale oxygen and give out carbon dioxide which is used by plants for photosynthesis.

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*Non-evaluative

The three inner zones, *i.e.*, lithosphere, mantle and core are studied by seismography. These are distinguished on the basis of properties which depend upon density and elasticity.

Let us now briefly discuss the composition of these zones.

1. The atmosphere. *The gaseous mixture surrounding the earth is called the atmosphere.* It contains mainly nitrogen (78·09%), oxygen (20·95%) and other gases such as CO_2, He, Ne, Ar, Kr and Xe (< 1%). The atmosphere extends not more than 60 km above the surface of the earth.

2. The hydrosphere. *The liquid phase of the earth (oceans, lakes etc.) is called the hydrosphere.* It covers about 80% of the earth's surface. There are a large number of elements present in sea water.

3. The crust or the lithosphere. The upper solid phase of the earth is called the crust or the lithosphere. Its thickness various from 10-50 km (Fig. 10.2). It consists of three types of rocks.

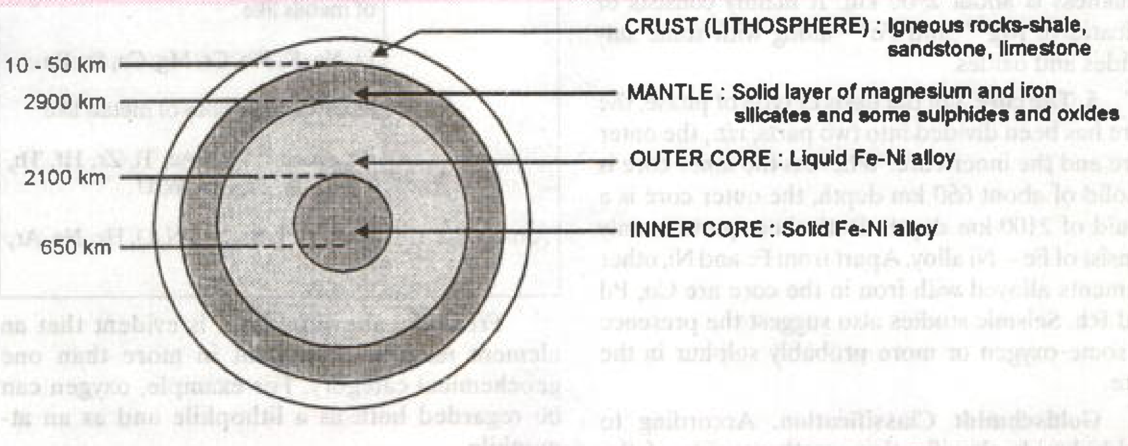

FIGURE 10.2. Main zones in the earth's interior.

(i) Igneous rocks. It is believed that the temperature deep down the earth is very high. *The extremely hot material present inside the earth is called* **magma.** Due to earthquakes, some vents are created in the upper layer of the earth. The high temperature inside the earth sometimes forces the magma out of the earth's surface through these vents in form of volcanic eruptions. This magma gets spread over the surface of the earth. With gradual cooling, over the years, it gets solidified in the form of rocks. Thus, *igneous rocks are formed by gradual cooling and solidification (i.e. fractional crystallization) over billions of years of the molten material coming out of the earth's surface during volcanic eruptions.* The word igneous implies formed by fire. These are mainly made up of aluminosilicates along with certain other ions such as Fe^{2+}, Mg^{2+}, Ca^{2+}, Na^{+} and K^{+}. These rocks cover about 4/5th of the earth's crust. Some important examples of igneous rocks are : *granite, basalt, gabbro*, etc.

(ii) Sedimentary or Stratified rocks. The weathering (selective extraction) of igneous rocks by water, carbon dioxide and humic acid (organic acid formed when water passes slowly through a mass of decaying vegetation) dissolves Na^{+}, Mg^{2+}, Ca^{2+}, Fe^{2+} etc. leaving behind insoluble residues consisting of TiO_2, Fe_2O_3 and SiO_2. These insoluble residues are ultimately broken into fine pieces called *sediments.* These sediments are then carried awaay by water to river banks and sea beds where they get deposited. With the passage of time new layers are deposited over the old ones. The bottom layers are ultimately converted into rocks by the pressure of overlying layers and presence of cementing material like lime. Thus, sedimentary rocks are composed mainly of minerals such as dolomite, limestone, silica, iron oxide, clay etc. The sedimentary rocks are also called *stratified rocks* since they occur in form of layers. *Limestone, sandstone, dolomite, shale etc.* are some important examples of sedimentary rocks.

(iii) Metamorphic rocks. *These rocks are formed by the structural modifications of the igneous and sedimentary rocks due to high temperature (caused by volcanic activity) or pressure (caused by earthquakes) or both.* Some important examples of metamorphic rocks are : *marble* (metamorphosed – lime stone), *quartzite* (metamorphosed sand stone) and *slate* (metamorphosed shale).

4. The mantle. The portion of the earth lying immediately below the crust is called the mantle. Its thickness is about 2900 km. It mainly consists of silicates of Mg^{2+} and Fe^{2+} along with some sulphides and oxides.

5. The core. On the basis of type of phase, the core has been divided into two parts, *viz.*, the outer core and the inner core. Whereas the inner core is a solid of about 650 km depth, the outer core is a liquid of 2100 km depth. Both these parts mainly consist of Fe – Ni alloy. Apart from Fe and Ni, other elements alloyed with iron in the core are Co, Pd and Rh. Seismic studies also suggest the presence of some oxygen or more probably sulphur in the core.

Goldschmidt Classification. According to Goldschmidt classification, earth consists of the following four zones :

1. Siderophil. *The innermost portion of the earth is called the iron core or the metallic core* or **siderophil** (*sideros* in Greek means iron). This covers both inner and outer cores as mentioned above. The elements present in siderophil are called *siderophiles.*

2. Chalcophil. *The layer of the earth surrounding the iron core* (*i.e.* mantle as mentioned above) *is called* **chalcophil.** Since this layer mainly contains sulphides of Cu, Zn, As and Pb, therefore, the elements present in this layer are called **chalcophiles** (*khalkos* in Greek means copper and brass).

3. Lithophil. *The outermost portion of the earth is called* **lithophil** (*lithos* in Greek means stone) and the elements present in this layer are called *lithophiles.*

4. Atmophil. *The gaseous mixture surrounding the crust or the lithosphere is called the* **atmophil.**

The distribution of the elements in these four different zones is different as shown in Table 10.1.

TABLE 10.1. Distribution of elements in different zones.

Zone	Constituents
Siderophil	Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt, Au
Chalcophil	P, S, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Te, Hg, Tl, Pb, Bi
Lithophil	Chlorides, sulphates and carbonates of metals like Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba Silicates and oxides of metals like Be, Al, Si, Y, La, Ac, Ti, Zr, Hf, Th, V, Nb, Ta, Cr, Mo, W, U
Atmophil	F, Cl, Br, I, B, C, Si, N, O, He, Ne, Ar, Kr, Xe

From the above table, it is evident that an element may be prominent in more than one geochemical category. For example, oxygen can be regarded both as a lithophile and as an atmophile.

10.4. Abundances of Elements in The Earth's Crust

Earth's crust is made up of light elements such as oxygen, silicon and aluminium. Oceanic crust is mainly basalt (which also contains magnesium and iron). Continental crust is mainly made up of two types of igneous rocks :

(*i*) *Light rocks, i.e.*, granite and related types containing 70% SiO_2 together with Al_2O_3.

(*ii*) *Heavy rock, i.e.*, basalt containing 40-50% silica together with MgO.

Aluminium is the second most abundant element in the light rocks and magnesium is the second most abundant element in the heavy rocks.

112 elements are known at present time. Out of these, 88 have been found in nature and the remaining have been synthesized. Oxygen constitutes nearly half (49·5) and silicon one-quarter of the total mass of elements in the earth's crust. The sixteen most abundant elements in the earth's crust and their percentages by weight are listed in Table 10.2.

TABLE 10.2. Sixteen most abundant elements in the Earth's Crust.

Atomic number	Element	Percentage (by weight)	Atomic number	Element	Percentage (by weight)
8	Oxygen	49·5	1	Hydrogen	0·9
14	Silicon	25·7	22	Titanium	0·6
13	Aluminium	7·5	17	Chlorine	0·2
26	Iron	4·7	15	Phosphorus	0·1
20	Calcium	3·4	25	Manganese	0·09
11	Sodium	2·6	6	Carbon	0·08
19	Potassium	2·4	16	Sulphur	0·06
12	Magnesium	1·9	56	Barium	0·04

(Total percentage weight of these elements = 99·77)

Two points which emerge from the about table are :

(*i*) Elements with low atomic numbers constitute a major portion of the earth's crust.

(*ii*) Elements with even atomic numbers are generally more abundant than elements with odd atomic numbers. There are, however some exceptions. For example gases (with even atomic numbers) occur only to a small extent because they probably escaped into the atmosphere during the condensation period.

10.5. Elements in Biological World

Many elements are accumulated in living organisms. For example,

(*i*) **Iodine** is *sea weeds*, (*ii*) **vanadium** in *sea cucumbers* (*iii*) **Magnesium** in chlorophyll, the green colouring pigment of plants. (*iv*) **Potassium** and iron also present in plant life. (*v*) **Carbon and hydrogen** are major constituents of all organic molecules (*bimolecules*) present in our body in one form or the other. Besides, these living organisms contain different elements in different parts. For example, (*i*) **Iron** in *haemoglobin* (blood).

(*ii*) **Zinc** in eyes of some animals and the enzyme carbonic anhydrase present in cells.

(*iii*) Traces of **Mn, Fe, Cu** in the *chloroplasts.*

It may be noted that very little is known as to why a particular element is present in a specific region of the living organism. However, it is known that their deficiency causes many disorders in the body. For example, deficiency of iron causes *anaemia* while that of iodine causes *goitre.*

Further, except iodine, no other element has been isolated from these biological sources.

10.6. Oceans as a Source of Elements

Oceans are a rich source of many useful substances, nutrients and minerals. For example,

(*i*) **Oil and natural gas** occur in continental shelf sedimentes.

(*ii*) **Gold** and **manganese** are present as sediments on the ocean floor.

(*iii*) Sea water contains a large number of dissolved salts by way of weathering of igneous rocks followed by extraction of elements by water. The different steps involved in this process are briefly described below :

(*i*) Igneous rocks consist of aluminosilicates of sodium, potassium, calcium etc. Rain water containing dissolved CO_2 dissolves these elements as their *bicarbonates* which go into sea water leaving behind clay and sand (called *detritus clay*).

Igneous rock

$$\left.\begin{array}{l} \underset{\textit{Calcium aluminosilicate}}{CaAl_2Si_2O_8} \\ + \underset{\textit{(Pot. aluminosilicate)}}{KAlS_3O_8} \\ + \underset{\textit{(Sod. aluminosilicate)}}{NaAlSi_3O_8} \end{array}\right\} + \underset{(H_2O + CO_2)}{\text{Rain water}}$$

$$\longrightarrow \underset{(Ca^{2+}, K^+, Na^+, HCO_3^-)}{\text{Stream of water}} + \underset{(Clay + SiO_2)}{\text{Detritus clay}}$$

(*ii*) Marine organisms convert Ca^{2+} and HCO_3^- ions to form $CaCO_3$ (shells) which form *sediments.*

$$Ca^{2+} + 2\,HCO_3^- \xrightarrow{\text{Marine organisms}} CaCO_3 + H_2O + CO_2$$

(*iii*) HCl injected by undersea volcanoes reacts with HCO_3^- to form chlorides of Na, K and Ca in sea water

$$HCl + HCO_3^- \longrightarrow Cl^- + H_2O + CO_2$$

The relative abundance of elements in sea water is shown in Fig. 10.3.

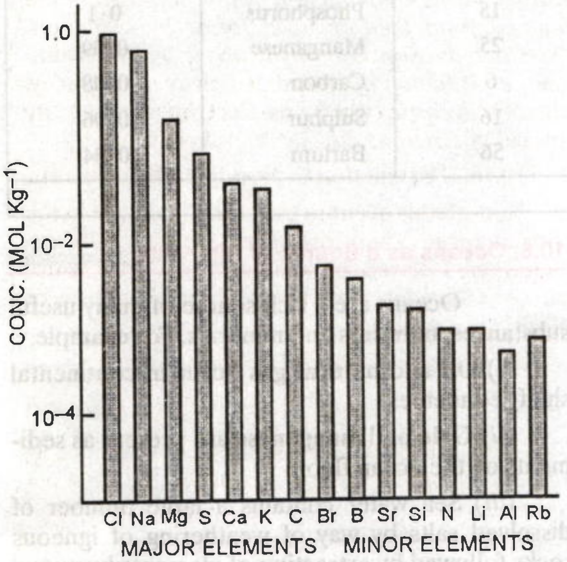

FIGURE 10.3. Elements in sea*.

Although sea water contains many elements but only four, *i.e., sodium, magnesium, chlorine and bromine* are commercially recovered from it.

Besides these, some rare metals are recovered from manganese nodules which are occasionally found in sea beds.

Huge amounts of metallic and non-metallic elements are present in sea water. Some important ones are Na^+, Mg^{2+}, Ca^{2+}, K^+, Sr^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, F^-, Br^-, I^- etc. In future, sea water may become an important source of many metals such as uranium and gold.

10.7. Modes of Occurrence of Elements

Elements may occur either in the *native (or free) state* or in the *combined state*. This is mainly due to the reason that different elements possess different chemical reactivities.

(i) Native state. Elements which are not attacked by moisture, oxygen and carbon dioxide of the air occur in the native state. For example, gold, platinum, noble gases etc.

(ii) Combined state. Elements which are readily attacked by moisture, oxygen and carbon dioxide of the air occur in the combined state in form of their compounds called *minerals*. In the combined state non-metals are found in the reduced form while metals are found in the oxidised form such as elements are generally present as oxides, carbonates, sulphides, silicates etc. as shown in Table 10.3.

TABLE 10.3. Important Types of Ores

Ore type	Examples
Native	Cu, Ag, Au, Hg, As, Bi, Sb, Pd, Pt, S, noble gases.
Oxides	$Al_2O_3.H_2O$ (diaspore) $Al_2O_3 \cdot H_2O$ (bauxite), Fe_2O_3 (haematite), Fe_3O_4 (magnetite), SnO_2 (cassiterite or tinstone), MnO_2 (pyrolusite), TiO_2, $FeCr_2O_4$ (iron chromite), WO_3, Cu_2O, ZnO (zincite).
Carbonates	$CaCO_3$ (calcite), $CaCO_3 \cdot MgCO_3$ (dolomite), $FeCO_3$ (siderite), $PbCO_3$, $BaCO_3$, $SrCO_3$, $ZnCO_3$ (calamine), $MnCO_3$, $CuCO_3 \cdot Cu(OH)_2$ (malchite).
Sulphides	Ag_2S (silver glance or argentite), Cu_2S (copper glance or chalcocite), copper pyrites ($CuFeS_2$), PbS (lead glance), ZnS (zinc blende), FeS, Bi_2S_3, NiS, CaS, MoS_3.
Halides	NaCl, KCl, AgCl (silver glance), $MgCl_2 \cdot 6\,H_2O$, NaCl and $MgCl_2$ (in sea water)
Sulphates	$BaSO_4$, $SrSO_4$, $PbSO_4$ $CaSO_4.2H_2O$(gypsum)
Silicates	$Be_3Al_2Si_6O_{18}$ (beryl), Zn_2SiO_4, $Sc_2Si_2O_7$ (thortveitite), $NiSiO_3$, $MgSiO_3$.
Phosphates	$CePO_4$, $LaPO_4$, $Th_3(PO_4)_4$ $LiF.AlPO_4$

10.8. Minerals Found in India

A variety of minerals are found in India. For example,

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*Non-evaluative

(*i*) **Orissa** and **Bihar** have the largest deposits of ores of *iron, manganese, chromium* in addition to *coal, mica* and *phosphates.*

(*ii*) **Madhya Pradesh** and **Maharashtra** have sizeable reserves of *maganese, chromium* and *bauxite.*

(*iii*) **Rajasthan** is rich is non-ferrous metals like *copper, zinc* and *lead.*

(*iv*) **Tamil Nadu** has large deposits of *iron, manganese, mica, limestone* and *lignite.*

A number of industries are producing iron, aluminium, zinc, gold etc. The Steel Authority of India (SAIL) is producing over 10 million tones of steel through a number of steel plants.

10.9. Occurrence of Metals—Minerals and Ores

Majority of the metals occur in the crust of the earth in the combined state in form of compounds called **minerals.** Thus,

The natural materials or the chemical compounds in which the metals occur in the earth are called **minerals.**

In other words, metals are extracted from minerals. But every mineral is not suitable for the extraction of the metal.

The mineral from which the metal is conveniently and economically extracted is called an ore. Thus, all ores are minerals but all minerals are not ores.

For example, iron is found in the crust of the earth as oxides, carbonates and sulphides. Out of these minerals of iron, oxides of iron are employed for extraction of the metal. *Thus, oxides of iron are called ores of iron.* Similarly, aluminium occurs in earth's crust in form of two minerals, *i.e.*, bauxite ($Al_2O_3.2H_2O$) and clay (Al_2O_3. $2SiO_2$. $2H_2O$). Out of these two minerals, aluminium can be conveniently and economically extracted from bauxite while no easy and cheap method is so far available for extraction of aluminium from clay. Therefore, *the ore of aluminium is bauxite*. Further, the main minerals of copper are *copper glance* (Cu_2S), *cuprite* (Cu_2O), *copper pyrites* ($CuFeS_2$), *malachite* ($CuCO_3.Cu(OH)_2$) etc. but copper can be conveniently extracted from copper pyrites. *Thus, copper pyrite is the ore of copper.*

10.10. Extraction of Elements

As stated above, only a few elements occur in the native state in nature while majority of them occur in the combined state. *In the combined state, metals usually occur in the oxidised form, (e.g.,* Fe_2O_3, Al_2O_3, SnO_2, MnO_2*) while non-metals occur in the reduced form such as* X^- (X = Cl, Br, I). Since the modes of occurrence of metals and non-metals are different, therefore, their methods of extraction or isolation from their natural sources are different. *Metals are usually obtained from their oxidised forms by reduction while non-metals are obtained from their reduced forms by oxidation. Whereas reduction is brought about by* **electronation**, *i.e. ; addition of electrons directly or indirectly, oxidation is carried out by* **de-electronation**, *i.e., by removal of electrons directly or indirectly.*

10.10.1. Extraction of Non-metallic elements

Non-metals occur in the combined state in the reduced form. Therefore, they are generally extracted or isolated by oxidation of their compounds. Consider, for example, the oxidation of chloride ion in water.

$$2\,Cl^-\,(aq) + 2\,H_2O\,(l) \longrightarrow 2\,OH^-\,(aq) + H_2\,(g) + Cl_2\,(g)$$

Since this oxidation cannot be carried out by ordinary chemical methods. Therefore, it is accomplished by electrolysis. The minimum potential difference required for the oxidation is 2·2 V. Similarly, fluorine is extracted by electrolysis of their fluorides. Elements like oxygen, nitrogen and noble gases are directly obtained from this. In contrast, carbon, sulphur and phosphorus are extracted either from native ores or by oxidation of their compounds occurring in nature. From the above discussion, it follows that there are no general methods available for extraction of non-metals. Therefore, the individual methods of their extraction will be discussed while dealing with the chemistry of these elements in unit 13.

10.11. Metallurgical Processes

The process of extracting metals from their ores is called metallurgy.

The process actually employed for the extraction of a metal depends upon its physical and chemical properties and the impurities associated with it. Since different metals have different physical and chemical properties, they have different methods of extraction. Therefore, *a single, universal method cannot be applied for the extraction of all the metals*. Still there are some procedures and processes which are common to the metallurgies of various metals. These are termed as *metallurgical operations*.

ADD TO YOUR KNOWLEDGE

Even 1600 years ago, Indians had a high level of skill in metallurgy. This is evident from the **Delhi Iron pillar** Near Kutab Minar. It is essentially made up of wrough iron (99·72%), carbon (0·08%), silicon (0·046%), sulphur (0·006%), phosphorus (0·114%) and manganese nil. Since 400 A.D., it has been existing without any rust or signs of decay.

This is primarily due to the reason that during finishing treatment given to the pillar, a thin film of magnetic oxide (Fe_3O_4) was applied on its surface.

Some important metallurgical operations are :

I. *Crushing and grinding of the ore*

II. *Concentration and benefaction of the ore.*

III. *Extraction of crude metal from the concentrated ore.*

IV. *Refining of the crude metal.*

These are briefly described below :

I. Crushing and grinding of the ore.

The ores usually occur in nature in form of big lumps. These lumps are broken into small pieces with help of *crushers or grinders*. This process is called **crushing.** These small pieces are then reduced to a fine powder with the help of *ball mill** or *stamp mill**. This process is called **Pulverisation.**

II. Concentraton or Benefaction of the ore (Ore-dressing).

Ores as they are obtained from earth's crust are never pure. They are usually associated with earthy and silicious impurities (in addition to the impurities of other minerals) called **gangue or matrix**. These impurities have to be removed from the ore before the extraction of the metal is actually done.

The removal of these unwanted earthy and silicious impurities (i.e. gangue or matrix) from the ore is called ore-dressing or concentration of ores and the process used to concentrate an ore is called the benefaction process.

The finely ground ore is concentrated by the following methods :

1. Hand picking. In case the impurities are quite distinct from the ore so that these may be differentiated by naked eye, these may be separated by hand picking.

2. Hydraulic Washing or Levigation or Gravity separation. *The process by which lighter earthy particles are freed from the heavier ore particles by washing with water is called* **levigation**. For this purpose, the ore is either agitated with water or washed with an upward stream of running water. The lighter impurities are washed away while heavier ore particles settle down.

This method is used when the ore particles are heavier than the earthy or rocky gangue particles. The oxide ores such as those of iron (*haematite), tin (tin stone)* and native ores of Au, Ag etc. are usually concentrated by this method. The process is carried out in specially designed tables called *Wilfley tables*.

3. Electromagnetic separation. *This method of concentration is employed when either the ore or the impurities associated with it are magnetic in nature.* For example, *chromite,* ($FeO \cdot Cr_2O_3 = FeCr_2O_4$) – an ore of chromium, magnetite (Fe_3O_4) – an ore of iron and pyrolusite (MnO_2) – an ore of manganese being magnetic are separated from non-magnetic silicious gangue by this method. Similarly, *tinstone or cassiterite* (SnO_2), an ore of tin being non-magnetic can be separated from magnetic impurities like those of tungstates of iron and manganese which are generally associated with it, by this method.

In this method, the powdered ore is dropped over a travelling belt moving around two rollers – one of which has an electromagnet in it. As the ore particles roll over the belt, the magnetic particles are attracted by the magnetic roller. As a result, two heaps are formed separately. The heap collected below the magnetic roller contains the magnetic particles while the heap formed away from the

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***A stamp mill** is a heavy stamp or bolt which rises and falls on a die below on which crushed ore is fed from one side. A ball mill, on the other hand, consists of a big steel tank containing a few steel balls or a few pieces of hard stone like flint in it. The steel tank is fed with crushed ore and water, and rotated. Steel balls fall on the crushed ore and reduce it to powder.

magnetic roller contains the non-magnetic impurities (Fig. 10.4). In case of tinstone, the tungstates being magnetic fall in a heap under the magnetic roller while the ore particles *i.e.* SnO_2 fall in a separate heap away from the magnetic roller.

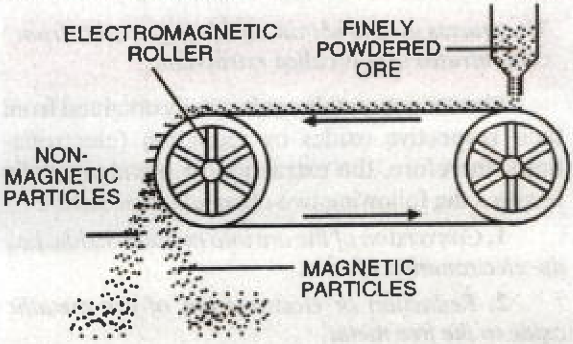

FIGURE 10.4. Electromagnetic separation.

4. Froth flotation. This method is widely used for the concentration of sulphide ores such as zinc blende (ZnS), copper pyrites ($CuFeS_2$), galena (PbS) etc. *This method is based upon the fact that the surface of sulphide ores is preferentially wetted by oils while that of gangue is preferentially wetted by water.*

The ore is crushed into a fine powder and mixed with water to form a suspension in a tank (Fig. 10.5). To this suspension are added **collectors** (*e.g.* pine oil, xanthates and fatty acids) which enhance the non-wettability of the ore particles and **froth-stabilizers** (*e.g.*, cresols and aniline) which stabilize the froth.

The suspension is violently agitated by the rotating paddle which draws in air causing frothing.

During this process, the ore particles which are preferentially wetted by the oil become lighter and thus rise to the surface along with the froth while the gangue particles which are preferentially wetted by water become heavier and thus settle down at the bottom of the tank. The froth is skimmed off. It is allowed to collapse and finally dried to get the concentrated ore.

If the mineral to be concentrated consists of sulphides of two metals, then by adjusting the proportion of oil to water, it is often possible to separate one sulphide from the other. Sometimes additional reagents called **depressants** are used to prevent one type of sulphide ore particles from forming the froth with air bubbles. For example sodium cyanide is used as a depressant to separate lead sulphide (PbS) ore from zinc sulphide (ZnS) ore. This is due to the reason that NaCN forms a zinc complex, $Na_2[Zn(CN)_4]$ on the surface of ZnS thereby preventing it from the formation of froth. Under these conditions only PbS forms froth and hence can be separated from ZnS ore.

$$4\,NaCN + ZnS \longrightarrow \underset{\text{Sod. tetracyanozincate (II)}}{Na_2[Zn(CN)_4]} + Na_2S$$

5. Leaching. *This process consists in treating the powdered ore with a suitable reagent (such as acids, bases or other chemicals) which can selectively dissolve the ore but not the impurities.*

In the **Baeyer process**, pure aluminium oxide (Al_2O_3) is obtained from the bauxite ore (which contains impurities of Fe_2O_3 and silicates) by treating the powdered ore with a strong (45%) solution

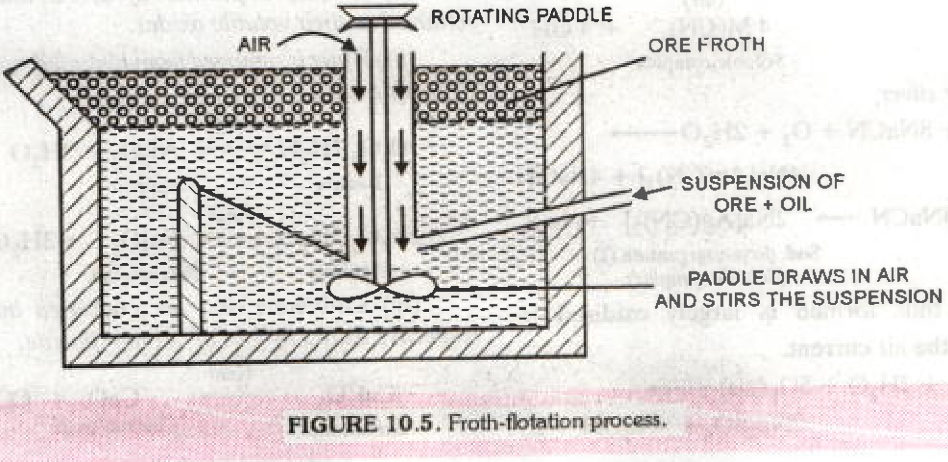

FIGURE 10.5. Froth-flotation process.

of NaOH when alumina (Al_2O_3) dissolves forming sodium meta-aluminate leaving behind impurities which are filtered off.

$$\underset{\text{Alumina}}{Al_2O_3 . 2H_2O\,(s)} + 2NaOH\,(aq) + H_2O\,(l) \longrightarrow \underset{\text{Sod. meta-aluminate}}{2Na[Al(OH)_4]\,(aq) \text{ or } 2NaAlO_2\,(aq)} + 4H_2O\,(l)$$

The solution of sodium aluminate is filtered, cooled and its pH adjusted downward either by dilution or by neutralization with CO_2 when aluminium hydroxide gets precipitated ; seeding with a little freshly precipitated aluminium hydroxide quickens the process.

$$Na[Al(OH)_4]\,(aq) \xrightarrow[\text{or } CO_2]{\text{Dilution}} Al(OH)_3\,(s) \downarrow + NaOH\,(aq)$$

Aluminium hydroxide, obtained as above, is filtered, washed and finally heated to about 1473 K to get pure alumina (Al_2O_3).

$$2\,Al(OH)_3 \xrightarrow{1473\text{ K}} Al_2O_3 + 3H_2O$$

Leaching is also used for extracting precious metals like silver and gold by converting these metals or their ores into their soluble complexes.

In this process, the finely powdered argentite or the native silver or gold is treated with a dilute solution (0.5 %) of sodium or potassium cyanide while a current of air is continuously passed. As a result, silver and gold pass into solution forming their respective soluble complex cyanides while the impurities remain unaffected which are filtered off. Thus :

$$4\,M + 8\,CN^- + 2\,H_2O + \underset{\text{(air)}}{O_2} \longrightarrow \underset{\text{Soluble complex}}{4\,M(CN)_2^-} + 4\,OH^-$$

(*i*) *For silver,*

$$4Ag + 8NaCN + O_2 + 2H_2O \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

$$\text{or } Ag_2S + 4NaCN \longrightarrow \underset{\substack{\text{Sod. dicyanoargentate (I)}\\ \text{(Soluble complex)}}}{2Na[Ag(CN)_2]} + Na_2S$$

Na_2S thus formed is largely oxidised to Na_2SO_4 by the air current.

$$4Na_2S + 2H_2O + 5O_2\text{(air)} \longrightarrow 2Na_2SO_4 + 4NaOH + 2S$$

(*ii*) *For gold,*

$$4Au + 8KCN + O_2 + 2H_2O \longrightarrow \underset{\substack{\text{Pot. dicyanoaurate (I)}\\ \text{(Soluble complex)}}}{4K[Au(CN)_2]} + 4\,KOH$$

III. Extraction of Crude Metals — Reduction/Oxidation

The process used to obtain metals in free state from concentrated ores is called extraction.

Since many metals can be easily obtained from their respective oxides by reduction (electronation), therefore, the extraction of metals acutally involves the following two chemical processes :

1. *Conversion of the ore into metallic oxide, i.e., de- electronation of ores.*

2. *Reduction or electronation of the metallic oxide to the free metal.*

1. Conversion of the ore into metallic oxide or de-electronation of ores. Metals are usually present in ores as hydrated oxides (hydroxides), carbonates and sulphides. Depending upon the nature of the minerals present in the ores, the following two methods are used for conversion of ores into their respective oxides.

(a) Calcination.

It is the process of converting an ore into its oxide by heating it strongly below its melting point either in absence or limited supply of air.

This method is commonly used to convert metal carbonates and hydroxides to their respective oxides. During the process of calcination, the following chemical changes occur :

(*i*) *Moisture is driven out.*

(*ii*) *Volatile impurities of S, As and P are removed as their volatile oxides.*

(*iii*) *Water is removed from hydrated oxides and hydroxide ores.*

$$\underset{\text{Bauxite}}{Al_2O_3.2H_2O} \xrightarrow{\text{Heat}} \underset{\text{Alumina}}{Al_2O_3} + 2H_2O$$

$$\underset{\text{Limonite}}{Fe_2O_3.3H_2O} \xrightarrow{\text{Heat}} \underset{\text{Ferric oxide}}{Fe_2O_3} + 3H_2O$$

(*iv*) *Carbonate ores are converted into their respective oxides by loss of carbon dioxide.*

$$\underset{\text{Limestone}}{CaCO_3} \xrightarrow{\text{Heat}} \underset{\text{Calcium oxide}}{CaO} + CO_2$$

$$\underset{\text{Dolomite}}{CaCO_3.MgCO_3} \xrightarrow{\text{Heat}} CaO + MgO + 2\,CO_2$$

$$\underset{\text{Malachite}}{CuCO_3.Cu(OH)_2} \xrightarrow{\text{Heat}} 2\,CuO + H_2O + CO_2$$

$$\underset{\text{Calamine}}{ZnCO_3} \xrightarrow{\text{Heat}} ZnO + CO_2$$

(v) It makes the ore porous and hence easily workable in subsequent stages. Calcination is usually carried out in a *reverberatory furnace* (Fig. 10.6).

The concentrated ore is placed on the hearth of the furnace and heated by flames deflected from the roof.

(b) Roasting. *It is the process of converting an ore into its metallic oxide by heating strongly at temperature insufficient to melt in excess of air.* This process is commonly used for sulphide ores. The following changes occur during roasting :

(i) Moisutre is removed.

(ii) Organic matter is destroyed.

(iii) Non-metallic impurities like that of sulphur, phosphorus and arsenic are oxidised and are removed as volatile gases.

$$S_8 + 8\,O_2 \longrightarrow 8\,SO_2 \uparrow \ (\textit{Sulphur dioxide})$$

$$P_4 + 5\,O_2 \longrightarrow P_4O_{10} \uparrow \ (\textit{Phosphorus pentoxide})$$

$$4\,As + 3\,O_2 \longrightarrow 2\,As_2O_3 \uparrow \ (\textit{Arsenious oxide})$$

(iv) Ores are generally converted into metallic oxides.

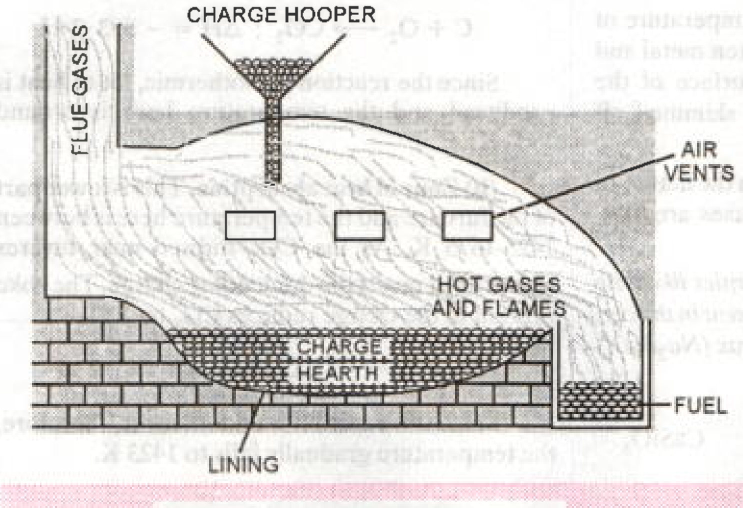

FIGURE 10.6. Reverberatory furnace.

$$\underset{\text{Zinc sulphide}}{2\,ZnS} + 3\,O_2 \longrightarrow \underset{\text{Zinc oxide}}{2\,ZnO} + 2\,SO_2 \uparrow$$

$$\underset{\text{Lead sulphide}}{2\,PbS} + 3O_2 \longrightarrow \underset{\text{Lead oxide}}{2\,PbO} + 2\,SO_2 \uparrow$$

(v) It makes the ore porous and hence easily workable in subsequent stages.

Like calcination, roasting is also carried out in a *reverberatory furnace* (Fig. 10.6). During roasting air vents are kept open while during calcination, air vents are either partially or completely closed.

2. Reduction or electronation of the oxide to the free metal. The roasted or the calcined ore is then converted into the free metal by reduction with a suitable reducing agent. The choice of the reducing agent, however, depends upon how difficult the reduction process is. If the metal to be extracted is very reactive like the alkali metals or the alkaline earth metals, then the reduction of the oxide can be done only by the electrolytic method. The oxides of less reactive metals like those of copper, lead, tin etc., can be reduced by a number of reducing agents. The final choice of the reducing agent is decided by the energetics and economics of the reduction process.

The various reduction processes have been divided into the following four categories :

(*a*) Chemical reduction

(*b*) Auto-reduction

(*c*) Displacement method

(*d*) Electrolytic reduction

(a) Chemical Reduction

(i) Carbon as a reducing agent – Smelting

The process of extracting the metal by reduction of its oxide ore with carbon (in form of coal, coke, charcoal and carbon monoxide) is called smelting.

In this process, the roasted or the calcined ore is mixed with a calculated quantity of carbon (coal or coke) and heated to a high temperature above its melting point in a reverberatory furnace when carbon reduces the metal oxide to the free metal. For example,

$$ZnO + C \longrightarrow Zn + CO \uparrow$$

$$SnO_2 + 2C \xrightarrow{1473-1573\ K} Sn + 2CO \uparrow$$

$$PbO + C \longrightarrow Pb + CO \uparrow$$

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO \uparrow$$

The carbon monoxide thus evolved or produced by incomplete combustion of carbon can also bring about the reduction of metal oxides to free metals as shown below :

$$ZnO + CO \xrightarrow{1600\ K} Zn + CO_2 \uparrow$$

$$Fe_2O_3 + CO \xrightarrow{823\ K} 2FeO + CO_2 \uparrow$$

$$FeO + CO \xrightarrow{1123\ K} Fe + CO_2 \uparrow$$

The metal thus produced is in the molten state and is tapped out from the furnace. Sometimes metals may be obtained in the vapour state, *e.g.*, Zn. In such cases, smelting cannot be carried out in an open furnace.

Flux. If the calcined or the roasted ore still contains non-fusible impurities of earthy matter, an additional substance called the flux is usually added during the reduction process. Thus,

Flux *is a substance which chemically combines with gangue (earthy impurities) which may still be present in the roasted or the calcined ore to form an easily fusible material called the* **slag.**

$$\text{Flux} + \text{Gangue} \longrightarrow \text{Slag}$$

The slag formed melts at the temperature of the furnace. It is insoluble in the molten metal and also being lighter floats over the surface of the molten metal from where it can be skimmed off from time to time.

Types of fluxes. Depending upon the nature of the impurities present in the ore, fluxes are classified into the following two types :

(i) Acidic fluxes. *For basic impurities like lime or metallic oxides (FeO, MnO etc.) present in the ore,* **acidic fluxes** *like silica (SiO_2) and borax ($Na_2B_4O_7 . 10H_2O$) etc. are used.*

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

$$\underset{(Basic\ impurities)}{FeO} + \underset{(Acidic\ flux)}{SiO_2} \longrightarrow \underset{(Fusible\ slag)}{FeSiO_3}$$

(ii) Basic fluxes. *For acidic impurities like silica (SiO_2), phosphorus pentoxide (P_4O_{10}) etc.* present *in the ore,* **basic fluxes** *like limestone ($CaCO_3$), magnesite ($MgCO_3$), haematite (Fe_3O_4) etc., are used.*

$$SiO_2 + CaCO_3 \longrightarrow CaSiO_3 + CO_2 \uparrow$$

$$\underset{(Acidic\ impurities)}{SiO_2} + \underset{(Basic\ flux)}{MgCO_3} \longrightarrow \underset{(Fusible\ slag)}{MgSiO_3} + CO_2 \uparrow$$

Production of Iron from the oxide ore

Iron is the most important industrial metal. Its extraction is carried out in a blast furnace (Fig. 10.7). It is a tall cylindrical furnace made of steel lined with fire clay refractory bricks. It is narrow at the top and has a double cup and cone arrangement for introduction of charge and outlet for waste gases. The charge consisting of calcined iron oxide (haematite, Fe_2O_3 and magnetite, Fe_3O_4), coke and limestone is fed into the top of the furnace. A blast of air pre-heated to about 1000 K is blown in by means of narrow pipes (called tuyeres) at the base of the furnace.

Reactions taking place in the furnace.

The following reactions occur in the blast furnace.

(i) Zone of combustion. Near the tuyeres, coke burns to form carbon dioxide.

$$C + O_2 \longrightarrow CO_2\ ;\ \Delta H = -393 \cdot 3\ kJ$$

Since the reaction is exothermic, lot of heat is produced and the temperature here is around 1800 K.

(ii) Zone of heat absorption. This is lower part of the furnace and the temperature here is between 1423-1673 K. As the CO_2 formed near tuyeres moves up, it meets the descending charge. The coke present in the charge reduces CO_2 to CO.

$$CO_2 + C \longrightarrow 2CO\ ;\ \Delta H = +163 \cdot 2\ kJ$$

Since this reaction is endothermic, therefore, the temperature gradually falls to 1423 K.

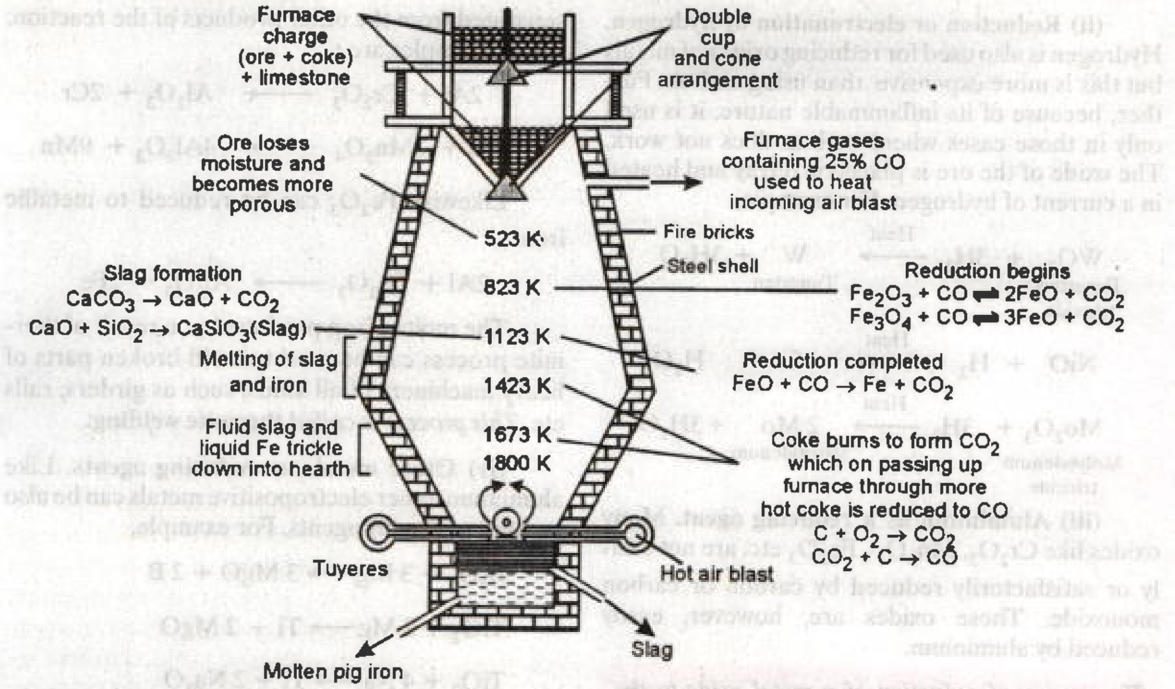

FIGURE 10.7. Blast furnace for the manufacture of pig or cast iron.

(iii) Zone of slag formation. It is the middle part of the furnace. The temperature here is around 1123 K. In this region, limestone decomposes to form CaO and CO_2. The CaO thus formed acts as a flux and combines with silica (present as an impurity) to form fusible calcium silicate slag

$$CaCO_3\,(s) \longrightarrow CaO\,(s) + CO_2\,(g)$$

$$CaO + SiO_2 \longrightarrow \underset{\text{Calcium silicate (slag)}}{CaSiO_3}$$

(iv) Zone of reduction. This is the upper part of the furnace. The temperature here is around 823 K. Here the ores are reduced to FeO by CO.

$$Fe_2O_3 + CO \xrightarrow{823\text{ K}} 2\,FeO + CO_2$$

$$Fe_3O_4 + CO \xrightarrow{823\text{ K}} 3\,FeO + CO_2$$

But the further reduction of FeO to Fe by CO occurs around 1123 K

$$FeO + CO \xrightarrow{1123\text{ K}} Fe + CO_2$$

However, direct reduction of iron ores, *i.e.* haematite, magnetite etc., which might have escaped reduction around 823 K, gets completely reduced to iron by carbon above 1123 K.

$$Fe_2O_3 + 3\,C \xrightarrow{>1123\text{ K}} 2\,Fe + 3\,CO$$

(v) Zone of fusion. This is the lower part of the furnace. Temperature here is in between 1423–1673 K. In this region, spongy iron melts and dissolves some C, S, P, SiO_2 etc. $CaSiO_3$ slag also melts in this region. Both the molten slag and molten iron trickle down into hearth where they form two separate layers. The molten $CaSiO_3$ slag being lighter forms the upper layer while molten iron being heavier forms the lower layer. The two liquids are periodically tapped off. The iron thus obtained from the furnace is called **pig iron or cast iron.**

(ii) Reduction or electronation by hydrogen. Hydrogen is also used for reducing oxides of metals but this is more expensive than using carbon. Further, because of its inflammable nature, it is used only in those cases where carbon does not work. The oxide of the ore is placed in a tray and heated in a current of hydrogen. For example,

$$\underset{\text{Tungsten trioxide}}{WO_3} + 3H_2 \xrightarrow{\text{Heat}} \underset{\text{Tungsten}}{W} + 3H_2O$$

$$NiO + H_2 \xrightarrow{\text{Heat}} Ni + H_2O$$

$$\underset{\text{Molybdenum trioxide}}{Mo_2O_3} + 3H_2 \xrightarrow{\text{Heat}} \underset{\text{Molybdenum}}{2\,Mo} + 3H_2O$$

(iii) Aluminium as a reducing agent. Many oxides like Cr_2O_3, Mn_3O_4, Fe_2O_3 etc. are not easily or satisfactorily reduced by carbon or carbon monoxide. These oxides are, however, easily reduced by aluminium.

The process of reduction of a metal oxide to the metal with the help of aluminium powder as the reducing agent is called aluminothermy or Goldschmidt thermite process.

In this process, *a mixture of aluminium powder and the metallic oxide (say Cr_2O_3, Mn_3O_4 etc.) called* **thermite** is ignited in a closed crucible by inserting a burning magnesium ribbon into the ignition mixture consisting of magnesium powder and barium peroxide (Fig. 10.8). This process is called **thermite process** or the **aluminothermic process.** Metals like manganese and chromium are obtained by this process.

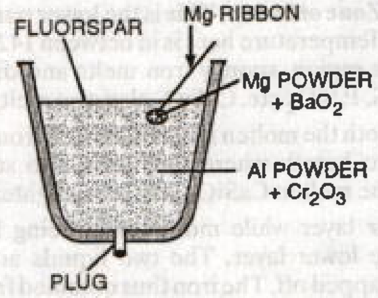

FIGURE 10.8. Aluminothermic process.

The ignition powder burns to produce a large amount of heat. As a result, the metals are obtained in the molten state and hence can be easily separated from the other products of the reaction. A few examples are :

$$2Al + Cr_2O_3 \longrightarrow Al_2O_3 + 2Cr$$

$$8Al + 3Mn_3O_4 \longrightarrow 4Al_2O_3 + 9Mn$$

Likewise Fe_2O_3 can be reduced to metallic iron.

$$2Al + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$$

The molten iron produced as a result of thermite process can be used to weld broken parts of heavy machinery of all kinds, such as girders, rails etc. *This process is called* **thermite welding.**

(iv) Other metals as reducing agents. Like aluminium, other electropositive metals can be also be used as usually agents. For example,

$$B_2O_3 + 3\,Mg \longrightarrow 3\,MgO + 2\,B$$

$$TiO_2 + 2\,Mg \longrightarrow Ti + 2\,MgO$$

$$TiO_2 + 4\,Na \longrightarrow Ti + 2\,Na_2O$$

Instead of using oxides of metals, their halides can also be used. For example, titanium can be obtained from titanium tetrachloride by reduction with magnesium **(Kroll's process).**

$$TiCl_4 + 2Mg \longrightarrow Ti + 2MgCl_2$$

(b) Auto-reduction or Self reduction or Self electronation.

Some metal sulphides can be used for the reduction of their own oxides. Thus, when the sulphide ores of the less active metals (whose oxides are unstable towards heat like Hg, Cu, Pb etc.) are roasted in an excess of air, a part of these sulphides are oxidised to their oxides which further react with more of the sulphide ore to yield the metal. *This process is called* **self-reduction or auto-reduction.** For example,

(*i*) $HgS\,(s) + O_2\,(g) \longrightarrow Hg\,(g) + SO_2\,(g)$

or $2\,HgS\,(s) + 3\,O_2\,(g) \longrightarrow 2\,HgO\,(s) + 2\,SO_2\,(g)$

$2\,HgO\,(s) \longrightarrow Hg\,(g) + O_2\,(g)$

also $2\,HgO\,(s) + HgS\,(s) \longrightarrow 3\,Hg\,(g) + SO_2\,(g)$

(*ii*) $\underset{\text{Galena}}{2PbS} + 3O_2 \longrightarrow 2PbO + 2SO_2$

$$2PbO + PbS \longrightarrow 3Pb + SO_2$$

Sometimes the sulphide ore may be oxidised to sulphate which is then reduced to the free metal by the excess of the sulphide ore.

$$PbS + 2O_2 \longrightarrow PbSO_4$$

$$PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2$$

(*iii*) $\underset{\text{Copper pyrites}}{2Cu_2S} + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

The roasting of the sulphides are discussed above is usually carried out in a reverberatory furance (Fig. 10.6).

(c) Displacement method.

Some metals are reduced by displacement by a more reactive metal from their soluble complexes. For example, silver and gold are obtained from their complex cyanides (obtained during leaching) by addition of more electropositive zinc metal.

$$2\,Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CH)_4] + 2\,Ag \downarrow$$

$$2\,K[Au(CN)_2] + Zn \longrightarrow K_2[Zn(CN)_4] + 2\,Au \downarrow$$

(d) Electrolytic method.

Active metals such as alkali metals, alkaline earth metals, aluminium etc. cannot be obtained by reduction of their respective oxides with carbon. This is due to the reason that the oxides of these metals are very stable and thus have to be heated very strongly with carbon in order to reduce them to the metallic state. Further, at such high temperatures, metals liberated combine with carbon forming their respective carbides. Thus, such metals are extracted by the electrolysis of their molten or fused oxides, hydroxides or chlorides. The metal is liberated at the cathode.

The process of extraction of metals by electrolysis of their fused salts is called electrometallurgy. In this process, electrons serve as the reducing agent.

Some important examples are :

(i) Electrolysis of NaCl. The *s*-block elements, *i.e.*, alkali (group 1) and alkaline earth materials (group 2) which occur as chlorides or oxosalts are converted into their chlorides. When electric current is passed through a fused chloride, metal (M^{n+}) ions are discharged at cathode and deposited. Similarly during the electrolysis of brine (NaCl solution) using mercury cathodes, the Na^+ is discharged at cathode and forms an amalgam. On the basis of electrochemical series, the liberation of H_2 should have occurred at the cathode. However, due to high H_2 overvoltage at the Hg cathode, liberation of Na occurs in preference to H_2 gas.

$$\underset{(Molten)}{NaCl} \longrightarrow Na^+ + Cl^- \quad (\textit{Ionization})$$

At cathode : $Na^+ + e^- \longrightarrow Na$ (*deposited*)

At anode : $Cl^- - e^- \longrightarrow Cl$

$$Cl + Cl \longrightarrow Cl_2 \uparrow$$

(ii) Electrolysis of alumina. Metals other than *s*-block elements can also be extracted by electrolysis of fused compounds. For example, in **Hall and Heroult process**, aluminium is obtained by electrolysis of a fused mixture of purified alumina (Al_2O_3) and cryolite (Na_3AlF_6) at 1150-1173 K, when molten aluminium collects at the cathode.

IV. Refining or Purification of Metals.

The metals obtained by any of the methods discussed above are still impure and hence are called crude metals. The impurities generally present in the crude metals are :

(*i*) *Other metals* – produced by simultaneous reduction of their respective oxides originally present in the ore.

(*ii*) *Non-metals* – like silicon and phosphorus formed by reduction in the furnace.

(*iii*) Unreacted oxides and sulphides of the metals, and

(*iv*) Substances taken up in the furnace, *e.g.*, residual slag, flux etc.

The crude metals are, therefore, purified or refined. The method actually used for purification depends upon the nature of the metal and the nature of the impurities to be removed.

The process of purifying the crude metals is called refining.

Some common methods used for refining of metals are discussed below :

1. Distillation Process. This method is employed for purification of volatile metals like zinc, mercury, cadmium etc. The impure metal is heated in an iron retort and the vapours are condensed in separate receivers. The pure metal distils over leaving behind the non-volatile (having higher boiling points) impurities in the retort.

2. Liquation Process. *This method is used for purification of such metals as contain impurities which are less fusible than the metals themselves, i.e., the melting points of the metals are lower than those of the impurities.* The crude metal is heated in an inert atmosphere of carbon monoxide on the sloping hearth of a reverberatory furnace (Fig. 10.9) when the metal melts and flows down into the receiver leaving the infusible impurities on the hearth. Metals like *tin* and *lead* are purified by this method.

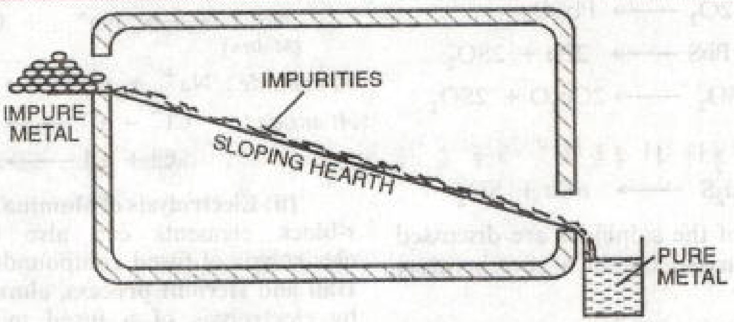

FIGURE 10.9. Liquation process.

3. Oxidation Process. *This process of metal refining is used when the impurities present have a greater affinity for oxygen and are thus oxidised more readily than the metal itself.* The impure metal is melted on the hearth of a suitable furnace and the molten metal thus obtained is brought in contact with air. The impurities are oxidised and form a scum on the surface of the molten metal from where it is skimmed off. Sometimes the oxide of the metal itself is added which supplies the necessary oxygen to the impurities for oxidation. For example, iron oxide is added to molten steel and copper oxide to molten copper. The various oxidation processes employed for different metals are briefly described below :

(*i*) **Bessemerisation.** This process is carried out in a specially designed furnace called a bessemer converter (Fig. 10.10). The impure metal is melted and a hot blast of air is passed through it when impurities are oxidised. Pig iron and copper are purified by this method.

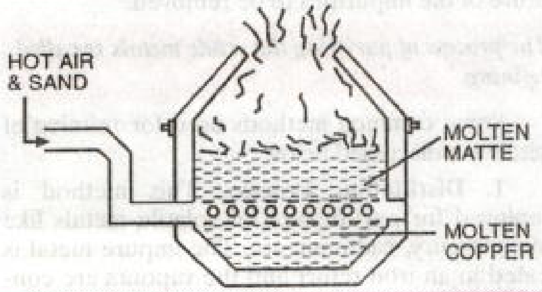

FIGURE 10.10. A Bessemer converter for refining of matte (impure copper).

Another converter which has been used is called the **Pierce-Smith converter.** It consists of a large horizontal steel drum resting upon rollers. Air is forced into the molten crude metal through tuyeres. During the process oxidation of impurities occurs and the heat thus evolved raises the temperature to about 2673 K.

(*ii*) **Cupellation.** *This method is applied when the impure metal contains impurities of other metals which form volatile oxides.* For example, last traces of lead are removed from silver by this process.

A cupel is an oval shaped pan with shallow hearth and made up of bone ash or cement. The impure metal is heated in a cupel in presence of a blast of air or oxygen. The impurities are converted into their volatile oxides which escape along with the blast of air or oxygen while the pure metal is left behind. Thus, when impure silver containing lead as impurity is heated in a cupel along with a blast of air, lead is oxidised to litharge (PbO) which being volatile escapes alongwith the blast while the shining mass of silver remains in the cupel.

(*iii*) **Poling.** *This method is employed when the crude metal contains impurities of the oxide of the metal itself.* For example, impure copper contains

Cu_2O and impure tin contains stannic oxide (SnO_2).

Air is blown through crude molten metal to which a suitable flux may be added. As a result, impurities get oxidised and escape either as gases such as CO_2, SO_2 etc. or pass into slag. The surface of molten metal is then covered with low sulphur coke, *i.e.*, anthracite (to prevent oxidation of the metal) and stirred with green wooden poles. At this high temperature of the molten metal, the wood liberates gases such as methane which reduce any oxide present in the metal (*i.e.* Cu_2O in blister copper) to copper metal.

$$3\,Cu_2O + CH_4 \longrightarrow 6\,Cu + 2H_2O + CO$$

4. Electro-refining. A large number of metals such as copper, silver, gold, lead, nickel, chromium zinc, aluminium etc. are refined by this method.

In this method, the impure metal is converted into a block which forms the anode while cathode is made up of a pure strip of the same metal (Fig. 10.11). These electrodes are suspended in an electrolyte which is the solution of a soluble salt of the metal usually a double salt of the metal. When electric current is passed, metal ions from the electrolyte are deposited at the cathode in the form of pure metal while an equivalent amount of metal dissolves from the anode and goes into the electrolyte solution as metal ions. The process takes place as under :

Anode : $M \longrightarrow M^{n+} + ne^-$

Cathode : $M^{n+} + ne^- \longrightarrow M$

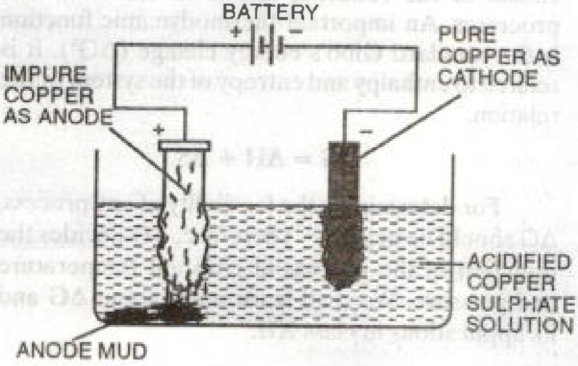

FIGURE 10.11. Electro-refining of metals.

The net result is the transfer of pure metal from the anode to the cathode. The voltage applied for electrolysis is such that the impurities of more electropositive metals remain as ions in the bath whereas impurities of the less electropositive metals remain unionized and settle down under the anode as *anode mud or anode sludge.* Thus in the electrolytic refining of copper, more basic metals like zinc remain in the solution as cations, whereas less basic metals like Au, Ag, Te etc. form the anode mud.

5. Zone refining (*Fractional crystallization*). *This method is employed for preparing extremely pure metals*. Germanium, silicon, boron, gallium and indium are purified by this method.

This method is based upon the principle that when a molten solution of the impure metal is allowed to cool, the pure metal crystallises out while the impurities remain in the melt.

In this method, the impure metal is converted into a bar which is heated at one end with a moving circular heater (Fig. 10.12) so that this end melts and forms a molten zone or the melt. As the heater is slowly moved along the length of the rod, the pure metal crystallises out of the melt whereas the impurities pass into the adjacent molten zone. This process is repeated several times till the impurities are completely driven to one end of the rod which is then cut off and discarded. *The process is usually carried out in an inert atmosphere to prevent the oxidation of the metal.* Semiconductors like silicon, germanium and gallium are purified by this method. *The elements thus obtained are of high purity.* For example germanium prepared by this method contains as little as 7-10 ppm of impurities.

6. Vapour-phase refining. In this method, *the crude metal is freed from impurities by first converting it into a suitable volatile compound by heating it with a specific reagent at a lower temperature and then decomposing the volatile compound at some higher temperature to give the pure metal.* This method is illustrated by the following two processes :

(*i*) **Mond process.** It is used for refining of nickel. When impure nickel is heated in a current of CO at 330–350 K, it forms volatile nickel carbonyl leaving behind the impurities. The nickel carbonyl thus obtained is then heated to a higher

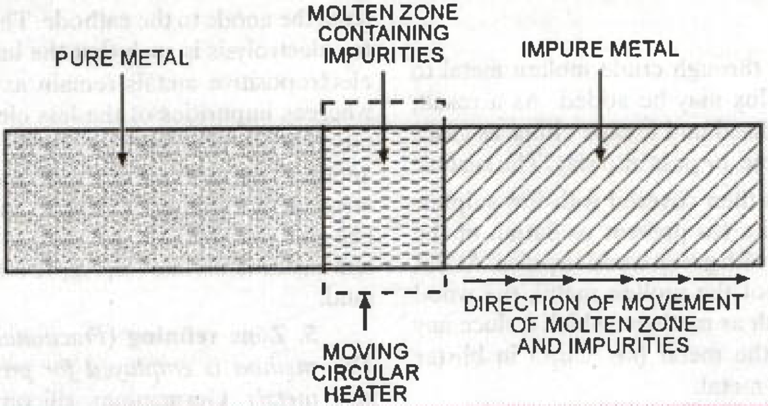

FIGURE 10.12. Zone-refining of metals.

temperature (450–470 K) when it undergoes thermal decomposition giving pure nickel.

$$\underset{\text{Impure}}{Ni} + 4\,CO \xrightarrow{330-350\text{ K}} \underset{\text{Nickel carbonyl}}{Ni(CO)_4}$$

$$Ni(CO)_4 \xrightarrow{450-470\text{ K}} \underset{\text{Pure}}{Ni} + 4\,CO$$

(*ii*) **Van Arkel method.** This method is used for preparation of utra-pure metals such as titranium and zirconium which are used in space technology. In this method, zirconium is heated in iodine vapours at about 870 K to form volatile zirconium tetraiodide which when heated over a tungsten filament at 2075 K decomposes to give pure zirconium.

$$\underset{(Impure)}{Zr\,(s)} + \underset{(I_2\,vapour)}{2\,I_2\,(g)} \xrightarrow{870\text{ K}} ZrI_4\,(g) \xrightarrow[\text{Tungsten filament}]{2075\text{ K}} \underset{(Pure)}{Zr\,(s)} + 2\,I_2\,(g)$$

Similarly,

$$\underset{(Impure)}{Ti(s)} + 2I_2(s) \xrightarrow{523\text{ K}} TiI_4(g) \xrightarrow{1700\text{ K}} \underset{(Pure)}{Ti(s)} + 2I_2(g)$$

7. Chromatographic method. This method is based upon the principle that *various components of a mixture are adsorbed to different extents on an adsorbent.* In column chromatography, an adsorbent such as Al_2O_3 is packed in a glass column. The mixture to be separated or purified is dissolved in a suitable solvent and applied to the top of the column. Depending upon their polarity, the components of the mixture are adsorbed to different extents on the column. When the column is extracted (or eluted) with a solvent (eluent), the weakly adsorbed component is eluted first followed by the more strongly adsorbed and so on. *This technique is especially suitable for such elements which are available only in minute quantities and the impurities are not very much different from the element to be purified.*

A flow-sheet diagram of the metallurgical processes discussed above is given in Fig. 10.13.

10.12. Thermodynamics of Metallurgy

Thermodynamic aspects of the reactions used in metallurgical operations are very important. These can help in deciding the temperature and the choice of the reducing agents in the reduction processes. An important thermodynamic function is the standard Gibb's energy change ($\Delta G°$). It is related to enthalpy and entropy of the system by the relation,

$$\Delta G = \Delta H + \Delta S.$$

For determining the feasibility of any process, ΔG should be negative. Therefore, ΔG decides the direction of the process at constant temperature and pressure. We shall learn more about ΔG and its applications in class XII.

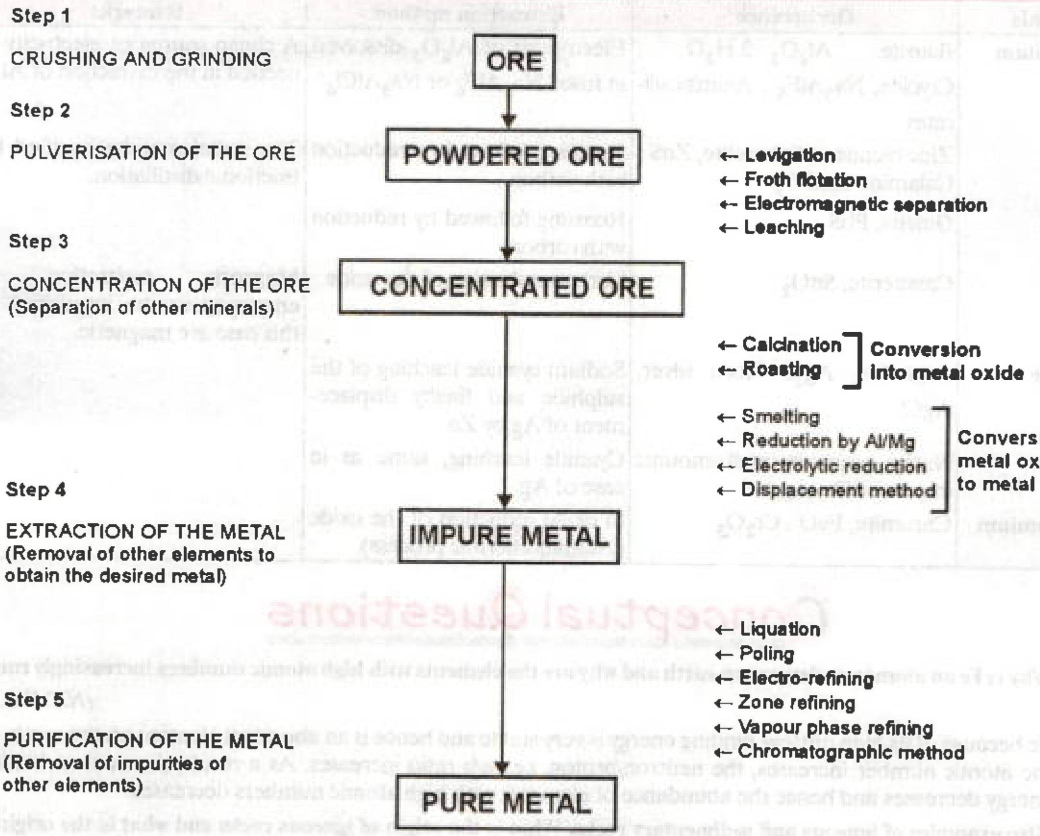

FIGURE 10.13. Flow-sheet diagram for general mutallurgical operations. In the above diagram, functions of the processes are given on the left white the methods used are written on the right.

Summary of the methods of extraction of some common metals

Metals	Occurrence	Extraction method	Remark
1. Lithium	Spodumene $LiAlSi_2O_6$; Lepidolite, $(Li, Na, K)_2 Al_2(SiO_3)_3 Fe(OH)$	Electrolysis of fused LiCl/KCl	Because of high reactivity these are extracted under anhydrous conditions
2. Sodium	Rock salt, NaCl ; Feldspar, $Na_3AlSi_3O_8$	Electrolysis of fused $NaCl/CaCl_2$, "	
3. Magnesium	Carnallite, $KCl.MgCl_2 \cdot 6H_2O$; Magnesite, $MgCO_3$	Electrolysis of fused MgO or $MgCl_2 / CaCl_2$	Carbon reduction is not possible with alkaline earths since a carbide is formed with them.
4. Calcium	Limestone, $CaCO_3$; Dolomite $MgCO_3 . CaCO_3$; Gypsum, $CaSO_4 . 2H_2O$	Electrolysis of fused $CaCl_2 / CaF_2$	"
5. Copper	Copper pyrites, $CuFeS_2$; Cuprite, Cu_2O ; Malachite, $CuCO_3 . Cu(OH)_2$	Roasting of sulphide. Initially formed Cu_2O reduces Cu_2S to Cu	It is an example of auto-reduction. Sulphuric acid leaching is also employed.

Metals	Occurrence	Extraction method	Remark
6. Aluminum	Bauxite, $Al_2O_3 . 2 H_2O$; Cryolite, Na_3AlF_6 ; Aluminosilicates	Electrolysis of Al_2O_3 dissolved in fused Na_3AlF_6 or Na_3AlCl_6	A cheap source of electricity is needed in the extraction of Al.
7. Zinc	Zinc blende or Sphalerite, ZnS ; Calamine $ZnCO_3$	Roasting followed by reduction with carbon	The metal may be purified by fractional distillation.
8. Lead	Galena, PbS	Roasting followed by reduction with carbon.	
9. Tin	Cassiterite, SnO_2	Carbon reduction of the oxide	Magnetic separation is employed as the impurities in this case are magnetic.
10. Silver	Argentite, Ag_2S Horn silver, AgCl	Sodium cyanide leaching of the sulphide and finally displacement of Ag by Zn.	
11. Gold	Native, occurs in small amounts in ores of Cu, Ag etc.	Cyanide leaching, same as in case of Ag.	
12. Chromium	Chromite, $FeO . Cr_2O_3$	Si or Al reduction of the oxide (Aluminothermic process)	

Conceptual Questions

Q. 1. **Why is Fe an abundant element on earth and why are the elements with high atomic numbers increasingly rare ?** ***(N.C.E.R.T.)***

Ans. Fe because of its high nuclear binding energy is very stable and hence is an abundant element on the earth. As the atomic number increases, the neutron/proton, *i.e.*, *n*/*p* ratio increases. As a result, the nuclear binding energy decreases and hence the abundance of elements with high atomic numbers decreases.

Q. 2. **Give examples of igneous and sedimentary rocks. What is the origin of igneous rocks and what is the origin of sedimentary rocks ?**

Ans. **Igneous rocks :** granite, basalt, gabbro etc.

Sedimentary rocks : limestone, sandstone, shale, dolomite etc.

Origin. Igneous rocks are formed by gradual cooling and solidification of magma.

Sediments are obtained by weathering of igneous rocks. These are brought by rain water, wind, CO_2 and humic acid to river banks, sea and lake beds where they get deposited to form sedimentary rocks.

Q. 3. **Metals like Cu, Ag, Zn, Hg and Pb occur in nature as sulphides rather than oxides ? Why ?**

Ans. The cations of these metals, *i.e.*, Cu^+, Zn^{2+}, Ag^+ and Hg^{2+} (*pseudo inert gas configuration*, $(n-1)\, s^2\, p^6\, d^{10}$) and Pb^{2+} (*inert pair configuration*, $((n-1)\, s^2\, p^6\, d^{10}\, ns^2)$) have high polarizing power and hence can easily polarize the bigger sulphide ion than the smaller oxide ion. As a result, sulphides of these metals are more stable than the oxides and hence these metals occur in nature in form of their sulphides rather than oxides.

Q. 4. **In general which metals do you expect to occur in the native state in nature ? Give examples.** ***(N.C.E.R.T.)***

Ans. Metals such as Cu, Ag, Au, Pt etc. which lie below hydrogen in the electrochemical series are not readily attacked by oxygen, moisture and CO_2 of the atmosphere and hence occur in the native state in nature.

Q. 5. **Copper and silver lie below in the electrochemical series and yet they are found in the combined state as sulphides in nature. Comment.** ***(N.C.E.R.T.)***

Ans. As explained in Q. 3, due to high polarising power of their cations, their sulphides are even more stable than the metals.

Q. 6. **Metals usually do not occur in nature as nitrates. Why ?**

Ans. Nitrates of all metals are soluble in water. Therefore, if metal nitrates were present in the crust of earth, these would be slowly and gradually washed by rain water into the sea. It is because of this reason that metals usually do not occur in nature as nitrates.

Q. 7. **How does NaCN act as a depressant in preventing ZnS from forming the froth ?** **(N.C.E.R.T.)**

Ans. NaCN combines with ZnS to form a complex, $Na_2[Zn(CN)_4]$ on the surface of ZnS and thus prevents it from forming the froth.

$$ZnS + 4\,NaCN \longrightarrow \underset{\text{Sod. tetracyanozincate (II)}}{Na_2[Zn(CN)_4]} + Na_2S$$

Q. 8. **Why is it advantageous to roast a sulphide ore to the oxide before reduction ?** (N.C.E.R.T.)

Ans. The standard free energies ($\Delta G°$) of formation of most of the sulphides are greater than those of CS_2 and H_2S (CS_2 is, in fact, is an endothermic compound). Therefore, neither carbon nor hydrogen can reduce metal sulphides to metal. In contrast, the standard free energies of formation of oxides are much lower than those of SO_2 and hence oxidation of metal sulphides to metal oxides is thermodynamically favourable. Therefore, it is the common practice to roast sulphide ore to the oxide before reduction.

Q. 9. **What is the thermodynamic consideration in the choice of a reducing agent in metallurgy ?** (N.C.E.R.T.)

Ans. For any spontaneous reaction, the free energy change (ΔG) must be negative

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

ΔH is the enthalpy change, during the reaction, T is the absolute temperature and ΔS is the change in entropy during the reaction.

Let us investigate the ΔG during the conversion of a metal into its oxide

$$M + O_2 \longrightarrow MO_2$$

In this reaction, dioxygen—a gas is used up, and metal oxide—a solid is formed. Since gases have higher entropy than liquids and solids, therefore, during this reaction, ΔS becomes negative. Thus, if temperature is raised, then $T\Delta S$ becomes more negative. Since $T\Delta S$ is subtracted in the equation, therefore, ΔG becomes less negative. *Thus, the free energy change increases with an increase in temperature.*

Consider the Ellingham diagram (Fig. 10.14) for some metal oxides.

From the diagram it is evident that metals for which free energy of formation of their oxides is more negative can reduce those metal oxides for which the free energy of formation of their respective oxides is less negative. In other words, any metal will reduce the oxide of other metals which lie above it in the Ellingham diagram because the free energy change will become more negative by an amount equal to the difference between the two graphs at that particular temperature. Thus Al reduces FeO, CrO and NiO in Thermite reaction but Al will not reduce MgO at temperature below 1773 K. From the above discussion, it is clear that thermodynamic considerations help us in choosing a suitable reducing agent in metallurgy.

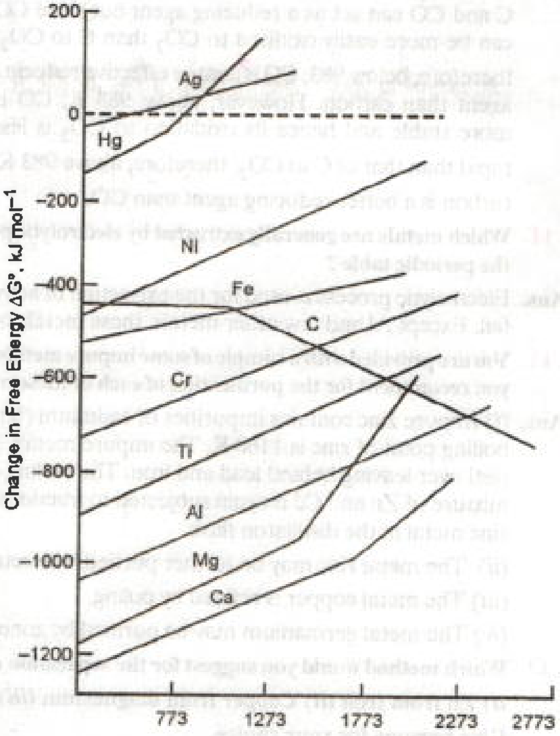

FIGURE 10.14. Ellingham diagram showing the change in free energy (ΔG) with temperature for oxides (based upon 1 mole of dioxygen in each case).

Q. 10. **Carbon monoxide is a more effective reducing agent than carbon below 983 K but above this temperature, reverse is true. How will you explain this ?** (N.C.E.R.T.)

Ans. When carbon reacts with dioxygen two reactions are possible :

$$C + O_2 \longrightarrow 2\,CO_2$$

$$2\,C + O_2 \longrightarrow 2\,CO$$

In the first reaction, the volume of CO_2 produced is the same as that of O_2 used, therefore, ΔS is very small and ΔG does not change with temperature. Thus, the graph of ΔG against T is almost horizontal (Fig. 10.15).

The second reaction produces two volumes of CO for every one volume of O_2 used. *Thus, ΔS is positive and hence ΔG becomes increasingly negative as the temperature increases.* Consequently its line on the Ellingham diagram slopes downwards (Fig. 10.15). The two lines for the reactions, $C \longrightarrow CO_2$ and $C \longrightarrow CO$ cross at 983 K. Below this temperature, the reaction leading to the formation of CO_2 is energetically more favourable but above 983 K, the formation of CO is preferred. In other words, below 983 K both C and CO can act as a reducing agent but since CO can be more easily oxidised to CO_2 than C to CO_2, therefore, below 983, CO is a more effective reducing agent than carbon. However, above 983 K, CO is more stable and hence its oxidation to CO_2 is less rapid than that of C to CO_2, therefore, above 983 K, carbon is a better reducing agent than CO.

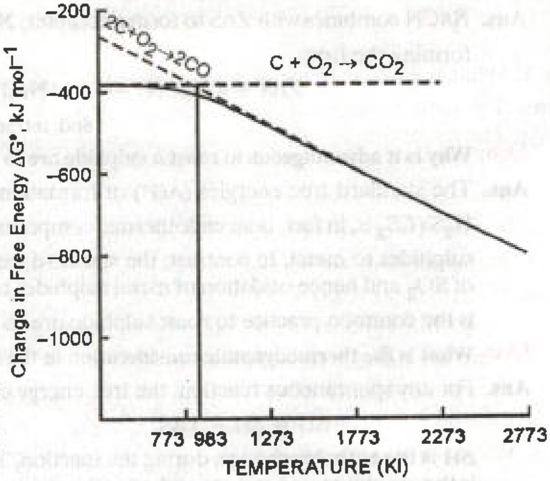

FIGURE 10.15. Ellingham diagram for carbon. (The composite curve is the solid line).

Q. 11. **Which metals are generally extracted by electrolytic processes ? Which positions these metals generally occupy in the periodic table ?** **(*N.C.E.R.T.*)**

Ans. Electrolytic process is used for the extraction of active metals like Na, Ca, Mg, Al etc. where all other methods fail. Except Al and few other metals, these metals belong to *s*-block elements.

Q. 12. **You are provided with a sample of some impure metals such as zinc, copper and germanium. Which methods would you recomment for the purification of each of these metals ?** **(*N.C.E.R.T.*)**

Ans. (*i*) Impure zinc contains impurities of cadmium (b.p. 1073 K), lead (b.p. 2024 K) and iron (b.p. 3273 K). The boiling point of zinc is 1180 K. The impure metals is distilled when zinc and cadmium with low boiling points distl over leaving behind lead and iron. The boiling points of Zn and Cd differ by about 100 K, therefore, the mixture of Zn and Cd is again subjected to fractional distillaton when low boiling Cd distils over leavng behind zinc metal in the distillaton flask.

(*ii*) The metal zinc may be further purfied by electrolytic refining as explained on page 10/17.

(*iii*) The metal copper is refined by poling.

(*iv*) The metal germanium may be purified by zone refining as explained on page 10/17-10/18.

Q. 13. **Which method would you suggest for the separation of the metals in the following mixtues ?**

(*i*) Zn from iron (*ii*) Copper from magnesium (*iii*) Rare earths.

Give reasons for your choice. **(*N.C.E.R.T.*)**

Ans. (*i*) Zn (b.p. 1180 K) can be easily separated from iron (b.p. 3273 K) by distillation.

(*ii*) A mixture of Cu and Mg metals is treated with dil. HCl when Mg dissolves forming $MgCl_2$ while copper remans unreacted. The impure copper thus obtained is purified by electrolytic refining. The $MgCl_2$ obtained above is made anhydrous by heating in a current of HCl gas. The anhydrous $MgCl_2$ thus obtained is added to a mixture of molten NaCl and $CaCl_2$ (973–1025 K) and electrolysed when pure Mg gets deposited on the cathode.

(*iii*) Rare earth metals (*i.e.*, lanthanides abbreviated as Ln) can be separated by fractional crystallization of their simple salts such as nitrates, sulphates, bromates, perchlorates, oxalates or preferably double salts such as $Ln(NO_3)_3 \cdot 3\,Mg(NO_3)_2 \cdot 24\,H_2O$ because they crystallize well. Since the solubilities decrease from La to Lu, therefore, salts at the Lu end of the series will crystallize first. The process has to be repeated a number of times to obtain good separations. Non-aqueous solvents such as diethyl ether have been used to separate $Nd(NO_3)_3$ and $Pr(NO_3)_3$.

Very Short Answer Questions CARRYING 1 MARK

Q. 1. What is a mineral ? How does it differ from an ore?

Ans. The natural materials or the chemical compounds in which the metals occur in the earth are called minerals. The mineral from which the metal is conveniently and economically extracted is called an ore. Thus, *all ores are minerals but all minerals are not ores.*

Q. 2. What types of ores are roasted ?

Ans. Sulphide ores are roasted to convert them into their oxides.

Q. 3. Metal sulphides occur mainly in rocks and metal halides in lakes and seas. Explain.

Ans. Metal halides being soluble in water, get dissolved in rain water and are carried to lakes and seas during weathering of rocks. On the other hand, metal sulphides being insoluble are left behind in the rocks as residue.

Q. 4. What are fluxes ? How are they useful ?

Ans. Flux is a substance which combines with gangue which may still be present in the roasted or calcined ore to form an easily fusible material called the slag.

Q. 5. What is a slag ?

Ans. A slag is an easily fusible material which is formed when gangue still present in the roasted or the calcined ore combines with the flux. For example, in the metallurgy of iron, CaO (flux) combines with silica gangue to form easily fusible calcium silicate ($CaSiO_3$) slag.

$$CaCO_3 \longrightarrow CaO + CO_2 \;;\; CaO + SiO_2 \longrightarrow \underset{(slag)}{CaSiO_3}$$

Q. 6. Why do some metals occur in the native state ?

Ans. Metals like Au and Pt, which are not reactive, *i.e.*, are not attacked by O_2, moisture and CO_2 of the air occur in the native state.

Q. 7. What do you mean by benefaction process ?

Ans. The process used to concentrate an ore is called the benefaction process.

Q. 8. What is gangue ?

Ans. The earthy and silicious impurities associated with the ores is called gangue.

Q. 9. Define aluminothermy.

Ans. The reduction of oxides of metals like Cr_2O_3, Fe_2O_3, Mn_3O_4 etc. to their metals by aluminium is called aluminothermy.

Q. 10. What is cupellation ?

Ans. Cupellation is a method used for refining of such metals which contain impurities of other metals which form volatile oxides. For example removal of last traces of Pb from Ag.

Q. 11. What is poling ?

Ans. Poling is a method used for refining of such metals which contain impurity of the oxide of the metal itself. For example, CuO in crude Cu.

Q. 12. What is the principle of zone refining ?

Ans. When the molten solution of an impure metal is allowed to cool, the pure metal crystallizes out while the impurities remain in solution.

Q. 13. What is Van Arkel method of obtaining ultrapure metals ?

Ans. The impure metal (Ti or Zr) is first converted into its volatile iodide by heating with I_2 at some low temperature and then decomposing the volatile iodide at a suitable high temperature to give the pure metal. For example,

$$\underset{(Impure)}{Zr\,(s)} + 2\,I_2\,(g) \xrightarrow{870\text{ K}} ZrI_4\,(g) \xrightarrow[\text{W filament}]{2075\text{ K}} \underset{(Pure)}{Zr\,(s)} + 2\,I_2\,(g)$$

Q. 14. Give the chemical formula of dolomite and carnallite.

Ans. $CaCO_3.MgCO_3$ and $KCl.MgCl_2.6H_2O$.

Q. 15. Give one important ore of aluminium.

Ans. Bauxite ($Al_2O_3 . 2H_2O$).

Q. 16. What is a depressant. Give one example.

Ans. Compounds which prevent the formation of froth in froth-flotation process are called depressants. For example NaCN, can be used as a depresant for ZnS in the separation of ZnS ore from PbS ore. It forms a layer of zinc complex, $Na_2[Zn(CN)_4]$ on the surface of ZnS and thus prevents it from forming the froth.

Q. 17. What is the role of a stabilizer in froth-flotation process ?

Ans. Chemical compounds like cresols and aniline which tend to stabilize the froth are called froth stabilizers.

Q. 18. Which is a better reducing agent at 983 K (or 710°C), carbon or carbon monoxide ? *(N.C.E.R.T.)*

Ans. CO. Above 983, CO being more stable does not act as a good reducing agent but carbon does.

Q. 19. Indicate the temperature at which carbon can be used as a reducing agent for FeO. *(N.C.E.R.T.)*

Ans. Above 1123 K, carbon can reduce FeO to Fe.

Q. 20. Is it true that under certain conditions Mg can reduce SiO_2 and Si can reduce MgO? *(N.C.E.R.T.)*

Ans. Below 1773 K, Mg can reduce SiO_2 but above 1773 K Si can reduce Mg.

Q. 21. How is ^{14}C obtained in the atmosphere ?

Ans. Due to nuclear reaction between cosmic rays and atmospheric nitrogen, *i.e.*, ${}^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H$

Q. 22. Why is the cosmic abundance of Fe very high ?

Ans. Due to its very high nuclear binding energy ?

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 10.1. to 10.6.

1. Explain why terestial and cosmic abundance of elements is different.
2. Why iron is an abundant element on earth and why are the elements with higher atomic numbers increasingly rare ?
3. Write short notes on : (*i*) Hydrosphere, (*ii*) Lithosphere (*iii*) Atmosphere and (*iv*) Biosphere.
4. Name a few elements present in the living organism.
5. Give a brief account of the various elements present in the sea- water.
6. Ocean is a storehouse of the elements. Comment.
7. Although sea water contains almost all the elements, yet only a few elements are recovered from it ?

Sec. 10.7. to 10.10.

8. How do the elements occur in nature ?
9. Why do a few elements occur in the native state while others do not ?
10. Differentiate between mineral and ores.
11. name the chief form of occurrence of the following in the earth's crust : *(N.C.E.R.T.)*
    (*a*) aluminium (*b*) calcium (*c*) sodium (*d*) lead
12. Giving appropriate examples (at least three), explain how the reactivity of a metal is related to its mode of occurrence in nature. *(N.C.E.R.T.)*
13. Predict the mode of occurrence of the following three types of metals : (*i*) Highly reactive (*i.e.*, Na) (*ii*) Moderately reactive (*i.e.*, Fe) (*iii*) Noble metal (*i.e.*, Au) *(N.C.E.R.T.)*
14. How do non-metals occur in nature ? How are they extracted/isolated from their natural sources ? *(N.C.E.R.T.)*

Sec.10.10. to 10.12.

15. Discuss some of the factors which need consideration before deciding on the method of extraction of metal from its ore. *(N.C.E.R.T.)*
16. Describe the principle of froth flotation process. What is the role of a stabilizer and of a depressant ? Give one example each. *(N.C.E.R.T.)*
17. Name three ores which are concentrated by froth flotation process. What is meant by a depressant ? *(N.C.E.R.T.)*

18. Differentiate between the following : (*i*) calcination and roasting, (*ii*) gangue and flux.
19. What is meant by concentration of ores ?
20. What is the purpose of roasting and calcination in metallurgical operations ?
21. What do you mean by leaching ? Explain with an example.
22. Explain the difference between leaching and levigation.
23. Silver ores and native gold have to be leached with metal cyanides. Suggest a reason for this.
24. Giving one example in each case, differentiate between
    (*i*) Hydrometallurgy and (*ii*) Electrometallurgy
25. What is a flux ? Discuss its types and uses in metallurgical operations.
26. What is aluminothermy ? Explain with one example.
27. What do you understand by the following terms ?
    (*i*) Roasting (*ii*) Calcination (*iii*) Smelting. *(N.C.E.R.T.)*
28. Name the metals which are associated with the following terms in their extraction from their ores :
    (*i*) Bessemer's converter (*ii*) Blast furnace (*iii*) Aluminothermic process (*iv*) Magnetic separation *(N.C.E.R.T.)*
29. The choice of a reducing agent in a particular case depends upon the thermodynamic factor. How far you agree with this statement ? Support your opinion with examples. *(N.C.E.R.T.)*
30. Is carbon a satisfactory reducing agent for all metal oxides ? Give reasons. *(N.C.E.R.T.)*
31. Describe the principle of each of the following processes in detail ?
    (*a*) Mond's process (*b*) Zone refining (*c*) Electrolytic refining. *(N.C.E.R.T.)*
32. What do you mean by vapour phase refining. Describe Van Arkel method used for purification of metals ?
33. Describe the principle of extraction of each of the following :
    (*i*) Sn from SnO_2 (*ii*) Zn from ZnO (*iii*) Cr from Cr_2O_3 *(N.C.E.R.T.)*
34. Name the process from which chlorine is obtained as a bye-product. What will happen if an aqueous solution of NaCl is subjected to electrolysis ? *(N.C.E.R.T.)*
35. Name the chief ores of tin, iron and aluminium. What methods are employed for the concentration and purification of their ores ? *(N.C.E.R.T.)*
36. Name the main steel plants which are operated by Steel Authority of India. *(N.C.E.R.T.)*
37. Write short notes on : (*i*) Liquation (*ii*) Poling (*iii*) Cupellation.
38. What is the basic difference between roasting and calcination ?
39. What is the main difference between cupellation and poling ?

Long Answer Questions CARRYING 5 or more MARKS

Sec. 10.1. to 10.8.

1. Discuss the origin of elements in this universe.
2. Discuss briefly the distribution of elements on earth.
3. Write the zones of the earth and discuss the distribution of elements in these zones.
4. Describe Goldschmidt's view regarding composition of the earth.
5. What are igneous and sedimentary rocks ? How were they formed during formation of earth ?

Sec 10.9. to 10.12.

6. What do you mean by the term 'concentration of ores'. Describe briefly the various methods used for this purpose.
7. Give a brief account of the various methods used for obtaining metals from the roasted or calcined ores.
8. What is meant by metallurgy ? Describe briefly the various methods employed for isolation of metals from their sulphide ores.
9. Give an appraisal of the methods used for reduction of metallic oxides to metals.
10. Discuss briefly the various methods used for refining of crude metals.

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Electrostatic concentration. *Principle.* The principle of electrostatic separation can be compared to the electromagnetic separation and depends upon the difference in the property of their conduction of electricity. Some particles are charged easily when brought into an electrostatic field of attraction while others are not and thus would be repelled by the electrode carrying the charge.

Example. When the ore containing lead sulphide and zinc sulphide is pulverized and fed upon a roller in a thin layer and subjected to the influence of an electrostatic field, lead sulphide, being a good conductor, is charged easily. It is repelled and thrown away from the roller. On the other hand, zinc sulphide being a poor conductor, is not influenced by the electrostatic field and falls just close to the roller.

2. Hydrometallurgy is the process of dissolving the ore in a suitable chemical reagent followed by extraction of the metal either by electrolysis or precipitation of the metal by a more electropositive metal. Ag and Au are extracted by this process.

$$4\,Ag + 8\,NaCN + O_2 + 2\,H_2O \longrightarrow 4\,Na[Ag(CN)_2] + 4\,NaOH$$

$$2\,Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2\,Ag\downarrow$$

3. Amalgamation. This process finds application in the extraction of noble metals like Au and Ag from their native ores. The principle of the method is that these metals combine with Hg to form amalgams. The crushed ore in the form of slurry is brought in contact with mercury coated over copper or brass plates. The metal particles of Au and Ag form an amalgam with mercury and are retained over the plates. The amalgam is scrapped off from the plates and distilled in iron retorts. Hg distils over leaving behind the metal.

C.B.S.E.-P.M.T. (MAINS) SPECIAL

Q. 1. Define amalgamation ? Discuss its use in the purification of gold and silver. Can Fe be purified by this method ?

Ans. Iron cannot be purified by this method since Fe does not form as amalgam.

Q. 2. Cinnabar (HgS) and galena (PbS) on roasting often give their respective metals but zinc blende (ZnS) does not. Explain.

Ans. On roasting all these sulphide ores are partly converted into their respective oxides. Since the oxides of mercury and lead are unstable while that of zinc is stable, therefore, oxides of mercury and lead bring about the reduction of their respective sulphides to the corresponding metals but zinc oxides does not reduce ZnS to Zn metal

$$HgS + \underset{(unstable)}{2\,HgO} \xrightarrow{\Delta} 3\,Hg + SO_2$$

$$PbS + \underset{(unstable)}{2\,PbO} \xrightarrow{\Delta} 3\,Pb + SO_2$$

$$ZnS + \underset{(Stable)}{2\,ZnO} \longrightarrow 3\,Zn + SO_2$$

Q. 3. Which of the following metals cannot be extracted by the smelting process ?

Al, Zn, Fe, Pb *(West Bengal J.E.E. 2003)*

Ans. Aluminium cannot be extracted by the smelting process because of the following reasons :

(*i*) Al is a highly electropositive element having very strong affinity for oxygen. Therefore, Al_2O_3 is a very stable compound and hence cannot be reduced by carbon.

(*ii*) Al_2O_3 when heated with carbon forms aluminium carbide.

$$2\,Al_2O_3 + 6\,C \longrightarrow Al_4C_3 + 6\,CO$$

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. During smelting, an additional substance is added which combines with impurities to form a fusible mass. The additional substance is called
   (*a*) Flux (*b*) Slag
   (*c*) Gangue (*d*) Ore.

2. The process of isolation of metals by dissolving the ore in a suitable chemical reagent followed by precipitation of the metal by a more electropositive metal is called
   (*a*) Electrometallurgy (*b*) Hydrometallurgy
   (*c*) Electro-refining (*d*) Zone-refining.

3. Smelting involves reduction of metal oxide with
   (*a*) Carbon (*b*) Carbon monoxide
   (*c*) Magnesium (*d*) Aluminium.

4. Zone-refining has been employed for preparing ultrapure samples of
   (*a*) Cu (*b*) Zn
   (*c*) Ge (*d*) Ag.

5. Which of the following is an ore of aluminium ?
   (*a*) Na_3AlF_6 (*b*) $Al_2O_3.2H_2O$
   (*c*) Al_2O_3 (*d*) $Al_2O_3.H_2O$

6. In the aluminothermite process, aluminium acts as
   (*a*) an oxidising agent (*b*) a flux
   (*c*) a reducing agent (*d*) a solder. *(I.I.T. 1983)*

7. In which of the following minerals, aluminium is not present ?
   (*a*) Cryolite (*b*) Mica
   (*c*) Fledspar (*d*) Fluorspar. *(I.I.T. 1993)*

8. An important ore of magnesium is
   (*a*) Malachite (*b*) Cassiterite
   (*c*) Carnallite (*d*) Galena. *(D.P.M.T. 1993)*

9. The salt which is least likely to be found in minerals is
   (*a*) Chloride (*b*) Sulphate
   (*c*) Sulphide (*d*) Nitrate. *(D.P.M.T. 1994)*

10. The extraction of which of the following metals involves bessemerisation.
    (*a*) Fe (*b*) Ag
    (*c*) Al (*d*) Cu. *(B.H.U. 1994)*

ANSWERS

1. *a* **2.** *b* **3.** *a* **4.** *c* **5.** *b* **6.** *c* **7.** *d* **8.** *c* **9.** *d* **10.** *d*

11. Which of the following metals is obtained by leaching the ore with dilute cyanide solution ?

(*a*) Silver (*b*) Titanium
(*c*) Vanadium (*d*) Zinc.

(A.I.I.M.S. 1994)

12. Which method of purification is represented by the equations.

$$\underset{\text{(Impure)}}{Ti} + 2I_2 \xrightarrow{500\text{ K}} TiI_4 \xrightarrow{1675\text{ K}} \underset{\text{(Pure)}}{Ti} + 2I_2$$

(*a*) Cupellation (*b*) Poling
(*c*) Van Arkel (*d*) Zone refining.

(A.I.I.M.S. 1994)

13. Which of the following benefaction processes is used for the mineral $Al_2O_3.2H_2O$?

(*a*) Froth-floatation (*b*) Leaching
(*c*) Liquation (*d*) Magnetic separation.

(A.I.I.M.S. 1990)

14. The process of concentrating Au and Ag ores is based upon their solubility in

(*a*) NH_3 (*b*) HNO_3
(*c*) HCl (*d*) KCN.

(C. .S.E. P.M.T. 1994)

15. Malachite is an ore of

(*a*) Iron (*b*) Zinc
(*c*) Copper (*d*) Mercury

(M.P.P.M.T. 1998)

16. Which of the following metals is sometimes found native in nature ?

(*a*) Aluminium (*b*) Copper
(*c*) Iron (*d*) Magnesium.

(M.P.C.E.E. 1999)

17. Which of the following metals is most abundant in the earth's crust ?

(*a*) Mg (*b*) Na
(*c*) Al (*d*) Fe. *(D.C.E. 1999)*

18. Heating pyrites to remove sulphur is called

(*a*) Smelting (*b*) Calcination
(*c*) Liquation (*d*) Roasting.

(M.P.P.M.T. 2000)

19. In the metallurgy of which of the following, cupellation process is used ?

(*a*) Copper (*b*) Silver
(*c*) Iron (*d*) Aluminium.

(M.P. P.M.T. 2000)

20. In the equation, $4\,M + 8\,CN^- + 2\,H_2O + O_2 \longrightarrow 4\,[M(CN)_2]^- + 4\,OH^-$, the metal M is

(*a*) Copper
(*b*) Iron
(*c*) Gold
(*d*) Zinc. *(M.P. C.E.E. 2000)*

21. Which of the following metals is leached by cyanide process.

(*a*) Ag (*b*) Na
(*c*) Al (*d*) Cu

(A.I.E.E.E. 2002)

22. Pyrolusite is a/an

(*a*) Oxide ore (*b*) Sulphide ore
(*c*) Carbide ore (*d*) Not an ore

(D.P.M.T. 2002)

23. In the extraction of copper from its sulphide ore, the metal is formed by reduction of Cu_2O with

(*a*) FeS (*b*) CO
(*c*) Cu_2S (*d*) SO_2

(A.I.I.M.S. 2003)

24. In the process of extraction of gold,

$$\text{Roasted gold ore} + CN^- + H_2O \xrightarrow{O_2} [X] + OH^-$$

$$[X] + Zn \longrightarrow [Y] + Au$$

Identify the complexes [X] and [Y]

(*a*) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_4]^{2-}$
(*b*) $X = [Au(CN)_4)]^{2-}$, $Y = [Zn(CN)_4]^{2-}$
(*c*) $X = [Au(CN)_2]^-$, $Y = [Zn(CN)_6]^{4-}$
(*d*) $X = [Au(CN)_4]^-$, $Y = [Zn(CN)_4]^{2-}$

(I.I.T. 2003)

25. The method of zone refining of metals is based on the principle of

(*a*) greater mobility of the pure metal than that of the impurity.
(*b*) higher melting point of the impurity than that of the pure metal.
(*c*) greater noble character of the solid metal than that of the impurity.
(*d*) greater solubility of the impurity in the molten state than in the solid.

(C.B.S.E. P.M.T. 2003)

ANSWERS

11. *a* **12.** *c* **13.** *b* **14.** *d* **15.** *c* 16. *b* 17. *c* 18. *d* 19. *b* 20. *c*
21. *a* **22.** *a* **23.** *c* **24.** *a* **25.** *d*

26. The methods chiefly used for the extraction of lead and tin from their ores are respectively

(*a*) Self reduction and Carbon reduction

(*b*) Self reduction and Electrolytic reduction

(*c*) Carbon reduction and Self reduction

(*d*) Cyanide process and Carbon reduction.

(I.I.T. 2004)

27. Vapour phase refining of nickel is carried out using

(*a*) I_2 (*b*) Cl_2

(*c*) HCl (*d*) CO

(*e*) NO *(Kerala E.E.E. 2004)*

28. Thomas slag is

(*a*) Calcium silicate (*b*) Calcium phosphate

(*c*) Barium phosphate (*d*) Strontium silicate

(*e*) Barium silicate *(Kerala E.E.E. 2004)*

29. Silver is obtained from $Na[Ag(CN)_2]$ by reaction with

(*a*) Fe (*b*) Na

(*c*) Zn (*d*) Au *(C.P.M.T. 2004)*

30. Which one of the following ores is best concentrated by froth- flotation method ?

(*a*) Malachite (*b*) Cassiterite

(*c*) Galena (*d*) Magnetite

(A.I.E.E.E. 2004)

31. During the extraction of iron, slag produced is

(*a*) CO (*b*) $FeSiO_3$

(*c*) $MgSiO_3$ (*d*) $CaSiO_3$

(J & K C.E.T. 2004)

32. Silver containing lead as an impurity is purified by

(*a*) Poling (*b*) Cupellation

(*c*) Levigation (*d* distillation

(J & K C.E.T. 2004)

33. Out of the following metals that cannot be obtained by electrolysis of the aqueous solution of their salts is

(*a*) Ag (*b*) Cr

(*c*) Cu (*d*) Mg

(J & K C.E.T. 2004)

34. In the froth-floatation process for benefaction of the ores, the ore particles float because

(*a*) they are light

(*b*) their surface is not easily wetted by water

(*c*) they bear electrostatic charge

(*d*) they are insoluble.

(M.L.N.R. Allahabad 1992 ; Karnataka C.E.T. 2004)

35. Mond's process is used for

(*a*) Ni (*b*) Al

(*c*) Fe (*d*) Cu *(A.F.M.C. 2004)*

HINTS/EXPLANATIONS to Multiple Choice Questions

7. Fluorspar is CaF_2.

9. All nitrates are soluble in water.

11. Silver dissolves in NaCN solution.

16. Copper is very slowly attacked by air, moisture and CO_2 and hence sometimes occurs in native state.

28. Calcium phosphate is called Thomas slag.

33. Since the reduction potential of Mg^{2+} (—2·37 V) is much lower than that of H_2O (—0·83 V), therefore, H_2O gets reduced in preference of Mg^{2+} ions.

34. Ore particles float because their surface is wetted by oil.

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The following questions consist of an 'Assertion' in column 1 and the 'Reason' in column 2. Use the following key to choose the appropriate answer.

(a) If both assertion and reason are CORRECT, and reason is the CORRECT explanation of the assertion.

(b) If both assertion and reason are CORRECT, but reason is NOT the CORRECT explanation of the assertion.

(c) If assertion is CORRECT, but reason is INCORRECT.

(d) If assertion is INCORRECT, but reason is CORRECT.

ANSWERS

26. *a* **27.** *d* **28.** *b* **29.** *c* **30.** *c* **31.** *d* **32.** *b* **33.** *d* **34.** *b* **35.** *a*

	Assertion (Column 1)	Reason (Column 2)
1.	Ti can be purified by van Arkel process.	TiI_4 is a volatile compound which decomposes at a high temperature
2.	Aluminothermy is used for extraction of chromium from chromium oxide.	Alumina has a high melting point.
3.	Ag and Au are extracted by leaching thier ores with a dilute solution of NaCN.	Impurities associated with these ores dissolve in NaCN.
4.	Carbonates and hydroxide ores are concentrated by froth floatation process.	In froth-floatation process pine oil is used because it preferentially wets the ore particles.

True/False Statements

Which of the following statements are true and which are false ?

1. Elements found in the combined state are often present as oxides, carbonates, sulphides and silicates.
2. A mixture of aluminium powder and the metallic oxide (Cr_2O_3 , Fe_2O_3) etc. is called fusion mixture.
3. The naturally occurring material in which the metal is present as stable compound in the earth's crust is called an ore.
4. The process employed to concentrate an ore is called the beneficiation process.
5. Leaching is a process by which a particular mineral in an ore can be dissolved selectively by using certain acids, bases or other reagents.
6. The removal of impurities from an ore by forming salts is called slagging operation.
7. Metals which are highly reactive cannot be obtained by electrolytic reduction.

Fill In The Blanks

1. An ore is a .... from which the metal can be extracted conveniently and economically.
2. The materials like stone, rock and earthy impurities present in naturally occurring ores are known as ......
3. A sulphide ore is generally roasted in order to convert it into ....
4. Highly electropositive metals like alkali metals are obtained by .... .
5. Low melting metals like lead are refined by .... .
6. Process of heating the ore in excess of air is known as.....
7. Sodium cyanide solution is used to extract .... from its ores.

Matching Type Questions

Match items given in Column A against those given in Column B.

Column A	Column B
1. Bauxite	(*a*) Flame test
2. Galena	(*b*) *s*-Block elements
3. Alkali metals are extracted by	(*c*) Froth-floatation
4. concentration of sulphide ore	(*d*) Fire extinguishers
5. concentation of ore	(*e*) Reducting agents
6. Sodium chloride	(*f*) Electrolytic method
7. Sodium bicarbonate is used in	(*g*) Benefication
8. Alkali metals are	(*h*) $Al_2O_3 . 2H_2O$
9. Alkaline earth metals are	(*i*) An ore of sodium
10. Magnesium does not give	(*j*) PbS

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*a*) **2.** (*b*) **3.** (*c*) **4.** (*d*).

TRUE/FALSE STATEMENTS

1. True **2.** False, thermite **3.** False, mineral **4.** True **5.** True **6.** True **7.** False.

FILL IN THE BLANKS

1. mineral **2.** gangue **3.** its oxide **4.** electrolytic reduction **5.** liquation **6.** roasting **7.** silver or gold.

MATCHING TYPE QUESTIONS

1. (*h*) **2.** (*j*) **3.** (*f*) **4.** (*c*) **5.** (*g*) **6.** (*i*) **7.** (*d*) **8.** (*e*) **9.** (*b*) **10.** (*a*)

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

2. *Correct explanation.* Al is a good reducing agent.
3. *Correct reason.* Ag and Au dissolve in NaCN solution to form their soluble complexes.
4. *Correct assertion.* Sulphide ores are concentrated by froth- floatation process.