

CHEMISTRY
(Skill Development Course)
(1st Semester)
Course No.: CHM-SEC-101
Separation and Purification Techniques

Unit-4: Metallurgical extraction

What is Metallurgy?

Metallurgy is a domain of materials science and engineering that studies the physical and chemical behavior of metallic elements, their inter-metallic compounds, and their mixtures, known as alloys.

Mineral :

The naturally occurring chemical substances in form of which the metals occur in the earth crust along with impurities are called minerals. Ex. Mineral of Aluminium – Bauxite, Cryolite, Clay, Feldspar, Mica.

Ore :

The mineral from which metal can be extracted easily & economically.

Ex. Fe – Fe₂O₃ (Haematite), Fe₃O₄ (Magnetite), FeSO₄ (Iron pyrite), FeCO₃ (Siderite)

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, SiO₂ etc.

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



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.

Different metals and their ores:

Metal	Ores	Composition
Aluminium	<ul style="list-style-type: none"> Bauxite Cryolite Kaolinite (a form of clay) 	$AlO_x(OH)_{3-2x}$, (where $0 < x < 1$) AlF_6Na_3 $[Al_2(OH)_4Si_2O_5]$
Iron	<ul style="list-style-type: none"> Haematite Magnetite Siderite Iron pyrites 	Fe_2O_3 Fe_3O_4 $FeCO_3$ FeS_2
Copper	<ul style="list-style-type: none"> Copper pyrites Malachite Cuprite Copper glance 	$CuFeS_2$ $CuCO_3 \cdot Cu(OH)_2$ Cu_2O Cu_2S
Zinc	<ul style="list-style-type: none"> Zinc blende or Sphalerite Calamine Zincite 	ZnS $ZnCO_3$ ZnO
Lead	<ul style="list-style-type: none"> Cerussite Galena Anglesite 	$PbCO_3$ PbS $PbSO_4$
Mercury	<ul style="list-style-type: none"> Cinnabar 	HgS
Silver	<ul style="list-style-type: none"> Silver glance/Argentite Horn silver 	Ag_2S $AgCl$
Potassium	<ul style="list-style-type: none"> Carnallite Indian nitre 	$KClMgCl_2 \cdot 6H_2O$ KNO_3
Fluorine	<ul style="list-style-type: none"> Cryolite Fluorspar 	Na_3AlF_6 CaF_2

Chemical metallurgy: The scientific approach to metallurgy involves chemical and physical metallurgy. Chemical metallurgy deals with the domain of the reduction and oxidation of metals. It is the science of obtaining metals from their ores, and of the consideration of the reactions of metals derived through a chemical approach. It involves the reactivity of metals, which includes the science of electrochemical (electrochemistry deals with the interaction between electrical energy and chemical change), and corrosive behaviors within metals.

Physical metallurgy: Physical metallurgy involves the mechanical, magnetic, electrical, and thermal properties of metals evaluated through the discipline of solid state physics (the study of rigid matter, or solids, by methods such as quantum mechanics, crystallography, electromagnetism, and metallurgy.) Physical metallurgy is a

systematic way of evaluating the physical properties of metals and alloys, and is basically the fundamental applications of the theory of phase transformation within metallic and alloyed substances.

Extractive metallurgy: Extractive metallurgy is a branch of metallurgical engineering where the processes and methods of the extraction of metals from their natural mineral deposits are studied. The field of ferrous and non-ferrous extractive metallurgy have specialties that are generically grouped into the categories, which are based on the process adopted to extract the metal:

- Mineral processing
- Hydrometallurgy
- Pyrometallurgy
- Electrometallurgy

Several processes can be used for the extraction of a given metal, depending on where that metal occurs naturally, and its chemical requirements.

Hydrometallurgy: This is concerned with extraction processes involving aqueous solutions used to extract the desired metal or metals from the raw ore.

Leaching process: The first step in the hydrometallurgical process is leaching, which involves dissolution of the valuable metals into the aqueous solution and/or a suitable solvent.

Purification and concentrating processes: After the solution is separated from the ore solids, the extract is often subjected to various processes of purification and concentration before the valuable metal is recovered either in its metallic state or as a chemical compound. This may include precipitation, distillation, adsorption, and solvent extraction. Final recovery processes The final recovery step may involve precipitation, cementation, or electrometallurgical processing.

Pyrometallurgy: Pyrometallurgy deals with the methods of extraction of metals from their ores and their refining and is based on physical and chemical changes occurring at high temperatures. There are 4 processes that are included in pyrometallurgical treatment. i.e.

1. Calcination
2. Roasting
3. Smelting
4. Refining

CALCINATION: Calcination is the thermal treatment of an ore that brings about its decomposition and elimination of volatile products i.e. carbon dioxide and water.

ROASTING: Roasting of an ore or a concentrate is a chemical process in which chemical conversion of ore is taken place by employing oxygen or other element. This process is used to remove Sulphur or other elements such as arsenic and tellurium in the form of a volatile oxide from an ore.

SMELTING: Heating process of production of metal or matte.

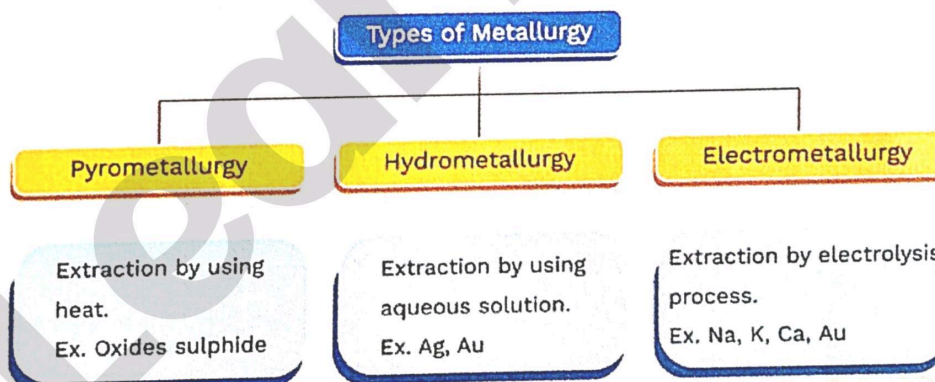
Electrometallurgy: This involves metallurgical processes that take place in some form of electrolytic cell. The most common types of electrometallurgical processes are:

Electrowinning - is an electrolysis process used to recover metals in aqueous solution, usually as the result of an ore having undergone one or more hydrometallurgical processes. The metal of interest is plated onto the cathode, while the anode is an inert electrical conductor.

Electro-refining - is used to dissolve an impure metallic anode (typically from a smelting process) and produce a high purity cathode.

Fused salt electrolysis process - is a process where the valuable metal has been dissolved into a molten salt (which acts as the electrolyte, with the valuable metal collecting on the cathode of the cell.) The fused salt electrolysis process is conducted at temperatures sufficient to keep both the electrolyte (molten salt) and the metal from being produced in the molten state.

Processing of ores: An ore is an occurrence of rock or sediment that contains sufficient minerals with economically important elements, typically metals, that can be economically extracted from the deposit. The ores are extracted from the earth through mining; they are then refined (often through the process of smelting) to extract the valuable element, or elements.



Extraction and Purification Process of Iron from hematite:

The extraction of iron from its ore is the third and the penultimate process in metallurgy, which is the process of separating metals from their ores. The common ores of iron are iron oxides. These oxides can be reduced to iron by heating them with carbon in the form of coke. Heating coal in the absence of air produces coke. Coke is cheap and it provides both the reducing agent and heat source for the reaction. The most commonly used iron ores are Hematite, Fe_2O_3 , and magnetite (Fe_3O_4).

The process of extraction of iron and their separation is followed by three major steps:

1. Concentration of Ore
2. Extraction of Iron from its concentrated ore
3. Purification of Iron

(1) Concentration of Ore

The extraction of iron begins with concentration through calcination which is a process in a limited supply of oxygen applied to ores to bring thermal decomposition. An ore of a metal is an impure source. It consists of many impurities other than metal such as sand, clay, etc. These impurities are known as gangue which is commercially useless so we must separate it from ore. This process is known as the concentration of ores. Concentration removes water and other impurities such as sulphur and carbonates.

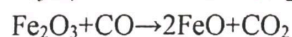
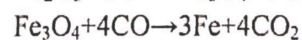
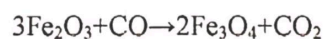
(2) Extraction of Iron from its Concentrated Ore

This concentrated ore is then mixed with limestone and coke which is fed into a blast furnace. The extraction of ore occurs in the blast furnace as follows:

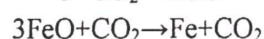
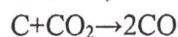
Blast refers to the combustion air being supplied above the atmospheric pressure. The blast furnace reduces the concentrated ore to its liquid chemical state. A blast furnace is used for smelting to produce industrial metals where the concentrated iron ore, coke, and limestone are fed from the top, and a blast of hot air is blown into the bottom. All these ingredients are crushed into small pieces and mixed and then put on a device called hopper which controls the input.

Hot air is blown from the bottom and coke is burned to give temperatures up to about 2200K. Burning coke provides the heat required for this process. At such temperatures, Coke reacts with the oxygen in the hot air to form Carbon Monoxide (CO). The CO and heat then move upwards and meet the raw material running down from the top. The temperature in the upper parts of the Blast Furnace is considerably lower than the 2200K at the bottom. In this part, Haematite Fe_2O_3 and Magnetite (Fe_3O_4) react to give Ferrous Oxide (FeO).

The reactions in the Blast furnace at lower temperatures (500K-800K),



At 900 – 1500 K, In the lower sections of the furnace,



(3) Purification of Iron

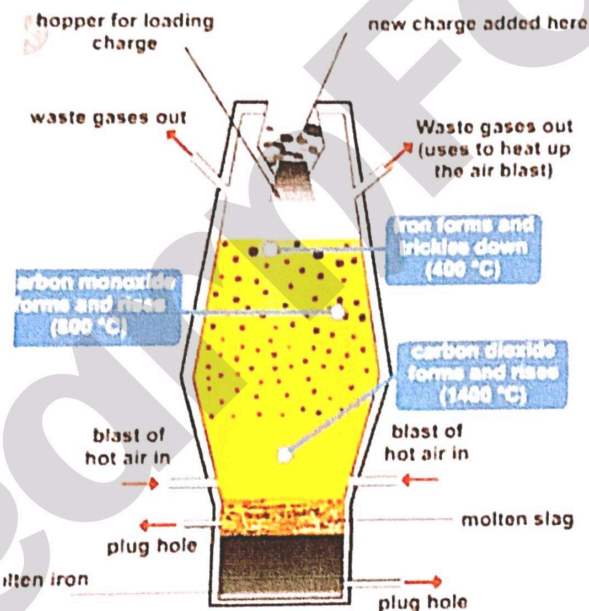
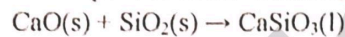
The limestone then decomposes to give CaO which removes the impurities such as silicate of the ore in the form of slag. It can then be easily separated out of molten iron. The iron manufactured in Blast

Furnaces contains about 3 – 4 % of Carbon and small quantities of other impurities such as sulphur, silicon, etc. This is called Pig Iron. It is a hard but brittle metal and the impurities hamper its strength. Carbon plays a very important role in influencing the brittleness and hardness balance in iron. To reduce the carbon content of pig iron, it is melted again with scraps of iron and coke and subjected to the blast of hot air. This kind of iron is known as Cast Iron and has a lower carbon content of about 2 – 3 %. This is even harder than pig iron.

Reactions involved in the purification of metals:

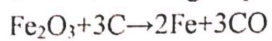


Then the calcium oxide reacts with silica impurities in the hematite, to produce slag.



Malleable Iron

Malleable Iron is the purest form of iron available commercially and is prepared from cast iron by heating cast iron in a furnace lined with Haematite (Fe_2O_3). The Haematite then reacts with Carbon in the cast iron to give pure iron and carbon monoxide gas.



Limestone then creates the slag. Impurities such as S, Si pass into the slag and the slag later can be easily separated to yield pure iron.

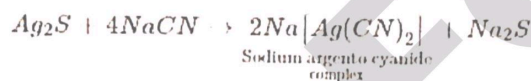
The iron minerals that are used as ores are hematite, magnetite, limonite, and siderite. Hematite is the most important iron ore.

Extraction of iron from its Oxides

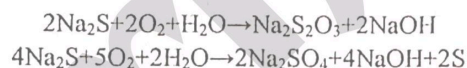
After concentration through calcination/roasting, oxide ores of iron are mixed with limestone and coke and then fed into a Blast furnace from its top. The oxide is reduced to metal here. When the molten pig iron is cooled at once, it is called white cast iron, which contains carbon in the form Fe_3C (cementite) and when the molten pig iron is cooled slowly, the iron is called grey cast iron, which contains carbon in the form of graphite.

Extraction and Purification Process of Ag from argentite:

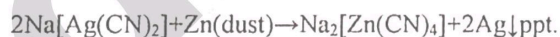
The important ore of silver are Argentite (Ag_2S) and Horn silver ($AgCl$).
Extraction of Silver from ore by cyanide process: In this process the finely powdered ore is concentrated by froth floatation process and then treated with dilute $NaCN$ and a current of air is passed into the solution so that Ag present in the ore is converted into soluble sodium argento cyanide complex.



The current of air passed into the solution oxidises Na_2S formed in the above reaction into $Na_2S_2O_3$, Na_2SO_4 and S and thus enables the above reversible reaction to proceed in forward direction.



Then the solution containing $Na[Ag(CN)_2]$ is



Precipitated Ag is purified by electrolytic method. The cathode is pure silver, anode is block of impure silver and electrolyte is 6% $AgNO_3$ with 1% HNO_3 . On passing current, impurities get deposited at the anode and pure silver at the cathode. Zn and Cu remain in solution while Au settles down as anode mud.

Extraction and Purification Process of Copper from Copper pyrites:

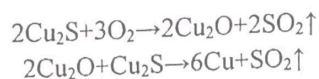
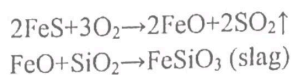
Extraction of copper from copper pyrites involves the following steps:

- (i) Concentration of ore: The ore is crushed and concentrated by froth floatation process.
- (ii) Roasting: The concentrated ore is roasted in excess of air. During the process of roasting, the moisture and volatile impurities are removed. Sulphur, Phosphorus, arsenic and antimony are removed as oxides, copper pyrite is partly converted into sulphide of copper and iron.



(iii) Smelting: The roasted ore is mixed with powdered coke and sand and is heated in a blast furnace to obtain matte (CuS+FeS) and slag. The slag is removed as waste.

(iv) Bessemerisation: The molten matte is transferred to Bessemer converter in order to obtain blister copper. Ferrous sulphide from matte is oxidized to ferrous oxide, which is removed as slag using silica.



(v) Refining: Blister copper contains 98% of pure copper and 2% of impurities and is purified by electrolytic refining. This method is used to get metals of a high degree of purity. For electrolytic refining of copper the following are used:

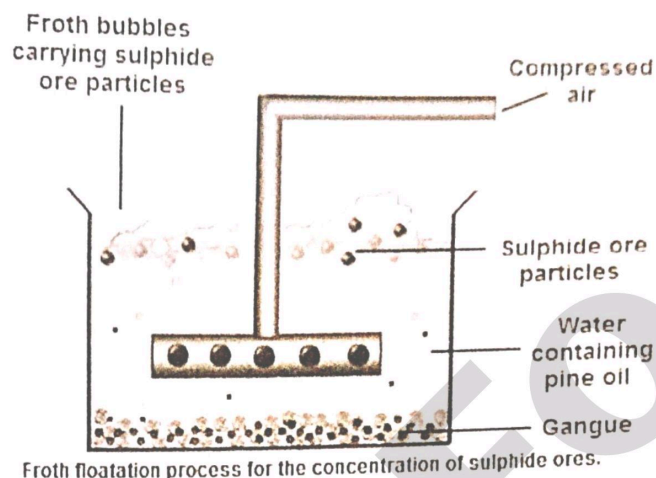
Cathode:	A	thin	plate	of	pure	copper	metal.
Anode:	A	block	of	impure	copper	metal.	

Electrolyte: Copper sulphate solution acidified with sulphuric acid. When electric current is passed through the electrolytic solution, pure copper gets deposited at the cathode and the impurities settle at the bottom of the anode in the form of sludge called anode mud.

Extraction and Purification of Zinc from Zinc Blend:

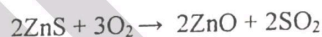
Concentration:

Zinc blende is concentrated by froth floatation process. The pulverized ore is kept in large tank containing water and pine oil. The mixture is agitated by passing compressed air. Ore forms froth and comes to the surface while impurities are left in water.

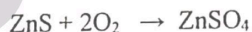


Roasting:

The concentrated ore is heated in excess supply of air above 900°C on the hearth of reverberatory furnace. During roasting, Zinc sulphide is converted to Zinc Oxide.

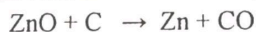


Small amount of ZnS may be oxidized to ZnSO_4 but above 900°C , ZnSO_4 decompose forming Zinc Oxide (ZnO)



Reduction (Smelting):-

ZnO obtained during roasting is mixed with coke and heated strongly where ZnO is reduced to Zn by carbon.



The reduction is done in vertical reflow. In this process roasted ZnO are mixed with coke in the ratio of 2:1 and small briquets are made. These briquets are fed into vertical reflow furnace, from the charging door. The reflow is heated externally by burning produce gas to about 1400°C . The vapour of Zn is fed to condenser where it condenses to give molten zinc called spelter zinc.

Extraction and Purification of Aluminium from Bauxite:

Aluminium is too high in the electrochemical series (reactivity series) to extract it from its ore using carbon reduction. The temperatures needed are too high to be economic. Instead, it is extracted by electrolysis. The ore

is first converted into pure aluminium oxide by the Bayer Process, and this is then electrolysed in solution in molten cryolite - another aluminium compound. The aluminium oxide has too high a melting point to electrolyse on its own.

Aluminium ore

The usual aluminium ore is *bauxite*. Bauxite is essentially an impure aluminium oxide. The major impurities include iron oxides, silicon dioxide and titanium dioxide.

Purifying the aluminium oxide - the Bayer Process

Reaction with sodium hydroxide solution

Crushed bauxite is treated with moderately concentrated sodium hydroxide solution. The concentration, temperature and pressure used depend on the source of the bauxite and exactly what form of aluminium oxide it contains. Temperatures are typically from 140°C to 240°C; pressures can be up to about 35 atmospheres.

High pressures are necessary to keep the water in the sodium hydroxide solution liquid at temperatures above 100°C. The higher the temperature, the higher the pressure needed. With hot concentrated sodium hydroxide solution, aluminium oxide reacts to give a solution of sodium tetrahydroaluminate.



The impurities in the bauxite remain as solids. All of these solids are separated from the sodium tetrahydroaluminate solution by filtration. They form a "red mud" which is just stored in huge lagoons.

Precipitation of aluminium hydroxide

The sodium tetrahydroaluminate solution is cooled, and "seeded" with some previously produced aluminium hydroxide. This provides something for the new aluminium hydroxide to precipitate around.



Formation of pure aluminium oxide

Aluminium oxide (sometimes known as alumina) is made by heating the aluminium hydroxide to a temperature of about 1100 - 1200°C.

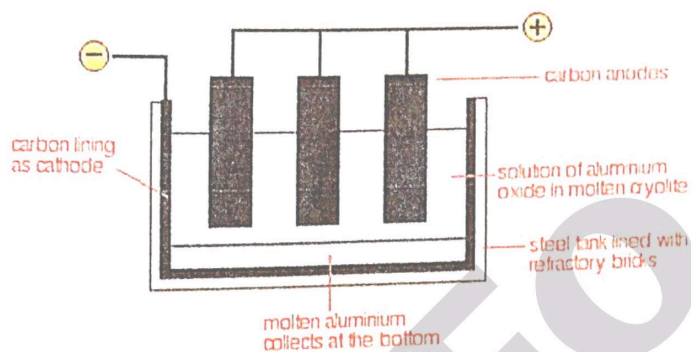


Conversion of the aluminium oxide into aluminium by electrolysis

The aluminium oxide is electrolysed in solution in molten *cryolite*, Na_3AlF_6 . Cryolite is another aluminium ore, but is rare and expensive, and most is now made chemically.

The electrolysis cell

The diagram shows a very simplified version of an electrolysis cell.



Although the carbon lining of the cell is labelled as the cathode, the effective cathode is mainly the molten aluminium that forms on the bottom of the cell.

Molten aluminium is syphoned out of the cell from time to time, and new aluminium oxide added at the top.

The cell operates at a low voltage of about 5 - 6 volts, but at huge currents of 100,000 amps or more. The heating effect of these large currents keeps the cell at a temperature of about 1000°C.

The electrode reactions

These are very complicated - in fact one source I've looked at says that they aren't fully understood. For chemistry purposes at this level, they are always simplified (to the point of being wrong! - see comment below).

This is the simplification:

Aluminium is released at the cathode. Aluminium ions are reduced by gaining 3 electrons.



Oxygen is produced initially at the anode.



However, at the temperature of the cell, the carbon anodes burn in this oxygen to give carbon dioxide and carbon monoxide.