TOPIC

5

SEMESTER-II (Period-V)

C12CH5

Chemistry of Selected Metals and their Compounds (contd)

LEARNING OBJECTIVE

Upon completion of this topic, learners will:

- Discuss the properties and uses of sodium, calcium, copper and their compounds and
- Demonstrate the preparation of copper, sodium and calcium.

5.1 EXTRACTION OF METALS—METALLURGY

A few most unreactive metals occur in nature in free state. Most of the metals occur in nature in oxidized form as their compounds. Therefore, metals are generally extracted by subjecting their ores to reduction by chemical methods or by electrolytic methods.

The process of extracting pure metal from its ore is known as metallurgy.

Some common steps involved in the metallurgical operations are:

I. *Crushing and grinding of the ore.*

II. *Concentration or benefication of the ore.*

III. *Preliminary treatment of the concentrated ore.*

IV. *Reduction.*

V. *Purification or refining of crude metal.*

I. CRUSHING AND GRINDING OF THE ORE

Most of the ores are obtained from the crust of the earth in the form of huge lumps. The huge lumps are broken into small pieces in the *jaw crushers.* They are further *pulverised in stamp mill* or *ball mill.*

II. CONCENTRATION OR BENEFICATION OF THE ORE

The ore obtained from the earth's crust is associated with rocky and silicious impurities. It is quite essential to get rid of these impurities so that they may not cause any interference in the process of extraction.

The removal of unwanted materials such as sand, clays, etc., from the pulverised ore is called **concentration, dressing** or **benefication of the ore.**

1. Hydraulic Washing, Levigation or Gravity Separation Method: This method is usually applicable to *oxide ores* in which the ore particles are heavier than the impurities. The powdered ore is washed with running stream of water. The lighter impurities are washed away leaving behind the heavier ore particles.

Native metals such as gold can be separated from sand and gravel by shaking and washing of earth with water in a pan or sieve. The process is known as **panning**.

2. Froth Floatation Process: This process is generally used for the concentration of *sulphide ores*. The finely powdered ore and *water* are taken in a tank. Additional reagents such as *pine oils, fatty acids,* etc., are added to the mixture. The contents are kept agitated by the blast of air. As a result of agitation the froth is produced.

The ore particles are preferentially wetted by the oil and are carried to the surface by the foam. The gangue material, which is preferentially wetted by water sinks to the bottom of the tank. The foam at the surface of the tank is transferred to the other tank where it is washed with water to recover the ore particles.

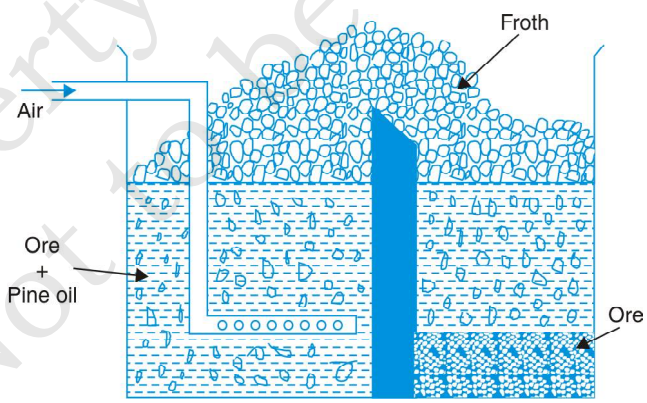

Fig. 5.1. Froth floatation process.

3. Magnetic Separation of Impurities: This method is usually employed when either the ore or the gangue is capable of being attracted by the magnetic field. The powdered ore is dropped over the belt revolving around the rollers, one of which is magnetic. The magnetic roller attracts the magnetic part of the ore and they are collected in the form of a heap near it. The non-magnetic part of the ore flies off and forms a heap away from the impurities.

4. Leaching: It is a chemical method for the concentration of the ore. In this process the powdered ore is dissolved selectively in acids, bases or other suitable reagents. The impurities remain undissolved as *sludge*. The solution of ore is filtered and the ore is recovered by precipitation or crystallisation.

III. PRELIMINARY TREATMENT OF THE CONCENTRATED ORE

The process of extraction of metal from the concentrated ore depends upon the nature of the ore as well as the nature of impurities present in the ore. Before the concentrated ore is subjected to final metallurgical operations in order to get the metal in the free state, the **preliminary chemical treatment** may be necessary. The objective of this preliminary chemical treatment is:

(*a*) *to get rid of impurities which would cause difficulties in the later stages*; and

(*b*) *to convert the ore into oxide of the metal* because it is easier to reduce an oxide than the carbonate or sulphide.

The processes employed for preliminary treatment are *calcination* and *roasting*.

1. CALCINATION

It is a process of heating the ore in a limited supply of air below its melting point. The process involves:

—the removal of volatile impurities,

—the removal of moisture,

—the decomposition of any carbonate ore into oxide.

$$Fe_2O_3.xH_2O \longrightarrow Fe_2O_3 + xH_2O(g)$$

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

$$CuCO_3 . Cu(OH)_2 \longrightarrow 2CuO + H_2O + CO_2$$

2. ROASTING

It is the process of heating the ore in the excess supply of air below its melting point. This process is employed when oxidation of the ore is required. As a result of roasting,

—moisture is driven away,

—volatile impurities are removed,

—the impurities like sulphur, phosphorus, arsenic are removed as their oxides,

—the ore undergoes oxidation to form metal oxide or sulphate.

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$2ZnS + 3O_2 \longrightarrow 2ZnO + SO_2$$

It is advantageous to roast a sulphide ore to the oxide before reduction because metal oxides can be reduced to metal by carbon and hydrogen much more easily than sulphides.

IV. REDUCTION

After the preliminary treatment, the ore may be subjected to reduction process by one of the following methods depending upon its nature:

1. Smelting or Reduction with Carbon. In this process, the roasted or calcined ore is mixed with suitable quantity of coke or charcoal (which act as *reducing agent*) and is heated to a high temperature above its melting point. During reduction, an additional reagent is also added to the ore to remove the impurities still present in the ore. This additional reagent is called **flux.** *Flux combines with the impurities to form a fusible product called* **slag.**

Flux + Impurities ⟶ Slag

The selection of flux depends upon the nature of impurities. If impurities are *acidic* in nature, the *flux is basic, such as, lime (CaO).* On the other hand, for *basic impurities,* an *acidic flux such as silica* (SiO_2) is used.

$$\underset{\text{(Basic impurity)}}{CaO} + \underset{\text{(Acidic flux)}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

2. Reduction with Aluminium. Certain metal oxides such as Cr_2O_3 and Mn_3O_4 are not easily reduced with carbon. In such cases aluminium is used as reducing agent because it is more electropositive than chromium or manganese. *The process of reduction of oxides with aluminium* is called **aluminothermy.** Some examples are:

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

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

The chemical methods are suitable for reduction of compounds of metals which are in the middle of the activity series.

V. PURIFICATION OR REFINING OF CRUDE METALS

The process of purification of impure metals is known as refining.

Depending upon the nature of the metal and the nature of the impurities present different methods are applied for the refining of metals. Some of the commonly used methods are discussed as follows:

1. Distillation. Volatile metals like zinc and mercury are purified by this method. The pure metal distils over and is condensed in a receiver. The non-volatile impurities are left behind in the retort.

2. Liquation. The method is used for easily fusible metals like bismuth, tin and lead. The crude metal is placed on the sloping hearth of a furnace and heated gently when the metal melts and flows down, leaving behind the infusible impurities which remain sticking to the floor of the hearth.

3. Electrolytic Refining or Electro-refining. This method is based on the phenomenon of electrolysis. Many metals like ***copper, silver, tin, gold, zinc, nickel and chromium*** are purified by electro-refining.

The impure metal is made anode whereas the thin sheet of pure metal is made cathode. Electrolyte is the solution of some salt of the metal. On passing electricity, the metal from the anode goes into solution as ions due to oxidation while pure metal gets deposited at the cathode due to the reduction of metal ions. The insoluble impurities settle down below the anode as **anode mud** whereas the soluble impurities go into solution. The reactions taking place at the two electrodes may be represented as:

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

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

5.2 GOLD

Gold is a chemical element with the symbol Au and atomic number 79, making it one of the higher atomic number elements that occurs naturally.

Occurrence

Since gold is very unreactive it occurs in free state in nature. The primary sources of gold are:

(*i*) *Alluvial gravel*. It is found in the beds of certain rivers. It is referred to as *alluvial gold.*

(*ii*) *Auriferous quartz.* Gold also occurs in the veins of quartz. This is called *relf gold.*

Extraction

The various steps involved in the extraction of gold are:

1. The concentrated ore is *roasted* to remove all the oxidisable impurities.

2. Treatment with KCN

The roasted ore is then treated with a solution of sodium cyanide or potassium cyanide for some days. In the presence of atmospheric oxygen, gold dissolves in the form of a complex.

$$4Au + 8NaCN + 2H_2O + O_2 \longrightarrow \underset{\text{Sodium dicyanoaurate (I)}}{4Na[Au(CN)_2]} + 4NaOH$$

3. Precipitation of Gold. From the solution the metal is precipitated by adding zinc shavings.

$$2Na[Au(CN)_2] + Zn \longrightarrow \underset{\text{Sodium tetracyanozincate (II)}}{Na_2[Zn(CN)_4]} + 2Au \downarrow$$

4. Purification. Gold obtained in the above process is impure and contains metals such as silver and copper as impurities. ***Removal of silver and copper impurities from impure gold is known as parting.*** It is achieved by boiling impure gold with conc. H_2SO_4. Silver and copper dissolve in hot conc. H_2SO_4 while the gold remains as such. Parting can also be done with conc. HNO_3.

Uses of Gold

1. For preparing ornaments.
2. For electrogilding (*i.e.*, gold plating by electrolysis).
3. For filling teeth, and in switch contacts.
4. For making compounds of gold.
5. For preparing alloys.

5.3 ALLUMINIUM

Occurrence

Aluminium is quite reactive element and hence does not occur in nature in the native form. Aluminium is the *most abundant metal* and the *third most abundant element* in the earth's crust. The important ores of aluminium are:

(*i*) *Bauxite*, $Al_2O_3.2H_2O$

(*ii*) *Cryolite,* Na_3AlF_6

(*iii*) *Feldspar*, $KAlSi_3O_8$.

EXTRACTION (From bauxite)

Aluminium metal is extracted from bauxite is a two stage process.

Stage 1. Involves the extraction of alumina (Al_2O_3) from bauxite.

Stage 2. Involves extraction of pure aluminium from Al_2O_3 by its electrolysis in molten cryolite [Na_3AlF_6]

Purification of Bauxite. Bauxite contains SiO_2, iron oxides and titanium (*IV*) oxide as impurities.

Bauxite is digested with a hot concentrated (45%) solution of sodium hydroxide at about 473–523 K and 35–36 bar pressure.

Alumina dissolves to form sodium tetrahydroxoaluminate (III), $Na[Al(OH)_4]$ leaving behind iron oxide and TiO_2.

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4]$$

Silica (SiO_2) also dissolves in sodium hydroxide to form soluble sodium trioxosilicate(IV), Na_2SiO_3.

$$SiO_2 + 2NaOH \longrightarrow 2Na_2SiO_3 + H_2O$$

The impurities are filtered out and CO_2 is bubbled. Through the filtrate containing sodium tetrahydroxo-aluminate(III) and sodium trioxosilicate(IV). At this stage the solution may be seeded with freshly precipitated aluminium hydroxide. Aluminium hydroxide precipitates leaving behind sodium trioxosilicate(IV) in solution. This is filtered and the precipitate of $Al(OH)_3$ is heated at 1473 K to obtain pure alumina.

$$Na[Al(OH)_4] + CO_2 \longrightarrow NaHCO_3 + Al(OH)_3 \downarrow$$

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

Uses of Aluminium

1. It is used for making angles used in windows.
2. It is a good conductor of electricity. Since it is not as good conductor as copper, thicker cables of aluminium are used for transmission of electricity.
3. Aluminium forms many useful alloys *e.g., magnalium* (Al and Mg), *duralumin* (Al, Cu, Mg and Mn). Aluminium alloys are used in aircraft and other transportation vehicles.
4. In the form of finely-divided powder, aluminium is used in antirust paints.
5. Aluminium foil is used for wrapping cigarettes, confectionery, etc.
6. Aluminium is used to produce metals such as chromium and manganese from their ores (*aluminothermic process*)

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

$$3MnO_2 + 4Al \longrightarrow 2Al_2O_3 + 3Mn$$

7. Aluminium utensils are extensively used for household purposes.

5.4 IRON

Iron is the second most abundant metal occurring in the earth's crust. It is an element of the first transition series.

Occurrence

The important ores of iron are:

1. *Haematite*, Fe_2O_3 (red oxide of iron)
2. *Magnetite*, Fe_3O_4 (magnetic oxide of iron)
3. *Limonite*, $Fe_2O_3.3H_2O$ (hydrated oxide of iron)
4. *Iron pyrites*, FeS_2
5. *Siderite or Spathic ore*, $FeCO_3$.

Extraction

The cast iron is generally extracted from haematite (Fe_2O_3). The various steps involved in the process are as follows:

1. Concentration. The ore is crushed with the help of jaw crushers into small pieces of about 5 cm size. The crushed ore is washed with a stream of water whereby lighter sand particles are washed away and the heavier ore particles settle down.

2. Calcination. The concentrated ore is heated strongly in the presence of air. This is called calcination. During calcination following changes take place:

- Moisture is driven out.
- Sulphur, arsenic and phosphorus impurities are expelled as their volatile oxides.
- Carbonate ore changes into oxide ore.

$$FeCO_3 \longrightarrow FeO + CO_2$$

- Ferrous oxide changes into ferric oxide.

$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

3. Smelting. After calcination the ore is subjected to reduction with carbon in a blast furnace (Fig. 5.2). The process is called **smelting.** Blast furnace is made up of steel, lined inside with fire resistant bricks. It has a cup and cone arrangement for the introduction of charge at the top, and at the base it has:

(*i*) a tapping hole for removing molten iron from time to time.

(*ii*) an arrangement for the introduction of hot air.

(*iii*) an outlet for slag.

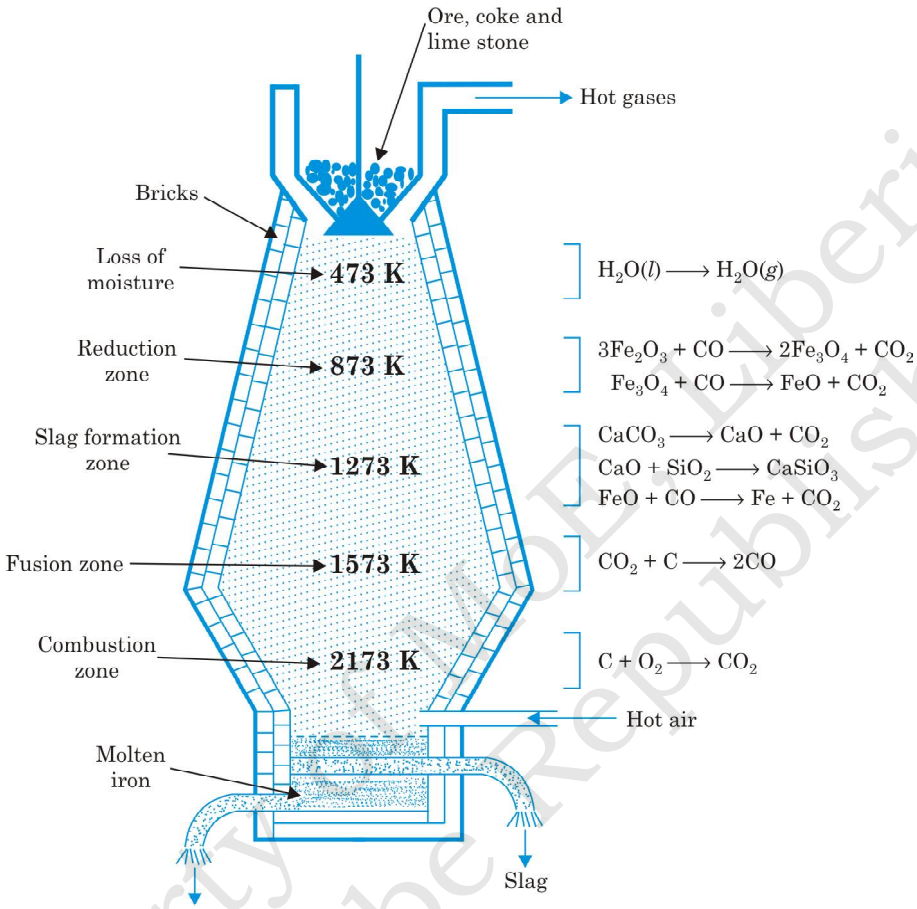

Fig. 2.2. Blast furnace for the manufacture of iron.

USES OF IRON

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

Alloys of Iron

Composition, Properties and Uses of Some Common Alloys

1. *Steel* Iron—98.5 to 99.5% Carbon—0.1 to 1.5% Traces of other impurities Hard, high tensile strength Construction, cables, machine parts, preparation of other alloy steels

2. *Stainless Steel* Iron—74% Carbon—0.5—1% Nickel—6 to 8% Chromium—18% Does not rust or corrode For household utensils, shaving blades, watch cases, etc.
3. *Magnalium* Magnesium—5% Aluminium—95% Tough, can be worked on the lathe ; does not stick to the tools Machined articles, cheap balances
4. *Duralumin* o *Duralium*Magnesium—2 Copper—4% Manganese—2% Aluminium—92% Light, tough, resists corrosion For making air ships, pressure cookers.
5. *Brass* Copper—60%Zinc—40% Resistant to corrosion, good ductility, high strength Utensils, screws and cartidge caps
6. *Bronze* Copper—90% Tin—10% Resistant to corrosion, hard, high tensile strength Control valves, statues, coins, medals, ship's propellers, etc.
7. *Solder* Lead—50% Tin—50% Low melting point. For soldering electrical wires.

5.5 STEEL

The amount of carbon present in steel is nearly intermediate between that contained in cast and wrought iron. The various steels contain carbon from 0.1 to 1.5%. The increase in carbon content in the steel decreases its ductility and increases its tensile strength.

Commonly used method for the production of steel:

1. Bessemer Process. The *Bessemer process* involves blowing a strong blast of air through the molten pig iron.

$$Si + O_2 \longrightarrow SiO_2$$
$$2Mn + O_2 \longrightarrow 2MnO$$
$$C + O_2 \longrightarrow CO_2$$

SiO_2 is slagged off with lime and MnO with silica in the form of their respective silicates.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$
$$SiO_2 + MnO \longrightarrow MnSiO_3$$

The slag floats on the surface whereas purified iron being denser than impure iron sinks to the bottom.

The Bessemer process produces iron containing less than 0.3 per cent carbon. If it is desired to obtain steel, the air blast is either shut off before all the carbon has burnt out, or a definite amount of pig iron rich

in carbon is added to the iron produced in the converter. Air is again blown through it for a short period in order to mix the ingredients.

Alloy Steels

The properties of steel can be modified by addition of other metals. *When steel is alloyed with at least one metal like nickel, chromium, vanadium, manganese, cobalt, tungsten, etc., an alloy steel is obtained.* Some of these alloy steels are given in below.

Some Alloy Steels

1. Nickel steel Ni 3.5% Hard, flexible, rust resistant For cables armour plates
2. Stainless steel Cr 18% Ni 8% Does not rust or corrode For household utensils, shaving blades, watch cases
3. Chrome-vanadium steel Cr 1% V 0.15% Tenacious and load bearingFor axles, springs and cog-wheels
4. Manganese steel Mn 12 to 15% Extremely hard and high melting For rock cru-sher, burglar proof safes
5. Tungsten steelW 14 to 20% Cr 3 to 8% Very hard and strong For cutting tools, springs
6. Invar Ni 36% Extremely low expansion on heating For clock pendulums
7. Alnico Al 12%, Ni 20%, Co 5% Highly magnetic For permanent magnets

Steel and alloy steels are preferred to the pure iron because they are stronger and resistant to corrosion. Iron undergoes corrosion (rusting).

5.6 TIN (S_N)

It is a chemical element belongign to the carbon family, Group 14 of the periodic table. It is a soft, silvery white metal with a bluish tinge, known to the ancients in bronze, an alloy with copper. Tin is widely used for plating steel cans used as food containers, in metals use for bearings, and in solder.

The origins of tin are lost in antiquity. Bronzes, which are copper-tin alloys, were used by humans in prehistory long before pure tin metal itself was isolated. Bronzes were common in early Mesopotamia, the Indus valley, Egypt, Israel, and Peru, Much of the tin used by the early Mediterranean peoples apparently came from the Scilly Isles and

Cornwall in the British Isles, where tin mining dates to at least 300–200 BCE. The symbol Sn for tin is an abbreviation of the Lating word for tin, *stannum*.

Occurrence and Distribution

The element is present in the igneous rocks of Earth's crust to the extent of about 0.001 per cent, which is scarce but not rare; its abundance is of the same order of magnitude as such technically useful elements as cobalt, nickel, copper, cerium and lead, and it is essentially equal to the abundance of nitrogen.

Tin occurs in grains of the native metal but chiefly as stannic oxide, SnO_2, in the mineral cassiterite, the only tin mineral of commercial significance. The metal is obtained from cassiterite by reduction (removal of the oxygen) with coal or coke in smelting furnaces. No high-grade deposits are knwon. The major sources are alluvial deposits, averaging about 0.01 per cent tin.

Properties of the Element

Tin is nontoxic, ductile, malleable, and adapted to all kinds of cold-working, such as rolling, spinning and **extursion**. The colour of pure tin is retained during exposure because a thin, invisible, protective film of stannic oxide is formed spontaneously by reaction with the oxygen of the air. The low melting point of tin and its firm adhesion to clean surfaces of iron, steel, copper and copper alloys facilitate its use as an oxidation resistant coating material.

Tin is attacked by strong acids and alkalies, but nearly neutral solutions do not affect it appreciably. Chlorine, bromine and iodine react with tin, but fluorine reacts with it only slowly at room temperature.

Uses

Tin-plating of iron protects the latter from corrosion; tin piping and valves maintain purity in water and beverages; molten tin is the base for (float) plate-glass production. Because pure tin is relatively weak, it is not put to structural uses unless alloyed with in which tin is in the + 4 oxidation state, is useful in making ceramic bodies opaque, as a mild abrasive, and as a weighting agent for fabrics. Tin fluoride and tin pyrophosphate, in which tin is in the + 2 oxidation state, are used in dentifrices. Organic tin comopounds act as stabilizers in certain plastics and as wood preservatives. A crystalline alloy with niobium is a superconductor at temperatures as high as 18 K (– 427°F) and retains this property in very strong magnetic fields.

Elemental tin is apparently non-toxic, and quantities of tin up to 300 parts per million, as dissolved by foods packaged in tin-plated containers and cooking utensils, are not harmful.

Tin forms two series of compounds: stannous, in which tin is in the + 2 oxidation state, and stannic, in which it is in the + 4 state, Some of the more commercially important stannous compounds are stannous chloride, $SnCl_2$, used in tin galvanizing and as a reducing agent in the manufacture of polymers and dyes; stannous oxide SnO, employed in making tin salts for chemical reagents and for plating; and stannous fluoride, SnF_2, an active ingredient in toothpastes. Stannic compounds of significance include stannic chloride, $SnCl_4$, widely used as a stabilizer for perfumes and as a starting material for other tin salts; and stannic oxide, SnO_2, a useful catalyst in certain industrail processess and a polishing powder for steel.

5.7 COPPER

Occurrence

Copper is found in combined as well as in free state.

The common ores of copper are:

1. ***Copper pyrites*, $CuFeS_2$**
2. *Copper glance*, Cu_2S
3. *Malachite*, $Cu(OH)_2.CuCO_3$
4. *Cuprite*, Cu_2O

Copper pyrites is the chief ore of copper.

Extraction

Most of the ores of copper are sulphide ores. These sulphide ores are roasted/smelted to obtain oxides which can then be easily reduced to metallic copper using coke :

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$Cu_2O + C \longrightarrow 2Cu + CO$$

In actual process the copper metal is extracted from copper pyrites ($CuFeS_2$) through the following steps :

1. Concentration

The ore is concentrated by froth floatation process.

2. Roasting

The concentrated ore is heated in the presence of excess of air in a reverberatory furnace. During heating temperature is kept below the melting point of the ore. Changes that take place during roasting are:

(*i*) Moisture is expelled.

(*ii*) Sulphur, arsenic and phosphorus impurities are expelled as their volatile oxides.

$$S + O_2 \longrightarrow SO_2 \uparrow$$
$$4As + 5O_2 \longrightarrow 2As_2O_5 \uparrow$$
$$4P + 5O_2 \longrightarrow 2P_2O_5 \uparrow$$

(*iii*) Copper pyrites ore is converted to ferrous sulphide and cuprous sulphide.

$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$

3. Smelting

Mixture of roasted ore, powdered coke and sand (flux) is heated in blast furnace.

In this furnace two changes take place:

(*i*) Oxidation of ferrous sulphide takes place and ferrous oxide, which is formed as a result of this, combines with silica (flux) to form fusible slag, $FeSiO_3$.

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$
$$\underset{\text{Impurity}}{FeO} + \underset{\text{Flux}}{SiO_2} \longrightarrow \underset{\text{Slag}}{FeSiO_3}$$

(*ii*) Cuprous oxide, which is formed as a result of oxidation, is partially converted back into cuprous sulphide.

$$Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$Cu_2O + FeS \longrightarrow Cu_2S + FeO$$

From the base of furnace molten mass called *matte* is removed which is nothing but cuprous sulphide (Cu_2S) containing some ferrous sulphide (FeS).

4. Bessemerisation

The *matte* is transferred to a *Bessemer converter* (Fig. 5.3). The converter can be tilted so that it can be emptied and the mass poured out when the process is over. A blast of hot air and silica (sand) is blown through *molten matte*.

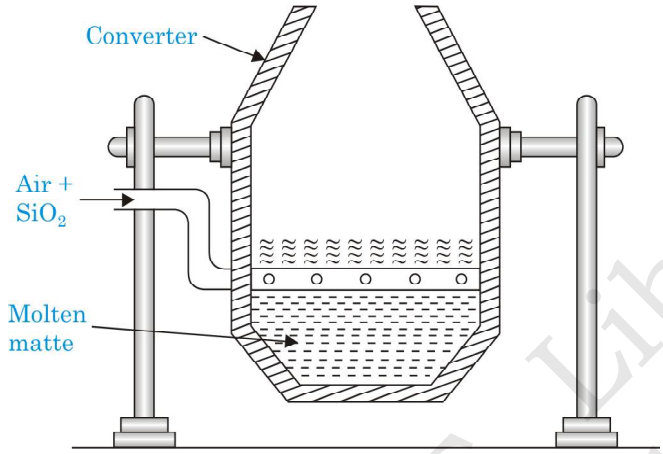

Fig. 5.3 Bessemer converter of copper.

The following reactions take place in the Bessemer converter:

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$

The iron oxide forms the slag with silica.

$$FeO + SiO_2 \longrightarrow \underset{\text{Slag}}{FeSiO_3}$$

The cuprous oxide reacts with more of Cu_2S to form copper.

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

After the reaction has been completed, the molten copper is poured off. As it cools, it gives up the sulphur dioxide dissolved in it which comes out in the form of bubbles thus giving the shape of blisters to the surface of copper which is, therefore, known as **Blister copper.**

5. Purification

(*i*) ***Poling.*** The blister copper is now purified by melting it in a reverberatory furnace where it is exposed to an oxidizing atmosphere. The impurities are either converted into slag or are expelled as volatile oxides. During this process the molten mass is stirred with long poles of green wood. The process is known as *poling*. The reducing gases evolved from the wood prevent the oxidation of copper.

Uses of Copper

1. Copper forms many useful alloys with metals such as Zn, Sn, Ni, etc.

2. It is extensively used for making electric cables and other electric appliances.
3. For electroplating and electrotyping.
4. For making utensils.
5. Copper is alloyed with gold and silver for making ornaments.

5.8 LEAD

Lead was one of the first metals known to man. Probably the oldest lead artifact is a figure made about 3000 BC. All civilizations, beginning with the anceint Egyptians, Assyrians, and Babylonians, have used lead for many ornamental and structural purposes. Many magnificient buildings erected in the 15th and 16th centuries still stand under their original lead roofs.

Lead Base Alloys

Becuse lead is very soft and ductile, it is normally usd commercially as lead alloys. Antimony, tin, arsenic and calcium are the most common alloying elements. Antimony generally is use to give greater hardness and strength, as in storage battery grids, seet, pipe and castings, Antimony contents of lead-antimony alloys can range from 0.5 to 25%, but they are usually 2 to 5%.

Lead-calcium alloys have replaced lead-antimony alloys in a number of applications, in particular, storage battery grids and casting applications. These alloy contain 0.02 to 0.15% Ca. More recently, aluminium has been added to calcium-lead and calcium-tin-lead alloys as a stabilizer for calcium. Adding tin to lead or lead alloys increases hardness and strength, but lead-tin alloys are more commonly use for their good melting, casting and wetting properties as in type metals and solders. Tin gives the alloy the ability to wet and bond with metals such as steel and copper; unalloyer lead has poor wetting characteristics. Tin combined with lead and bismuth or cadmium forms the principal ingredient of many low-melting alloys.

Uses

1. The most significant applications of lead and lead alloys are lead-acid storage batteries, ammunition, cable sheating, and building construction materials. Other important applications include counterweights, battery clamps and other cast products such as: bearings, ballast, gaskets, type metal, terneplate, and foil. Lead in various forms and combinations is finding incrased application as a material for controlling sound and mechnanical vibrations. Also, in many forms it is important as shielding against x-rays and, in the nuclear industry, gamma rays. In addition, lead is used as an alloying element in steel and in copper alloys to improve machinability and other characteristics, and it is used in fusible (low-melting) alloys for fire sprinkler systems.
2. **Battery Grids.** The largest use of lead is in the manufacture of lead-acid storage batteries. These batteries consist of a series of grid plates made from either cast or wrought calcium lead or antimonial lead that is pasted with a mixture of lead oxides and immersed in sulfuric acid.
3. **Type metals.** A class of metals used in the printing industry, generally consist of lead-antimony and tin alloys. Small amounts of copper are added to increase hardness for some applications.
4. **Cable Sheathing.** Lead sheathing extruded around electrical power and communication cables gives the most durable protection against moisture and corrosion damage, and provides mechanical protection of the insulation. Chemical lead, 1% antimonial lead, and arsenical lead are most commonly employed for this purpose.
5. **Lead base bearing alloys.** which are called lead-base babbitt metals, vary widely in composition but can be categorized into two groups.

   Alloys of lead, tin, antimony, and, in many instances, arsenic.

   Alloys of lead, calcium, tin and one or more of the alkaline earth metals.
6. **Ammunition.** Large quantities of lead are used in ammunition for both military and sporting purposes. Alloys use for shot contain up to 80% 5B and 2% As; those use for bullet cores contain upto 2% Sb.
7. **Terne Coatings:** Long terne steel sheet is carbon steel that has been continuously coated by various hot dip processes with terne metal (lead with 3 to 15% Sn). Its excellent solderability and

special corrosion resistance make the produce well-suited for this application.

8. **Lead Foil.** Generally, known as composition metal foil, is usually made by rolling a sandwich of lead between two sheets of tin, producing a tight union of the metals.
9. **Fusible Alloys.** Lead alloyed with tin, bismuth, cadmium, indium or other elements either alone or in combination, forms alloys with particularly low melting points. Some of these alloys, which melt at temperatures even lower than the boiling point of water, are referred to as fusible alloys.
10. **Anodes** made of lead alloys are used in the electrowinning and plating of metals such as manganese, copper, nickel and zinc. Rolled lead-calcium-tin and lead-silver alloys are the preferred anode materials in these applications, because of their high resistance to corrosion in the sulfuric acid used in electrolytic solutions. Lead anodes also have high resistance to corrosion by seawater, making them economical to use in systems for the cathodic protection of ships and offshore rigs.

5.9 ALLOYS

*An **alloy** is a homogeneous mixture of two or more metals, or metals and non-metals.*

The alloys are prepared to improve the mechanical properties like hardness and tensile strength, to resist the atmospheric and chemical corrosion, to produce sound and workable casting, and to lower the melting point.

*An alloy containing mercury as one of the metals is known as an **amalgam**.*

Some examples of common alloys are:

Brass, contains copper and zinc metals.

Bronze, contains copper and tin metals.

Stainless steel, contains iron, carbon, chromium and nickel.

Object of Preparation of Alloys

The main objects of making alloys are given below:

1. ***To increase the hardness.*** For example, pure iron is very soft and stretches easily when hot. But if it is mixed with a small amount of carbon (about 0.05%), it becomes hard and strong. Similarly, gold is alloyed with copper or silver to increase the hardness. The ornaments made from pure gold (24 carat gold) are

easily deformed. In order to avoid this, gold is alloyed with copper or silver to make ornaments. In India, generally, 22 carat gold is used for making ornaments. 22 Carat gold contains 22 parts pure gold and 2 parts either copper or silver.

2. ***To increase the tensile strength.*** For example, magnalium which is an alloy of magnesium and aluminium has greater tensile strength than the constituent metals.
3. ***To increase resistance to corrosion.*** For example, stainless steel which is an alloy of iron, chromium, nickel and carbon does not undergo corrosion.
4. ***To modify chemical reactivity.*** For example, sodium amalgam is less reactive than sodium.
5. ***To lower the melting point.*** For example, soldering metal (an alloy of tin and lead).
6. ***To produce good casting.*** For example, type metal.

Preparation of Alloys

Alloys are generally prepared by any of the following methods:

1. By melting the main metal, and then, dissolving the other components in it in a definite proportion. The melt is then allowed to solidify to obtain the alloy.
2. By compressing together the various constituents of the alloy under high pressure.
3. By simultaneous electrodeposition of metals.

Types of Alloys

There are two types of alloys:

1. *Ferrous alloys*. These are the alloys which contain iron as one of the constituents, such as nickel steel, stainless steel, etc.
2. *Non-ferrous alloys*. These are the alloys which do not contain iron as one of the constituents, such as bronze, brass, etc.

5.10 CEMENT

Cement is a general name given to a powdered material which initially have a plastic flow when mixed with water, but sets into a hard solid structure in several hour with varying degree of strength and bonding properties. It was discovered in 1824 by an English Meson Joseph Aspdine.

Chemically, cement is *fine ground mixture of calcium aluminates and silicates of varying composition which hardens into a rigid solid mass after treatement with water*. It is called **portland cement** because

of the resemblance of the hardened mass to ***portland rock***, a famous building stone of England.

Composition of Portland Cement

Portland cement is a dirty greyish heavy powder containing calcium aluminates and silicates. The silicates and aluminates which form more than 90% of the cement are:

- Tricalcium silicate ($3CaO.SiO_2$)
- Dicalcium silicate ($2CaO.SiO_2$)
- Tricalcium aluminate ($3CaO.Al_2O_3$)

Of these, tricalcium silicae is most important.

Raw Material for Clinker Production

The essential *raw materials* for the production of cement are **limestone** and **clay** which supply all the *four principle ingredients*; CaO, Al_2O_3, SiO_2 and Fe_2O_3. Calcium oxide and iron oxide are obtained from ***calcareous materials*** like limestone,chalk, calcium carbonate sluge etc. Silica and alumina are obtained from ***siliceous or argillaceius materials*** like clay, blast furnace slag, slate etc.

Production of Cement

FORMATION OF CEMENT CLINKERS

The raw materials, **lime** and **clay** are mixed and subjected to following processing.

1. Physical Treatment of Raw Materials

(*a*) Dry Process: In this process, the calcareous and argillaceous materials are ***mixed*** in the ratio 3 : 1, ***crushed***, ***dried***, ***sieved*** and then ***ground to a fine powder***. The mixture is now ready for the chemical treatment in the kiln.

(*b*) Wet Process: In this process, the rocky matter is ***crushed*** and water is sprinkled over it. The resulting materials is ground in the wet conditions to form a ***slurry***. The slurry, which contains 35-40% of water, is stored in large tanks equipped with mechanical stirrers. It is then fed into the kiln.

2. Chemical Treatment

It involves ***calcination*** of the mixture of **limestone** and **clay**. *Dry mixture* from the dry process or the *slurry* from the wet process is fed into the rotary kiln (Fig. 5.4) for calcination.

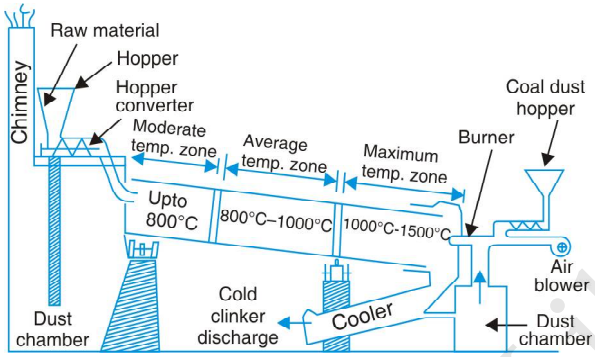

Fig.5.4 Rotary kiln for manufacture of portland cement.

The charge is introduced at upper end and it travels down as the kiln rotates.

The charge is heated by burning ***fuels*** like ***pulverized coal*** or, ***fossil fuel***, or ***oil*** or ***natural gas***. The hot fuel gases are made to enter at the lower end of the kiln with the help of a blower. As the charge moves forward, it meets higher temperatures till it reaches the lower end where the temperature is highest (around 1400 C). The charge takes 2 to 3 hours to cover the journey in the kiln. Reactions taking place in the rotary kiln in three major zones are as follows:

(*a*) *Maximum Temperature Zone (1000°C–1500°C)*: The main reactions between lime, alumina and silica takes place near the lower end of kiln resulting in formation of calcium silicates and aluminates as shown below.

$$2CaO + SiO_2 \longrightarrow \underset{\text{Dicalcium silicate}}{2CaO.SiO_2}$$

$$3CaO + Al_2O_3 \longrightarrow \underset{\text{Tricalcium aluminate}}{3CaO.Al_2O_3}$$

$$3CaO + SiO_2 \longrightarrow \underset{\text{Tricalcium silicate}}{3CaO.SiO_2}$$

$$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow \underset{\text{Tetracalcium alumino ferrite}}{4CaO.Al_2O_3.FeO_3}$$

(*b*) *Moderate Temperature Zone (up to 800°C):* At 100°C, the removal of free moisture takes place. At 500°C, kaolin ($Al_2O_3,2SiO_2.2H_2O$) present in clay breaks up into amorphous silica and alumina.

(*c*) *Average Temperature Zone (up to 800°C–1500°C):* Limestone decomposes to form lime and carbon dioxide.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Moreover, due to high temperature in this zone, about 20-30% of mass melts and combines with solids mass to form pebbles (which vary in size) and are called **cement clinkers.**

The burnt gases (containing a good amount of dust) are made to pass through a dust chamber, where most of dust is retained and gases are allowed to escape through chimney.

The hot clinkers from the rotary kiln go to coolers which consist of series of tubes parallel to kiln in which air is forced through. As a result of this, the clinkers cool down while the air gets heated. The hot air is then used for the combustion of the fuel as an economy measure.

Formation and Packing of Cement

The cooled **clinkers** are mixed with 3-5% of **gypsum $CaSO_4.2H_2O$**, along with certain *dispersing* and *water proofing agents* and then ground to a fine powder. Since pure finely powdered, clinkers set very rapidly, therefore, gypsum has to be added to retard the setting of cement. The powdered material is passed through fine sieves and finally it is sent to the automatic packing machines where it is packed in jute or polythene bags.

Setting of Cement

When cement is mixed with water and left as such for some time, it becomes a hard mass. This is known as **setting of cement**.

$$3CaO.Al_2O_3 + 6H_2O \xrightarrow{\text{Hydration}} \underset{\text{Colloidal gel}}{3CaO.Al_2O_3.6H_2O}$$

$$2CaO.SiO_2 + xH_2O \xrightarrow{\text{Hydration}} \underset{\text{Colloidal gel}}{2CaO.SiO_2.xH_2O}$$

$$4CaO.Al_2O_3.Fe_2O_3 + 6H_2O \xrightarrow{\text{Hydration}} \underset{\text{Colloidal gel}}{3CaO.Al_2O_3.6H_2O + Fe_2O_3.CaO}$$

At the same time some $Ca(OH)_2$ and $Al(OH)_3$ are formed as precipitates due to hydrolysis.

$$3CaO.SiO_2 + H_2O \xrightarrow{\text{Hydrolysis}} Ca(OH)_2 + 2CaO.SiO_2$$

$$3CaO.Al_2O_3 + 6H_2O \xrightarrow{\text{Hydrolysis}} 3Ca(OH)_2 + 2Al(OH)_3$$

Setting of cement is an exothermic process. Hence, cement structures have to be cooled during setting by sprinkling water.

Uses of Cement

1. Cement on a very large scale is used in building construction. For this purpose it is generally used in the form of a ***thick paste*** of cement, sand and water in appropriate proportion.
2. In the form of **concrete**, it used for the construction of floors, and roads. **Concrete** is a mixture of *cement*, *sand*, *gravel or small pieces of stone* along with *water*. It sets into an exceedingly hard structure.
3. In the form of **reinforced concrete** it is used in building roofs and bridges, etc. Reinforced concrete is the concrete which is made more stronger by embeding into it the steel frames or wire netting. The structures made of reinforced concrete are extremely strong because in these structures the compression strength of cement is coupled with tensile strength of steel.
4. It is also used in making *asbestos sheets*.

5.11 ENVIRONMENTAL IMPACT OF CEMENT PRODUCTION

Although cement is very useful in buildings and construction work, yet the cement production has adverse effect on the environment in the following way. One of the major pollutants released from cement plants is ***cement dust***. Its harmful effects are as under:

- It increases the concentration of particulate matter in air.
- The heavy metals present in the cement dust cause disturbance in various metabolic activities which further retards the growth process.
- It also causes breathing problems and lungs infections.
- Direct contact of cement dust with skin become the cause of many allergies and skin diseases.
- Cement kiln-dust gets accumulated on the soil and researchers have reported that it changes the soil alkalinity which is harmful for the crops.

EXERCISE

I. Objective Type Questions

Select the most appropriate choice from the options given as (a), (b), (c) and (d) after each question:

1. The impurities associated with the ore after mining are collectively called
   (*a*) flux (*b*) slag (*c*) minerals (*d*) gangue.
2. An ore after levigation is found to have acidic impurities. Which of the following can be used as flux during smelting operation ?
   (*a*) H_2SO_4 (*b*) $CaCO_3$
   (*c*) SiO_2 (*d*) Both $CaCO_3$ and SiO_2.
3. In which of the following minerals, aluminium is not present?
   (*a*) Fluorspar (*b*) Cryolite (*c*) Feldspar (*d*) Mica
4. The process in which metal oxide is reduced to metal by aluminium is called
   (*a*) smelting (*b*) aluminothermy
   (*c*) hydrothermy (*d*) no specific name.
5. Which of the following metals can be extracted by smelting?
   (*a*) Aluminium (*b*) Magnesium (*c*) Iron (*d*) None of these.
6. In the froth-floatation process for benefication 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.
7. Which of the following benefication processes is used for the mineral bauxite ?
   (*a*) Froth floatation (*b*) Leaching
   (*c*) Liquation (*d*) Magnetic separation.
8. Heating an ore in the absence of air below its melting point is called
   (*a*) leaching (*b*) roasting (*c*) smelting (*d*) calcination.
9. Cement is
   (*a*) Mixture of various elements
   (*b*) Single compound of definite composition
   (*c*) Mixture of aluminates and silicates of alkali metals
   (*d*) Mixture of calcium aluminates and silicates.

10. The credit of discovery of portland cement goes to
(*a*) Rutherford (*b*) Joseph Aspdin
(*c*) Joseph Pristlay (*d*) Linus Pauling.

11. Which of the following is not a constituent of Portland cement?
(*a*) CaO (*b*) Fe_2O_3 (*c*) Al_2O_3 (*d*) B_2O_3.

12. The colour of portland cement is
(*a*) Greyish white (*b*) Greyish black
(*c*) Bluish white (*d*) White.

13. In the rotary kiln the product that we get is
(*a*) Clinkers (*b*) Concrete
(*c*) Gypsum (*d*) Powdered cement.

14. The formula of gypsum is
(*a*) $CaSO_4.\frac{1}{2}H_2O$ (*b*) $CaSO_4$
(*c*) $CaSO_4.2H_2O$ (*d*) $CaSiO_3$.

II. Fill in the Blanks

Complete the following sentences by supplying appropriate words:

1. Froth floatation process is generally employed for ..... ores.
2. The most abundant metal in earth's crust is ..... .
3. The purification of crude metal is referred to as ..... .
4. The process of reduction of oxides by aluminium is known as ..... .
5. The process of removal of gaugue from ore is known as ..... .
6. Aluminium is obtained from Al_2O_3 by ..... reduction.
7. In the metallurgical process for electrorefining of the metal, the anode is made of ..... metal.
8. Slag is a product formed during smelting by combination of ..... and impurities.
9. The most important silicate component of the cement is .....
10. The charge introduced in the lime kiln consists .....
11. The temperature in the rotary kiln ..... as we move down the kiln.
12. The formation silicates/aluminates in the kiln occurs at the temperature range of .....
13. Concrete is a name given to .....

III. Discussion Questions

1. What is metallurgy? Write common steps involved in the metallurgical operations.
2. Write various steps involved in extraction of gold.
3. How would you extract aluminium from bauxite?
4. Write important ores of iron.
5. Discuss the process of extraction of iron from haematite.
6. Discuss the process of extraction of copper from copper pyrites.
7. What do you mean by alloy? Give some examples.
8. What is cement. Write down its compostion.
9. Write down steps involved in the production of cement.
10. Write short notes on:
    (a) Setting of cement
    (b) Environmental impact of cement production.