General Principles and Processes of Isolation of Elements - Part 1

Objectives

After going through this lesson, the learners will be able to understand the following:

- Explain the terms minerals, ores
- Analyse various methods used for concentration and benefaction of ore
- The use of calcination and roasting processes to obtain various metal oxides from their respective ores
- The principles of oxidation and reduction as applied to the extraction procedures

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Introduction

The development of human civilization passed from the Stone Age to Bronze Age and then Iron Age to our modern developed society—a society that is dependent on metals and alloys for its very existence.

Since the discovery of copper the metallurgical knowledge of the ancient man developed over thousands of years to investigate and understand the nature and use of the available native metal. The prehistoric man basically used six metals which were: gold, silver, copper, tin, lead, and iron.

Over the years the metallurgical knowledge evolved from an art to a science. The advancements in the knowledge of metallurgical processes became synonymous with the development of civilization (Table 1).

Table1: Chronological list of developments in the use of materials

Date	Development	Location
9000 B.C.	Earliest metal objects of wrought native copper	Near East
6500 B.C.	Earliest life-size statues, of plaster	Jordan
5000–3000 B.C.	Chalcolithic period: melting of copper; experimentation with smelting	Near East
3000–1500 B.C.	Bronze Age: arsenical copper and tin bronze alloys	Near East
3000–2500 B.C.	Lost-wax casting of small objects	Near East
2500 B.C.	Granulation of gold and silver and their alloys	Near East
2400–2200 B.C.	Copper statue of Pharaoh Pepi I	Egypt
2000 B.C.	Bronze Age	Far East
1500 B.C.	Iron Age (wrought iron)	Near East
700–600 B.C.	Etruscan dust granulation	Italy
600 B.C.	Cast iron	China
224 B.C.	Colossus of Rhodes destroyed	Greece
200–300 A.D.	Use of mercury in gilding (amalgam gilding)	Roman world
1200–1450 A.D.	Introduction of cast iron (exact date and place unknown)	Europe
Circa 1122 A.D.	Theophilus's *On Divers Arts*: the first monograph on metalworking written by a craftsman	Germany
1252 A.D.	Diabutsu (Great Buddha) cast at Kamakura	Japan
Circa 1400 A.D.	Great Bell of Beijing cast	China
16th century	Sand introduced as mold material	France
1709	Cast iron produced with coke as fuel, Coalbrookdale	England
1715	Boring mill or cannon developed	Switzerland
1735	Great Bell of the Kremlin cast	Russia
1740	Cast steel developed by Benjamin Huntsman	England
1779	Cast iron used as architectural material, Ironbridge Gorge	England
1826	Zinc statuary	France
1838	Electrodeposition of copper	Russia, England
1884	Electrolytic refining of aluminum	United States, France

Source: M. Goodway, History of Casting, Casting, Vol 15, Metals Handbook, 9th ed., ASM International, 1988, p 15–23

Qus 1: Which of the metals occur in their native state and why?

Ans: Metals like Au, Ag, Pt, etc. occur in their native state since they are unreactive.

A few elements like carbon, sulphur, gold and noble gases, occur in free state while others in combined forms in the earth's crust. The extraction and isolation of an element from its combined form involves various principles of chemistry. A particular element may occur in a variety of compounds. The process of metallurgy and isolation should be such that it is chemically feasible and commercially viable. Still, some general principles are common to all the extraction processes of metals. For obtaining a particular metal, first we look for minerals which are naturally occurring chemical substances in the earth's crust obtainable by mining. Out of many minerals in which a metal may be found, only a few are viable to be used as sources of that metal. Such minerals are known as ores.

Often, an ore contains only a desired substance. It is usually contaminated with earthly or undesired materials known as gangue. The extraction and isolation of metals from ores involve the following major steps:

- Concentration of the ore,
- Isolation of the metal from its concentrated ore, and
- Purification of the metal.

The entire scientific and technological process used for isolation of the metal from its ores is known as Metallurgy**.**

In the present episode, we shall describe various steps for effective concentration of ores.

Occurrence of Metals as Minerals in the Earth's Crust

Elements vary in abundance. Among metals, aluminium is the most abundant. It is the third most abundant element in earth's crust (8.3% approx. by weight). Iron is the second most abundant metal in the earth's crust. It forms a variety of compounds and their various uses make it a very important element. It is one of the essential elements in biological systems as well. Selection of ore forms a very crucial step in the metallurgy of a metal, as this decides on the economic viability of the process. The principal ores of aluminium, iron, copper and zinc are shown in (Table 2):

Table 2: Principal Ores of Some Important Metals

Metal	Ores	Composition
Aluminium	Bauxite	$AlO_x(OH)_{3-2x}$ [where 0 < x < 1]
	Kaolinite (a form of clay)	$[Al_2(OH)_4 Si_2O_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrites	FeS_2
Copper	Copper pyrites	$CuFeS_2$
	Malachite	$CuCO_3.Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

Qus 2: Why do metals exist in the form if their carbonates, hydroxides and sulphides in nature and not in the form of their nitrates?

Ans: Nitrates of various metals are soluble in water so can be washed away by rain water which goes into the ground as underground water since the metals are present in the earth's crust.

Qus 3: Name the important ores of tin and iron.

Ans: For **Sn**: Cassiterite (SnO_2)

For **Fe** : Haematite (Fe_2O_3) and Magnetite (Fe_3O_4)

Qus 4: Why is iron never found in the free state?

Ans: Iron has two stable oxidation states Fe^{2+} and Fe^{3+}, as a result has a tendency to get oxidised in presence of air and moisture so is reactive and not found in the native state.

Concentration of Ores

This is the first step in the metallurgy as unwanted impurities i.e. the gangue is removed in this step. Removal of the unwanted materials (e.g., sand, clays, etc.) from the ore is known as **concentration, dressing or benefaction**. Before concentration, ores are crushed, powdered and graded to a reasonable size.

It involves several steps and selection of these steps depends upon the differences in physical or chemical properties of the compound of the metal present and that of the gangue. The type of the metal, the available facilities and the environmental factors are also taken into consideration while selecting the method of concentration. Some of the important procedures are:

Hand Picking

In cases where the sizes of impurity particles differ from the size of the ore particles , the impurities can be removed manually by picking with hand. Generally rocky particles and other coarse earthy material are removed by this method.

Hydraulic Washing

The concentration process of an ore by Hydraulic Washing method may be compared with washing of pulses to remove any dirt or small stones before cooking.

Principle: Difference in gravities of the ore and the gangue particles. It is therefore a type of gravity separation method.

Method: In one such process, an upward stream of running water is used to wash the powdered ore. The lighter gangue particles are washed away and the heavier ores are left behind. The method has been in use for concentration of ores of tin and lead as these are heavy and settle to the bottom, whereas the dirt (gangue) is washed off (Figure 1).

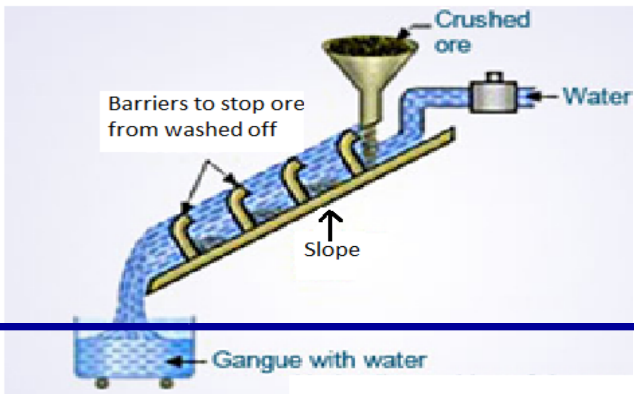


Figure 1: Hydraulic washing

Magnetic Separation

You all must have played with magnets and used them for simple separation of magnetic substances like iron filings from other components of a heterogeneous mixture in your lower classes. This method uses the same technique for concentration of ore.

Principle: Differences in magnetic properties of the ore components.

If either the ore or the gangue (one of these two) is capable of being attracted by a magnetic field, then such separations are carried out.

Method: The ground ore is carried on a conveyor belt which passes over a large electromagnetic roller. The magnetic component gets carried away with the roller whereas the non-magnetic component drops first and makes a heap. The magnetic component being carried away with the conveyor belt forms a separate heap. This method has been in use for concentration of iron ores (Figure 2).

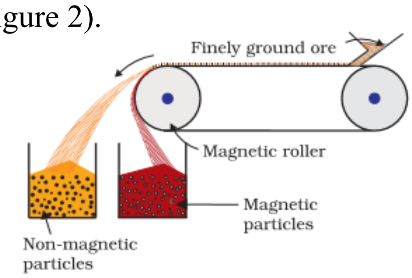
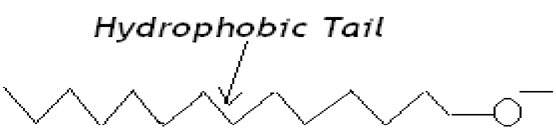


Fig. 6.1: Magnetic separation (schematic)

Figure 2: Magnetic separation (schematic)

Froth Floatation Method

You all have studied about the cleansing action of soap, where the long chain fatty acid has a hydrophobic tail and a hydrophilic head. In water, soap or detergent molecules have a unique orientation that keeps the hydrocarbon portion of the detergent molecule away from-water by forming micelles. These micelles lead to the formation of froth which pulls the dirt and cleans the linen.



Soap or Detergent molecule

The story about concentration of copper ore containing copper sulphide is very interesting; it is based on the same daily washing technique used in every household. Before we learn about the scientific technique let us learn how having a scientific attitude of asking questions and seeking their answers is so important in life and how it leads to innovations.

An Innovative Washerwoman

A washerwoman had an innovative mind. While washing a miner's overalls, she noticed that sand and similar dirt fell to the bottom of the washtub. What was peculiar, the copper bearing compounds that had come to the clothes from the mines, were caught in the soapsuds and so they came to the top along with the froth and when light fell on the froth it had a shine like gold. One of her clients was a chemist, Mrs. Carrie Everson. The washerwoman told her experience to Mrs. Everson. The latter investigated the property and quality of the shiny material coming to the top with soap froth. He thought that the idea could be used for separating copper compounds from rocky and earthy materials on a large scale. This way an invention happened. At that time only those ores were used for extraction of copper, which contained large amounts of the metal. Invention of the Froth Floatation Method made copper mining profitable even from the low-grade ores. World production of copper soared and the metal became cheaper (Figure 3).

Principle: Difference in the wetting characteristics of ore and gangue. The mineral particles are wetted by oils while the gangue particles by water. This method has been in use for removing gangue from sulphide ores.

Method:

1. In this process, first a suspension of the powdered ore is made with water.
2. Collectors and froth stabilisers are added to the suspension. The Collectors enhance non wetting ability of the mineral particles in water. Examples of collectors are pine oils, fatty acids, xanthates,etc.
3. Froth stabilisers as the name suggests stabilise the froth. Examples are cresols, aniline etc.
4. A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed by the collector's light and thus carries the mineral particles alongwith it to the top. It is then easily removed from the top.
5. It is then dried for recovery of the ore particles.

6. Sometimes, the ore obtained from nature is a mixture of sulphide of two metals, for example, an ore containing ZnS and PbS. In such cases the two sulphide ores are separated by adjusting the proportion of oil to water or by using 'depressants'. For example, in case of the ore containing ZnS and PbS, the depressant used is NaCN. It selectively prevents ZnS to come to the top and stick to the froth, but allows PbS to come with the froth. NaCN forms a coordination complex with ZnS, thus depressing it.

$$ZnS + 4\,NaCN \longrightarrow Na_2\,[Zn(CN)_4] + Na_2S$$

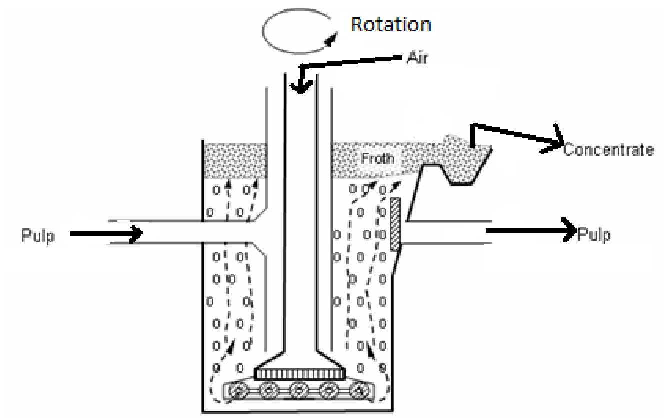


Figure 3: Froth floatation process

Qus 5: How does NaCN act as a depressant in preventing ZnS from forming froth?

Ans: NaCN forms a layer of Zinc complex $Na_2Zn(CN)_{4,}$ thereby preventing froth formation.

Leaching

In metallurgical process the concept of Learning is used to convert the metal ore into a soluble compound and then filter off the impurities as residue. In general Leaching means to separate soluble constituents of a mixture by passing a suitable liquid through it. Leaching is often used if the ore is soluble in some suitable solvent.

The following examples illustrate the procedure:

a. **Leaching of Alumina from Bauxite**: The principal ore of aluminium, bauxite, usually contains SiO_2, iron oxides and titanium oxide (TiO_2) as impurities. Concentration is carried out in following steps:

1. Digesting the powdered ore with a concentrated solution of NaOH at 473–523 K and 35–36 bar pressure. This way, Al_2O_3 is leached out as sodium aluminate leaving the impurities behind. SiO_2 too forms sodium silicate, but it is removed in subsequent steps:

$$AL_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$$

2. The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated.

$$2Na[Al(OH)_4](aq) + CO_2(g) \rightarrow AL_2O_3.xH_2O(s) + 2NaHCO_3(aq)$$

3. At this stage freshly prepared samples of hydrated Al_2O_3 are added to the solution to induce precipitation. This process is called seeding, so, we may say that the solution is seeded with a fresh sample of Al_2O_3.

4. The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3:

$$Al_2O_3.xH_2O\ (s) \xrightarrow{1470K} Al_2O_3\ (s) + x.H_2O(g)$$

b. **Metallurgy of Silver and Gold**: In case of metallurgy of silver and gold, metal is recovered in following steps:

1. The respective metal is converted to a soluble metal cyanide complex by treating with dilute solution of NaCN or KCN in the presence of air (for O_2). This water soluble complex is easily leached out as following:

$$4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq)$$

(soluble metal cyanide complex)

(M=Ag or Au)

2. The metal is obtained later by from its soluble complex by replacement with Zn, which forms a more stable; tetracyano zincate complex:

$$2[M(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2M(s)$$

Extraction of Crude Metal from Concentrated Ore

The method used for the extraction of the metal from the concentrated ore depends upon the nature of the metal. Based on their reactivity, the metals have been grouped into the following three categories :

- Metals of low reactivity (low in the activity series)
- Metals of medium reactivity (In the middle of the activity series)
- Metals of high reactivity (At top of the activity series)

Reducing the metal compound to the metal

Steps Involved in Extraction of Metal from its Ore

Metals of high reactivity	**Metals of medium reactivity**	**Metals of low reactivity**	**Noble metals**
K, Na, Ca, Mg, Al	Zn, Fe, Pb	Cu, Hg	Ag, Au
Ore	Ore	Ore	
↓	↓	↓	Found in native state only need to be purified usually by leaching
Crush	Crush	Crush	
↓	↓	↓	
Concentration of the ore	Concentration of the ore	Concentration of the ore	
↓	↓	↓	
Melt	Conversion of ore to its oxide by calcination or roasting	Melt	
↓	↓	↓	
Electrolysis of molten ore	Reduction of oxide to metal	Electrolysis of molten ore	
↓	↓	↓	
Pure metal	Purification to get pure metal	Pure metal	

Thus for metals of medium or low reactivity the concentrated ore must be converted into a form which is suitable for reduction. Usually the ore is converted to oxide before reduction. Oxides are easier to reduce. Thus isolation of metals from concentrated ore involves two major steps viz:

a. Conversion to oxide
b. Reduction of the oxide to metal.

a. Conversion to Oxide: Conversion of concentrated ore to oxide can be carried out by either calcinations or roasting.

I. Calcination: Calcination involves the strong heating of concentrated ore in absence of air. On strong heating the volatile impurities escape leaving behind the metal oxide. Calcination is the process in which an ore is heated strongly in the absence of air:

i. To convert a carbonate ore into metal oxide,
When calamine ore (zinc carbonate) is heated strongly in the absence of air, it decomposes to form zinc oxide and carbon dioxide

$$ZnCO_3(s) \xrightarrow{\text{calcination}} ZnO\ (s)\ + CO_2(g)$$

$$CaCO_3.MgCO_3(s) \rightarrow CaO(s)\ +\ MgO(s)\ +\ 2CO_2(g)$$

ii. to remove water from hydrated ores, and
iii. to remove volatile impurities from the ore

$$Fe_2O_3.xH_2O(s) \rightarrow Fe_2O_3\,(s)\ +\ xH_2O(g)$$

II. Roasting: In roasting, the ore is heated in a regular supply of air in a furnace at a temperature below the melting point of the metal. In this process a sulphide ore is strongly heated in the presence of air to convert it into metal oxide and to remove volatile impurities.

When zinc blende (zinc sulphide) is strongly heated in air (roasted), it forms zinc oxide and sulphur dioxide:

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

Some other reactions involving sulphide ores are:

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

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

The sulphide ores of copper are heated in a reverberatory furnace. If the ore contains iron, it is mixed with silica before heating. Iron oxide forms iron silicate (SLAG) and copper is produced in the form of copper matte which contains Cu_2S and FeS.

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

$$FeO + SiO_2 \rightarrow FeSiO_3\,(slag)$$

The SO_2 produced is utilised for manufacturing H_2SO_4 .

Comparison between Calcination and Roasting

S.No.	Calcination	Roasting
1	Carried out for carbonate ores, to convert the ore into its oxide. $CaCO_3 \xrightarrow{Heat} CaO + CO_2$	Carried out for sulphide ores, to convert the ore into its oxide. $ZnS + O_2 \xrightarrow{Heat} ZnO + SO_2$
2	Heating concentrated ore strongly in absence of air.	Heating concentrated ore strongly in presence of air
3	Removal of moisture, CO_2 and other volatile impurities	Removal moisture, CO_2, impurities of sulphur, arsenic etc.

b. Reduction of oxide to the metal: Reduction of the metal oxide usually involves heating it with some other substance acting as a reducing agent (C or CO or even another metal). The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide.

$$M_xO_y + yC \rightarrow xM + yCO$$

Some metal oxides get reduced easily while others are very difficult to be reduced. In any case, heating is required and the concept is called **pyrometallurgy** (Pyro is for heat).

As you know reduction may be understood as:

1. Gain of electron or electronation
2. Loss of Oxygen

To understand the variation in the temperature requirement for thermal reductions (pyrometallurgy) and to predict which element will suit as the reducing agent for a given metal oxide (M_xO_y), Gibbs energy interpretations are made. You will study the prediction of a good reducing agent and the suitable temperature for reduction of metal oxide to metal in the next module of this chapter.

Summary

Metals are required for a variety of purposes. For this, we need their extraction from the minerals in which they are present and from which their extraction is commercially feasible. These minerals are known as ores. Ores of the metal are associated with many impurities. Removal of these impurities to certain extent is achieved in concentration steps. The concentration of ore may be brought about by choosing a suitable process out of: Hydraulic Washing, magnetic separation, froth floatation or leaching. The method of reducing the concentrated ore to metal depends upon whether the metal belongs to high, medium, low or extremely low reactivity.The concentrated ore of medium or low reactivity is then usually converted to metal oxide by either calcination or roasting. In general the metal sulphides are roasted and metal carbonates or hydrates are calcined before reduction to metal.

Qus 6: Why are carbonate and sulphide ores generally converted into their oxides ?

Ans: Since a metal can be obtained more easily from its oxide by reduction so carbonate and sulphide ores of metals are converted into their oxides.

Qus 7 : Why can carbon reduce copper oxide to copper but not calcium oxide to calcium?

Ans: carbon reduces copper oxide to copper but not calcium oxide to calcium because it has more affinity for oxygen than copper but less affinity for oxygen than calcium.