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Extractive Metallurgy

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29. EXTRACTIVE METALLURGY

1. OCCURRENCE OF METALS

The earth's crust is the largest source of metals, besides some soluble salts of metals found in sea water. The mode of occurrence of a metal is largely dependent on its chemical nature. Those metals, which are relatively inert, occur in free or native state (i.e. in uncombined state) but most of the metals are reactive and hence are found in a combined state.

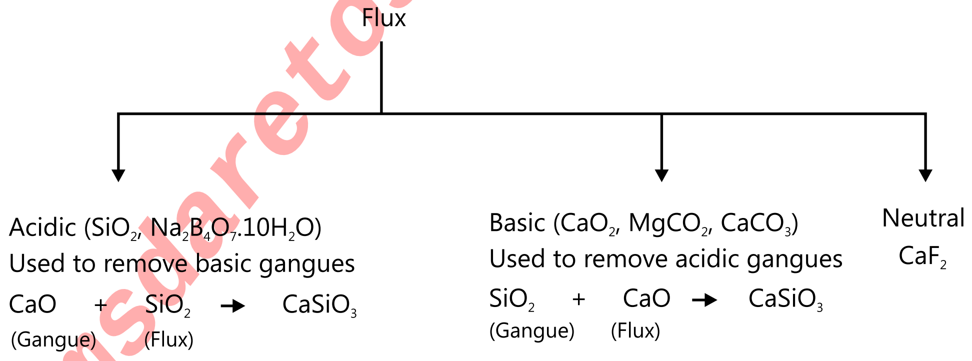
Mineral: The compounds of a metal which are naturally available in the earth's crust and can be obtained by mining are called minerals. A mineral may consist of one or more metallic compounds, having almost a fixed composition.

Ore: The minerals from which a metal can be extracted economically and conveniently are called ores.

Some important terminologies used in the process are:

Gangue or Matrix: Gangue or matrix are the non-metallic impurities present in the ore. In fact, impurities associated with an ore is known as gangue.

Flux: Flux are chemical substances which are generally added to an ore in order to remove the impurities or gangue. E.g., CaO, SiO_2 etc.



Flowchart 29.1: Classification of flux

Slag: Gangue + Flux → Slag

"Slag" is the fusible, light and floatable substance formed due to the reaction between gangue and the flux.

PLANCESS CONCEPTS

All ores are minerals but all minerals are not ores.

Vaibhav Krishnan (JEE 2009, AIR 22)

2. TYPES OF ORES

Ores may be classified mainly into following 4 classes:-

(a) **Native ores:** They contain the metal in a free state, and are found in the association of rock or alluvial impurities like clay, sand etc. Silver, gold, platinum etc. occur as native ores. Sometimes, lumps of almost pure metals are also found. These are called nuggets.

(b) **Oxidized ores:** These ores consist of oxides or oxysalts (e.g. carbonates, phosphates, sulphates and silicates) of metals.

Table 29.1: Some important ores of metals

Metal	Ores	Composition
Aluminium	Bauxite	$AlO_x(OH)_{3-2x}$ [where $0 < X < 1$] Al_2O_3
	Diaspore	$Al_2O_3.H_2O$
	Corundum	Al_2O_3
	Kaolinite (a form of clay)	$[Al_2\ (OH)_4\ Si_2O_5]$
Iron	Hematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrite	FeS_2
	Limonite	$Fe_2O_3.3H_2O$
Copper	Copper pyrite	$CuFeS_2$
	Copper glance	Cu_2S
	Cuprite	Cu_2O
	Malachite	$CuCO_3.Cu(OH)_2$
	Azurite	$2CuCO_3.Cu(OH)_2$
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO
Lead	Galena	PbS
	Anglesite	$PbSO_4$
	Cerrusite	$PbCO_3$
Magnesium	Carnallite	$KCl.MgCl_2.6H_2O\ [K_2MgCl_4.6H_2O]$
	Magnesite	$MgCO_3$
	Dolomite	$MgCO_3\ CaCO_3$
	Epsom salt (Epsomite)	$MgSO_4\ 7H_2O$
	Langbeinite	$K_2Mg_2(SO_4)_3$
Tin	Cassiterite (Tin stone)	SnO_2
Silver	Silver glance (Argentite)	Ag_2S
	Pyrargyrite (Ruby Silver)	Ag_3SbS_3
	Chlorargyrite (Horn silver)	$AgCl$.
	Stefinite	Ag_2SbS_4
	Prousitite	Ag_2AsS_3

Illustration 1: Which metals are supposed to occur in the native state in nature? **(JEE MAIN)**

Sol: Elements below hydrogen in the electrochemical series like Cu, Ag. Au etc, exist as native ores.

Illustration 2: Match the ores listed in column I with their correct chemical formula listed in column II. **(JEE ADVANCED)**

Column I	Column II
(A) Cassiterite	(p) $FeCO_3$
(B) Siderrte	(q) SnO_2
(C) Cerussite	(r) $PbSO_4$
(D)Anglesite	(s) $PbCO_3$

Sol: SnO_2 is called cassiterite or tin stone, $FeCO_3$ is called siderite. $PbCO_3$ is called cerussite and $PbSO_4$ is called anglesite. So correct match is A → q; B → p; C → s and D → r.

3. PRINCIPAL STEPS IN THE RECOVERY OF A METAL FROM ITS ORE

The isolation and extraction of metals from their ores involve the following major steps:

(a) Crushing of the ore

(b) Dressing or concentration of the ore

(c) Isolation of the crude metal from its ore

(d) Purification or refining of the metal

3.1 Crushing of the Ore

Ore is first crushed by jaw crushers and ground to a powder (pulverization of the ore) with the help of equipment like ball mills and stamp mills.

3.2 Concentration of the Ore

The removal of unwanted, useless impurities from the ore is called dressing, concentration or benefaction of the ore. It involves several steps, and, selection of these steps depends on the difference in the physical properties of the compound of the metal and that of the gangue. Hence, this process can be carried out by two methods of separation - Physical and Chemical.

Physical Methods of separation:

(a) Gravity separation or levigation

(b) Magnetic separation

(c) Froth floatation

Chemical methods of separation, i.e. leaching.

3.2.1 Physical Methods of Separation

Hydraulic Washing/Gravity Separation/ Levigation:

It is based on the difference in the densities of the gangue and ore particles. In this, the powdered ore is agitated with water or washed with an upward stream of running water. The lighter particles of sand, clay etc. are washed away leaving behind heavier ore particles. For this, either hydraulic classifier or wilfley table is used. This method is generally used for the concentration of oxide and native ores.

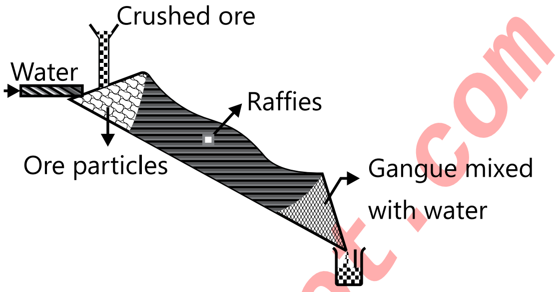


Figure 29.1 : Representation of gravity separation using wilfley table

Electromagnetic Separation: It is based on the differences in magnetic properties of the ore components. It is used when either the ore or the impurities associated with it are magnetic in nature. A magnetic separator consists of a belt (of leather or brass) moving over two rollers, one of which is magnetic. When the powdered ore is dropped on the belt at the other end, the magnetic component of the ore is attracted by the magnetic roller and falls nearer the roller while non-magnetic impurities fall away from it.

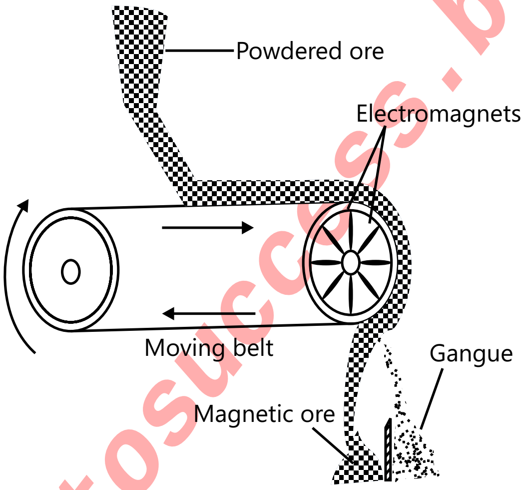


Figure 29. 2 : Electromagnetic separation using Electromagnets

Examples: Chromite ore ($FeO.Cr_2O_3$) is separated from non-magnetic silicious impurities and cassiterite ore (SnO_2) is separated from magnetic Wolframite ($FeWO_4 + MnWO_4$).

PLANCESS CONCEPTS

- Gravity separation utilizes the difference in density between the ore and the impurity.
- Magnetic separation is used to separate the magnetic impurities/ore from non-magnetic ores/impurities.

Nikhil Khandelwal (JEE 2009, AIR 94)

Froth Floatation Process: This process is used to separate the sulphide ore from the impurity in the ore. It is based upon the differential wetting of the ore by oil and the impurity by water. In this process, the ore is ground to fine powder and mixed with water to form a slurry mixture. Any one of the oily components, such as pine oil, eucalyptus oil, crude coal tar cresols, etc. is added together with sodium ethyl xanthate as a collector. Air, which acts as an agitator, creates bubbles through the mixture. Finally, the ore is floated to the froth and silicious impurities are settled at the bottom of the tank. Then the froth is collected into a separate container and washed thoroughly and dried. The oil added acts as a frothing agent. It reduces the surface tension of the water and helps to produce a stable froth. Reagents such as aniline or cresol are used to stabilize the froth. The formation of bubble involves an increase in air-water surface that means doing work against surface tension. The energy required to create a bubble of radius r is $2 \times 4 \pi r^2 \times E$. It is the energy required to create a unit surface area and it is directly proportional to the surface tension. The froth floatation process is usually applied for sulphide ores and the schematic representation is shown in figure. Sodium ethyl xanthate acts as a collector of sulphide ore.

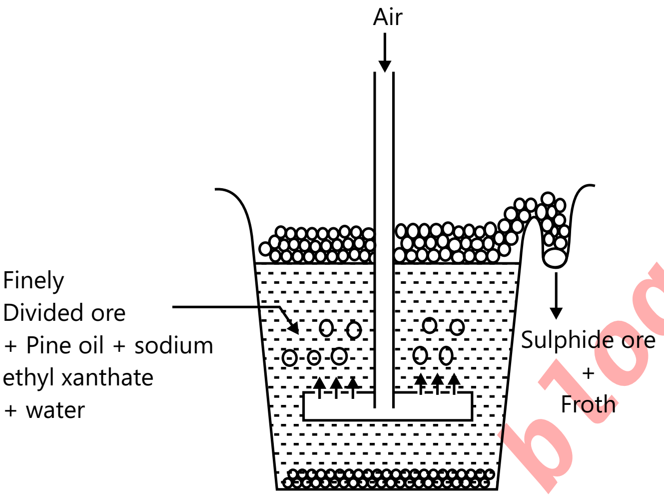


Figure 29.3: Froth floatation process for sulphide ore

The hydrophobic end prefers to stay in the air and the hydrophilic end prefers to stay in the water. Since the molecule has both hydrophobic and hydrophilic parts, the best place for it to stay is the air-water interface and hence it exhibits floating characteristics. The hydrophilic end attracts the sulphide particles and forms surface coated particles as shown in figure.

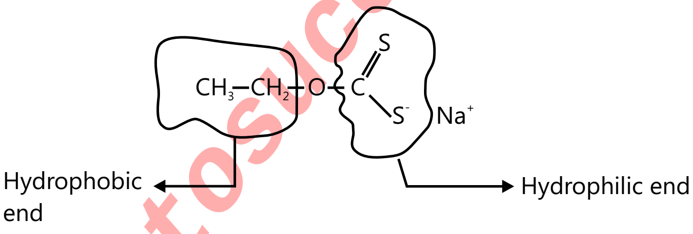


Figure 29.4-a: Bonding between dirt particle and sodium ethyl xanthate

Finally, the collected sulphide particles are floated to the froth and transferred to a separate container, washed with huge amounts of water, dried and sent for the next step of extraction.

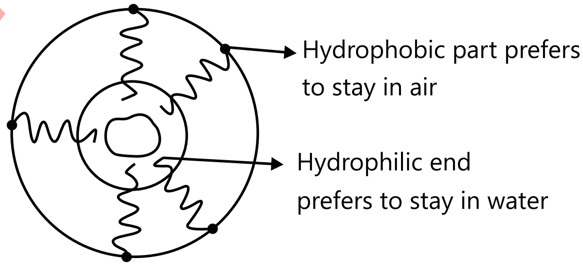
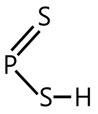


Figure 29.4-b: Sodium ethyl xanthate at the air water interface

(a) The other alkyl groups in xanthate may be amyl ($C_5H_{11}-$), octyl $\left(C_8H_{17}^-\right)$, etc. instead of the ethyl group.

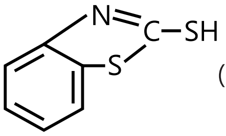
(b) The other collectors that may be used are;

- **(i)** Sodium lauryl sulphate : $C_{12}H_{25}-O-SO_3$ Na
- **(ii)** Trimethyl cetly ammonium bromide: $C_{16}H_{12}N^+(Me)_3)Br^-$
- **(iii)** Dicresyl dithiophosphate: $(CH_3-C_6H_4-O)_2$



(also called acrofloat)

- **(iv)** Mecraptobenzthiazole:



(also called floatogen)

The overall ore collecting process occurs through adsorption and depends upon the unbalanced forces on the solid surface.

Activator is a substance that is added to help the collector stay attached to the particles to be floated and hence, improves the floating characteristics of the ore. For example, the floating characteristic of ZnS is poor, compared to that of CuS. Hence $CuSO_4$ is used as an activator to form a coating of CuS on the ZnS surface and improve its floating characteristics.

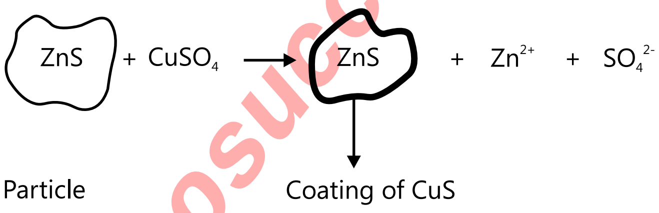


Figure 29.4-c: Action of activator

Accordingly, using suitable activators, the froth flotation process can also be applied for non sulphide ores. For example, Na_2S is a suitable activator for malachite ($CuCO_3$. Cu $(OH)_2$) and anglesite ($PbSO_4$) in which the coatings of CuS and PbS are formed by the activator, respectively.

A depressant is a substance that is added to suppress the floating characteristic of the ore particles. For example, galena (PbS) is associated with another sulphide impurity ZnS, which also rises to the surface with the froth. The reagent NaCN/KCN is used to suppress the floating characteristics of ZnS by forming soluble complex with KCN.

$PbS(s) + NaCN/KCN \rightarrow$ No reaction $ZnS(s) + 4[NaCN/KCN] \rightarrow [Zn(CN)_4]^{2-} + 4\,[Na^+/\,K^+] + S^{2-}$

PLANCESS CONCEPTS

- Froth floatation is used to separate the sulphide ores from its impurities.
- Froth floatation is based on the principle of differential wetting of the ore by oil and impurities by water.
- Activator is a substance that helps the collector to stay attached to the particles to be floated.
- Depressant is a substance which suppresses the floating characteristic of the ore.

Saurabh Gupta (JEE 2010, AIR 443)

Illustration 3: How does NaCN act as a depressant in preventing ZnS from forming the froth? **(JEE MAIN)**

Sol: NaCN reacts with ZnS and forms a layer of $Na_2[Zn(CN)_4]$ complex on the surface of ZnS and prevents it from the formation of froth.

Illustration 4: What is the role of a stabilizer in the froth floatation process? **(JEE MAIN)**

Sol: Froth can last for a longer period in the presence of a stabilizer.

3.2.2 Chemical Methods/Leaching

Leaching: Leaching is often used if the ore is soluble in some suitable solvent, e.g, acids, bases and suitable chemical reagents.

Leaching of alumina from bauxite: The principal ore of aluminium, bauxite, usually contains SiO_2, iron oxide and titanium oxide (TiO_2) as impurities. The concentration is carried out by 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 (and also SiO_2 as sodium silicate) leaving behind the impurities, iron oxide and titanium oxide.

$Al_2O_3(s) + 2NaOH\,(aq) + 3H_2O\,(l) \rightarrow 2Na\,[Al\,(OH)_4](aq)$

The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated. At this stage, the solution is seeded with freshly prepared samples of hydrated Al_2O_3 which induces the precipitation.

$2Na\,[Al\,(OH)_4](aq) + CO_2(g) \rightarrow Al_2O_3.xH_2O(s) + 2NaHCO_3(aq)$

The sodium silicate remains in the solution and hydrated alumina is filtered, dried and heated to give back pure Al_2O_3: $Al_2O_3.xH_2O(S) \xrightarrow{1470K/caloination} Al_2O_3(s) + xH_2O\,(g)$

These steps comprise the Bayer's process.

Other examples: In the metallurgy of silver and that of gold, the respective metal/ore is leached with a dilute solution of NaCN or KCN in the presence of air (or O_2) from which the metal is obtained later by displacement with zinc scrap.

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

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

PLANCESS CONCEPTS

Leaching is based on the difference of reactivity of the ore and impurity towards acids and bases.

Neeraj Toshniwal JEE 2009, AIR 21

3.3 Extraction of Concentrated Ore from Crude Metal

The concentrated ore must be converted into a form which is suitable for reduction. Usually the sulphide ore is converted to oxide before reduction. Oxides are easier to reduce. Thus isolation of metals from concentrated ore involves two major steps as given below.

(i) Conversion to oxide (ii) Reduction of the oxide to metal

3.3.1 Conversion to Oxide

Conversion of ore into oxide is carried out in two ways depending upon the nature of ore.

Calcination: It is a process of heating the concentrated ore strongly in a limited supply of air or in the absence of air. The process of calcination brings about the following changes:

(a) The carbonate ore gets decomposed to form the oxide of the metal, e.g.

$FeCO_3$ (siderite) $\xrightarrow{\Delta}$ $FeO + CO_2$; $PbCO_3$ (cerrussite) $\xrightarrow{\Delta}$ $PbO + CO_2$

$CaCO_3$ (calcite ore / lime stone) $\xrightarrow{\Delta}$ $CaO + CO_2$

$ZnCO_3$ (calamine) $\xrightarrow{\Delta}$ $ZnO + CO_2$

$CuCO_3 . Cu(OH)_2$ (malachite) $\xrightarrow{\Delta}$ $2CuO + H_2O + CO_2$

$MgCO_3 . CaCO_3$ (dolomite) $\xrightarrow{\Delta}$ $MgO + CaO + 2CO_2$

(b) Water of crystallization present in the hydrated oxide ore is lost as moisture, e.g.

$2Fe_2O_3 . 3H_2O$ (limonite) $\xrightarrow{\Delta}$ $2Fe_2O_3(s) + 3H_2O\ (g) \uparrow$

$Al_2O_3 . 2H_2O$ (bauxite) $Al_2O_3(s) + 2H_2O\ (g) \uparrow$

(c) Organic matter, if present in the ore, gets expelled and the ore becomes porous. Volatile impurities are removed.

Roasting: It is a process of heating the concentrated ore (generally sulphide ore) strongly in the excess of air or O_2 below its melting point. Roasting is an exothermic process; once started, it does not require additional heating. The process of roasting does the following things:

(a) Roasting at moderate temperature: Some portion of the sulphide ores like galena (PbS), Zinc blende (ZnS) is converted into metallic oxide. If the temperature is fairly low (about 500°C) and the concentration of SO_2 in the gaseous environment is more, sulphate may be produced, that is stable, and high temperature is needed to decompose them.

$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$; $2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$

$PbS + 2O_2 \xrightarrow{\Delta} PbSO_4$; $ZnS + 2O_2 \xrightarrow{\Delta} ZnSO_4$

Sometimes roasting may not bring about complete oxidation.

$2CuFeS_2$ (copper pyrite) $+ 4O_2 \rightarrow Cu_2S + 2FeO + 3SO_2$

(b) Roasting at high temperature: The sulphide ores of some of the metals like Cu, Pb, Hg, Sb etc., when heated strongly in the free supply of air or O_2 are reduced directly to the metal rather than to the metallic oxides, e.g. Cu_2S (copper glance) $+ O_2 \rightarrow 2Cu + SO_2$

PbS (galena) $+ O_2 \rightarrow Pb + SO_2$; HgS (cinnabar) $+ O_2 \rightarrow Hg + SO_2$

The reduction of the sulphide ore directly into metal by heating it in air or O_2 is known by various names, like self-reduction, auto-reduction, air-reduction etc. The SO_2 produced is utilized for the manufacture of H_2SO_4.

(c) It removes easily oxidisable volatile impurities like arsenic (as As_2O_3)), sulphur (as SO_2), phosphorus (as P_4O_{10}) and antimony (as Sb_2O_3).

4M (M=As, Sb) $+ 3O_2 \rightarrow 2M_2O_3\uparrow$; $S + O_2 \rightarrow SO_2\uparrow$; $P_4 + 5O_2 \rightarrow P_4O_{10}\uparrow$

These oxides being volatile, escape as gases through the chimney.

(d) When the concentrated tin stone ore SnO_2 (ore of Sn), is heated strongly in a free supply of air (roasting), the impurities of CuS and FeS present in the ore are converted into $CuSO_4$ and $FeSO_4$ respectively

$CuS + 2O_2 \xrightarrow{\Delta} CuSO_4$; $FeS + 2O_2 \xrightarrow{\Delta} FeSO_4$

Both calcination and roasting are generally carried out in a reverberatory furnace. In case of roasting, the air holes are kept open, while they are partially or completely closed during calcination.

Slag Formation: In many extraction processes, an oxide is added deliberately to combine with other impurities to form a stable molten phase immiscible with molten metal, called a slag. The process is termed as smelting.

The principle of slag formation is essentially the following:

Non metal oxide (acidic oxide) + Metal oxide (basic oxide) → Fusible (easily melted) slag

Removal of unwanted basic and acidic oxides: For example, FeO is the impurity in the extraction of Cu from copper pyrite. $2CuFeS_2 + 4O_2 \rightarrow Cu_2S + 2FeO + 3SO_2$

$$\underbrace{Cu_2S\ +\ FeO}_{\text{(Roasted phsite)}} + SiO_2 \rightarrow \underset{\text{(upper layer)}}{FeSiO_3\left(\text{Fusible slag}\right)} + \underset{\text{(lower layer)}}{Cu_2S\ \left(\text{matte}\right)}$$

Matte also contains a very small amount of iron (II) sulphide.

To remove unwanted acidic impurities like sand and P_4O_{10}, smelting is done in the presence of limestone.

$CaCO_3 \rightarrow CaO + CO_2$; $CaO + SiO_2 \rightarrow CaSiO_3$ (fusible slag)

$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$ (fusible slag - Thomas slag)

Properties of a Slag:

(a) Slag is a fusible mass.

(b) It has a low melting point.

(c) It is lighter and is immiscible with the molten metal. It is due to these properties that the slag floats as a separate layer on the molten metal and so, can be easily separated from the metal. The layer of the slag on the molten metal prevents the metal from being oxidised.

Types of Flux: Flux are of two types, viz, acidic flux and basic flux.

(a) Acidic flux: It is an acidic oxide (oxide of a non-metal) like SiO_2, P_2O_5, B_2O_3 (from borax). It is used to remove basic impurities like CaO, FeO, MgO etc. The acidic flux combines with a basic impurity to form a slag.

(b) Basic flux: It is a basic oxide (i.e. oxide of a metal) like CaO (obtained from lime stone, $CaCO_3$), MgO (from magnesite. $MgCO_3$), haematite (Fe_2O_3) etc. It is used to remove acidic impurities like SiO_2, P_2O_5 etc. The basic flux combines with an acidic impurity to form a slag.

Thus, slag can be defined as a fusible mass, which is obtained when a flux reacts with an infusible, acidic or basic impurity present in the oxide ore.

PLANCESS CONCEPTS

- In Calcination, the concentrated ore is heated to a high temperature in the absence of air.
- In Roasting, the concentrated ore is heated to a high temperature in the presence of air.

Aman Gour (JEE 2012, AIR 230)

3.3.2 Reduction of the Oxide to Metal

The free metal is obtained by reduction of a compound, using either a chemical reducing agent or by an electrolysis.

Reduction with Carbon: A large number of commercial processes come under this category. Carbon can be used to reduce a number of oxides and other compounds, and because of the low cost and availability of coke, this method is widely used. The disadvantages are that, high temperature is needed, which is expensive and necessitates the use of the blast furnace.

$PbO + C \rightarrow Pb + CO$ (extraction of lead)

$2Fe_2O_3 + 3C \rightarrow 4Fe$ (spongy iron) $+ 3CO_2$

$ZnO + C \xrightarrow{1200°C} Zn + CO$ (extraction of zinc)

$SnO_2 + 2C \text{ (anthracite)} \xrightarrow{1800°C} Sn + 2CO$ (extraction of tin)

$MgO + C \xrightarrow[\text{electric furnace}]{1200°C} Mg + CO$

Reduction with CO: In some cases CO produced in the furnace itself, is used as a reducing agent.

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$; $Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$

$PbO + CO \rightarrow Pb + CO_2$; $CuO + CO \rightarrow Cu + CO_2$

The reduction process of carbon or carbon monoxide is usually carried out in a blast furnace. There are some disadvantages of using carbon as a reducing agent e.g.:

(a) Some metallic oxides like CaO give metallic carbides instead of metals. $CaO + 3C \xrightarrow{\Delta} CaC_2 + CO$

(b) During the cooling of the products, in many cases, reformation of the oxide and carbon may take place.

$$MgO + C \underset{\text{cool}}{\overset{\Delta}{\rightleftharpoons}} Mg + CO$$

Reduction by other Metals: If the temperature needed for carbon to reduce an oxide is too high, for economical or practical purposes, reduction by other metals is done. Also, certain metallic oxides cannot be reduced by carbon because the affinity of oxygen for the metal is greater than its affinity for carbon. Such metallic oxides (Cr and Mn) can be reduced by a highly electropositive metal such as aluminium that liberates a large amount of energy (1675 kJ/mol) on oxidation to Al_2O_3. The process is known as Goldschmidt or aluminothermic process and the reaction is known as thermite reaction.

Cr_2O_3 is mixed with a requisite amount of Al-powder (this mixture is called thermite mixture) and is placed on a large fire-clay crucible. An intimate mixture of Na_2O_2 or BaO_2 and Mg powder (called ignition mixture or igniter) is placed in a small depression made in the thermite mixture. The crucible is surrounded by sand, which prevents the loss of heat by radiation. A piece of Mg ribbon is struck into the ignition mixture and the charge is covered by a layer of fluorspar (CaF_2) which acts as a heat insulator. Now the Mg-ribbon is ignited so that the ignition mixture catches fire and flame is produced, leading to a violent reaction between Mg and BaO_2 with the evolution of a large amount of heat.

$Mg + BaO_2 \rightarrow BaO + MgO + Heat$

Heat produced in the above reaction makes Cr_2O_3 and Al powder to react together.

$Cr_2O_3 + Al \rightarrow 2Cr\ (l) + Al_2O_3$

Molten Cr-metal formed settles down at the bottom of the crucible.

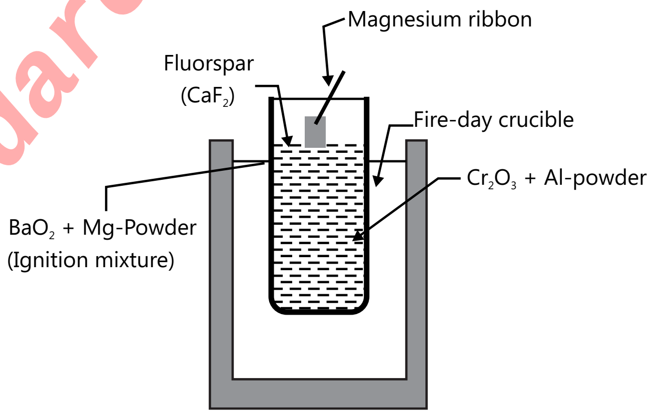


Figure 29.5: Reduction of Cr_2O_3 by Al-powder (Aluminothermic process)

In this process, thermite mixture consisting of Fe_2O_3 and Al-powder in 3: 1 ratio is placed in a funnel-shaped crucible, lined internally with magnesite, with a plug hole at its bottom. The thermite mixture is covered with a mixture of BaO_2 and Mg-powder (ignition mixture) in which a piece of Mg ribbon is inserted. The ends of the iron pieces to be welded are thoroughly cleaned and surrounded by a fire-clay mould. When the Mg ribbon is ignited, the ignition mixture catches fire and Fe_2O_3 gets reduced to Fe by Al-powder.

$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$ (molten); $\Delta H = -3230$ kJ (The reaction is used for thermite welding)

$3Mn_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9\,Mn$; $B_2O_3 + 2Al \rightarrow 2B + Al_2O_3$ (extraction of boron)

As it is a strongly exothermic reaction, it proceeds with explosive violence and only initial heating is needed.

Magnesium Reduction Method: Magnesium is used in a similar way to reduce oxides. In certain cases where the oxide is too stable to reduce, electropositive metals are used to reduce halides.

$TiCl_4 + 2\,Mg \xrightarrow[1000\text{–}1150°C]{\text{kroll process}} Ti + 2\,MgCl_2$; $TiCl_4 + 4Na \xrightarrow{\text{IMI process}} Ti + 4NaCl$

Advantages of using Na and Mg as reducing agents are, the higher reducing power of the metals and solubility of their halides in water, so that the reduced metals can be washed free from impurities.

Self Reduction method: This method is also called auto-reduction method or air reduction method. If the sulphide ore of some of the less electropositive metals like Hg, Cu, Pb, Sb, etc. are heated in air, a part of these is changed into oxide or sulphate. Then that reacts with the remaining part of the sulphide ore to give its metal and SO_2.

Examples: $2HgS + 3O_2 \rightarrow 2HgO + 2SO_2$; $2HgO + HgS \rightarrow 3Hg + SO_2$

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$; $2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$

$2PbS + 3O_2 \rightarrow 2PbO + 2\,SO_2$; $2PbO + PbS \rightarrow 3Pb + SO_2$

The extraction of Pb by heating its sulphide ore (PbS) in air can also be represented as

$PbS + 2O_2 \rightarrow PbSO_4$; $PbSO_4 + PbS \rightarrow 2\,Pb + 2SO_2$

Electrolytic Reduction Method: It presents the most powerful method of reduction and gives a very pure product. As it is an expensive method compared to chemical methods, it is used either for very reactive metals, such as magnesium or aluminum, or for the production of samples of high purity. Electrolytic reduction of copper has the additional advantage of allowing the recovery of valuable minor contaminants such as silver.

(a) **In aqueous solution:** Electrolysis can be carried out conveniently and cheaply in an aqueous solution, so that the products do not react with water. Copper and zinc are obtained by electrolysis of the aqueous solution of their sulphates.

(b) **In other solvents:** Electrolysis can be carried out in solvents other than water. Fluorine reacts violently with water and it is produced by electrolysis of KHF_2 dissolved in anhydrous HF.

(c) **In fused melts:** Elements that react with water are often extracted from fused melts of their ionic salts. Aluminum is obtained by the electrolysis of a fused mixture of Al_2O_3 and cryolite $Na_3[AlF_6]$. Both sodium and chlorine are obtained from the electrolysis of fused NaCl. In this case, upto two-thirds by weight of $CaCl_2$ is added as an impurity to lower the melting point from 803 to 505°C.

Electrochemical Principles of Metallurgy: Electrolytic reduction can be regarded as a technique for driving a reduction by coupling it through electrodes and external circuits to a reactive or a physical process with a more negative ΔG. The free energy available from the external source can be assessed from the potential it produces, across the electrodes, using the thermodynamic relation:

$\Delta G = -nFE$ ... (i) where, n is the number of electrons transferred, F is Faraday's constant (F = 96.5 kJ/mol) and E° is the electrode potential of the redox couple, formed in the system.

Hence, the total Gibb's energy of the coupled internal and external process is $\Delta G + \Delta G\,(\text{external}) = \Delta G - nFE_{ext}$

If the potential difference of the external source exceeds $E_{ext} = -\dfrac{\Delta G}{nF}$ then, the reduction is thermodynamically feasible. Thus, the overall process occurs with a decrease in free energy. More reactive metals have large negative values of the electrode potential. So their reduction is difficult. If the difference of two E° values corresponds to a positive E° and consequently negative $\Delta G°$ in equation (i), then the less reactive metal will come out of the solution and the more reactive metal will go to the solution, e.g., $Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

Hydrometallurgy: The processing of extraction of ores and minerals as well as metals and their compounds at relatively low, often ambient temperatures employing an aqueous solution is known as hydrometallurgy. Occasionally, organic reagents are also used. This method of extraction is generally used for low grade ores. Copper is extracted by hydrometallurgy from a low grade ore. It is leached out using acid and bacteria. The solution containing Cu^{+2} is treated with scrap iron or H_2.

$CuSO_4 + Fe \rightarrow Cu(s) + FeSO_4$

A hydrometallurgical process for the extraction of metals from ores, concentrates, or secondary materials essentially contains three basic steps—dissolution of the valuable metal in the aqueous solution (leaching), purification of the leach solution and the subsequent recovery of metal from the purified solutions either by electrolysis or by adding some electropositive metal to it. Some of the metals obtained by hydrometallurgy are as follows:

Extraction of Ag and Au: Metals like Au and Ag can be precipitated for their salt solution by electropositive metals e.g. Zn. Metallic Ag is dissolved from its ore in a dilute NaCN solution, and the solute so obtained, is treated with scrap Zn when Ag is precipitated. Air is blown into the solution to oxidize Na_2S. Leaching the metals like silver, gold with CN^- is an oxidation reaction ($Ag \rightarrow Ag^+$ or $Au \rightarrow Au^+$)

$Ag_2S(s) + 4CN^-(aq) \rightarrow 2\,[Ag\,(CN)_2]^-\,(aq) + S^{2-}(aq)$

$2[Ag\,(CN)_2]^-\,(aq) + Zn(s) \rightarrow [Zn(CN)]^{2-}\,(aq) + 2Ag\,(s)$

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

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

Here Zn acts as a reducing agent.

The leaching pitch blends with H_2SO_4 or sodium carbonate to dissolve uranium:

$U_3O_8 + 3Na_2CO_3 + \frac{1}{2}\,O_2 \rightarrow 3Na_2UO_4 + 3CO_2;\ U_3O_8 + 3\,H_2SO_4 + \frac{1}{2}\,O_2 \rightarrow 3UO_2SO_4 + 3H_2O$

Precipitation of Mg $(OH)_2$ from sea water using lime solution:

$MgCl_2 + Ca\,(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$

Oxidation Reduction: Besides reductions, some extractions are based on oxidation particularly for non-metals.

(a) A very common example of extraction based on oxidation is the extraction of chlorine from brine (chlorine is found abundantly in sea water as common salt). $2Cl^-(aq) + 2H_2O(l) \rightarrow 2OH^-(aq) + H_2(g) + Cl_2(g)$

The $\Delta G°$ for this reaction is + 422 kJ, when it is converted to $E°$ (using $\Delta G° = -nE°F$), we get $E° = -2.2$ V. Naturally, it will require an external e.m.f. that is greater than 2.2 V. But the electrolysis requires an excess potential to overcome some other hindering reactions. Thus, Cl_2 is obtained by electrolysis giving out H_2 and aqueous NaOH as by-products. Electrolysis of molten NaCl is also carried out. But in that case, Na metal is produced and not NaOH.

Illustration 5: Common impurities present in Bauxite are:

(A) CuO (B) ZnO (C) Fe_2O_2 (D) SiO_2 **(JEE ADVANCED)**

Sol: (C) Red Bauxite contains Fe_2O_3 as impurity.

(D) White Bauxite contains SiO_2 as impurity

Illustration 6: Which metals are generally extracted by the electrolytic reduction and why? **(JEE MAIN)**

Sol: More reactive and electropositive elements acts as strong reducing agents like. Sodium, aluminium, magnesium etc. Hence they cannot be extracted by any of the chemical methods.

3.4 Purification or Refining of Metal

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

3.4.1 Thermal Refining

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

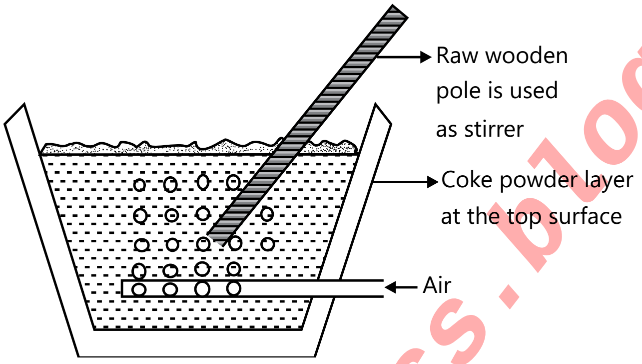
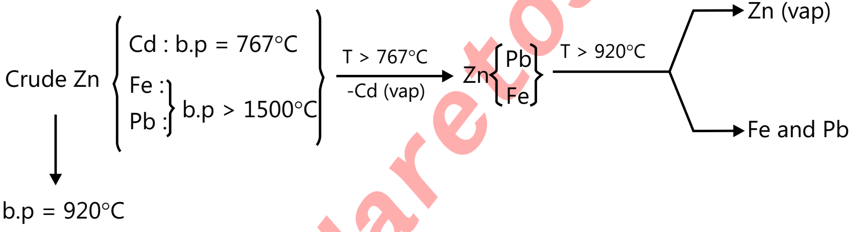


Figure 29.6: Diagrammatic representation of oxidation by air and poling

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

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



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

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

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

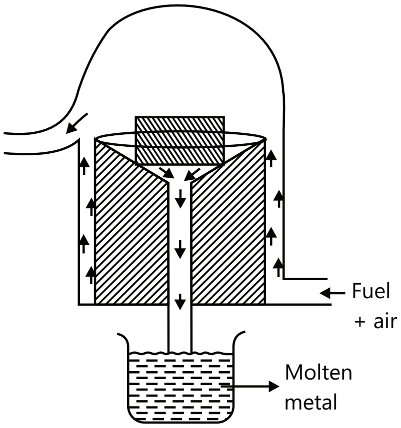


Figure 29.7: Diagrammatic representation for liquation

Zone Refining: Metals like Si, Ge and Ga of high purity (which are used in semiconductors) are purified by this method. This process is known as ultra-purification, because it results in the impurity level decreasing to ppm level. Zone refining is based upon fractional crystallization, as the impurity prefers to stay in the melt and on solidification only the pure metal solidifies on the top surface of the melt. In this process, a ring furnace is heated to a suitable temperature for melting the metal rod (figure (a)), producing a thin zone throughout the cross-sectional area as shown in Figure (b). It is desirable that the diameter of the rod, d, is small enough to give a uniform melt.

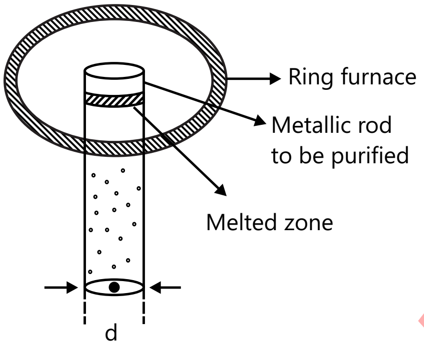


Figure 29.8-a: Metal rod heated by ring furnace

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

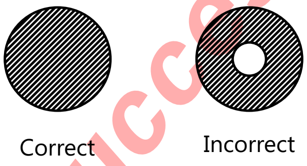


Figure 29.8-b: Cross-sectional view of the metal rod

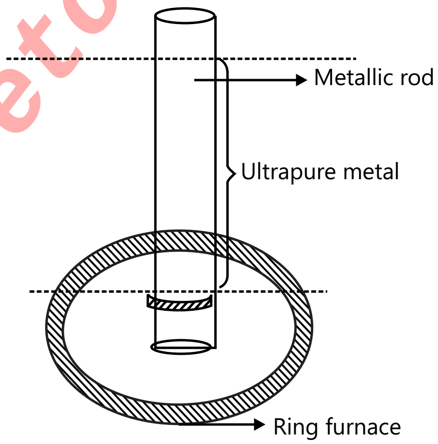


Figure 29.8-c: Ring furnace moving down the metal rod

Vapour Phase Refining: The two essential criteria for the vapour refining process are listed below:

(a) The intermediate compound formed has to be volatile.

(b) The intermediate compound formed has to be relatively unstable, i.e. it should decompose on heating at a practically achievable temperature.

This refining technique is used in the following purification processes:

(i) Mond's process (for purification of nickel):

$$\underset{\text{Impure}}{\text{Ni(s)} + 4\text{CO(g)}} \xrightarrow{50\text{–}80^\circ\text{C}} \underset{\text{volatile}}{\text{Ni(CO)}_4\text{(g)}} \xrightarrow{150\text{–}180^\circ\text{C}} \underset{\text{Pure}}{\text{Ni(s)}} + \underset{\text{Recycled}}{4\text{CO(g)}}$$

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

(ii) Van-Arkel-de Boer process (for purification of zirconium, boron and titanium):

$$\underbrace{\text{Zr or Ti}}_{\text{impure}} \xrightarrow[250^\circ\text{C}]{I_2\text{(vap)}} \underbrace{\text{ZrI}_4 \text{ or TiI}_4}_{\text{Volatile}} \xrightarrow[\text{on gestem filsment}]{1400^\circ\text{C}} \underbrace{\text{Zr(s) or Ti(s)}}_{\text{pure}} + \underset{\text{recycled}}{2I_2\text{(g)}}$$

$$\underset{\text{impure}}{\text{B}} + \frac{3}{2}I_2\text{(vap)} \rightarrow \underset{\text{volatile}}{\text{BI}_3} \xrightarrow{\Delta} \underset{\text{Pure}}{\text{B}} + \underset{\text{recycled}}{\frac{3}{2}I_2\text{(g)}}$$

3.4.2 Electro Refining

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

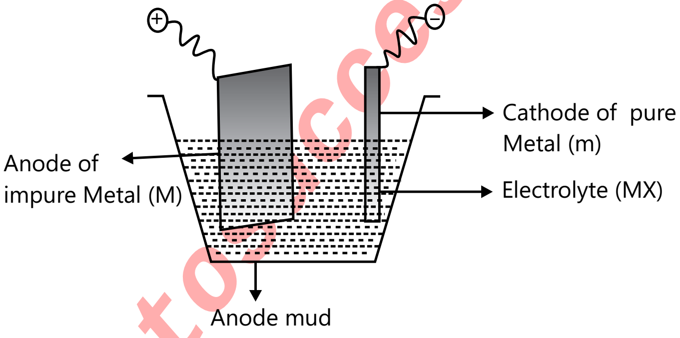


Figure 29.9: Diagrammatic representation of electro refining

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

Reactions at the electrodes: At cathode: $M^{n+} + ne^- \rightarrow M$

At anode : (i) $M \rightarrow M^{n+} + ne^-$ (wanted) (ii) $X^{n-} \rightarrow \frac{1}{2}X_2 + ne^-$ (unwanted)

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

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

The metallic impurities having lower oxidation potential than that of the metal to be refined are separated in the form of anode mud at the bottom. The suitable electrolytes used in general for respective metals are:

Cu: $CuSO_4$ solution
Zn: $ZnSO_4$ solution
Au: $AuCl_3$ solution
Sn: $SnSO_4$ solution
Ag: $AgNO_3$ solution
Al: Al_2O_3 + (Na_2AlF_6) melt + BaF_2
Ni : $N_2(NO_3)_2$ solution
Pb: $PbSiF_6$ solution

PLANCESS CONCEPTS

- In the Poling process, a wooden pole is used and the hydrocarbons reduce the metal oxide impurities to refined metal.
- Fractional distillation utilizes the difference in the boiling points between the metal and its impurities.
- Liquation is applicable to metals having much lower melting points, as compared to its impurities.
- Zone refining is based upon fractional crystallization, as the impurity prefers to stay in the melt and the pure metal solidifies on cooling.
- Mond's process is used for nickel, as $Ni(CO)_4$ is volatile and on high temperature decomposes to give back pure nickel metal.
- Van arkel de boer's process is used for purification of Zr, B and Ti, as their iodides are volatile and on higher temperature gives back the pure metal. Electro refining is used for purification of Cu, Zn, Sn , Ag, Au, Ni, Pb and Al. Anode consists of impure metal and cathode consists of pure metal.

B Rajiv Reddy (JEE 2012, AIR 11)

4. THERMODYNAMICS OF EXTRACTION: ELLINGHAM DIAGRAM OF A METAL

The standard electrode reduction potential of metal provides a very good indicator, or, the ease or difficulty of extracting the metal from its compounds. However, since most metals of industrial importance are obtained by the chemical reduction of their oxide, the free energy changes occurring during these processes are of more fundamental importance. Despite the fact that redox reactions do not always reach equilibrium, thermodynamics can at least be used to identify which reactions are feasible. For a spontaneous reaction the change in free energy ΔG must be negative,

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

It is sufficient to consider ΔG because it is related to the equilibrium constant through $\Delta G = -RT\ln K$.

Here, a negative value of ΔG corresponds to $K > 1$ and, therefore, a favorable reaction. Reaction rates are also relevant, but at a high temperature, reactions are often fast and we can normally assume that any thermodynamically permissible process can occur. The problem of extracting a metal from its ore is essentially concerned with decomposing the oxide of the metal (apart from simple binary compounds such as metal sulfides and chlorides that occur in nature). Most metal ores consist essentially of a metal oxide in association with one or more nonmetal oxides. Ores like carbonates, sulphides etc. are also converted to oxides, prior to reduction.

The free energy of formation, ΔG is the standard free energy of the reaction.

$$x\,M + \frac{y}{2}O_2 \rightarrow M_xO_y \qquad \text{... (i)}$$

or $$\frac{2x}{y}M + O_2 \rightarrow \frac{2}{y}M_xO_y \qquad \text{... (ii)}$$

ΔG is the free energy of formation per mole of O_2 consumed.

If the standard free energy of formation, ΔG has a negative sign at a given temperature, then the oxide can be expected to form spontaneously from the metal plus oxygen. If ΔG has a positive sign, the oxide will be expected to decompose spontaneously into its elements.

The free energy of formation of an oxide can now be determined, provided we know the entropy of the formation.

$$\Delta G = \Delta H - T\Delta S \qquad \text{... (iii)}$$

In reaction (ii) oxygen is used up in the course of the reaction. Gases have a more random structure (less ordered) than liquid or solids. In this reaction, the entropy or randomness decreases, and hence ΔS is negative (provided that neither the metal nor its oxide M_xO_y are vaporized). Thus, if the temperature is raised then TΔS becomes more negative. Since, TΔS is subtracted in equation (ii), ΔG becomes less negative. Thus, the change in free energy decreases with increase in temperature. The free energy change that occurs when 1 mol of common reactant (in this case O_2) is used, may be plotted graphically against the temperature for a number of reaction of metals to their oxides. This graph is shown in the following figure and is called an Ellingham diagram for oxides. Similar diagrams can be produced for 1 mol of S, giving Ellingham diagram for sulphides and similarly for halides using 1 mol of halogen.

This figure shows a number of oxide plots with slopes defined by $\Delta G / T = -\Delta S$. It is noted that the entropy change in reaction (ii) is roughly the same for all metal oxides, provided that the boiling point of neither the metal nor oxide is exceeded. Thus, below the boiling point of metal, the slope of all the graphs are roughly the same, since TΔS factor is the same whatever the metal may be. When the temperature is raised, a point will be reached where the graph crosses the ΔG = 0 line. Below this temperature the free energy of formation of oxide is negative, so the oxide is stable. Above this temperature the free energy of formation of the oxide is positive, and the oxide becomes unstable and should decompose into metal and oxygen. This explains why HgO_3 for instance, decomposes spontaneously into its elements when heated. Theoretically, all oxides can be decomposed to give metal and oxygen, if a sufficiently high temperature can be attained. In practice, that is easily attainable and these metals can be extracted by thermal decomposition of their oxides. The diagram predicts that MgO and ZnO ought to decompose if heated strongly enough, but it does not hold out much hope for obtaining, say, pure Mg by straight forward heating of the oxide to a high temperature where the boiling point of the metal is exceeded. However the slope increases, since the reaction now involves a larger entropy change as the randomness increases in reactants. For example, $2Mg\ (g) + O_2(g) \rightarrow 2MgO(s)$

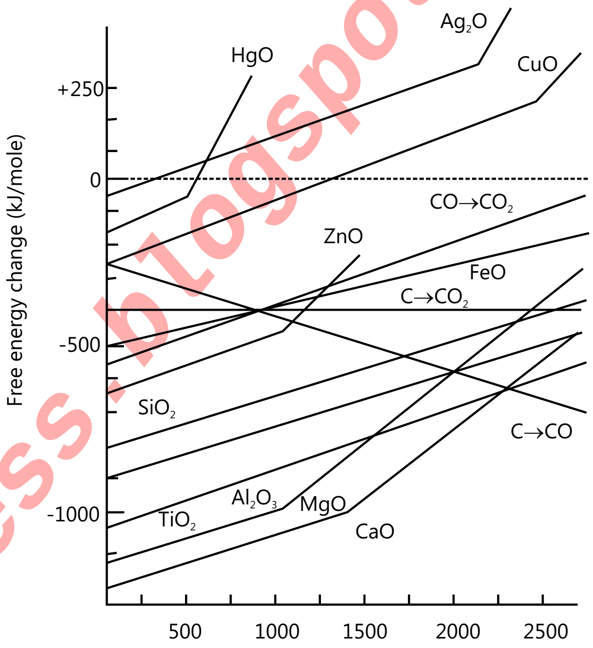


Figure 29.10: Free energy vs temperature ˚C

Here, three moles of gas phases are converted into solid phases in the reaction. This takes place above 1120°C, which is the boiling point of Mg. Similarly Hg—HgO line changes slopes at 365°C. Several of the plots show abrupt changes in the slopes. These breaks occur at temperatures at which the metal undergoes a phase transition. A smaller effect is seen at the melting point. If, however the oxide undergoes a phase change, there will be an increase in the entropy of the oxide, and at such a point the curve becomes less steep. For example in the case of Pb, the oxide (PbO) boils, while lead is liquid. In these instances the entropy change becomes positive for the reaction and hence the slope ΔG/T changes sign, and, the situation reverts to normal once the boiling point of Pb is reached.

In principle, when the plot of one metal lies below that of another, the first metal is capable of reducing the oxide of the second. A vertical line drawn on the Ellingham plot of the metal oxides at any T gives the sequence of the stabilities of metal oxides. A metal forming a more stable oxide (higher - ΔG) will be the potential reducing agent for a less stable oxide. If the two lines intersect, the free energy change for the reduction will be zero at that temperature and equilibrium results, but a change of temperature will make the reaction to proceed, provided no kinetic barriers (activation energy) exist. Thus, Mg metal will reduce CuO and FeO, but not CaO. Also, it is seen that at room temperature (27°C) the order of the reducing ability approximates that of standard electrode potential.

Although the SiO_2 line is above the MgO line, Si can successfully reduce MgO to free metal. Upto 1100°C, the normal boiling point of Mg, the ΔG plot for formation of SiO_2 and MgO are parallel. However, above 1100°C the plot for MgO changes slope, owing to the increased entropy effect, and above 1700°C the reaction between Si and MgO proceeds with decrease in free energy. In practice, the reaction is further enhanced by the distillation of Mg metal from the reaction mixture.

$2\ MgO + Si \rightarrow 2\ Mg + SiO_2$

Carbon/Carbon Monoxide as reducing agent: In figure, the plot corresponding to the change $C(s) + O_2(g) \rightarrow CO_2(g)$ is shown by a horizontal line. For this reaction ΔS is relatively small because in this case one mole of gaseous product is formed while one mole of gaseous reactant is used up. ΔG for this reaction is almost independent of temperature. The plot for CO_2 is relatively high in the figure, and at a lower temperature, C will reduce only a few of the metal oxides as shown. However, the slopes of the plots for several of the metals are such that they cross the CO_2 plot; hence, theoretically these metals can be reduced by C at an elevated temperature. An alternative reaction involving carbon and oxygen is the formation of CO.

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

Since two gaseous products are formed from one mole of a gaseous reactant, this process is accompanied by an increase in entropy. Hence, the slope of the corresponding line is negative as shown, by the downward sloping line in the figure. If the temperature is high enough, C should reduce all the metal oxides, being converted into CO. The plot for the reaction of CO with oxygen is also shown. There are three curves for carbon, corresponding to complete oxidation of C to CO_2, partial oxidation to carbon monoxide, and oxidation of CO to carbon dioxide. The three curves pass through a common point at 710°C. Thus, the free energies of formation of CO_2 from carbon monoxide and carbon dioxide from carbon are identical.

$2CO(g) + O_2(g) \rightarrow 2\,CO_2(g)$ $\Delta G = x$ kJ/mol ; $C(s) + O_2(s) \rightarrow CO_2(g)$ $\Delta G = x$ kJ/mol

Subtracting one equation from the other and rearranging, the following is obtained:

$$CO_2(g) + C(s) \rightarrow 2CO(g)\ \Delta G = 0$$

i.e. an equilibrium is set. It is clear, that, below a temperature of 710°C, CO is a more effective reducing agent than carbon, but above this temperature, the reverse is true. All three oxidation curves for the carbon system lie above that for the oxidation of zinc, until a temperature of approximately 1000°C is reached. At this point, carbon is thermodynamically capable of reducing ZnO to Zn. Since this temperature is greater than the boiling point of Zn (907°C), it will be formed as a vapour. The overall equation for reduction is $ZnO(s) + C(s) \rightarrow Zn(g) + CO(g)$

It is interesting to note that the value of carbon as a reducing agent is due to a marked increase in disorder that takes place when carbon (an ordered solid) reacts with one mole of oxygen to give two moles of CO. The net effect is an extra mole of gas and hence an increase in disorder (an increase in entropy). It is a fact, that, in the region of 2000°C, carbon is thermodynamically capable of reducing most metal oxides to metal. Thus, for most metal oxides, a reducing agent is required and we should consider the overall reaction obtained by subtracting the metal oxidation from one carbon oxidation as

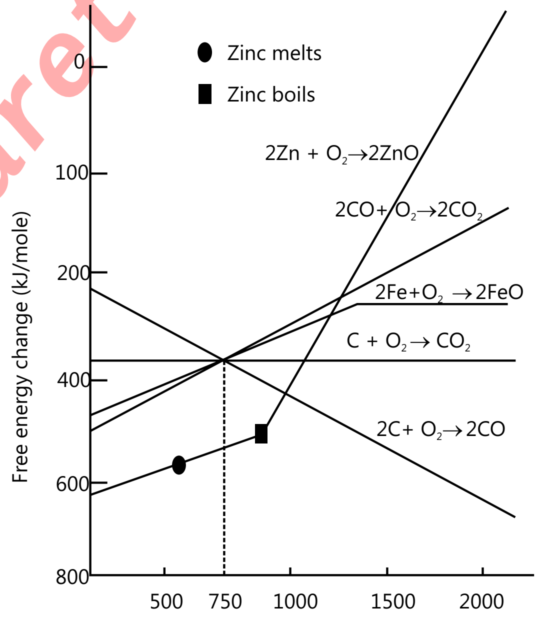


Figure 29.11: Free energy vs temperature ˚C

$$\Delta G_{overall} = \Delta G_{(O)} - \Delta G_{(M)}$$

Metals as reducing agents: Metal oxide reduction is thermodynamically favorable for temperatures at which the line for the metal oxide is above any one of the lines for carbon oxidation. The ΔG for metal oxide reduction by carbon is negative.

Note: The Gibb's energies of formation of most sulphides are greater than that for CS_2. In fact, CS_2 is an endothermic compound. Therefore, the $\Delta_F G°$ of M_xS is not compensated. So reduction of M_xS is difficult. Hence, it is common practice to roast sulphide ores to corresponding oxides prior to reduction. Similar principles apply to other types of reduction. For instance, if the plot of $\Delta G_{(M)}$ lies above $\Delta G_{(M')}$, M′ is now taking the place of C. When $\Delta G = \Delta G_{(M')} - \Delta G_{(M)}$ is negative, the reaction is, $M'O + M \rightarrow M + M'O$

Hydrogen as a reducing agent: Hydrogen is not a very effective reducing agent for obtaining metals from their oxides. The reason is that ΔS is negative for the reaction: $\underset{\text{3 moles of gas}}{2H_2(g) + O_2(g)} \longrightarrow \underset{\text{2 moles of gas}}{2H_2O(g)}$ as the products are less disordered. The plot of ΔG against T therefore rises with temperature, meaning that not many metal oxide plots are intersected. H_2 will therefore reduce oxides such as Cu(I) oxide and Cu(II) oxide, but not the oxides of Al, Mg, and Ca. Oxides of iron are reduced only with difficulty. In the case of magnetic iron oxide, Fe_3O_4, an equilibrium composition is readily established.

In the case of W, Mo, and Co, ΔG is above that of H_2O so that H_2 can reduce these oxides.

$MoO_3 + 3H_2 \longrightarrow Mo + 3H_2O$; $GeO_2 + 2H_2 \longrightarrow Ge + 2H_2O$

$Co_3O_4 + 4H_2 \longrightarrow 3Co + 4H_2O$; $WO_3 + 3H_2 \longrightarrow W + 3H_2O$

This method is not widely used because many metals react with H_2 at elevated temperatures.

PLANCESS CONCEPTS

- If in Ellinghams diagram, a metal A is placed above metal B then metal A can be reduced by metal B.
- The free energy change increases with temperature because the slope is ΔS which is negative.

Rohit Kumar (JEE 2012, AIR 79)

Illustration 7: The reaction $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2\,Cr$ ($\Delta G° = -421$ kJ) is thermodynamically feasible as is apparent from the Gibb's energy value. Why does it not take place at room temperature? **(JEE MAIN)**

Sol: Certain amount of activation energy is essential even for such reactions which are thermodynamically feasible, therefore heating is required.

Illustration 8: Is it true, that under certain conditions, Mg can reduce Al_2O_3 and Al can reduce MgO? What are those conditions? **(JEE MAIN)**

Sol: Below 1350ºC, Mg can reduce Al_2O_3 and above 1350°C, Al can reduce MgO, as evident from the Ellingham diagram.

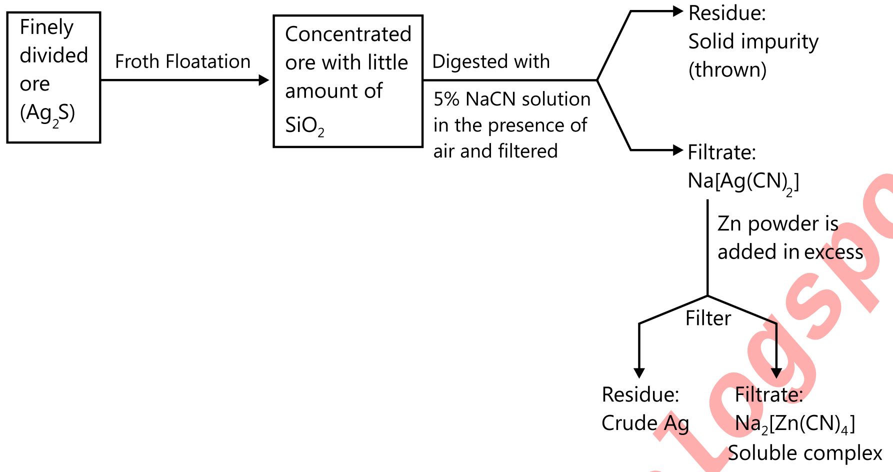
5. METALLURGY OF SOME IMPORTANT METALS

5.1 Extraction of Silver

Important ores of silver are

(a) Argentite or silver glance: Ag_2S
(b) Ruby silver: Ag_3SbS_3
(c) Horn silver: AgCl

There are three processes commonly used for the extraction of Ag; The cyanide process is described below. The other two processes, i.e. Parke's process and Pattinson's process are beyond the scope of discussion. Cyanide process or Mc-Arthur Forest Process: This process is depicted in the flow diagram given in figure.



Flowchart 29.2: For Mc-arthur forest for extraction of silver

Reactions taking place at the different stages in the cyanide process are as follows:

(i) $Ag_2S + 4Na\,CN(excess) \rightleftharpoons 2[Ag(CN)_2]^{-} + Na_2S + 2Na^{-}$

$4Na_2S + 5O_2(air) + 2H_2O \rightarrow 2Na_2SO_4 + 4NaOH + 2S$

Since the above reaction is reversible, the conversion ratio is not good. Hence the process is carried out in the presence of air which converts the Na_2S produced into Na_2SO_4 and S, and the overall reaction becomes unidirectional.

(ii) In the step involving the precipitation of Ag, a little excess of Zn powder is added by which $Na[Ag(CN)_2]$ becomes the limiting reagent, otherwise the loss of Ag will be more. Here Zn is chosen because it is more electropositive as compared to Ag and the replacement reaction occurs very easily. $2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag\downarrow$

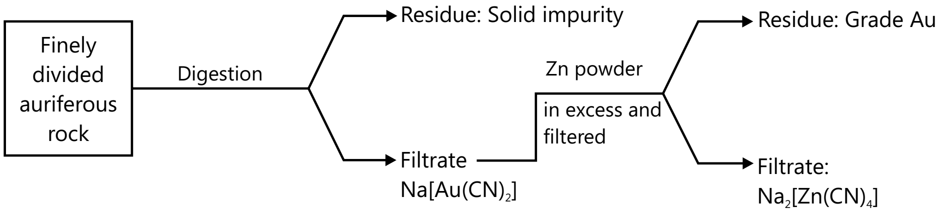
Refining of Ag: Refining of silver is carried out by electrolytic process.

$$\underset{(\text{Zn, Cu, Au as impurity})}{\text{Crude Ag}} \xrightarrow[\text{(mobius procces)}]{\text{electro refining}} \underset{(\text{upto } 99.6 - 99.9\% \text{ pure Ag})}{\text{Pure Ag}}$$

Electrolyte : $AgNO_3$ solution + 10% HNO_3
Cathode : Pure Ag strip
Anode : Impure Ag slab
Reactions at the electrodes:
At cathode : $Ag^+ + e^- \rightarrow Ag$
At anode : $Ag \rightarrow Ag^+ + e^-$

5.2 Extraction of Gold

The flow diagram of different stages involved in the cyanide process for extraction of gold is shown in figure.



Flowchart 29.3: Cyanide process for extraction of gold

Auriferous rock is rock of quartz contaminated with gold linings.

Reactions taking place in different steps are:

In step 1: $4Au + 8NaCN + 2H_2O + O_2 \rightarrow 4Na[Au(CN)_2] + 4NaOH$

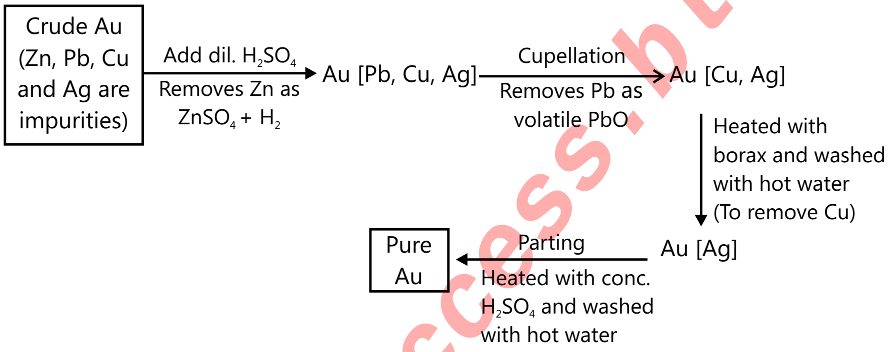
Here, oxidation of Au is not possible without the presence of air and NaCN acts as a complexing agent.

In step 2: $2Na[Au(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Au\downarrow$

Refining of Au: The steps involved in the refining of Au are given in figure. In the third step, on heating with borax, the soluble metaborate of Cu, i.e. $Cu(BO_2)_2$ is formed and washed out with water. Similarly, in the fourth step also, Ag dissolves out as Ag_2SO_4 leaving behind pure Au.

Note:

- The removal of Ag can also be carried out using chlorine or by electrolysis.
- Cupellation is a process, where crude gold is taken in a small bowl called cupell and melted in the presence of air. Due to the high oxygen affinity of Pb, it is converted into PbO (volatile) which escapes from the system.



Flowchart 29.4: Refining of gold

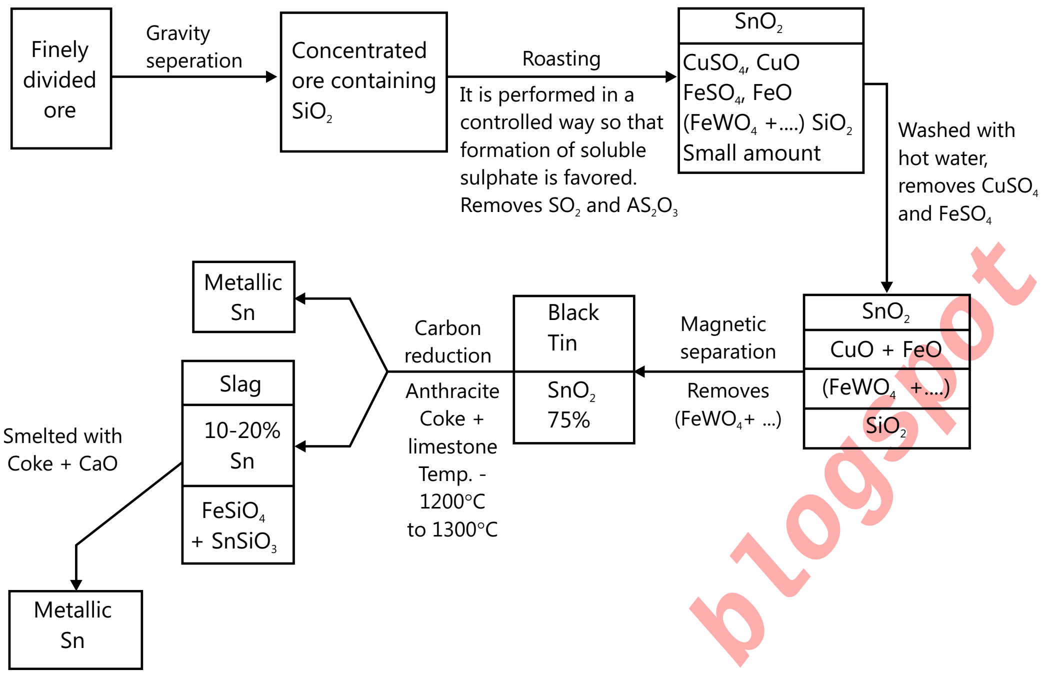
PLANCESS CONCEPTS

- Extraction of gold from auriferous rock is done in 2 steps; first it is oxidised by oxygen and treated with NaCN and then it is reduced by zinc.
- During refining, firstly, dilute H_2SO_4 removes Zn, then cupellation removes Pb, Cu is removed after heating with borax and washing with water and finally parting's process removes Ag.

Krishan Mittal (JEE 2012, AIR 199)

5.3 Extraction of Tin

An important ore of tin is cassiterite or tin stone (1-5% SnO_2 present in it). The main impurities present in the ore are sand (SiO_2), pyrite of Cu and Fe, and wolframite [$FeWO_4 + MnWO_4$]. The for extraction of Sn is depicted below.



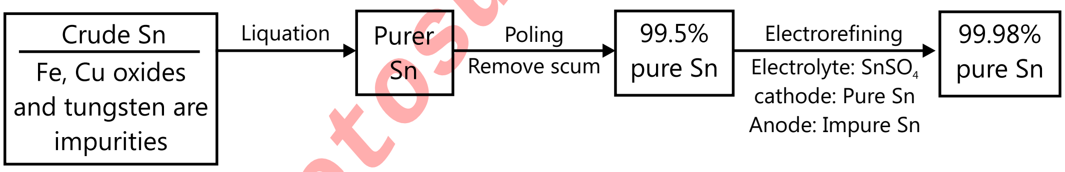
Flowchart 29.5: Extraction of tin

The reactions taking place in the extraction of Sn are:

1. In step 1: $SnO_2 + 2C \rightarrow Sn + 2CO\downarrow$

2. In step 2: $SnSiO_3 + CaO + C \rightarrow Sn + CaSiO_3 + CO\downarrow$

Refining of Sn: The steps involved in the refining of Sn are shown below.



Flowchart 29.6: Refining of tin

PLANCESS CONCEPTS

- Extraction of tin involves gravity separation, followed by roasting, followed by magnetic separation and finally carbon reduction. The slag is also smelted.
- In refining, liquation is followed by poling's process and finally by electro refining.

T P Varun (JEE 2012, AIR 64)

5.4 Extraction of Magnesium

The important ores of magnesium are:

1. Magnesite : $MgCO_3$
2. Dolomite : $MgCO_3.CaCO_3$
3. Carnallite : $KCl.MgCl_2.6H_2O$

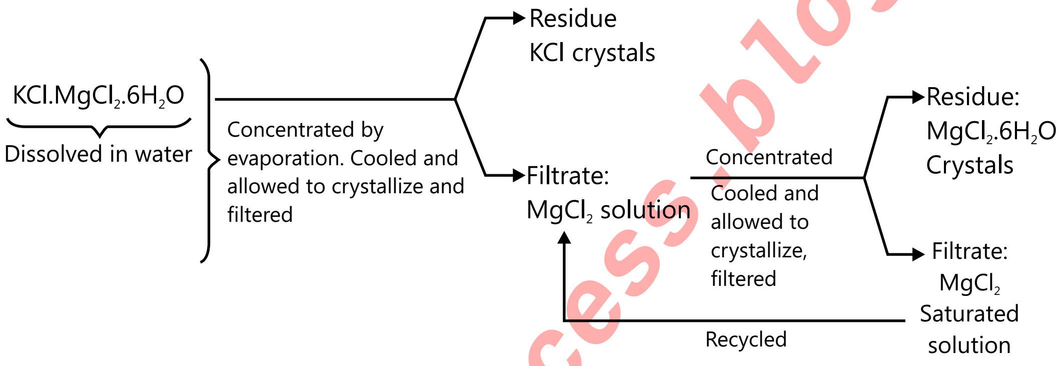
4. Kainite : $K_2SO_4.MgSO_4.MgCl_2.6H_2O$
5. Kieserite : $MgSO_4.H_2O$
6. Asbestos : $CaMg_3(SiO_3)_4$
7. Spinel : $MgO.A_2O_3$

Two processes recommended for extraction of Mg are electrolytic reduction and carbon reduction. The latter is a very costly process due to very high temperature requirement.

(a) Electrolytic reduction: The process for extraction of magnesium consists of the following three steps.

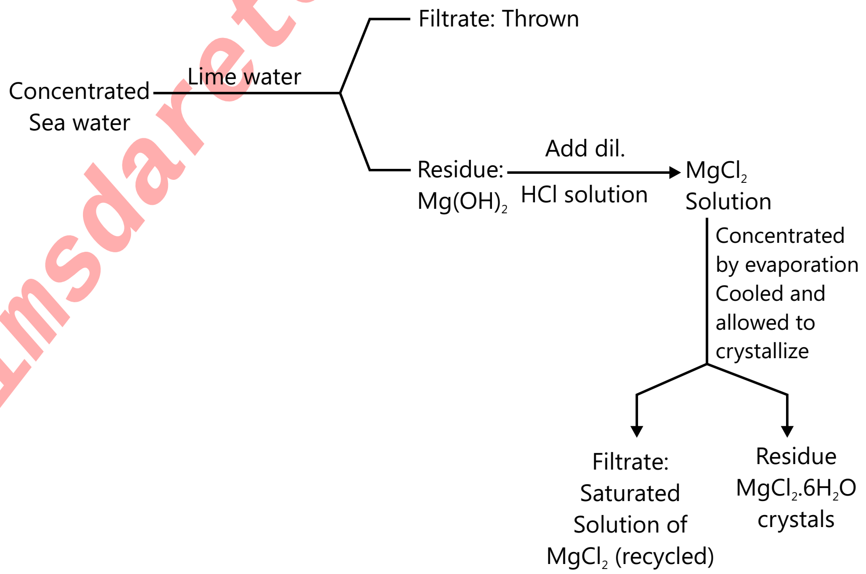
Step 1: Preparation of hydrated $MgCl_2$

(i) From Carnallite ($KCl.MgCl_2.6H_2O$): The steps involved in the preparation of hydrated $MgCl_2$ from Carnallite are depicted in figure. The principle behind this process is that KCl is less soluble as compared to $MgCl_2$ and crystallizes first.



Flowchart 29.7: Preparation of hydrated $MgCl_2$ from carnallite

(ii) From sea water: Sea water consists of a lot of $MgCl_2$. The process for extraction of $MgCl_2$, from sea water is known as Dow sea water process. The steps involved in the process are depicted in figure. The principle behind this process is that $Ca(OH)_2$ is soluble in water while $Mg(OH)_2$ is sparingly soluble in water.



Flowchart 29.8: Preparation of hydrated $MgCl_2$ from sea water

Step 2: Conversion of hydrated $MgCl_2$ to anhydrous $MgCl_2$: On direct heating of $MgCl_2.6H_2O_2$, anhydrous $MgCl_2$ cannot be obtained due to its hydrolysis: $MgCl_2 . 6H_2O \xrightarrow{\Delta} Mg(OH)Cl + HCl\uparrow + 5H_2O\uparrow$

$$Mg(OH)Cl \rightarrow MgO + HCl\uparrow$$

Also, MgO formed is an unwanted substance in the electrolytic reduction step due to its very high melting point (i.e. 2850°C). Hence hydrated $MgCl_2$ is heated to 175°C in vacuum, in a current of dry HCl gas, and $MgCl_2$ (anhydrous) is formed.

$$MgCl_2.6H_2O \xrightarrow{\Delta} MgCl_2 + 6H_2O;\ MgCl_2 + H_2O \rightarrow Mg(OH)Cl + HCl$$

When dry HCl is present in the system, the hydrolysis equilibrium shifts towards left but due to increase in thermal energy of the system, the decomposition reaction continues and results in anhydrous $MgCl_2$. An alternative method for preparation of anhydrous $MgCl_2$ involves heating calcined magnesite. (MgO) to 1000°C in a current of dry Cl_2 gas.

$$MgCO_3 \xrightarrow[\Delta]{} MgO + CO_2;\ MgO + C + Cl_2 \xrightarrow{-1000^\circ C} MgCl_2 + CO\downarrow$$

Step 3: Electrolytic reduction of anhydrous $MgCl_2$: The schematic representation of electrolytic reduction of anhydrous $MgCl_2$ is shown in figure:

$MgCl_2 \rightarrow Mg^{2+} + 2Cl^- : NaCl \rightarrow Na^+ + Cl^-$

At cathode : $Mg^{2+} + 2e^- \rightarrow Mg$;

At anode : $2Cl^- - 2e^- \rightarrow Cl_2$

The container for electrolytic cell has to be covered and the air present inside is removed by passing the coal gas through an opening (not shown in the diagram) to prevent the oxidation of Mg formed, which is floating on the top surface of the molten electrolyte.

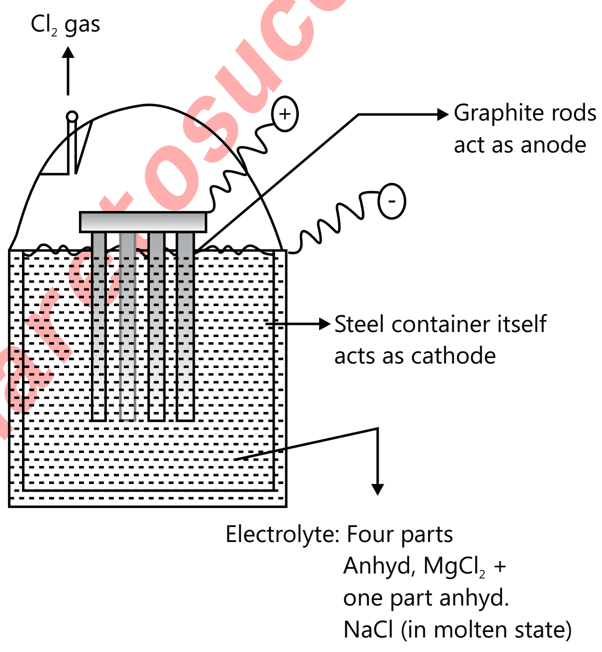


Figure 29.12: Electrolytic reduction of anhydrous $MgCl_2$

The electrolyte in the molten state consists of four parts of anhydrous $MgCl_2$ and one part anhydrous NaCl. One part of NaCl is added to reduce the melting temperature of the electrolyte from 1200 °C (m.p. of pure $MgCl_2$) to 700°C and at the same time electrical conductivity of the melt is also increased.

Fused carnallite may also be used as an electrolyte because both Na and K are more electropositive as compared to Mg and hence Mg^{2+} is preferably discharged at the cathode.

(b) Carbon reduction process: In this process for extraction of magnesium, initially MgO is produced from calcination of $MgCO_3$, which is then directly heated with coke powder at around 2000 °C in a closed electric furnace. $MgCO_3 \rightarrow MgO + CO_2$; $MgO + C \rightarrow Mg\uparrow + CO\uparrow$

Mg thus obtained comes out in the vapour form and cooled suddenly to about 200 °C by dilution with a large volume of H_2 gas to prevent reoxidation of Mg.

Note: Boiling point of Mg is –1100 °C.

(c) Other processes: Some other processes used for extraction of magnesium are:

(i) Thermal reduction of $MgCl_2$: The mixture of anhydrous $MgCl_2$ and CaC_2 is heated at 1500°C and the vapours of Mg are collected in the same way as in the carbon reduction process.

$MgCl_2 + CaC_2 \rightarrow CaCl_2 + Mg + 2C$

(ii) Pidgeon process: Here the calcined mixture of dolomite and powder of ferrosilicon (80% Si) is heated to 1200°C in a closed container. Mg is vaporized and collected in a condenser.

$CaCO_3 + MgCO_3 \rightarrow CaO + MgO + 2CO_2$; $2MgO + 2CaO + Si \rightarrow 2Mg\uparrow + 2CaSiO_3$

PLANCESS CONCEPTS

Extraction of magnesium involves the following steps - preparation of hydrated $MgCl_2$ and conversion of hydrated $MgCl_2$ to anhydrous $MgCl_2$

Aishwarya Karnawat (JEE 2012, AIR 839)

5.5 Extraction of Aluminium

The important minerals of Al are:

1. Hydrated oxides: Bauxite ($Al_2O_3.3H_2O$) Gibbsite ($Al_2O_3.3H_2O$)
   china clay or Kaolin ($Al_2O_3.2H_2O$) Diaspore ($Al_2O_3.H_2O$)
2. Oxide : Corundum (Al_2O_3)
3. Sulphate : Alunite [$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$]
4. Fluoride : Cryolite ($3NaF.AlF_3$)
5. Aluminate : Spinel ($MgO.Al_2O_3$)
6. Silicate : Feldspar ($K_2O.Al_2O_3.6SiO_2$)

Bauxite is the ore most commonly used for extraction of aluminium. Bauxite is of two types:

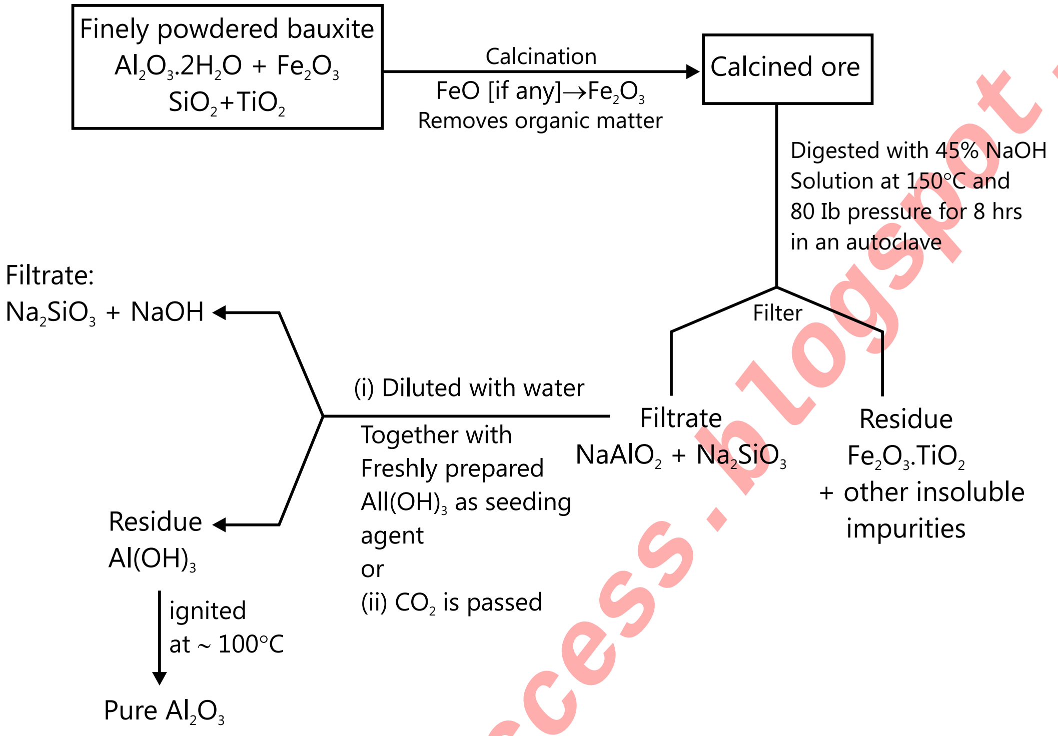
1. Red bauxite: $Al_2O_3.2H_2O + Fe_2O_3$ (major impurity) $+ SiO_2 + TiO_2$
2. White bauxite: $Al_2O_3.2H_2O + SiO_2$ (major impurity) $+ Fe_2O_3 + TiO_2$

The main steps involved in the extraction of Al from bauxite are:

1. Beneficiation of bauxite and preparation of pure alumina.
2. Electrolytic reduction of pure alumina.
3. Electrorefining of aluminium.

Beneficiation of bauxite: Different processes adopted for beneficiation of red and white bauxite are described below.

Bayer's process: This is used for beneficiation of red bauxite. Various stages of the process are depicted in the figure.



Flowchart 29.9: Bayer's process for beneficiation of bauxite

The reaction involved in the above process are:

In step 1: $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^-$; $SiO_2 + 2NaOH \rightarrow NaSiO_3 + H_2O$

In step 2: $[Al(OH)_4]^- \underset{OH}{\rightleftarrows} \underset{white}{Al(OH)_3\downarrow} \rightleftarrows Al^{3+} + 3H_2O$ Since $Al(OH)_3$ is amphoteric in nature, it gets dissolved in alkali as well as in acid as shown in the reactions above. Hence to get $Al(OH)_3$ from $[Al(OH)_4]^-$, the pH of the medium is to be reduced, but care has to be taken, that the pH is not low enough to dissolve it further in the form of Al^{3+}. The decrease in pH can be done by:-

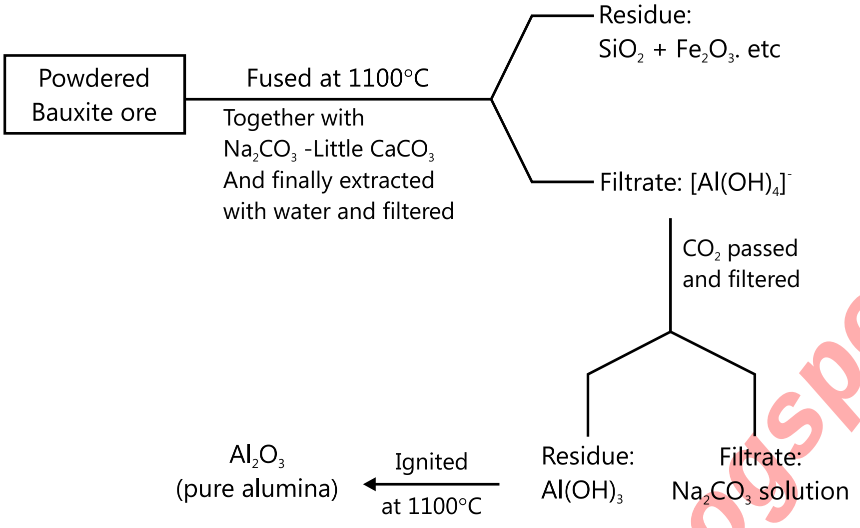
- Adding large amounts of water which increases the volume and decreases the pH. But without the seeding agent (which provides the nucleus of the precipitate) the precipitation is delayed.
- Acidification which reduces the pH of the medium. But here a strong acid is not recommended to avoid any further dissolution of $Al(OH)_3$ in the form of Al^{3+}. Hence weak acids like CO_2 gas are passed, which reacts as follows: $CO_2+2OH^- \rightarrow CO_3^{2-}+ H_2O$

  $CO_2 + H_2O \rightarrow H_2CO_3$ [weak enough to dissolve $Al(OH)_3$] ; $[Al(OH)_4]^- \rightleftharpoons Al(OH)_3\downarrow + OH^-$

  OH^- ions are consumed in the above reaction and the formation of $Al(OH)_3$ is favoured.

Note: The Bayer's process cannot be adopted for white bauxite because the major impurity SiO_2 is also separated out along with Al_2O_3 and finally Al_2O_3, of inferior quality is formed.

Hall's process: This process is adopted for beneficiation of low grade red bauxite. Various stages of the process are depicted in the flow diagram in Figure.



Flowchart 29.10: Hall's process for beneficiation of low grade red bauxite

The reactions involved in the above process are:

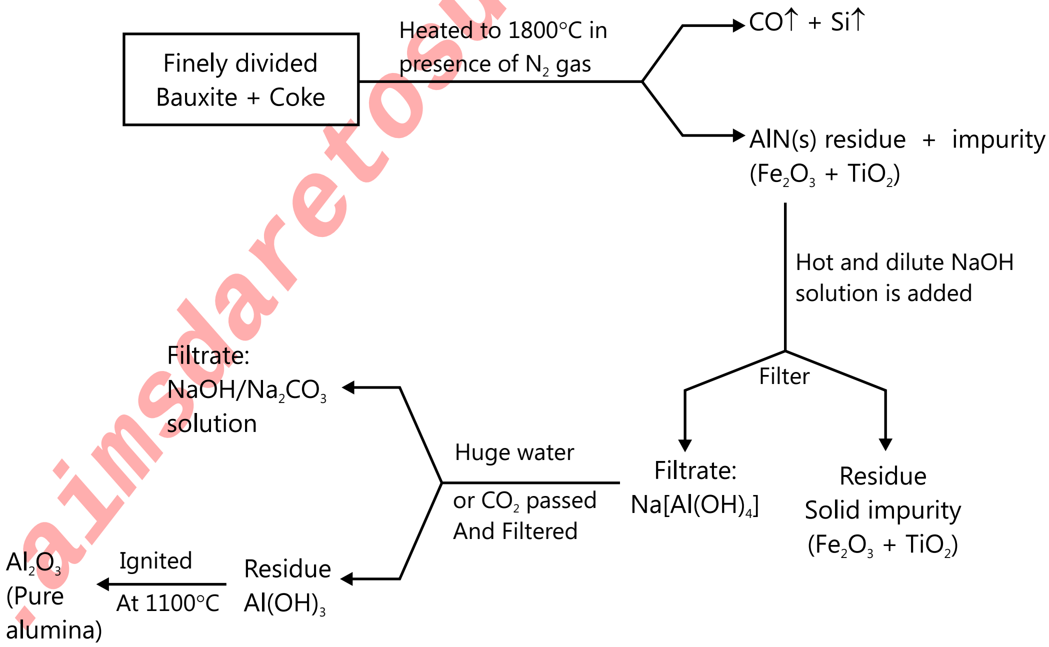
In step 1: $Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_3 + CO_2\uparrow$; $SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2\uparrow$

$Fe_2O_3 + Na_2CO_3 \rightarrow 2NaFeO_2 + CO_2\uparrow$; $CaO + SiO_2 \rightarrow CaSiO_3$

In step 2: $2NaAlO_2 + CO_2 + 3H_2O \rightarrow 2Al\,(OH)_3\downarrow + Na_2CO_3$

In step 3: $2Al\,(OH)_3 \xrightarrow[-3H_2O]{\Delta} Al_2O_3 + 3H_2O$

Serpeck's process: This process is used for beneficiation of white bauxite. Various steps of this process are depicted in the flow diagram in figure.



Flowchart 29.11: Serpeck's process for beneficiation of white bauxite

The reactions involved in the above process are:

In step 1: $Al_2O_3 + 3C + N_2 \rightarrow 2AlN(s) + 3CO$; $SiO_2 + 2C \rightarrow Si\uparrow + 2CO\uparrow$

In step 2: $AlN + NaOH + 3H_2O \rightarrow Na[Al(OH)_4] + NH_3\uparrow$

In step 3: $Na[Al(OH)_4] \xrightleftharpoons{H_2O} Al(OH)_3^{-} + NaOH$

or $[Al(OH)_4]^- \rightleftharpoons Al(OH)_3\downarrow + OH^-$; $CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$

Electrolytic reduction of pure Al_2O_3: In the electrolytic reduction of Al_2O_3 i.e. molten alumina (20 %) mixed with cryolite (60%) and fluorspar (20 %) is taken in an iron tank with carbon lining that acts as the cathode. A graphite rod hanging from the top acts as the anode. A powdered coke layer is maintained at the top figure.

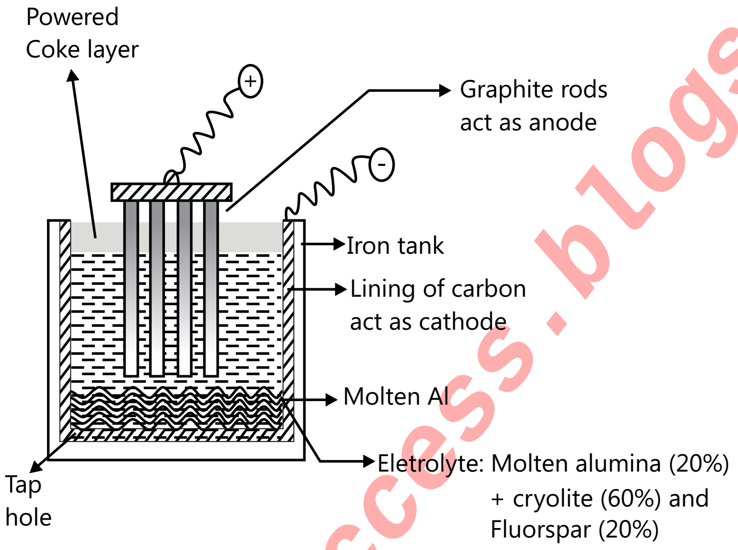


Figure 29.13: Electrolytic reduction of alumina.

On electrolysis, molten Al is deposited at the cathode and since Al is heavier compared to the electrolyte, it gets deposited at the bottom, while oxygen gas is liberated at the anode.

(a) **Reactions** $Al_2O_3 \rightarrow Al^{3+} + 3O^{2-}$

At the cathode: $Al^{3-} + 3e^- \rightarrow Al$

Since Na and Ca are more electropositive than Al, only Al^{3+} gets deposited at the cathode.

At the anode: $2O^{2-} \rightarrow O_2 + 4e^-$

(b) **Functions of fluorspar (CaF_2): (i)** It reduces the melting temperature of the mixture to 900°C from 2050°C (Melting point of pure Al_2O_3) and saves on the fuel cost.

(ii) It also improves the electrical conductivity of the melt, compared to that of molten Al_2O_3

(c) **Functions of cryolite: (i)** It acts as a solvent and helps dissolve Al_2O_3.

(ii) It also helps to reduce the melting temperature of the mixture.

Alternative theory for electrolytic reaction at the anode can explain the dissolution of Al_2O_3.

$AlF_3\,3NaF \rightarrow Al^{3+} + 3Na^- + 6F^-$, $Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}$ and $CaF_2 \rightarrow Ca^{2+} + 2F^-$

Since the $[F^-] >>> [O^{2-}]$, F^- ions get discharged at the anode first which in turn react with Al_2O_3 and liberate O_2 at the anode. $2F^- \rightarrow F_2 + 2e^-$; $3F_2 + Al_2O_3 \rightarrow 2AlF_3 + \frac{3}{2}O_2$

(d) **Function of the coke powder layer at the top: (i)** The oxygen liberated at the anode corrodes the anode surface, reacting with graphite to produce CO and CO_2 and finally the anode cuts down at the bottom and electrical connectivity is lost.

At the junction of liquid-solid-air interface, the energy available is maximum (this can be proved thermodynamically) and corrosion is maximum at this point. To prevent this corrosion, the coke powder (having a large surface area for reaction) layer is kept at the top, which reacts with liberated oxygen.

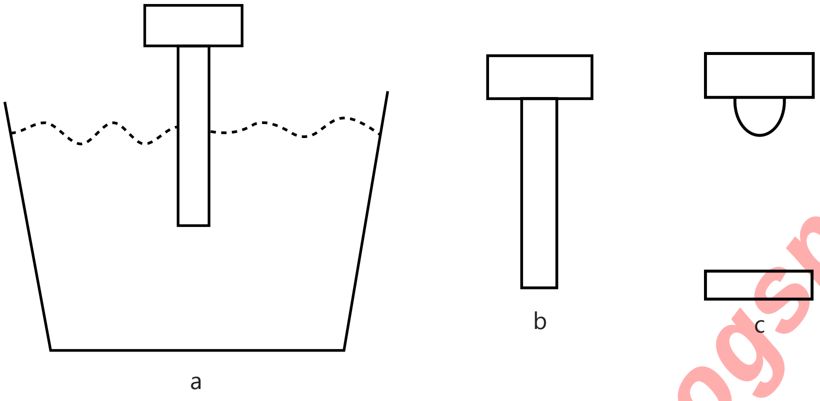


Figure 29.14: Corrosion of graphite anode

(ii) The surface becomes rough unlike the shiny mirror like molten electrolyte; and the radiation loss of heat is also prevented.

Electro Refining of Aluminium: Impure aluminium mixed with copper melt is taken in an iron tank with graphite lining. The layer of pure Al acts as the cathode. The graphite rods at the top are essential for electrical connection.

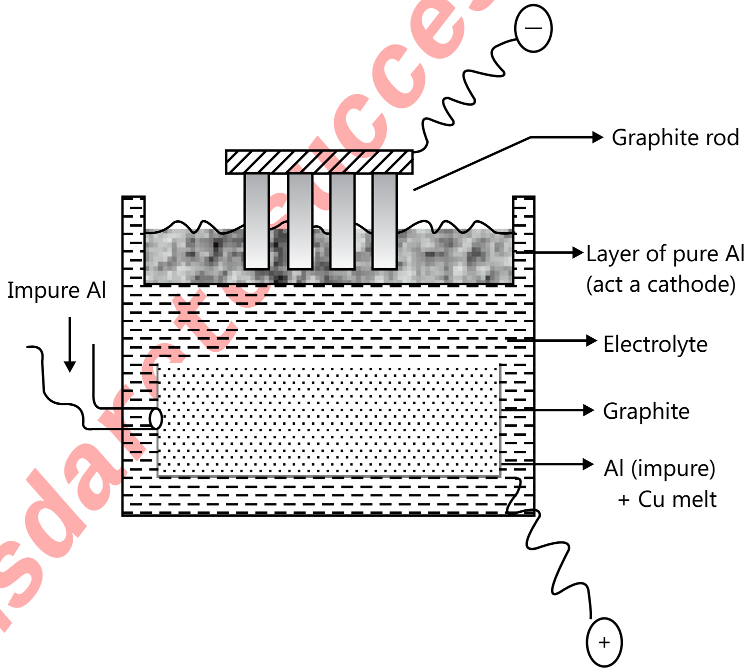


Figure 29.15: Electrorefining of aluminium

Here, the electrolyte is the molten mixture of cryolite and BaF_2 saturated with Al_2O_3. BaF_2 is added instead of CaF_2 to adjust the density in such a way that it exists as a separate middle layer. Similarly in impure Al, the Cu melt is deliberately added to increase the density in such a way that it exists as a separate bottom layer.

The reactions involved in the process are: At the anode: $Al \rightarrow Al^{3+} + 3e^-$

Here, the top surface of bottom layer acts as the anode and Al only enters into the electrolyte as Al^{3+} because

$E^o_{Al^3/Al^{3+}} > E^o_{Cu/Cu^{2+}}$

At the cathode: $Al^{3+} + 3e^{-} + \rightarrow Al$

Here, the bottom surface of the top layer (the pure Al melt) acts as the cathode and Al^{3+} enters as Al from the electrolyte.

Note:

(a) Impurities like Fe, Si and Cu remain intact in the bottom layer.

(b) When the thickness of the top layer is increased to a certain limit, it is drained out into a separate container.

  (i) Pure Al_2O_3 is not used as the electrolyte because:

  - The melting point of Al_2O_3 is 2050°C, hence the power consumption is very high.
  - Al obtained at this temperature gets volatilized and the loss is very high.
  - Aluminium is lighter than Al_2O_3 and floats at the top surface and volatilizes easily, as well as attacked by the oxygen, liberated at the anode.

  (ii) The aqueous solution of Al salt cannot be used as an electrolyte because hydrogen is discharged at the cathode in preference to Al, as the discharge potential of H^+ is smaller compared to Al^{3+}. For example, if $Al\,(NO_3)_3$ is used, then the reactions involved are

$$Al\,(NO_3)_3 \rightarrow Al^{3+} + 3NO_3^{-}\,;\ H_2O \rightarrow H^+ + OH^-$$

At the cathode: $2H^+ \xrightarrow{+2e^-} H_2$

At the anode: $4OH^- \rightarrow 2H_2O + O_2\uparrow + 4e^-$

(b) Molten $AlCl_3$ is not chosen as electrolyte because, being covalent in nature, it is a poor conductor of electricity. It also sublimes easily.

PLANCESS CONCEPTS

(a) Main steps involved in the extraction of Al from Bauxite are:

  (i) Beneficiation of bauxite and preparation of pure alumina.

  (ii) Electrolytic reduction of pure alumina.

  (iii) Electro refining of aluminium.

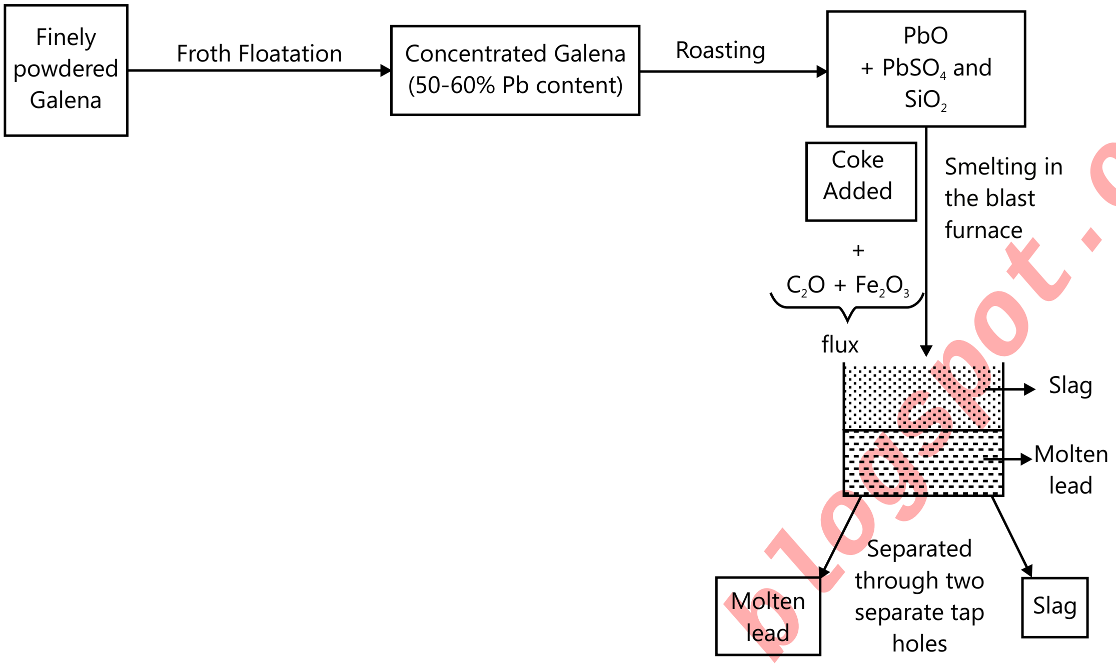
(b) Beneficiation of bauxite includes 3 different processes namely Bayer's process, Hall's process and Serpeck's process, depending on the nature of ore.

Saurabh Chaterjee (JEE Advanced 2013, AIR)

5.6 Extraction of Lead

The important ores of lead are:

1. Galena : PbS
2. Cerrusite : $PbCO_3$
3. Anglesite : $PbSO_4$
4. Crocoisite : $PbCrO_4$
5. Lanarkite : $PbO.PbSO_4$



Flowchart 29.12: Carbon reduction process for extraction of lead

The ore used commercially for extraction of lead is galena. Depending upon the impurity content, lead can be extracted from galena by one of the following two processes:

(a) Carbon reduction (when the impurity content is high enough)

(b) Self-reduction (when the impurity content is low)

The reactions involved at various stages of the process are:

1. In the froth floatation step: PbS does not react with NaCN solution while ZnS gets dissolved in NaCN solution and its floating characteristics are completely lost.

$$ZnS + NaCN \rightarrow \underbrace{Na_2[Zn(CN)_4] + Na_2S}_{\text{Both soluble}} \; ; PbS + NaCN \rightarrow \text{No reaction}$$

2. In the roasting step: $PbS + \frac{3}{2}O_2 \rightarrow PbO + SO_2\uparrow$

$PbS + 2O_2 \rightarrow PBSO_4$ (minor) ; $PbO + SiO_2 \rightarrow PbSiO_3$ (minor)

Function of lime: Since lime is more basic compared to PbO, CaO reacts preferably with SiO_2 and its presence acts as a negative catalyst towards the formation of $PbSiO_3$ and $PbSO_4$, It also helps to keep the mass porous and helps to complete reaction.

3. In the smelting step: Initially coke is burnt in a blast of air to produce CO and CO_2

$C + O_2 \rightarrow CO_2$; $C + CO_2 \rightarrow 2CO$

Pb formation reaction $PbO + C \rightarrow Pb(l) + CO\uparrow$

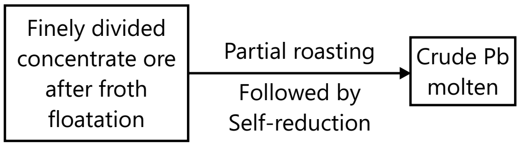
$PbO + CO \rightarrow Pb(l) + CO_2\uparrow$; $PbSO_4 + 4C \rightarrow PbS + 4CO$

Pbs (unreacted) + $2PbO \rightarrow 3Pb\ (l) + SO_2\uparrow$; $PbS + PbSO_4$ (if any) $\rightarrow 2Pb(l) + 2SO_2\uparrow$

Slag formation reaction: $CaO + SiO_2 \rightarrow CaSiO_3$

$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$; $FeO + SiO_2 \rightarrow FeSiO_3$

Self-reduction process: The steps involved in the self-reduction process are shown in the flow diagram. The reactions involved in the process are:

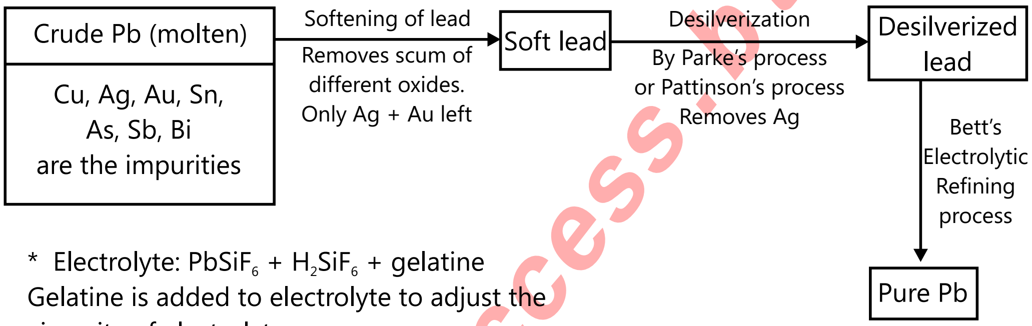


Flowchart 29.13: Self-reduction process for extraction of lead

1. In the roasting step: $PbS + \frac{3}{2}O_2 \rightarrow PbO + SO_2$; $PbS + 2O_2 \rightarrow PbSO_4$
2. In the self-reduction step: $PbS + 2PbO \rightarrow 3Pb + SO_2\uparrow$; $PbS + PbSO_4 \rightarrow 2Pb + 2SO_2\uparrow$

Note: After partial roasting, air blasting is stopped and heating is continued for self-reduction reactions.

Refining of Lead: The steps for refining of lead are given in the in figure.



* Electrolyte: $PbSiF_6 + H_2SiF_6$ + gelatine
Gelatine is added to electrolyte to adjust the viscosity of electrolyte
Anode: Impure Pb.
Cathode: pure Pb strip

Flowchart 29.14: Refining of lead

PLANCESS CONCEPTS

(a) Depending on the impurity content, one of 2 following processes is used:

(i) Carbon reduction. **(ii)** Self-reduction.

(b) Carbon reduction involves froth floatation, roasting and smelting.

(c) Self reduction involves roasting followed by self-reduction steps.

Mredul Sharda (JEE Advanced 2013, AIR)

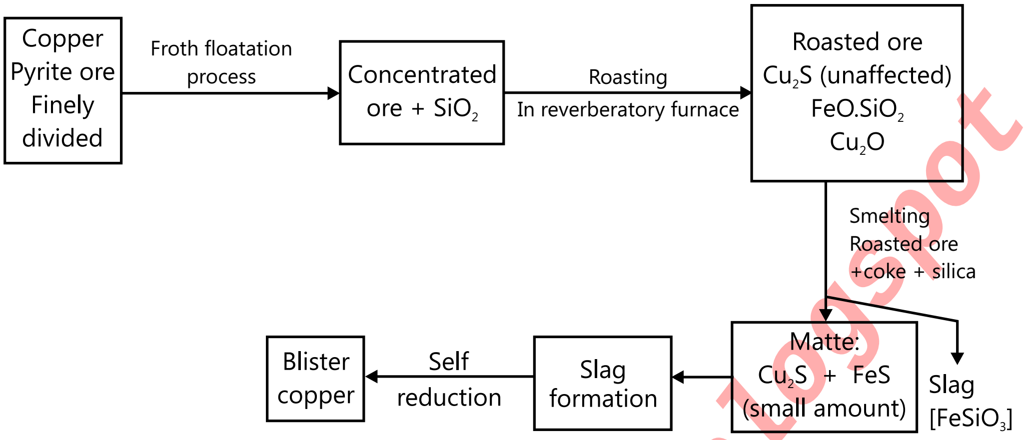
5.7 Extraction of Copper

The important ores of Cu are:

1.	Chalcocite or copper glance	: Cu_2S
2.	Copper pyrite or chalcopyrite	: $CuFeS_2$
3.	Cuprite or ruby copper	: Cu_2O
4.	Malachite	: $Cu(OH)_2.CuCO_3$
5.	Azurite	: $Cu(OH)_2.2CuCO_3$

Less important ores of copper are chrysocolla ($CuSiO_3.2H_2O$) and malonite (CuO).

The chief ore used for extraction of copper is copper pyrite ($Cu_2S.FeS.FeS_2$). The flow diagram for extraction of copper from copper pyrite is depicted in figure.



Flowchart 29.15: For extraction of copper from copper pyrite

The Changes and reactions involved in the above process are:

(a) **In the roasting step:** Roasting is done with excess of air and at temperatures below the fusion temperature of the ore, $Cu_2S.Fe_2S + O_2 \rightarrow Cu_2S + 2FeS + SO_2\uparrow$; $Cu_2S.Fe_2S_3 + 4O_2 \rightarrow Cu_2S + 2FeO + 3SO_2\uparrow$

Since iron is more electropositive as compared to copper, its sulphide is preferentially oxidized and Cu_2S remains unaffected. If any Cu_2O (little amount) is formed, it also reacts with unreacted FeS to give back

$$Cu_2S.\ Cu_2S + \frac{3}{2}O_2 \rightarrow Cu_2O + SO_2\uparrow;\ Cu_2O + FeS \rightarrow Cu_2S + FeO$$

(b) **In the smelting step:** Coke is used here as fuel to maintain such temperature that keeps the mixture in the molten state. $FeS + \frac{3}{2}O_2 \rightarrow FeO + SO_2\uparrow$

$$Cu_2O + FeS \rightarrow Cu_2O + FeO;\ FeO + SiO_2 \rightarrow FeSiO_3\ (slag)$$

Slag being lighter, floats as an immiscible layer on the top surface of Cu_2S (matte) and is removed through a separate hole.

(c) **In the Bessemer converter:** The raw material for the Bessemer converter is matte, i.e. $Cu_2S + FeS$ (little). Here air blasting is initially done for slag formation and SiO_2 is added from an external source.

$$FeS + \frac{3}{2}O_2 \rightarrow FeO + SO_2\uparrow;\ SiO_2 + FeO \rightarrow FeSiO_3\ (slag)$$

During slag formation, the characteristic green flame is observed at the mouth of the Bessemer converter which indicates the presence of iron in the form of FeO. Disappearance of this green flame indicates that the slag formation is complete. Then air blasting is stopped and slag is removed.

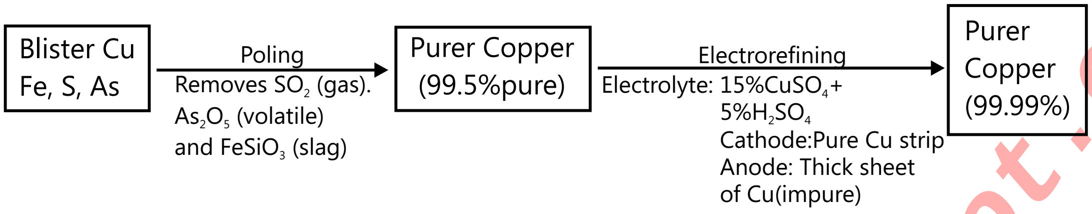
Again air blasting is restarted from partial roasting before self-reduction, until two-thirds of Cu_2S is converted into Cu_2O. After this, only heating is continued for the self-reduction process.

$$Cu_2S + \frac{3}{2}O_2 \rightarrow Cu_2O + SO_2\uparrow;\ Cu_2S + 2Cu_2O \rightarrow 6Cu\ (l) + SO_2\uparrow$$

And $Cu_2S + 2O_2 \rightarrow Cu_2SO_4$; $Cu_2S + Cu_2SO_4 \rightarrow 4Cu + 2SO_2\uparrow$

Thus the molten Cu obtained is poured into a large container and allowed to cool and during cooling, the dissolved SO_2 comes up to the surface and forms blisters. It is known as blister copper.

Refining of blister copper: Blister Cu contains 2-3% impurity (mainly Fe, S and As). The steps involved in its refining are depicted in the flow diagram in figure.



Flowchart 29.16: Refining of blister copper

In the poling step: The little Cu_2O formed is reduced to metallic Cu by the reducing gases produced from charring of green wooden pole. The powdered anthracite (coke) spread on the top surface of the molten mass also helps to produce a reducing environment.

In the electrorefining step, the impurities like Fe, Ni, Zn get dissolved in the solution, while Au, Ag and Pt are deposited as anode mud below the anode.

PLANCESS CONCEPTS

- Extraction of copper includes froth floatation, followed by roasting, then smelting and finally by bessemerization.
- Refining of copper includes poling's process followed by electrorefining.

Vaibhav Krishnan (JEE 2009, AIR 22)

5.8 Extraction of Zinc

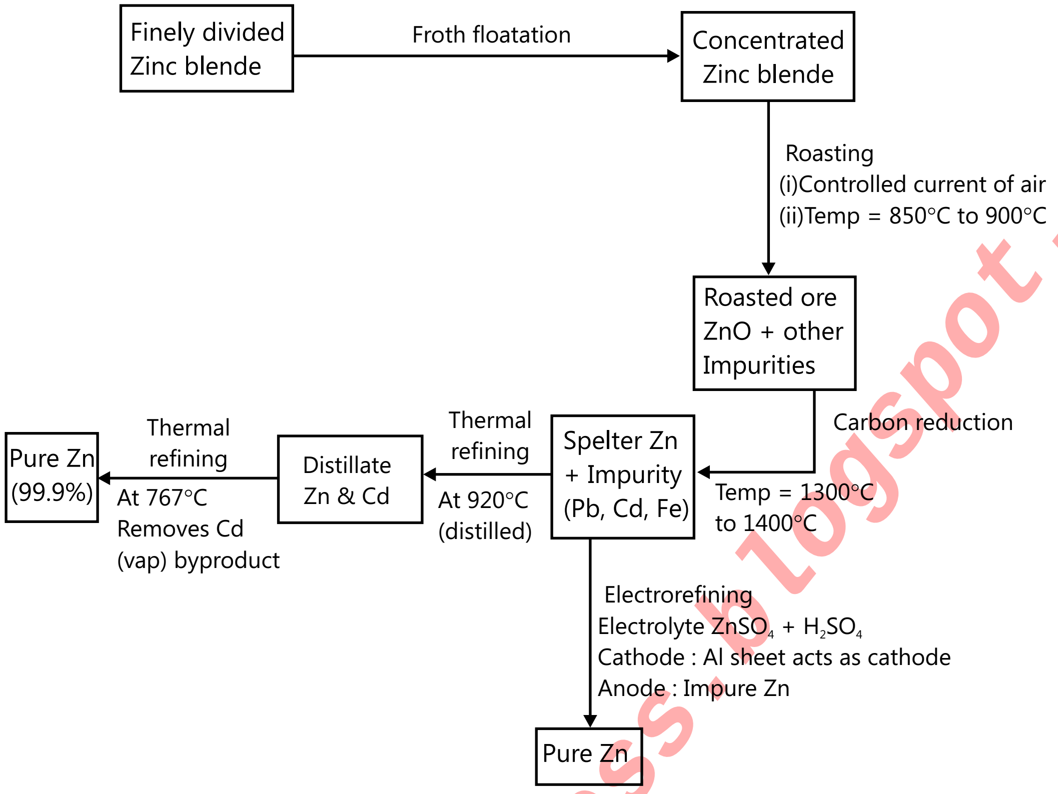
The various ores of zinc are:

1. Zinc blende : ZnS
2. Zincite : ZnO
3. Franklinite : ZnO Fe_2O_3
4. Calamine : $ZnCO_3$
5. Willemite : $ZnSiO_3$
6. Electric calamine : $ZnSiO_3.ZnO.H_2O$

The chief ore used for extraction of zinc is zinc blende, which is also known as Black Jack due to the invariable association of galena (PbS) that is black in colour. Sometimes, calamine is also used to extract Zn by carbon reduction process.

The flow diagram for extraction and refining of zinc from zinc blende is depicted in figure. The changes and reactions involved at various stages of zinc extraction are:

(a) **In the froth floatation step:** This is done in two steps to separate out PbS and ZnS depending upon their different floating characteristics. On addition of pine oil, PbS floats first and is removed. Then more pine oil is added and ZnS floats on the top.



Flowchart 29.17: For extraction and refining of zinc from zinc blende

(b) **In the roasting step:** During roasting, the temperature has to be above 850°C and the air current must be controlled. ZnS is converted into $ZnSO_4$, which converts back to ZnS during carbon reduction of roasted ore.

$$ZnS + \frac{3}{2}O_2 \xrightarrow[850°C]{\text{above}} ZnO + SO_2\uparrow$$

$$ZnS + 2O_2 \xrightarrow[850°C]{\text{below}} ZnSO_4;\ ZnSO_4 + 4C \xrightarrow[\text{carbon reduction}]{\text{during}} ZnS + 4CO\uparrow$$

(c) **In the smelting step:** During smelting, excess coke is used, to stop the production of CO_2 .Otherwise, Zn reduced will be converted back to ZnO. Hence if any CO_2 is produced, it is allowed to convert into CO by the reaction with coke.

$$ZnO + C \rightarrow Zn + CO$$

$$2ZnO + C \rightleftarrows 2Zn + CO_2 \text{ (this reaction is reversible) ; } CO_2 + C \rightarrow 2CO$$

The temperature during smelting is kept above 1300°C, though the b.p. of Zn is 920°G. The temperature is kept much higher, compared to that required for vapourizing of zinc in the furnace. This is done because the reaction of carbon dioxide with coke is highly endothermic and brings down the temperature to below 920°C and the evaporation of Zn is affected. Hence, the temperature is maintained at 1300°C-1400°C.

(d) **In the electrorefining step:** For electrorefining of Zn (crude), Al sheet is used as cathode instead of pure Zn strip. This is because the electrolyte used is $ZnSO_4 + H_2SO_4$ (dil.), and in dil. H_2SO_4. Zn gets dissolved, while Al does not. $Zn + H_2SO_4$ (dil) $\rightarrow ZnSO_4 + H_2\uparrow$

$Al + H_2SO_4$ (dil) $\rightarrow$ No reaction; $2Al + 6H_2SO_4$ (cocn.) $\rightarrow Al_2(SO_4)_3 + 3SO_2 + H_2O$

Reactions at the electrode: $ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-}$

At the cathode: $Zn^{2+} + 2e^- \rightarrow Zn$

At the anode: $OH^- \rightarrow OH + e^-$; $4OH \rightarrow 2H_2O + O_2\uparrow$

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

PLANCESS CONCEPTS

Extraction and refining of zinc includes froth floatation, followed by roasting, then smelting and finally refined by either thermal refining or electrorefining.

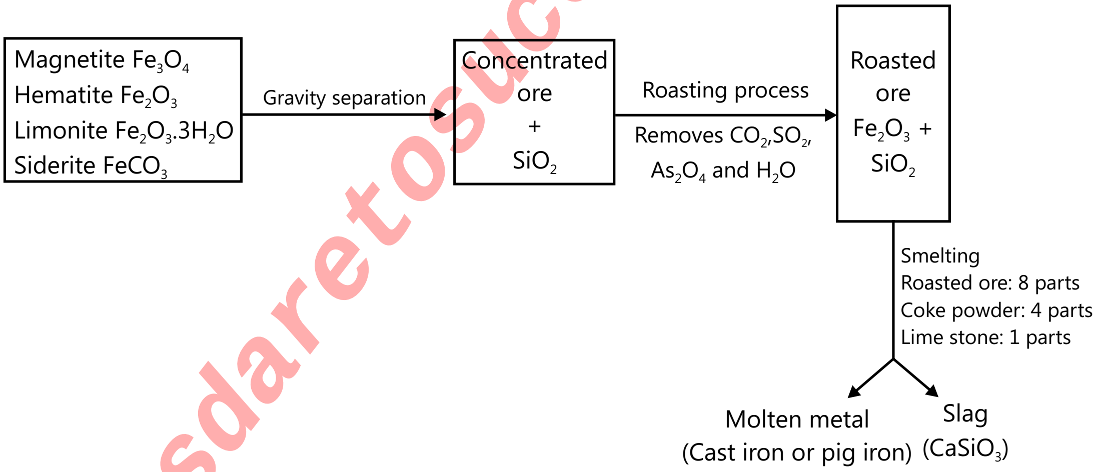
Nikhil Khandelwal (JEE 2009, AIR 94)

5.9 Extraction of Iron

The various ores of iron are:

1.	Hematite	: Fe_2O_3
2.	Magnetite	: Fe_3O_4
3.	Brown hematite or limonite	: $Fe_2O_3.3H_2O$
4.	Siderite or spathic iron are	: $FeCO_3$
5.	Iron pyrite	: FeS_2

The chief ore used for extraction of iron is hematite, while FeS_2 is never used because iron obtained from this ore contains a lot of Sulphur, which makes it brittle and useless. The flow diagram for extraction of iron from different ores is depicted in figure.



Flowchart 29.18: For extraction of iron from hematite

The reaction at various steps of the iron extraction are:

(a) In the roasting step:

$$Fe_3O_4 \rightarrow FeO + Fe_2O_3$$

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

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

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

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

(b) **In the smelting step:** The various changes taking place during smelting in the blast furnace are shown in figure.

The reactions involved are:

At 600-900°C: $\underbrace{Fe_2O_3}_{\text{(Partially reduced)}} + 3CO \rightarrow 2Fe + 3CO_2\uparrow$

At 900-1000°C; $CaCO_3 \rightarrow CaO + CO_2\uparrow$; $CO_2 + C \rightarrow 2CO\uparrow$

At 1000-1300°C ; $Fe_2P_3 + 3C \rightarrow 2Fe + 3CO\uparrow$;
$CaO + SiO_2 \rightarrow CaSiO_3$ (stag)

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

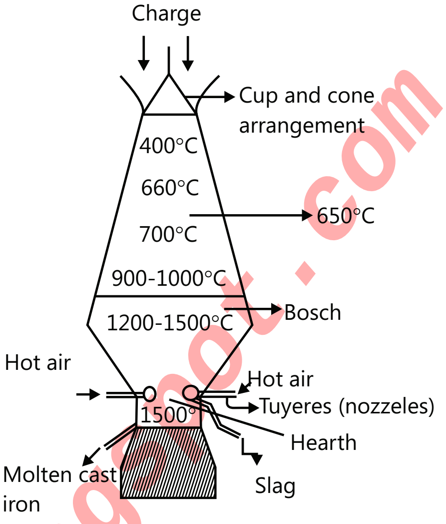


Figure 29.16: Smelting in the blast furnace

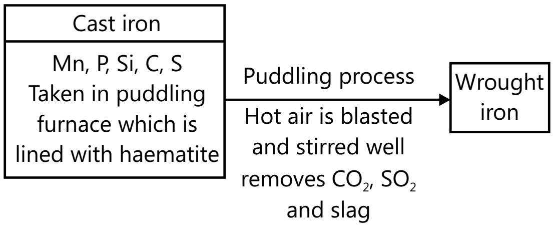
$MnO + 2C \rightarrow Mn + 2CO$; $SiO_2 + 2C \rightarrow Si + 2CO$

$Ca_3(PO_4)_2$ present in the limestone reacts with SiO_2 to produce slag and P_2O_5 is reduced by coke to produce P_4 as impurity: $Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + 2P_2O_3$; $2P_4O_5 + 10C \rightarrow P_4 + 10CO\uparrow$

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

Purification of iron or preparation of wrought iron

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



Flowchart 29.19: For preparation of wrought iron from cast iron

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

$S + O_2 \rightarrow SO_2\uparrow \qquad C + O_2 \rightarrow CO_2\uparrow$

$3S + 2Fe_2O_3 \rightarrow 4Fe + 3SO_2\uparrow$

$3Si + 2Fe_2O_3 \rightarrow 4Fe + 3SiO_2$

$3Mn + Fe_2O_3 \rightarrow 2Fe + 3MnO$; $MnO + SiO_3 \rightarrow MnSiO_3$ (slag)

$3C + 2Fe_2O_3 \rightarrow 2Fe + 3CO\uparrow$; $4P + 5O_2 \rightarrow P_2O_5$; $Fe_2O_3 + P_2O_5 \rightarrow 2FePO_4$ (slag)

Byproducts of iron extraction

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

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

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

%C	Type of steel
0.15-0.3	Mild steel
0.3-0.6	Medium steel

0.6-0.8	High carbon steel
0.8-1.4	Tool steel

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

Different elements present in steel provide different properties as described below:

Element	Properties imparted
P above 0.05%	Imparts low tensile strength and cold brittleness.
Mn	Imparts high hardness and increases tensile strength, e.g. rail road contains 13% Mn.

Cr and Ni Imparts stainless characteristics by producing impervious coating of their oxides on the surface.

N (above 0.01%) Makes steel brittle as well as difficult to weld.

C improves hardness and strength.

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

(a) Puddling process: This process involves stirring of molten iron in a reverberatory furnace by rods, which are consumed in the process

(b) Bessemer and Thomas process

(c) Siemens open hearth process

(d) Basic oxygen process (also called Linz Donawitz (L.D) process)

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

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

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

- If the cast iron contains Mn, but not P, S, Si, then the lining used is silica brick and the process is known as the acid Bessemer process.
- If the cast iron contains acidic impurities such as Si, S, P, a lining of calcined dolomite (CaO.MgO) or magnesia (MgO) is used and the process is called basic Bessemer process. In this process, the P_2O_3 formed from P combines with lime and forms basic slag $[Ca_3(PO_4)_2.CaO]$, which is known as Thomas slag. It is a valuable byproduct and is sold as phosphate fertilizer.

Some heat treatment processes related to steel

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

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

(c) Tempering: The hard and brittle steel is healed to a 200-300°C temperature range and cooled very slowly to room temperature by which the brittleness of the steel disappears while the hardness remains same. This process is called as tempering.

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

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

PLANCESS CONCEPTS

- Extraction of iron includes gravity separation followed by roasting and then smelting to give pig or cast iron.
- Puddling's process is used for purification of iron and converts pig iron to wrought iron.

Saurabh Gupta (JEE 2010, AIR 443)

Illustration 9: Auto reduction process issued in extraction of:

(A) Cu (B) Hg (C) Al (D) Fe **(JEE ADVANCED)**

Sol: (A) and (B) $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$; $HgS + 2HgO \rightarrow 3Hg + SO_2$

Illustration 10: Why is sulphide ore roasted to convert it into the oxide before reduction? **(JEE MAIN)**

Sol: $\Delta_t G°$ of most sulphide ores are greater than those of CS_2 and H_2S. Hence neither carbon nor hydrogen is a suitable reducing agent for the metal sulphides. Moreover the roasting of a sulphide to the oxide is quite advantageous thermodynamically because $\Delta_t G^0$ of oxides are much lower than those of SO_2.

POINTS TO REMEMBER

Metallurgy	A collection of processes used for the extraction of metals from their ores which includes its purification and alloy formation
Ore	A mineral from which one or more metals can be extracted easily and profitably.
Flux	A substance used to reduce the m.p. of ore or react with gangue to convert it to slag.
Gangue or matrix	Earthly impurities present with minerals
Pyrometallurgy	Method of thermal reduction (using reducing agent and heat) of ore to metal.
Hydrometallurgy	Method of extraction of metals using leaching and displacement employing cheaper and reactive metal.
Leaching	Method of reacting an ore with some reagent to collect the required metal as water soluble salt.
Smelting	Heating purified oxide form of ore with coke. It may give metal or matte. It is generally known as carbon reduction method.
Aluminothermy	Method of reducing oxide of a metal by heating with powdered aluminium.

JEE Main/Boards

Exercise 1

Q.1 Copper can be extracted by hydrometallurgy but not zinc. Explain.

Q.2 Out of C and CO, which is a better reducing agent at 673 K?

Q.3 How is leaching carried out in case of low grade copper ores?

Q.4 Why is zinc not extracted from zinc oxide, through reduction using CO?

Q.5 Name the common elements present in the anode mud in electrolytic refining of copper. Why are they so present?

Q.6 State the role of silica in the metallurgy of copper.

Q.7 What is meant by the term "chromatography"?

Q.8 How is 'cast iron' different from 'pig iron"?

Q.9 Differentiate between "minerals" and "ores".

Q.10 Out of C and CO. which is a better reducing agent for ZnO?

Q.11 What is the role of graphite rod in the electrometallurgy of aluminium?

Q.12 Describe a method for refining nickel.

Q.13 Giving examples, differentiate between 'roasting' and 'calcination".

Q.14 Why copper matte is put in silica lined converter?

Q.15 What is the role of cryolite in the metallurgy of aluminium?

Q.16 What types of ores are roasted?

Q.17 Name one each of (a) acidic flux (b) basic flux.

Q.18 What is gangue?

Q.19 What name is given to carbon reduction process for extracting the metal?

Q.20 Outline the principles of refining of metals by the following methods:

(i) Zone refining (ii) Electrolytic refining

(iii) Vapour phase refining

Q.21 What is the role of depressant in froth floatation process?

Q.22 Why is the extraction of copper from pyrites more difficult than that from its oxide ore through reduction?

Q.23 Explain:

(i) Zone refining (ii) Column chromatography

Q.24 Write down the reactions taking place in different zones in the blast furnace during the extraction of iron.

Q.25 Write chemical reactions taking place in the extraction of zinc from zinc blende.

Q.26 What criterion is followed for the selection of the stationary phase in chromatography'?

Q.27 How can you separate alumina from silica in a bauxite ore associated with silica? Give equations, if any?

Q.28 The value of $\Delta_r G^0$ for formation of $Cr_2 O_3$ is -540 kJ $mol^{-1}$and that of Al_2O_3 is - 827 kJ mol^{-1}. Is the reduction of Cr_2O_3 possible with Al?

Q.29 The choice of a reducing agent in a particular case depends on thermodynamic factor. How far do you agree with this statement? Support your opinion with two examples.

Q.30 Name the processes from which chlorine is obtained as a by-product. What will happen if an aqueous solution of NaCl is subjected to electrolysis?

Q.31 Predict conditions under which Al might be expected to reduce MgO.

Exercise 2

Single Correct Choice Type

Q.1 In presence of oxygen, removal of sulphur from an ore is included in

(A) Calcination (B) Roasting

(C) Smelting (D) Fluxing

Q.2 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

Q.3 Pyrolusite is a/an

(A) Oxide ore (B) Sulphide ore

(C) Carbide ore (D) Not an ore

Q.4 The metal always found in the free state is

(A) Au (B) Zn (C) Cu (D) Na

Q.5 In the extraction of iron, the slag produced is?

(A) CO (B) $FeSiO_3$ (C) $MgSiO_3$ (D) $CaSiO_3$

Q.6 Which alloy of aluminium is used in aircraft industry

(A) Duralumin (B) Magnalium

(C) Nickeloy (D) alunico

Q.7 The common impurities present in the bauxite ore are

(A) Fe_2O_3 and CuO (B) Fe_2O_3 and PbO

(C) $Fe_2O_3$and SiO_2 (D) SiO_2 and CuO

Q.8 The material used in solar cell contains

(A) Si (B) Sn (C) Ti (D) Cs

Q.9 Cyanide process is used for the extraction of:

(A) Ag (B) Hg (C) Cu (D) Zn

Q.10 During smelting, an additional substance is added which combines with impurities to form a fusible product. It is known as

(A) Slag (B) Mud (C) Gangue (D) Flux

Q.11 Purification of silicon element used in semi-conductors is done by

(A) Zone refining (B) Heating

(C) Froth floatation (D) Heating in vacuum

Q.12 Aluminothermic process is used for metallurgy of

(A) Pb (B) Ag

(C) Al (D) None of these

Q.13 In electrorefining of copper some gold is deposited as

(A) Anode mud (B) Cathode mud

(C) Cathode (D) Electrolyte

Q.14 Poling process is used

(A) For the removal of Cu_2O from Cu

(B) For the removal of Al_2O_3 from Al

(C) For the removal Fe_2O_3 from Fe

(D) In all the above

Q.15 Which of the following is not a basic flux?

(A) $CaCO_3$ (B) CaO (C) SiO_2 (D) MgO

Q.16 Zone refining is a method to obtain

(A) Very high temperature

(B) Ultra pure Al

(C) Ultra pure metal

(D) Ultra pure oxides

Q.17 Mac Arthur process is use for

(A) Ag (B) Fe (C) Cl (D) O_2

Q. 18 Use of electrolysis is

(A) Electroplating (B) Electrorefining

(C) Both (A) and (B) (D) None of these

Q.19 Calcination is used in metallurgy for removal of

(A) Water and sulphide (B) Water and CO_2

(C) CO_2 and H_2S (D) H_2O and H_2S

Q.20 In blast furnace, maximum temperature is in

(A) Zone of fusion

(B) Zone of combustion

(C) Zone of slag combustion

(D) Zone of reduction

Q.21 Of the following which cannot be obtained by electrolysis of the aqueous solution of their salts?

(A) Ag (B) Mg and Al (C) Cu (D) Cr

Q.22 Van Arkel method of purification of metals involves converting the metal into a

(A) Volatile stable compound

(B) Volatile unstable compound

(C) Non-volatile stable compound

(D) None of the above

Q.23 In the froth floatation process for the purification of ores, the ore particles float because

(A) They are light

(B) Their surface is hydrophobic i.e., not easily wetted by water

(C) They bear electrostatic charge

(D) They are insoluble

Q.24 Which method of purification is represented by the following equations?

$$Ti + 2I_2 \xrightarrow{773K} TiI_4 \xrightarrow{1675K} Ti + 2I_2$$

(A) Cupellation (B) Poling

(C) Van Arkel (D) Zone refining

Q.25 Calcination is the process of heating the ore

(A) In a blast furnace (B) In absence of air

(C) In presence of air (D) None of these

Q.26 Which one of the following metals cannot be extracted by carbon reduction process?

(A) Pb (B) Al (C) Hg (D) Zn

Q.27 Cyanide process is used for obtaining

(A) Cr (B) Ag (C) Cu (D) Zn

Previous Year's Questions

Q.1 Which of the following mineral does not contain Al ***(1992)***

(A) Cryolite (B) Mica

(C) Feldspar (D) Fluorspar

Q.2 Which of the following is not an ore ***(1982)***

(A) Bauxite (B) Malachite

(C) Zinc blende (D) Pig iron

Q.3 Copper can be extracted from ***(1978)***

(A) Kupfernickel (B) Dolomite

(C) Galena (D) Malachite

Q.4 Among the following statements, the incorrect one is ***(1997)***

(A) Calamine and siderite are carbonates

(B) Argentite and cuprite are oxides

(C) Zinc blende and pyrites are sulphides

(D) Malachite and azurite are ores of copper

Q.5 Which ore contains both iron and copper ***(2005)***

(A) Cuprite (B) Chalcocite

(C) Chalcopyrite (D) Malachite

(A) If both assertion and reason are true and reason is the correct explanation of assertion, then mark (A)

(B) If both assertion and reason are true but reason is not the correct explanation of assertion, then mark (B)

(C) If assertion is true but reason is false, then mark (C)

(D) If both assertion and reason are false, then mark (D)

Q.6 Assertion: Gold is recovered from its solution containing aurocyanide complex by adding zinc dust. ***(1982)***

Reason: Zinc is more electropositive than gold.

Q.7 Assertion: Zinc is used and copper is not used in the recovery of Ag from the complex $[Ag(CN)_2]^-$. ***(1995)***

Reason: Zinc is a powerful reducing agent than copper.

Q.8 Assertion: Coke and flux are used in smelting. ***(1998)***

Reason: The phenomenon in which ore is mixed with suitable flux and coke is heated to fusion is known as smelting.

Q.9 Assertion: Leaching is a process of reduction. ***(1999)***

Reason: Leaching involves treatment of the ore with a suitable reagent so as to make it soluble while impurities remains insoluble.

Q.10 Assertion: Ethyl xanthate is used as a collector in froth floatation process. ***(1999)***

Reason: Collectors depress the floatation property of one of the components of the ore and thus help in the separation of different minerals present in the same ore.

Q.11 Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly? ***(2008)***

(A) Metal sulphides are thermodynamically more stable than CS_2

(B) CO_2 is thermodynamically more stable than CS_2

(C) Metal sulphides are less stable than the corresponding oxides

(D) CO_2 is more volatile than CS_2

Q.12 Which method of purification is represented by the following equation: $Ti+2I_2 \rightarrow TiI_4$ ***(2012)***

(A) Zone refining (B) Cupellation

(C) Poling (D) Van Arkel

Q.13 In the context of the Hall-Heroult process for the extraction of Al, which of the following statements is false? ***(2015)***

(A) CO and CO_2 are produced in this process

(B) Al_2O_3 is mixed with CaF_2 which lowers the melting point of the mixture and brings conductivity

(C) Al^{3+} is reduced at the cathode to form Al

(D) Na_3AlF_6 serves as the electrolyte

Q.14 Which one of the following ores is best concentrated by froth floatation method? ***(2016)***

(A) Siderite (B) Galena

(C) Malachite (D) Magnetite

Q.15 Galvanization is applying a coating of ***(2016)***

(A) Cr (B) Cu (C) Zn (D) Rb

JEE Advanced/Boards

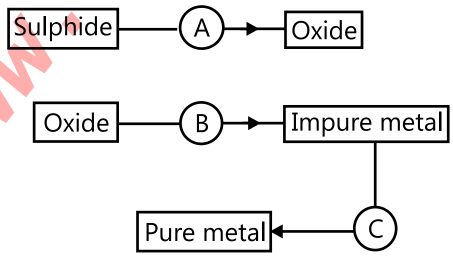
Exercise 1

Q.1 What is Goldschmidt Thermite Process?

Q.2 Al_2O_3 can't be reduced by carbon to get Al metal. Explain.

Q.3 Cu can reduce Ag^+ to metallic Ag but Ag can't reduce Cu^{2+} to metallic Cu. Explain.

Q.4 A metal is in combined state as sulphide. Identify the steps (A), (B), (C)



Q.5 Write chemical equations for metallurgical processes to represent:

(a) Roasting of galena (PbS).

(b) Reduction of Cu_2O using charcoal as a reducing agent.

(c) deposition of pure silver from an aqueous solution of Ag^+.

Q.6 Why zinc and not copper is used for the

recovery of metallic silver from the complex $[Ag(CN)_2]^-$?

Q.7 Sodium is prepared by the electrolysis of molten NaCl but not by the electrolysis of its aqueous solution.

Q.8 Elements of alkali metal group are strong reducing agent. Explain.

Q.9 In the metallurgy of iron, why limestone is added to the ore.

Q.10 What is the actual reducing agent of haematite in blast furnace?

Q.11 Write chemical equations to represent the most probable outcome in each of the following. If no reaction is likely to occur, state so:

(i) $CdCO_3 \xrightarrow{\Delta}$

(ii) $MgO \xrightarrow{\Delta}$

(iii) $SnO_2 + CO \xrightarrow{\Delta}$

(iv) $CdSO_4\ (aq) \xrightarrow{\text{electrolysis}}$

(v) $2HgO \xrightarrow{\Delta}$

(vi) $MgO + Zn \xrightarrow{\Delta}$

Q.12 Why graphite is used as anode but not diamond?

Q.13 The following reactions take place during the extraction of copper from copper ore:

(i) $2Cu_2S(\ell) + 3O_2(g) \rightarrow 2Cu_2O(\ell) + +2SO_2(g)$

(ii) $2Cu_2O(\ell) + Cu_2S(\ell) \rightarrow 6Cu(\ell) + SO_2(g)$

Identify the oxidizing and reducing agents.

Q.14 Dolomite ($MgCO_3.CaCO_3$) can also be treated to get $MgCl_2$ which in turn is electrolyzed to get Mg. (Dow natural brine process). Give reactions of this process.

Q.15 $[CaCO_3.MgCO_3] \xrightarrow{\Delta} CaO.MgO$

$CaO.\ MgO \xrightarrow[1150°C]{Fe/Si} Mg + Fe + Ca_2SiO_4$

Name this process.

Q.16 Convert Mg into MgO.

Q.17 (i) A black mineral (A) on treatment with dilute sodium cyanide solution in presence of air gives a clear solution of (B) and (C).

(ii) The solution of (B) on reaction with zinc gives precipitate of a metal (D).

(iii) (D) is dissolved in dilute HNO_3 and the resulting solution gives a white precipitate (E) with dilute HCl.

(iv) (E) on fusion with sodium carbonate gives (D).

(v) (E) dissolves in aqueous solution of ammonia giving a colourless solution of (F). Identify compounds (A) to (F) and give chemical equations for reactions in steps (i) to (iv).

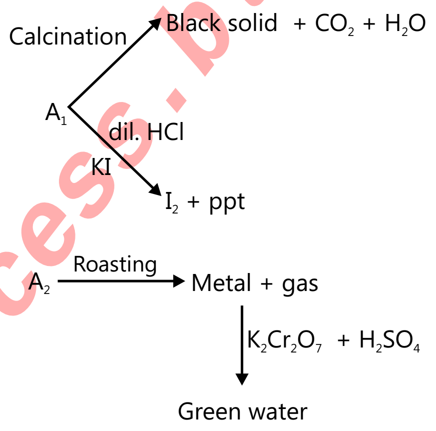
Q.18 Name two metals which are used for reduction in metallurgical process. Give one chemical equation for each

Q.19 Aluminium metal is frequently used as a reducing agent for the extraction of metals such as chromium or manganese from their respective oxides. Why?

Q.20 What is the function of basic furnace linings in steels manufacture?

Q.21 Write down reactions involved in the extraction of Pb. What is the oxidation number of lead in litharge?

Q.22 A_1 and A_2 are two ores of metal M. A_1 on calcination gives black precipitate, CO_2 and water?



Q.23 Gold is also extracted by cyanide process as in case of silver. Outline the reactions.

Q.24 How is Ag extracted from silver coin?

Q.25 In the purification of bauxite ore as preliminary step in the production of Al, $[Al(OH)_4]^-$ can be converted to $Al(OH)_3$ by passing CO_2 through it. Write an equation for the reaction that occurs.

Q.26 When the ore hematite is burnt in air with coke around 2000°C along with lime, the process not only produces steel, but also produces a silicate slag that is useful in making building material such as cement. Discuss the same and show through balanced chemical equation.

Q.27 Explain the following

(i) In the metallurgy of iron, lime-stone is added to the ore.

(ii) Although Au is soluble in aqua-regia, Ag is not.

Exercise 2

Single Correct Choice Type

Q.1 Sulphide ores are generally concentrated by

(A) Froth floatation (B) Roasting

(C) Gravity (D) Reduction by carbon

Q.2 Which method of purification is represented by the following equations?

$$Ti + 2I_2 \xrightarrow{523K} TiI_4 \xrightarrow{1700K} Ti + 2I_2$$

(A) Cupellation (B) Poling

(C) Van Arkel (D) Zone refining

Q.3 Cryolite is

(A) Na_3AlF_6 and is used in the electrolysis of alumina for decreasing electrical conductivity

(B) Na_3AlF_6 and is used in the electrolysis of alumina for lowering the melting point of alumina

(C) Na_3AlF_6 and is used in the electrolytic purification of alumina

(D) Na_3AlF_6 and is used in the electrolysis of alumina

Q.4 Cassiterite is an ore of

(A) Mn (B) Ni (C) Sb (D) Sn

Q.5 When an aqueous solution of sodium chloride is electrolysed using platinum electrodes, the ions discharged at the electrodes are

(A) Sodium and hydrogen

(B) Sodium and chloride

(C) Hydrogen and chloride

(D) Hydroxyl and chloride

Q.6 The luster of a metal is due to

(A) Its high density

(B) Its high polishing

(C) Its chemical inertness

(D) Presence of free electrons

Q.7 Which metal can't be obtained from electrolysis?

(A) Ca (B) Mg

(C) Cr (D) All of the above

Q.8 The function of flux during smelting of ores is to:

(A) Make the ore porous

(B) Remove gangues

(C) Facilitate reduction

(D) Precipitate slag

Q.9 The chemical composition of slag formed during the smelting process in the extraction of copper is:

(A) $Cu_2O + FeS$ (B) $FeSiO_3$

(C) $CuFeS_2$ (D) $Cu_2S + FeO$

Q.10 The chemical process in the production of steel from haemotite ore involves:

(A) Reduction

(B) Oxidation

(C) Reduction followed by oxidation

(D) Oxidation followed by reduction

Q.11 In the commercial electrochemical process for alumniuim extraction, the electrolyte used is

(A) $Al(OH)_3$ in NaOH solution

(B) An aqueous solution of $Al_2(SO_4)_3$

(C) A molten mixture of Al_2O_3 and Na_3AlF_6

(D) A molten mixture of $AlO(OH)$ and $Al(OH)_3$

Q.12 Calcination is used in metallurgy to remove

(A) H_2O and H_2S (B) H_2O and CO_2

(C) CO_2 and H_2S (D) H_2O and H_2S.

Q.13 The metallic luster exhibited by sodium is

explained by the presence of

(A) Na^+ ions

(B) Conducting electrons

(C) Free protons

(D) A body-centred cubiclattice.

Q.14 Stainless steel contains

(A) Fe, Cr, Cu (B) Fe, Cr, Ni

(C) Fe, Ni, C (D) Fe, Ni, Cu

Q.15 Which one of the following beneficiation processes is used for the mineral, $Al_2O_3.2H_2O$?

(A) Froth floatation (B) Leaching

(C) Liquation (D) Magnetic separation

Q.16 The extraction of which of the following metals involves bessemerisation ?

(A) Fe (B) Ag (C) Al (D) Cu

Q.17 One of the characteristic properties of non-metals is that they

(A) Are reducing agents

(B) Form basic oxides

(C) Form cations by electron gain

(D) Are electronegative

Q.18 In the froth floatation process for the purification of ores, the ore particles float because

(A) They are light

(B) Their surface is hydrophobic i.e., not easily wetted by water

(C) They bear electrostatic charge

(D) They are insoluble

Q.19 Which is not a basic flux?

(A) $CaCO_3$ (B) Lime (C) SiO_2 (D) CaO

Q.20 The substance which is added to remove impurities is known as

(A) Slag (B) Flux (C) Gangue (D) Catalyst

Q.21 Electrolytic reduction method is used in the extraction of

(A) Highly electronegative elements

(B) Highly electropositive elements

(C) Transition metals

(D) Noble metals

Q.22 The role of calcination in metallurgical operations is

(A) To remove moisture

(B) To decompose carbonate

(C) To drive off organic matter

(D) To achieve all the above

Comprehension Type

A black coloured compound (A) on reaction with dil H_2SO_4 form a gas 'B' and a solution of compound (C). When gas B is passed through solution of compound (C), a black coloured compound A is obtained which is soluble in 50% HNO_3 and forms blue coloured complex 'D' with excess of NH_4OH and chocolate brown ppt. 'E' with $K_4[Fe(CN)_6]$

Q.23 'A' is

(A) CuS (B) FeS (C) PbS (D) HgS

Q.24 'B' is

(A) H_2S (B) SO_2 (C) NH_3 (D) SO_3

Q.25 'C' is

(A) CuS (B) $CuSO_4$ (C) $Cu(NO_3)_2$ (D) $HgSO_4$

Q.26 'D' is

(A) $Cu(OH)_2$ (B) $[Cu(NH_3)_2]SO_4$

(C) $[Cu(NH_3)_4](NO_3)_2$ (D) $[Cu(NH_3)_6]SO_4$

Q.27 'E' is

(A) $Cu_2[Fe(CN)_6]$ (B) $Cu_4[Fe(CN)_6]$

(C) $Cu_3[Fe(CN)_6]_2$ (D) None of these

Assertion Reasoning Type

(A) If both assertion and reason are true and reason is the correct explanation of assertion, then mark (a)

(B) If both assertion and reason are true but reason is not the correct explanation of assertion, then mark (b)

(C) If assertion is true but reason is false, then mark (c)

(D) If both assertion and reason are false, then mark (d)

Q.28 Assertion: Calamine is a ore of boron.

Reason: Boric acid is a tribasic acid.

Q.29 Assertion: FeS_2 is also known as fools' gold.

Reason: FeS_2 has yellow metallic appearance.

Q.30 Assertion: Pb^{4+} can be reduced easily to Pb^{2+}.

Reason: Pb^{2+} is paramagnetic.

Q.31 Assertion: Diamond is harder than graphite.

Reason: Graphite is more stable than diamond.

Q.32 Assertion: Carbon dioxide and nickel react to form tetracaronyl nickel (0).

Reason: Ni(CO)$_4$ decomposes on heating to form Ni and CO.

Previous Years Questions

Q.1 Which ore contains both iron and copper ***(2005)***

(A) Cuprite (B) Chalcocite

(C) Chalcopyrite (D) Malachite

Q.2 Extraction of zinc from zinc blende is achieved by ***(2007)***

(A) Electrolytic reduction

(B) Roasting followed by reduction with carbon

(C) Roasting followed by reduction with another metal

(D) Roasting followed by self-reduction

Q.3 Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of ***(2008)***

(A) Nitrogen (B) Oxygen

(C) Carbon dioxide (D) Argon

Q.4 Oxidation states of the metal in the minerals haematite and magnetite, respectively, are ***(2011)***

(A) II, III in haematite and III in magnetite

(B) II, III in haematite and II in magnetite

(C) II in haematite and II, III in magnetite

(D) III in haematite and II, III in magnetite

Q.5 Addition of high proportions of manganese makes steel useful in making rails ***(1998)***

(A) Gives hardness to steel

(B) Helps the formation of oxides of iron

(C) Can remove oxygen and sulphur

(D) Can show highest oxidation state of +7

Q.6 Extraction of metal from the ore cassiterite involves ***(2011)***

(A) Carbon reduction of an oxide ore

(B) Self-reduction of a sulphide ore

(C) Removal of copper impurity

(D) Removal or iron impurity

Paragraph

Copper is the most noble of the first row transition metals and occurs in small deposits in several countries. Ores of copper include chalcanthite ($CuSO_4 .5H_2O$), atacamite ($Cu_2Cl(OH)_3$, cuprite (Cu_2O), copper glance (Cu_2S) and malachite ($Cu_2(OH)_2CO_3$). However, 80% of the world copper production comes from the ore chalcopyrite ($CuFeS_2$). The extraction of copper from chalcopyrite involves partial roasting, removal of iron and self-reduction. ***(2010)***

Q.7 Partial roasting of chalcopyrite produces

(A) Cu_2S and FeO (B) Cu_2O and FeO

(C) CuS and Fe_2O_3 (D) Cu_2O and Fe_2O_3

Q.8 Iron is removed from chalcopyrite as

(A) FeO (B) FeS (C) Fe_2O_3 (D) $FeSiO_3$

Q.9 In self-reduction, the reducing species is

(A) S (B) O^{2-} (C) S^{2-} (D) SO_2

Q.10 Match the following Metals listed in column I with extraction processes listed in column II. ***(1979)***

Column I	Column II
(A) Silver	(p) Fused salt Electrolysis
(B) Calcium	(q) Carbon Reduction
(C) Zinc	(r) Carbon monoxide reduction
(D) Iron	(s) Amalgamation
(E) Copper	(t) Self reduction

Q.11 Write the chemical reactions involved in the extraction of silver from argentite. ***(2000)***

Q.12 Write the balanced chemical equation for developing photographic films.

Q.13 Write balanced chemical equation for developing a black and white photographic film. Also give reason, why the solution of sodium thiosulphate on acidification turns milky white and give balance equation of this reaction. ***(2005)***

Q.14 Given the number of water molecule (s) directly bonded to the metal center in $CuSO_4 . 5H_2O$. ***(2009)***

Q.15 Given the coordination number of Al in the crystalline state of $AlCl_3$. ***(2009)***

Q.16 Extraction of zinc from zinc blende is achieved by, ***(2007)***

(A) Electrolytic reduction

(B) Roasting followed reduction by reduction with carbon

(C) Roasting followed by reduction with another metal

(D) Roasting following by self-reduction

Q.17 Match the conversions in column I with the type (s) of reaction (S) give in column II. ***(2008)***

Column I	Column II
(A) $PbS \rightarrow PbO$	(p) Roasting
(B) $CaCO_3 \rightarrow CaO$	(q) Calcination
(C) $ZnS \rightarrow Zn$	(r) Carbon reduction
(D) $Cu_2S \rightarrow Cu$	(s) Self reduction

Q.18 Sulfide ores are common for the metals ***(2013)***

(A) Ag, Cu and Pb (B) Ag, Cu and Su

(C) Ag, Mg and Pb (D) Al, Cu and Pb

Q.19 The carbon-based reduction method in NOT used for the extraction of ***(2013)***

(A) Tin from SnO_2

(B) Iron from Fe_2O_3

(C) Aluminium from Al_2O_3

(D) Magnesium from $MgCO_3.CaCO_3$

Q.20 Match the anionic species given in column I that are present in the ore (s) given in column II ***(2015)***

Column I	Column II
(A) Carbonate	(p) Siderite
(B) Sulphide	(q) Malachite
(C) Hydroxide	(r) Bauxite
(D) Oxide	(s) Calamine
	(s) Argentite

Q.21 Extraction of copper from copper pyrite $\left(CuFeS_2\right)$ involves ***(2016)***

(A) Crushing following by concentration of the ore by froth-flotation

(B) Removal of iron as slag

(C) Self-reduction step to produce 'blister copper' following evolution of SO_2

(D) Refining of 'blister copper' by carbon reduction

PlancEssential Questions

JEE Main/Boards

Exersice 1

Q.2 Q.6 Q.15

Q.21 Q.27 Q.30

Exersice 2

Q.8 Q.24

Previous Years' Questions

Q.9

JEE Advanced/Boards

Exersice 1

Q.4 Q.12 Q.17

Q.20 Q.27

Exersice 2

Q.2 Q.13 Q.32

Previous Years' Questions

Q.3 Q.10 Q.15

Answer Key

JEE Mains/Boards

Exercise 2

Single Correct Choice Type

Q.1 B **Q.2** C **Q.3** A **Q.4** A **Q.5** D **Q.6** A **Q.7** C
Q.8 A **Q.9** A **Q.10** D **Q.11** A **Q.12** D **Q.13** A **Q.14** A
Q.15 C **Q.16** C **Q.17** A **Q.18** C **Q.19** B **Q.20** B **Q.21** B
Q.22 A **Q.23** A **Q.24** C **Q.25** B **Q.26** B **Q.27** A

Previous Years' Questions

Q.1 D **Q.2** D **Q.3** D **Q.4** B **Q.5** C **Q.6** A **Q.7** B
Q.8 B **Q.9** D **Q.10** C **Q.11** A **Q.12** D **Q.13** D **Q.14** B
Q.15 C

JEE Advanced/Boards

Exercise 2

Single Correct Choice Type

Q.1 A **Q.2** C **Q.3** B **Q.4** D **Q.5** C **Q.6** D **Q.7** C
Q.8 D **Q.9** B **Q.10** D **Q.11** C **Q.12** C **Q.13** C **Q.14** B
Q.15 B **Q.16** D **Q.17** D **Q.18** B **Q.19** C **Q.20** B **Q.21** B
Q.22 D

Comprehension Type

Q.23 A **Q.24** A **Q.25** B **Q.26** C **Q.27** A

Assertion Reasoning Type

Q.28 D **Q.29** C **Q.30** C **Q.31** C **Q.32** D

Previous Years' Question

Q.1 C **Q.2** B **Q.3** B **Q.4** D **Q.5** A, C **Q.6** A, D **Q.7** B
Q.8 D **Q.9** C **Q.10** A $\rightarrow$ s; B $\rightarrow$ p; C $\rightarrow$ q; D $\rightarrow$ q, r; E $\rightarrow$ t **Q.16** B
Q.17 A $\rightarrow$ p; B $\rightarrow$ q; C $\rightarrow$ p, r; D $\rightarrow$ p, s **Q.18** A **Q.19** C, D
Q.20: A $\rightarrow$ p, q, s; B $\rightarrow$ t; C $\rightarrow$ q, r; D $\rightarrow$ r **Q.21** A, B, C

Solutions

JEE Main/Boards

Exercise 1

Sol 1: The reduction potential of zinc and iron is lower than that of copper. In hydrometallurgy, Zn/Fe can be used to displace Cu from the solution

$Fe_{(s)} + Cu^{2+}_{(aq.)} \longrightarrow Fe^{2+}_{(aq.)} + Cu_{(s)} \downarrow$

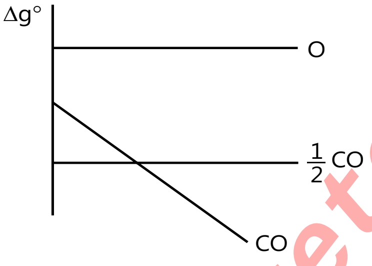
But to displace Zn, more reactive metals i.e. Na, K are required but they violently react with water and gives hydrogen gas.

$K + H_2O \longrightarrow KOH + \frac{1}{2}H_2 \uparrow$

$\therefore$ By hydrometallurgy, Cu can be extracted but not Zn.

Sol 2: Ellingham diagrams.

In this range of temperature, diagrams show that carbon monoxide act as stronger reduction agent than carbon.



$2CO + O_2 \rightarrow 2CO_2$

has more negative free energy than

$2C + O_2 \rightarrow 2CO$

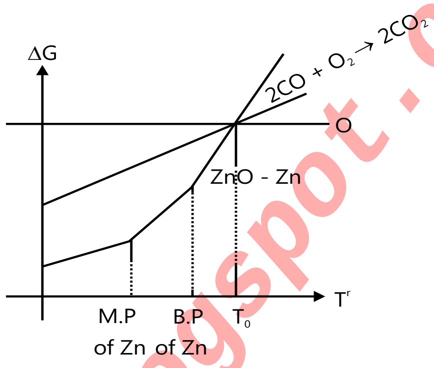
$\therefore$ In the upper part of furnace, haematite is reduced by CO even in the presence of C.

Sol 3: In case of low grade copper ores, such as chalcopyrites, Ag is used to reduced the remaining copper.

$Cu^{2+} + 2Ag \rightarrow Cu + 2Ag^{+}$

and by formation of shiny Ag_2S layer, it is confirmed that Cu got reduced.

Sol 4: Ellingham diagram clearly indicates that the CO graph cut at much higher temperature to Zinc oxide's graph.



$T_0 > T_{B.P\ of\ Zn}$ So, Zn will be in vapour form and its very tough to maintain such high temperature in furnace for long time and at this temperature, carbon forms carbides.

Sol 5: Element present in the anode mud:- Se, Te, Ag, Au, Pt and Sb

These elements are very less reactive and are not affected during the purification process. Hence, they settle down below anode as anode mud.

Sol 6: In the process of Bessemerisation, air is blown into molten matte with silica. So, by self reduction CuS gets reduced to Cu but at same time, FeS also gets converted to FeO but to avoid further reaction, silica is added.

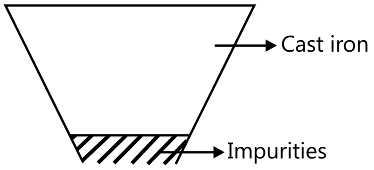
$FeO + SiO_2 \rightarrow FeSiO_3$ (Slag)

Thomas slag

By this, molten copper gets separated out.

Sol 7: Refer Theory - Chromatography

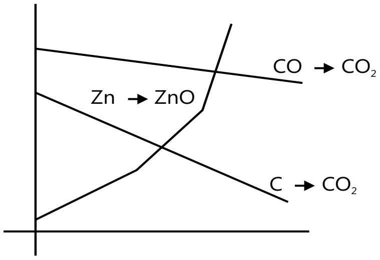
Sol 8: The composition difference between cast and Pig iron is, Pig iron has 4% carbon content whereas cast iron has at least 2% carbon content.



After extracting from furnace, we get pig iron and we put them in a case from which impurities can be cut out so there is difference of amount in impurity.

Sol 9: Minerals are the substances in which metals are present either in native or combined forms but ores are that minerals from which metal can be extracted economically and conveniently.

Sol 10: From Ellingham diagram, graph of C cuts the Zn graph at lower temperature than CO.



$\therefore$ $ZnO + C \rightarrow Zn + CO, \quad \Delta G_1$

$ZnO + CO \rightarrow Zn + CO_2, \quad \Delta G_2$

$|\Delta G_1| > |\Delta G_2|$ so, first reaction is favourable

$\therefore$ C is better reducing agent than CO.

Sol 11: Graphite rod is used as an anode and graphite line iron as cathode during the electrolysis of alumina.

Sol 12: Refer theory

Sol 13: Refer theory

Sol 14: Copper matte contains sulfides of copper and iron. While reducing, it is Bessemer converter by self-reduction, CuS gets converted to Cu but to avoid Fe in the final product, silica is used which forms slag with FeO

$FeO + SiO_2 \rightarrow \underset{\text{(slag)}}{FeSiO_3}$

Sol 15: Generally, aluminium is extracted by using electrometallurgy, but for that purpose Al should be in molten state. But, melting point of aluminium is very high. So, to increase the solubility and to decrease the melting point, cryolite is added.

Sol 16: Roasting is a process in which ore is heated in presence of oxygen to convert it into corresponding oxides. So the ores whose oxides can be easily reduced by C/CO or by self reduction are roasted. E.g. CuS, FeS, but ores of Al, Na, K cannot be roasted.

Sol 17: (a) Acidic flux:- Used to remove basic gangues

E.g. SiO_2, $Na_2B_4O_7.10H_2O$

(b) Basic flux:- Used to remove acidic gangues

E.g. CaO, $MgCO_3$, $CaCO_3$.

Sol 18: Gangue:- (Matrix)

These are the non-metallic impurities present in the ore. In fact, impurities associated with an ore is known as gangue.

Sol 19: Refer theory

Sol 20: (1) Zone Refining: Fractional crystallisation :-Based on difference in solublities of impurities in molten and solid state.

E.g. Ge, Ga, Si etc (To extrapurify the metal)

(2) Electrolytic Refining: Faraday's law of electrolysis

Metals which are not reduced by C/CO, are reduced by this method. E.g. Na, Ca, K, Al etc.

(3) Vapour phase refining:

$Ni + 4CO \rightarrow [Ni(CO)_4] \xrightarrow{\Delta} Ni\downarrow + 4CO$ Purification by forming volatile carbonyl complex.

Sol 21: Froath floatation:- Based on the different wetting property of the ore and gangue with oil and water. Depressants are used to depress the frothing tendency of the frothing agent Eg. NaCN, KCN

Example: In the selective froth floatation of PbS, ZnS can be depressed using depressant.

$Zn + 4CN^- \rightarrow [Zn(CN)_4]^{2-}$

Sol 22: Copper pyrites $\rightarrow CuFeS_2$ composes sulfides of CuS and FeS both.

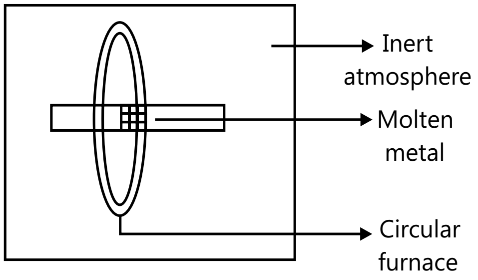
While extracting copper from pyrites, when we oxidise the ore $2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$, ferrous oxide also gets formed which has to be removed by slag formation

$$\left.\begin{array}{l} CuS + O_2 \rightarrow CuO + SO_2 \\ 2CuO + CuS \rightarrow 3Cu + SO_2 \end{array}\right\} \text{Self reduction}$$

But in simple oxide 'CuO', it can be easily reduced by carbon reduction

$CuO + C \rightarrow Cu + CO_2\uparrow$

Sol 23: (i) Zone Refining: Method to obtain metals of very high purity metals like Ge, Ga, Si etc. This method is based on difference in solubilities of impurities in molten and solid state. This refining is as shown below:



Heater melts that part of metal and impurities flows in the molten part and by moving this, eventually get at the end and cut out, this process is repeated several times.

(ii) Column Chromatography:- This technique is based on different adsorbing power of different metal ions on a surface. This technique is used for that metals whose separation is difficult. Eg. Lanthanoids, actinoids.

Sol 24: At 600-900°C: $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

At 900-1000°C ; $CaCO_3 \rightarrow CaO + CO_2$; $CO_2 + C \rightarrow 2CO$

Sol 25: Extraction of any ore is done in 3 parts.

(i) Concentration:- froth floatation process.

(ii) Roasting:-

$$\begin{tikzcd} 2ZnS + 3O_2 \arrow[r] & 2ZnO + 2SO_2 \arrow[d, "\text{Carbon Reduction}"] \\ ZnO + C \arrow[r] & Zn + CO \end{tikzcd}$$

(iii) Purification:- fractional distillation & electrolysis.

Sol 26: Refer theory

Sol 27: Silica in alumina is a natural impurity and before electrolysis, this impurity should be removed. So any of the following chemical process can be used to purify alumina from bauxite.

(i) Bayer's process:- Finely powdered

$$\text{Bauxite} \xrightarrow[FeO \rightarrow Fe_2O_3]{\text{Roasted}} \text{Roasted ore}$$

$$\text{Roasted ore} \xrightarrow[\substack{\text{High pressure, filtered} \\ Fe_2O_3 \text{ as residue}}]{\text{Caustic soda solution}}$$

$$\text{Filtrate (Sod. aluminate + Sod. Silicate)} \xrightarrow[\text{filtered}]{CO_2} Al(OH)_3 \xrightarrow{\Delta} \text{Pure } Al_2O_3$$

(ii) Hall's process:

Finely Bauxite:

Finely Bauxite:-

$$\xrightarrow[\text{Fused, extracted with water}]{Na_2CO_3} \text{Solution} + (\text{Residue } SiO_2 + Fe_2O_3)$$

$$\begin{tikzcd} \text{Filtrate } (Na_2CO_3) \arrow[r, "CO_2", "50^\circ - 60^\circ \text{ \& filtered}"'] & \text{ppt. } Al(OH)_3 \arrow[d, "\Delta"] \\ & \text{Pure } Al_2O_3 \end{tikzcd}$$

(iii) Serpeck's Process:-

$$\text{Finely powdered bauxite ore} \xrightarrow[\Delta \text{ to } 1800^\circ C]{\text{Coke} + N_2}$$

$$\begin{tikzcd} \text{silica reduced to Si which volatises} + & AlN \arrow[d, "H_2O"] \\ \text{Pure } Al_2O_3 & Al(OH)_3 \arrow[l, "\Delta"'] \end{tikzcd}$$

Sol 28: Refer Elingham diagram

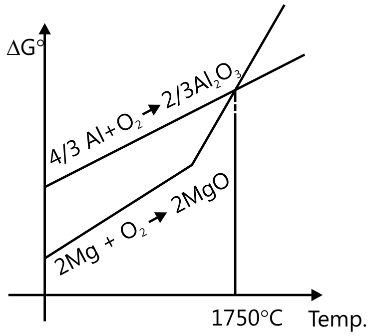
Sol 29: Yes, Reducing agent's selection widely depends on thermodynamic factor because free energy is the factor which decides the reaction feasibility.

E.g. (1) In the upper part of blast furnace, carbon monoxide is better reducing agent than carbon because in that temperature range, ΔG of CO's reaction is less than for C.

(2) Reduction of ZnO is not feasible by carbon because it can be only possible at high temperature at which both compounds are in vapour phase.

Sol 30: In the electrolysis of NaCl, Cl_2 is obtained as a by-product

Sol 31: Ellingham Diagram:-



Reduction of MgO by Al is feasible at very high temperature around 1750°C

$2Al + 3MgO \rightarrow 3Mg\downarrow + Al_2O_3$

Because ΔG is negative after this temperature. So, aluminothermite is not useful to extract Mg from MgO. Thus, electrolytic reduction is used.

Exercise 2

Sol 1: (B) During roasting, air is blown to convert metal sulphides into metal oxides.

$$FeS + \frac{3}{2}O_2 \rightarrow FeO + SO_2$$

Sol 2: (C) Cu can be reduced by self-reduction. So,

$$Cu_2S + \frac{3}{2}O_2 \rightarrow Cu_2O + SO_2\ ;\ 2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

Sol 3: (A) Pyrolusite $\rightarrow MnO_2$

Sol 4: (A) Ag, Au, Hg, Pt are chemically inert metals.

Sol 5: (D) $\underset{\text{lime}}{CaO} + \underset{\text{silica}}{SiO_2} \longrightarrow \underset{\text{slag}}{CaSiO_3}$

Sol 6: (A) Duralumin an alloy of aluminium is used in aircraft industry

Sol 7: (C) Bauxite ore impurities:- $\underset{\text{Acidic}}{SiO_2} + \underset{\text{impurities}}{Fe_2O_3}$

Sol 8: (A) Si is a semi-conductor.

Sol 9: (A)
$$\begin{tikzcd}
Ag + 2CN^- \arrow[r] & Ag(CN)_2^- \arrow[d, "Zn,\ 2CN^-"] \\
& Ag + [Zn(CN)_4]^{2-}
\end{tikzcd}$$

Sol 10: (D) Flux + Gangue $\rightarrow$ slag.

Sol 11: (A) Zone refining:- Purification is done at microscopic level because we need ultra-purified element to use in semi-conductors. Zone refining is based on fractional crystallisation.

Sol 12: (D) None of this elements can be reduced by Al but other example are Cr, Mn, Ti, etc.

Sol 13: (A) Anode mud are the elements which get deposited in the bottom of anode Eg. Ag, Au, Pt.

Sol 14: (A) Poling:- Molten metal is stirred with green anode poles which releases hydrocarbon (gas) which reduces the oxide e.g. Cu

$Cu_2O + CO \rightarrow 2Cu + CO_2\ ;\ Cu_2O + H_2 \rightarrow 2Cu + H_2O$

Sol 15: (C) SiO_2 is an acidic flux $\underset{\text{Acidic}}{SiO_2} + \underset{\text{Basic}}{CaO} \longrightarrow CaSiO_3$

Sol 16: (C) Zone refining is a method to obtain ultra pure metal.

Sol 17: (A) Mac Arthur process is basically cyanide process.

Sol 18: (C) Electroplating: To deposit a specific metal on some other to protect the inner ore is done by electrolysis.

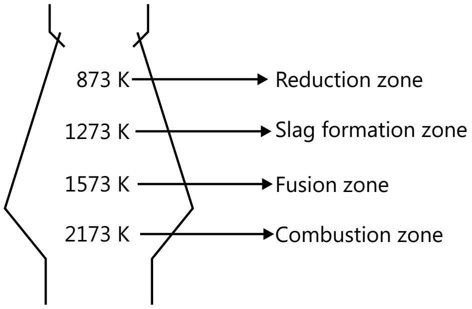
Electrorefining: Electrochemical series decide which metal to be deposited first on anode and using it, we can remove the impurities by electrolysis.

Sol 19: (B) Calcination: Ore is heated at high temperature in the absence of air.

E.g. Applied for carbonate and hydrated ores.

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

Sol 20: (B)



Sol 21: (B) Mg and Al's aqueous solution on electrolysing gives hydrogen at anode.

∴ Molten mixture is used.

Sol 22: (A) Van-Arkel method:- Metal is converted into a volatile stable compound (e.g., Iodine) and impurities are not affected during compound formation

E.g. Zr, Ti

$Ti + 2I_2 \rightarrow TiI_4\ (g)$

$Ti\ I_4(g) \xrightarrow{1700K} Ti_{(S)} + 2I_{2(g)}$

Sol 23: (A) In the froth floatation process for the purification of ores, the ore particles float because they are light.

Sol 24: (C) Van arkle method is used.

Sol 25: (B) Calcination is the process of heating the ore in absence of air.

Sol 26: (B) Highly electropositive metal can not be reduced because it requires high temperature at which carbide formation occurs.

Sol 27: (A) Cyanide process is used for obtaining Cr.

Previous Years' Questions

Sol 1: (D) Fluorspar (CaF_2), Cryolite (Na_3AlF_6), Feldspar ($KAlSi_3O_8$), Mica ($K_2O.3Al_2O_3.6SiO_2.2H_2O$).

Sol 2: (D) Pig iron → It is the most impure form of iron and contains highest proportion of carbon (2.5 – 4%)

Malachite → $Cu(OH)_2.CuCO_3$

Zinc blende → ZnS

Bauxite → $Al_2O_3.2H_2O$

Sol 3: (D) Malachite ($Cu(OH)_2.CuCO_3$).

Sol 4: (B) Cuprite (Cu_2O) and Argentite (Ag_2S).

Sol 5: (C) Among cuprite [Cu_2O], Chalcocite [Cu_2S], Chalcopyrite [$CuFeS_2$] & Malachite [$Cu(OH)_2.CuCO_3$].

Sol 6: (A) Au is recovered from the solution by the addition of electropositive metal.

$2NaAu(Cu)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2Au\uparrow$

Soluble complex

Sol 7: (B) Both assertion and reason are true and reason is the correct explanation of assertion.

Sol 8: (B) Both assertion and reason are true but reason is not the correct explanation of assertion. Non-fusible mass present in ore in mixing with suitable flux are fused which are then reduced by coke to give free metal.

Sol 9: (D) Leaching is a process of concentration.

Sol 10: (C) Assertion is true but reason is false. Collectors absorb themselves on polar groups to grains of ores and thus derive them on the surface to pass on into the froth.

Sol 11: (A) Metal sulphides are thermodynamically more stable than CS_2

Sol 12: **(D)** Van Arkel method

$$Ti(s) + 2I_2(g) \xrightarrow{523K} TiI_4(g)$$

$$TiI_4(g) \xrightarrow{1700K} Ti(s) + 2I_2(g)$$

Sol 13: (D) 13 In the context of the Hall-Heroult process for the extraction of Al, Na_3AlF_6 serves as the electrolyte

Sol 14: (B) Galena = Pbs

For sulphur ores froth floatation is carried out.

Sol 15: (C) Galvanization is applying a coating of Zn.

JEE Advanced/Boards

Exercise 1

Sol 1: Goldschmidt thermite process:- Reduction by powdered aluminium. This process is employed in cases where metals have very high m.pt and are to be extracted from their oxides.

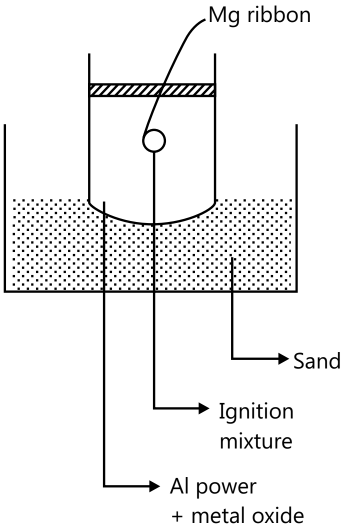
Process:-

$Mg + BaO_2 \rightarrow BaO + MgO + Heat \rightarrow$(in large amount)

Ignition mixture

$Cr_2O_3 + Al \xrightarrow{\Delta} 2Cr(\ell) + Al_2O_3 + Heat$

E.g. Reduction of Cr, Ti, W, Mn etc.



Sol 2: $Al_2O_3 + C \rightarrow 2Al + CO_2$

ΔG of this reaction is negative at very high temperature, so there are 2 reasons that it is not useful:-

(i) Such high temperature is difficult to achieve in furnace for very long time and at such temperature, Al_2O_3 will also be in vapour phase.

(ii) At high temperature, C instead of reducing forms carbide Al_4C_3 with aluminium.

Sol 3: Redox reaction depends upon standard reduction potential of that metals.

$E^o_{Ag^+/Ag} - E^o_{Cu^{2+}/Cu} > 0$ and to fease the reaction, E° should be positive of that whole reaction.

$\therefore\ Cu + 2Ag^+ \rightarrow 2Ag + Cu^{2+}$

Oxidation half:- $Cu \rightarrow Cu^{2+} + 2e^-$; $E_1 = -\ E^o_{Cu^{2+}/Cu}$

Reduction half:- $Ag^+ + e^- \rightarrow Ag$;$E_2 = E^o_{Ag^+/Ag}$

$$E^o_{Reaction} = 2E^o_{Ag^+/Ag} - E^o_{Cu^{2+}/Cu} > 0$$

Sol 4:

$$\text{Sulphide} \xrightarrow[\text{Roasting}]{} \text{Oxide}$$

$$\begin{tikzcd}
\text{Oxide} \arrow[r, "\text{Carbon Reduction}"'] & \text{Impure metal} \arrow[d, "\text{Electrolysis (Purification)}"] \\
& \text{Pure metal}
\end{tikzcd}$$

E.g. $FeS \xrightarrow[\Delta]{O_2} FeO \xrightarrow{C+CO} \underset{(\text{inpure})}{Fe} \longrightarrow \underset{(\text{pure})}{Fe}$

Sol 5: (a)

$$\begin{tikzcd}
PbS + \frac{3}{2}O_2 \arrow[r] \arrow[dr] & PbO + SO_2 \\
& Pb_3O_4 + SO_2
\end{tikzcd}$$

(b) $Cu_2O + C \rightarrow 2Cu + CO$

(c) $Ag^+_{(aq.)} + e^- \longrightarrow Ag_{(s)}$

Sol 6: $E^o_{(OP)}$ of Zn is more positive than E^o_{OP} of Cu and this Zn is more powerful reductant than Cu and thus, Zn can easily replace Ag from $[Ag(CN)_2^-]$

$Zn + [Ag(CN)_2^-] \longrightarrow Ag + [Zn(CN)_4]^{2-}$ E_1, K_1

$Cu + [Ag(CN)_2]^- \longrightarrow Ag + [Cu(CN)_4]^{2-}$ E_2, K_2

$K_1 >> K_2$ because $|E_1| > |E_2|$

Furthermore, Zn being cheaper in comparison to Cu.

Sol 7: Instead of molten NaCl, if we use aqueous solution of NaCl, then, at cathode, Na^+ ions are not discharged at cathode on the contrary, H^+ ions get discharged to form H_2.

$H^+ + e^- \rightarrow \frac{1}{2}H_2 \uparrow$

At anode, $Cl_2\uparrow$ will form irrespective of solvent.

In molten NaCl, there is no competition for Na^+ to get discharged at cathode.

$Na^+_{(aq.)} + e^- \longrightarrow Na_{(s)}$

Sol 8: The members of group 1 i.e. alkali metals have low ionization potential value and thus possess high electropositive character as well as high oxidation potential which enables then to get easily oxidised so that's why they are strong reducing agent but they are not widely used because they react violently with water

$Na + H_2O \rightarrow NaOH + H_2\uparrow$

Sol 9: In blast furnace, lime stone, $CaCO_3$ is useful in fusion zone, where at 800°C – 1200°C, $CaCO_3$ gets dissociated in CaO + CO_2 and it acts as flux, which reacts with acidic gangue SiO_2 to form slag.

$CaCO_3 \rightarrow CaO + CO_2$

$CaO + SiO_2 \rightarrow CaSiO_3$ (slag)

Sol 10: In blast furnace, temperature differs widely from top to bottom.

So, in different temperature range different compound behaves as a reducing agent.

At 300 – 800°C,

CO is better reducing agent than C

$3Fe_2O_3 + C \rightarrow 2Fe_3O_4 + CO$

$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$

$FeO + CO \rightarrow Fe + CO_2$

For this, in zone of combustion.

$C + O_2 \rightarrow CO_2$

$CO_2 + C \rightarrow 2CO$

Sol 11: (i) $CdCO_3 \xrightarrow{\Delta} CdO + CO_2$

Thermal decomposition

(ii) $MgO \xrightarrow{\Delta}$ No reaction

(iii) $SnO_2 + CO \xrightarrow[\text{Reduction}]{\Delta} Sn + 2CO_2$

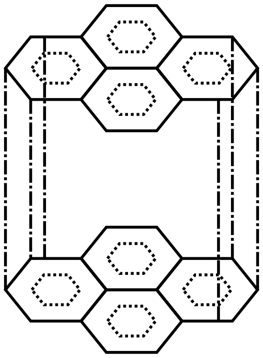
(iv) $CdSO_4(aq) \xrightarrow[\text{electrolysis}]{} \underbrace{H_2SO_4 + O_2}_{\text{at anode}} + \underbrace{Cd}_{\text{at cathode}}$

(v) $2HgO \xrightarrow{\Delta} Hg + O_2$

Thermal decomposition

(vi) $MgO + Zn \xrightarrow{\Delta}$ NO reaction

Sol 12: Graphite and diamond, both are isomers but their physical properties differ widely.



Graphite conducts electricity because there exist free electrons between two sheets of graphite. On the other hand, diamond is a bad conductor because it does not have free electrons and during electrolysis, it is important for anode to conduct electricity and complete the circuit.

Sol 13: (i) $$2\underset{\substack{\downarrow\\ \text{Reducing}\\ \text{agent}}}{Cu_2\overset{-2}{S}} + 3\underset{\substack{\downarrow\\ \text{Oxidising}\\ \text{agent}}}{O_2}(g) \longrightarrow 2Cu_2O(\ell) + 2\overset{+4}{S}O_2(g)$$

(ii) $$2\underset{\substack{\downarrow\\ \text{Oxidising}\\ \text{agent}}}{\overset{+1}{Cu_2}O_{(\ell)}} + \underset{\substack{\downarrow\\ \text{Reducing}\\ \text{agent}}}{Cu_2\overset{-2}{S}_{(g)}} \longrightarrow 6Cu_{(\ell)} + \overset{+4}{S}O_{2(g)}$$

Sol 14: Calcination:-

$MgCO_3.CaCO_3 \xrightarrow[\Delta]{\text{Calcination}} MgO + CaO + 2CO_2\uparrow$

Dolomite

$MgCl_2 + CaCO_3\downarrow \xrightarrow{CO_2} MgCl_2 + CaCl_2$

Now, electrolysis of $MgCl_2$ gives Mg

$Mg^{2+} + 2e^- \rightarrow Mg$ Anode reaction

$2Cl^- \rightarrow Cl_2\uparrow + 2e^-$ Cathode reaction

Sol 15: Calicnation

Sol 16:
$$\begin{tikzcd}
Mg \arrow[r, "HNO_3"] \arrow[d, "Cl_3"] & Mg(NO_3)_2 \arrow[r, "\Delta"] & MgO \\
MgCl_2 \arrow[r, "KHO"] & Mg(OH)_2 \arrow[ur, "-H_2O"'] &
\end{tikzcd}$$

Sol 17:
$$\begin{tikzcd}
\substack{(A)\\ \text{Black}\\ \text{mineral}} \arrow[r, "\text{Dil.}", "NaCN+O_2"'] & (B) + (C) \arrow[d, "Zn"] & & \\
& \substack{(D)\downarrow\\ \text{Metal}} \arrow[r, "\text{Dil.}", "HNO_3"'] & {} \arrow[r, "\text{Dil.}", "HCl"'] & \substack{(E)\downarrow\\ \text{White ppt}} \arrow[d, "aq.\ NH_3"] \arrow[ll, bend left, "\text{fusion with}", "Na_2CO_3"'] \\
& & & \substack{(F)\\ \text{Colourless}}
\end{tikzcd}$$

(A) →(D) leaching process

∴ these are the compounds of Ag

∴ (A) Ag_2S

(B) $[Ag(CN)_2]^- Na^+$

(C) Na_2S

(D) Ag

(E) AgCl

(F) $[Ag(NH_3)_2]Cl$

Sol 18: (i) Aluminium:- Gold Schimdt process:-

$Al + Mn_3O_4 \rightarrow Mn + Al_2O_3$

(ii) Fe is also used

$Fe + HgS \rightarrow Hg + FeS$

Sol 19: Aluminium metal is frequently used as a reducing agent for the extraction of metal such as Cr and Mn from their respective oxides because aluminium is more electropositive than Cr/Mn. The process of reduction is known as Aluminothermite process (Gold shmidt process)

$Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr; \Delta H = -ve$

$3Mn_3O_4 + 8Al \rightarrow 4Al_2O_3 + 9Mn; \Delta H = -ve$

Sol 20: During the extraction of iron (Fe) from haematite (Fe_2O_3) it contains some impurities such as P_4O_{10} or SO_2, which are acidic in nature. So, to remove this gangue as slag basic lining of lime (CaO) or magnesia (MgO) is used

$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$

$MgO + SO_2 \rightarrow MgSO_3$

Sol 21: Lead is extracted from its mineral galena (PbS).
(i) It is firstly concentrated by froth floatation process.

(ii) Roasting in reverbatory furnace

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

$PbS + 2O_2 \rightarrow PbSO_4$

The idea of Cu ores come from calcined black solid and ppt. after reaction with KI.

Sol 22: A_1 will be malachite i.e., $CuCO_3.Cu(OH)_2$

A_2 will be copper glance i.e., Cu_2S The confirmatory reaction are

(a) For malachite

(i) $CuCO_3.Cu(OH)_2 \xrightarrow{\text{Calcinations}} \underset{\text{Black solid}}{2CuO} + CO_2\uparrow H_2O$

(ii) $CuCO_3.Cu(OH)_2 \xrightarrow{HCl} CuCl_2 + CO_2\uparrow + H_2O$

$CuCl_2 \xrightarrow{KI} \underset{\text{ppt(D)}}{Cu_2I_2}\downarrow + KCl + I_2$

(b) For copper glance

$Cu_2S \xrightarrow[O_2]{\text{Roasting}} Cu_2O + SO_2$

$Cu_2S + Cu_2O \rightarrow Cu + SO_2$

SO_2 is the gas which gives green colour with acidified $K_2Cr_2O_7$ as

$3SO_2 + \underset{\text{orange}}{K_2Cr_2O_7} + H_2SO_4 \rightarrow K_2SO_4 + \underset{\text{green}}{Cr_2(SO_4)_3} + 4H_2O$

Now reduction of AgCl,

(i) $2AgCl + Na_2CO_3 \rightarrow Ag_2CO_3 + 2NaCl$

$Ag_2CO_3 \xrightarrow{\Delta} 2Ag\downarrow + CO_2\uparrow + \frac{1}{2}O_2\uparrow$

(ii) Cyanide process with AgCl.

Sol 23: Cyanide process is a type of leaching process which a chemical reaction is used to extract metal from ore. In this process, crushed rock containing traces of gold is treated with 0.1 – 0.2% solution of NaCN and aerated O_2 (air) oxidized free metal to Au^+ which complexes with CN^-

$4Au + 8CN^- + 2H_2O + O_2 \rightarrow 4[Au(CN)_2]^- + 4OH^-$

The pure metal is displaced from solution by an active metal

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

Sol 24: Silver coin contains Ag, Au and Cu also. So, to extract silver, it should undergo various processes.

So, individually every metal impurities can be removed.

Silver coin

$$\begin{tikzcd}(Cu+Ag+Au) \arrow[r, "\text{Conc.}", "HNO_3"'] & (Cu^{2+}+Ag^{+}+Au^{3+})NO_3^- \arrow[d, "NaCl"] \\ & AgCl\downarrow \text{ (white ppt.)} \\ & AuCl_3\downarrow\end{tikzcd}$$

Now, since Ag, Au, both are noble metals, they possess similar chemical properties.

But due to difference in physical properties, Au can be removed by fractional distillation.

After oxidising minerals,

The roasted mineral is smelted into lead

$2PbO + PbS \rightarrow 3Pb + SO_2\uparrow$

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

→ Self reduction

PbO (litharge) oxidation state → +2

Purification is done by cupellation, polling and most importantly, electrolysis.

Sol 25: In the purification of bauxite, due to impurities such as silica (SiO_2) and other silicates, Bauxite is converted into alumina by Bayer's process. During this process, CO_2 is passed through it. Aqueous solution of CO_2 is acidic. Hence, CO_2 when passed into $[Al(OH)_4]^-$ solution makes it acidic. Hence, $Al(OH)_3$ is precipitated.

$CO_2 + H_2O \rightarrow H_3O^+ + HCO_3^-$

$[Al(OH)_4]^- + H_3O^+ \rightarrow Al(OH)_3\downarrow + 2H_2O$

Sol 26: Haematite ore majorily contain [Fe_2O_3/FeO)] but also contains silica (SiO_2). So, during roasting in blast furnance, carbon reduction is done along with lime. So, silica can be removed as slag.

$$CaO + SiO_2 \rightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

Simultaneously, Fe also gets reduced

$$C + O_2 \rightarrow CO_2\ ;\ CO_2 + C \rightarrow 2CO$$

$$3CO + Fe_2O_3 \rightarrow \underset{\text{(Steel)}}{2Fe} + 3CO_2$$

So difference in densities make them easily separable at the bottom of furnace and this calcium silicate because of its hard nature is widely used in cement industry.

Sol 27: (ii) Au and Ag both are generally chemically inert but they differ during their reaction with HCl + HNO_3

$$Au + 4HCl + 3HNO_3 \rightarrow \underset{\text{soluble}}{HAuCl_4} + 3NO_2 + 3H_2O$$

$$Ag + HCl + HNO_3 \rightarrow \underset{\text{insoluble}}{AgCl} + NO_2 + H_2O$$

So, in Aquaregia, Au forms a soluble complex compound, $HAuCl_4$ but Ag forms a precipitate which do not dissolve.

Exercise 2

Single Correct Choice Type

Sol 1: (A) Sulphides have fundamental property based on the different wetting property of the ore and gangue with oil and water.

Sol 2: (C) Van Arkel

This is vapour phase refining process by forming volatile complex compound.

Sol 3: (B) Cryolite-Na_3AlF_6 is used during the electrolysis of alumina to increase the electrical conductivity and decrease the melting point of alumina (Al_2O_3).

Sol 4: (D) Cassiterite is an ore of Sn.

Sol 5: (C) Discharging of element at cathode and anode depends upon various factors mainly on

(i) standard reduction potential

(ii) Nature of electrode

Using platinum and graphite electrode, we get different products so it is entirely experimental.

Sol 6: (D) Metal makes lattices in which nucleus is arranged in specific array of position but valence electrons are free to move into whole lattice this property gives lustre to a metal.

Sol 7: (C) For Cr, instead of electrolysis, we can use more cheaper process, aluminothermite, because electrolysis gives high yield but it's a very costly process.

Sol 8: (D) Flux's basic use is to combine with gangues/matrix or other impurities and then remove them by slag formation.

E.g. Formation of $CaSiO_3$ in extraction of iron (Fe).

Sol 9: (B) In extraction of Cu, FeO is a gangue to remove it, SiO_2 (silica) is added and it forms

Thomas slag

$$\underset{\text{Gangue}}{FeO} + \underset{\text{Flux}}{SiO_2} \longrightarrow \underset{\text{Thomas slag}}{FeSiO_3}$$

Sol 10 (D) In blast furnace

$$\begin{tikzcd} FeO/Fe_2O_3 \arrow[r] \arrow[d, "\text{Roasting}"] & Fe_3O_4 \arrow[r, "\text{(Carbon Reduction)}"'] & Fe \\ Fe_3O_4 & & \end{tikzcd}$$

Sol 11: (C) Al_2O_3 is used in molten state because aqueous solution will give H_2 at cathode and Na_3AlF_6 is used to increase the conductivity of Al_2O_3 and to decrease the melting point of mixture.

Sol 12: (C) Calcination is used in metallurgy to remove CO_2 and H_2S

Sol 13: (C) The metallic luster exhibited by sodium is explained by the presence of Free protons

Sol 14: (B) Stainless steel:- Fe + Cr + Ni

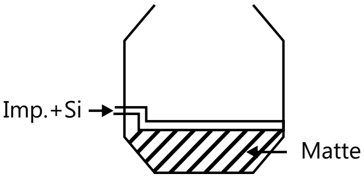
Sol 15: (B) Leaching:-

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

$$2NaAlO_2 + 4H_2O \rightarrow 2Al(OH)_3 + 2NaOH$$

$$2Al(OH)_3 \xrightarrow[1200]{\Delta} Al_2O_3 + 3H_2O$$

Sol 16: (D) Bessemerisation of Cu



Bessemer converter

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

$2CuS + SiO_2 \rightarrow FeSiO_3$ (slag)

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

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

Sol 17: (D) Generally they are more electronegative than metals.

Sol 18: (B) In the froth floatation process for the purification of ores, the ore particles float because their surface is hydrophobic i.e. not easily wetted by water

Sol 19: (C) SiO_2 Acidic flux.

Sol 20: (B) Flux + Gangue $\rightarrow$ slag

Sol 21: (B) E.g. Na, K, Ca, Al, etc.

Group I, II metals.

Sol 22: (D) The role of calcination in metallurgical operations is to remove moisture, to decompose carbonate,to drive off organic matter.

Comprehension type

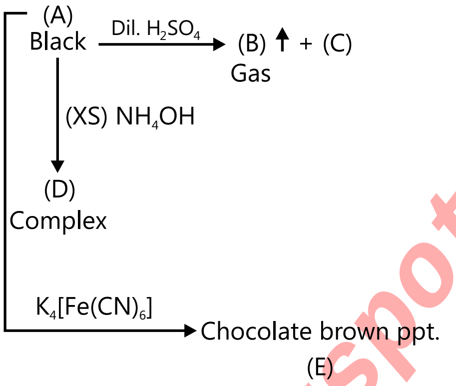
Sol 23: (A) CuS

Sol 24: (A) H_2S

Sol 25: (B) $CuSO_4$

Sol 26: (C) $[Cu(NH_3)_4](NO_3)_2$

Sol 27: (A)



Chocolate brown ppt. form with Cu metal

(E) is $Cu_2\,[Fe(CN)_6]$

Assertion Reasoning Type

Sol 28: (D) Calamine ($ZnCO_3$)

(R) Boric acid is monobasic acid

$B(OH)_3 + H_2O \rightarrow [B(OH)_4]^- + H^+$

Sol 29: (D) Based on experiments.

Sol 30: (C) Pb^{4+} is easily reduced to Pb^{2+} because of inert pair effect.

(R) Pb^{2+} is diamagnetic.

Sol 31: (C) Diamond is hardest natural occurring substance because of its strong 4 valence lattice.

(R) Graphite is more stable because of electrical conductivity and availability of free electrons.

Sol 32: (C) Mond's Process:-

$$Ni + 4CO \xrightarrow{\Delta} \underset{\substack{\text{volatile stable} \\ \text{complex compound}}}{Ni(CO)_4} \xrightarrow{\Delta} Ni\downarrow + 4CO$$

Previous Years' Questions

Sol 1: (C) Chalcopyrite contain both iron and copper.

Sol 2: (B) Zinc blende contain ZnS which is first roasted partially and then subjected to reduction with carbon

$ZnS + O_2 \rightarrow ZnO + SO_2$ Roasting

$ZnO + C \xrightarrow{\Delta} Zn + CO\uparrow$ Carbon reduction

Sol 3: (B) A water soluble complex with silver and dilute aqueous solution of NaCN is $Na[Ag(CN)_2]$. In the cyanide process, the native silver is crushed and treated with aqueous NaCN solution and aerated.

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

Sol 4: (D) Haematite is Fe_2O_3, in which oxidation number of iron is III. Magnetite is Fe_3O_4 which is infact a mixed oxide ($FeO.Fe_2O_3$), hence, iron is present in both II and III oxidation state.

Sol 5: (A, C) Addition of manganese to iron improve hardness of steel as well as remove oxygen and sulphur.

Sol 6: (A, D) The important ore of tin is cassiterite (SnO_2). Tin is extracted from cassiterite ore by carbon reduction method in a blast furnace.

$SnO_2 + 2C \rightarrow Sn + 2CO$

The product often contain traces of iron which is remov-ed by blowing air through the melt to oxidize to FeO which then floats to the surface.

$2Fe + O_2 \rightarrow 2FeO$

Sol 7: (B) $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2\uparrow$

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

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2\uparrow$

Sol 8: (D) $FeO + SiO_2 \rightarrow FeSiO_3$ (slag)

Sol 9: (C) $Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$

In Cu_2S, sulphur is S^{2-} and in SO_2, sulphur is in +4 state. Hence, S^{2-} is acting as a reducing agent.

Sol 10: (A) A →s; B → p; C→ q; D → q, r; E→ t

Silver is extracted by amalgamation process

$Ag + Hg \rightarrow Ag(Hg) \xrightarrow{\text{Distillation}} Ag(s) + Hg(g)\uparrow$

(B) Calcium is extracted by electrolysis of fused $CaCl_2$.

(C) Zinc is extracted by carbon reduction method

$ZnO + C \rightarrow Zn + CO$

(D) Iron is extracted by both, carbon reduction method and CO reduction methods

$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

(E) Copper is extracted by self-reduction methods

$Cu_2S + O_2 \rightarrow Cu_2O + SO_2$

$Cu_2O + Cu_2S \rightarrow Cu + SO_2$

Sol 11: $4NaCN + Ag_2S \rightarrow 2Na[Ag(CN)_2] + Na_2S$

$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag$

Sol 12: The common photographic film is coated with AgBr and during developing of photographic film, the unreacted AgBr is removed by $Na_2S_2O_3$ as

$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

Sol 13: $2AgBr + C_6H_4(OH)_2$ (Hydroquinone) →

$2Ag + 2HBr + C_6H_4O_2$

(developer) quinone

$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

(b) $Na_2S_2O_3 + 2H^+ \rightarrow 2Na^+ + H_2SO_3 + S\downarrow$

Colloidal

Sulphur

Sol 14: Four, the complex has formula $[Cu(H_2O)_4]\,SO_4.H_2O$

Sol 15: In crystalline state, $AlCl_3$ has rock-salt like structure with coordination number of Al = 6.

Sol 16: (B) Extraction of zinc from zinc blende is achieved by

Sol 17: A → p; B → q; C → p, r; D → p, s

PbS → PbO - Roasting

$CaCO_3 \rightarrow CaO$ - Calcination

ZnS → Zn - Roasting, Carbon reduction

$Cu_2S \rightarrow Cu$ - Roasting, Self reduction

Sol 18: (A)

Sulfinde ore of Ag → Argentite (Ag_2S)

Pb → Galena (PbS)

Cu → Copper glance (Cu_2S)

Hence (A) is correct.

Sol 19 : (C, D) Fe_2O_3 and SnO_2 undergoes C reduction. Hence (C) and (D) are correct.

Sol 20: $A \rightarrow p, q, s; B \rightarrow t; C \rightarrow q, r; D \rightarrow r$

Siderite	$FeCO_3$
Malachite	$CuCO_3.Cu(OH)_2$
Bauxite	$AlO_x(OH)_{3-2x};\ 0 < x < 1$
Calamine	$ZnCO_3$
Argentite	Ag_2S

Sol 21: (A, B, C) Extraction of copper from copper pyrite ($CuFeS_2$) involve crushing following by concentration of the ore by froth-flotation, removal of iron as slag, self-reduction step to produce 'blister copper' following evolution of SO_2

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