

Metallurgical Extraction

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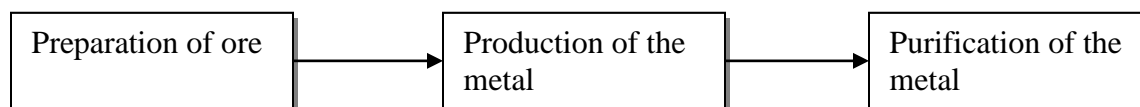
1. Metallurgical extraction

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1. Extraction of Elements and Metallurgy

Metallurgy is the science and technology of separating metals from their ores and of compounds alloys. An alloy is a solid solution either of two or more metals, or of a metal or metals with one or more non-metals. Minerals which are naturally occurring chemical substances in the earth's crust obtainable by mining. Out of many minerals in which a metal may be found, only a few are viable to be used as sources of that metal. Such minerals are known as **ores**. Rarely, an ore contains only a desired substance. It is usually contaminated with earthly or undesired materials known as gangue.

Recovery of a metal from its ores involves three principal steps (three P's)

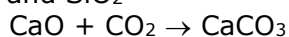


1.1 The Occurrence and Isolation of the Elements

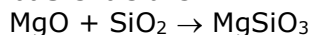
Most metals occur in nature as **minerals**; **silicates** and **aluminates** are the most abundant minerals, but they are difficult to concentrate and reduce and therefore generally unimportant for commercial source of metals. Other minerals are **oxides** as **haematite (Fe₂O₃)** and **rutile (TiO₂)** and **sulphides** as **cinnabar (HgS)** and **galena (PbS)**.

The early transition metals on the left hand side of the d-block generally occur as oxides, and the more electronegative, late transition metals on the right hand side of the d-block occurs as sulphides. Less electronegative (more electropositive) metals can form ionic compounds by losing electrons to oxygen (and thus oxides are possible). More electronegative (less electropositive) metals tend to form covalent sulphide minerals with less electronegative sulphur.

Oxides of the s-block metals are strongly basic hence, form carbonates and silicates with acidic oxides as CO₂ and SiO₂



basic acidic



Basic acidic

Only gold and platinum-group metals (Ru, Os, Rh, Ir, Pd, and Pt) are sufficiently unreactive to occur as free metals (in natural state).

The most abundant elements in the earth's crust' (by weight) are shown in Table.

1.1 The Most Abundant Elements

	Element	% of Earth's Crust
1.	Oxygen	46.4
2.	Silicon	28.2
3.	Aluminium	8.32
4.	Iron	5.63
5.	Calcium	4.15
6.	Sodium	2.36
7.	Magnesium	2.14
8.	Potassium	2.09
9.	Titanium	0.57
10.	Hydrogen	0.14
11.	Phosphorus	0.112
12.	Manganese	0.106

This indicates:

- Oxygen is the most abundant element.
- Aluminium is the most abundant metal.
- First five elements comprise almost 92% by weight, and
- First ten elements make up over 99.5% of the earth's crust.
- Other very abundant elements are nitrogen (78% of the atmosphere) and hydrogen, which occurs as water in the ocean.

1.2 Principal Ores of Some Important Metals.

Metal	Ore	Formula
Aluminium	Bauxite	$\text{Al}_2\text{O}_3 \cdot x \text{H}_2\text{O}$
Chromium	Chromite	FeCr_2O_4
Copper	Chalcopyrite	CuFeS_2
Iron	Haematite	Fe_2O_3
Lead	Galena	PbS
Manganese	Pyrolusite	MnO_2
Mercury	Cinnabar	HgS
Tin	Cassiterite	SnO_2
Titanium	Rutile	TiO_2
	Ilmenite	FeTiO_3
Zinc	Sphalerite	ZnS

1.3 Principal Types of Minerals Representing as Anions

Type	
Uncombined metals	Ag, Au, Bi, Cu, Pd, Pt
Carbonates	CaCO_3 (calcite, limestone), MgCO_3 (magnesite), $\text{CaCO}_3 \cdot \text{MgCO}_3$ (dolomite), PbCO_3 (cerussite), ZnCO_3 , (smithsonite)
Halides	CaF_2 (fluorite), NaCl (halite), KCl (sylvite), Na_3AlF_6 (cryolite)
Oxides	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ (bauxite), Cu_2O (cuprite), MnO_2 (pyrolusite), SnO_2 (cassiterite), Al_2O_3 (corundum), Fe_2O_3 (haematite), TiO_2 (rutile), ZnO (zincite), Fe_3O_4 (magnetite)
Phosphates	$\text{Ca}_3(\text{PO}_4)_2$ (phosphate rock), $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (hydroxyapatite)
Silicates	$\text{NaAlSi}_3\text{O}_8$ (albite), $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$ (talc)
Sulphides	Ag_2S (argentite), CdS (greenockite), Cu_2S (chalcocite), FeS_2 (pyrite), HgS (cinnabar), PbS (galena), ZnS (sphalerite)
Sulphates	BaSO_4 (barite), CaSO_4 (anhydrite), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite)

Benefaction of Ores

Most of the ores available in nature contain large amount of impurities, i.e., **gangue**. The pretreatment of ores, based on physical properties and without bringing out any major chemical change in the ore, is known as **benefaction** or **concentration of the ore or ore-dressing**.

1.4 Following table summarises the various methods adopted for the ore-dressing.

	Method	Ores specification	Process
1.	Gravity separation (Tabling) by hydraulic washing	Based on the difference in the specific gravities of the ore and gangue. Cassiterite or tin-stone, chromite and pitchblende are concentrated	Crushed ore is kept on top of a slope table, which is made vibrates. A stream of water is passed in the direction perpendicular to the slope. The lighter particles are thrown up by vibration and are removed by water stream
2.	Magnetic separation	Based on the difference in magnetic properties of minerals. If the ore but not the gangue is attracted by a magnetic field, it can be concentrated to yield a sample which is rich in metal. Magnetite (Fe_3O_4), haematite (Fe_2O_3), wolframite (FeWO_4), chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) and ilmenite ($\text{FeO} \cdot \text{TiO}_2$) separated from non-magnetic impurities	The pulverized mineral is passed over a rubber belt which moves on a pulley in a magnetic field. The non-magnetic gangue particles fall off in a vertical position when the belt passes over a pulley, but the magnetic ore clings to the belt. When the belt is out of magnetic field, the ore separates. <div style="text-align: center;"> </div>
3.	Froth flotation process	Used to concentrate sulphide ores; based on the difference in wettability of different minerals	Some times depressants are used to prevent certain type of particles from forming the froth with bubbles. NaCN is used as a depressant in the separation of ZnS and PbS. NaCN acts as a depressant for ZnS but does not prevent PbS from the formation of the froth, due to complex formation $\text{ZnS} + 4\text{NaCN} \rightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + \text{Na}_2\text{S}$
4.	Leaching	Useful in case the ore is soluble in a suitable solvent. Pure Al_2O_3 is obtained from the bauxite ore in the Bayer's process by leaching; also employed in	Leaching of bauxite $\text{Al}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq}) + 3\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_4^-$ $\xrightarrow[\text{CO}_2]{\text{dilution}} \text{Al}(\text{OH})_3 + \text{OH}^- \xrightarrow{\Delta} \text{Al}_2\text{O}_3$ Leaching of silver and gold

		concentration of silver and gold ores when leaching is done using NaCN in presence of air.	$4M + 8CN^- + 2H_2O + O_2 \rightarrow [M(CN)_2]^-$ <p style="text-align: right;"><i>soluble</i></p> <p>(M = Ag or Au)</p> $Ag_2S + 4CN^- \rightarrow 2[Ag(CN)_2]^- + S^{2-}$
5.	Calcination	Used when concentrated ore is in the form of hydroxide or carbonate; volatile matter is burnt away. It is done in a reverberatory furnace.	$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$ $CaCO_3 \xrightarrow{\Delta} CaO + CO_2$
6.	Roasting	Sulphide ore is heated in a regular supply of air at a temperature below the melting point of the metal. It converts sulphide into oxide or sulphate; part of sulphide may also act as a reducing agent.	$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$ $2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$ $2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$ <p>Process is carried out in a reverberatory furnace.</p>

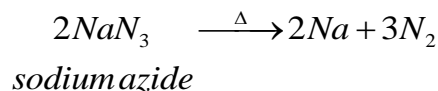
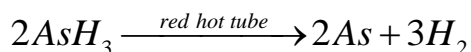
Separation and Extraction of Elements

The different methods for separating and extracting elements may be divided into five classes:

Mechanical Separation: A surprisingly large number of elements occur in the free elemental state. They have remained in the native form because they are unreactive as Cu, Ag, Au and Pt.

- Au is found in the native form, as grains in quartz, as nuggets and in the silt of river beds because of very high density (19.3 g cm^{-3}). Ag and Cu are sometimes found in the native form as nuggets. All the three metals lie below hydrogen and other reactive metals in electrochemical series and thus are easily displaced to the metallic form.
- Palladium and platinum are also found as native metals.
- Liquid droplets of Hg are found associated with cinnabar, HgS.
- Diamonds are found in the earth and are obtained by mechanical separation of large amount of earth and rock.

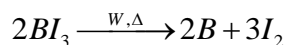
Thermal Decomposition Method: A few compounds will decompose into their constituent elements simply by heating:



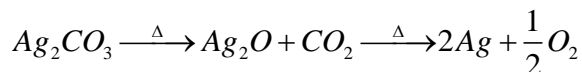
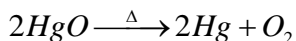
- In Mond's process:

$$Ni(CO)_4 \xrightarrow{230^\circ C} Ni + 4CO$$

$$ZrI_4 \xrightarrow{W, \Delta} Zr + 2I_2$$



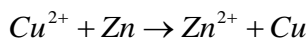
- In Van Arkel-de-Boer process:



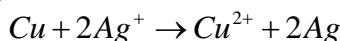
Oxides of the metals lying below Hg (and that of Hg) in electrochemical series decompose on heating, giving metal.

Displacement of Element by Another: In principle any element may be displaced from solution by another element which is higher in electrochemical series (ECS).

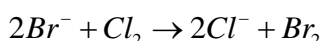
- **Zn displaces Cu from CuSO₄ solution** since Zn is above Cu in ECS:



- **Cu displaces Ag from AgNO₃ solution** due to the same fact.



Sea water has Br⁻. Cl₂ can oxidize Br⁻ to Br₂



This method is quite applicable when displaced metal costlier than the other metal which is oxidised. **ECS** is in **order Li>K>Ca>Na>Mg>Al>Mn>Zn>Fe>Cu>Hg>Ag>Au**

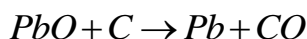
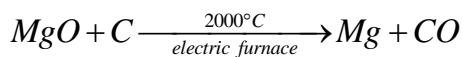
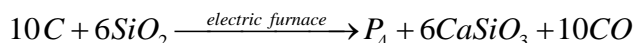
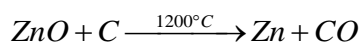
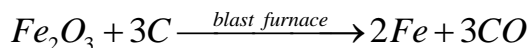
A reaction is spontaneous if reducing agent is above oxidizing agent in ECS.

Zn and Mg can reduce Fe²⁺ to Fe (in prevention of rust) since both are above Fe in ECS.

High Temperature Chemical Reduction Methods:

Once an ore has been concentrated, it is reduced to the free metal, either by chemical reduction or by electrolysis. The method used depends on the activity of the metal as measured by its standard reduction potential. The most active metals have the most negative standard reduction potentials and are the most difficult to reduce; the least active metals have the most positive standard reduction potentials and are the easiest to reduce.

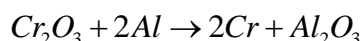
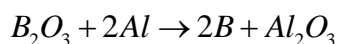
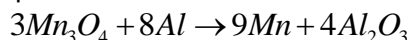
- **Reduction by carbon:**



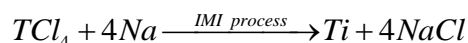
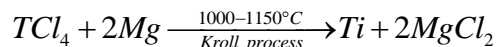
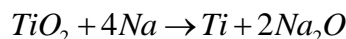
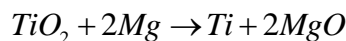
- **Reduction by another metal:**

If the temperature needed for carbon to reduce an oxide is too high for economic or practical purpose, the reduction may be affected by another highly electropositive metal such as aluminium, which liberates a large amount of energy (1675 kJ mol⁻¹) on oxidation to Al₂O₃.

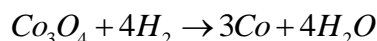
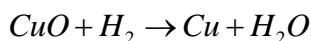
This is the basis of the thermite process:



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:



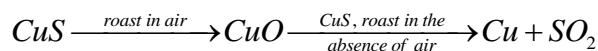
- **Reduction of oxides with H₂:**



This method is not widely used, because many metals react with H₂ at elevated temperatures forming hydrides. Also there are chances of explosion of H₂ with O₂.

- **Self reduction:**

Sulphides of Cu, Pb and Sb when roasted in air are converted partially into oxides. On further roasting in the absence of air, self reduction takes place:



It is carried out in a **Bessemer converter** or **Pierce – Smith converter**.

Electrolytic Reduction

To get metal of high purity, electrochemical refining is done making impure metal as anode.

- **In an aqueous solution**

It is used in cases when the electrolyte is soluble in water and products do not react with it. Copper, Zn, Ag and other metal are obtained by the electrolysis of aqueous solution of their salts (ZnSO₄, AgNO₃, CuSO₄). Impure metal is oxidised at anode and is deposited at the cathode (of pure metal).

- **In fused metals:**

Na, K, Ca, Mg etc., react with H₂O hence, these metals are extracted by electrolysis of fused halides.

- Na and Cl₂ are obtained by electrolysis of fused NaCl.
- Al is obtained by the electrolysis of used mixture of Al₂O₃ and Na₃ [AlF₆] (cryolite).

- **In other solvents:**

Electrolysis can be carried out in solvents other than water. F₂ reacts violently with H₂O hence, it is produced by electrolysis of KHF₂ in HF.

1.5 Reduction Methods for Producing Some Common Metals

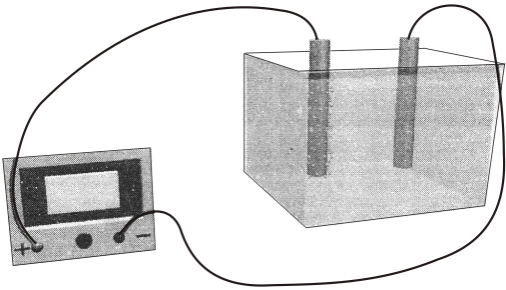
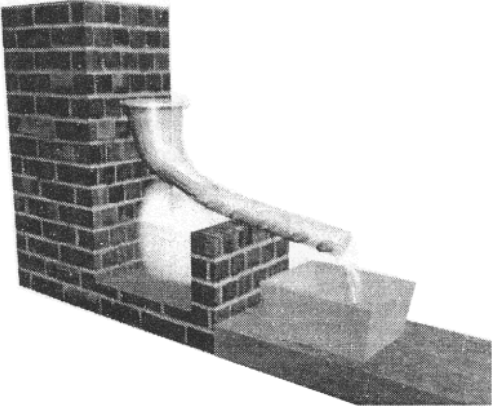
	Metal	Reduction Method
Least active	Au, Pt	None; found in nature as the free metal
	Cu, Ag, Hg	Roasting of the metal sulphide.
	V, Cr, Mn, Fe	Reduction of the metal oxide with carbon, hydrogen or a more active metal
	Al	Electrolysis of molten Al_2O_3 in cryolite
Most active	Li, Na, Mg	Electrolysis of the molten metal chloride

1.6 Some Specific Reduction Processes

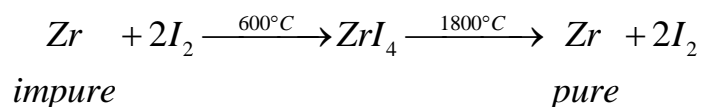
Metal	Compound (ore)	Reduction Process	Comments
Mercury	HgS (cinnabar)	Roast reduction; heating of ore in air $\text{HgS} + \text{O}_2 \xrightarrow{\Delta} \text{Hg} + \text{SO}_2$	
Copper	Sulphides such as Cu_2S (chalcocite)	Blowing of oxygen through purified molten Cu_2S $\text{Cu}_2\text{S} + \text{O}_2 \xrightarrow{\Delta} 2\text{Cu} + \text{SO}_2$	Preliminary ore concentration and purification steps required to remove FeS impurities
Zinc	ZnS (sphalerite)	Conversion to oxide and reduction with carbon $2\text{ZnS} + 3\text{O}_2 \xrightarrow{\Delta} 2\text{ZnO} + 2\text{SO}_2$ $\text{ZnO} + \text{C} \xrightarrow{\Delta} \text{Zn} + \text{CO}$	Process also used for the production of lead from galena PbS

Iron	Fe ₂ O ₃ (haematite)	Reduction with carbon monoxide $2C(\text{coke}) + O_2 \xrightarrow{\Delta} 2CO$ $Fe_2O_3 + 3CO \xrightarrow{\Delta} 2Fe + 3CO_2$	
Titanium	TiO ₂ (rutile)	Conversion of oxide to halide salt and reduction with an active metal $TiO_2 + 2Cl_2 + 2C \xrightarrow{\Delta} TiCl_4 + 2CO$ $TiCl_4 + 2Mg \xrightarrow{\Delta} Ti + 2MgCl_2$	Also used for the reduction of UF ₄ obtained from UO ₂ , pitchblende
Tungsten	FeWO ₄ (wolframite)	Reduction with hydrogen $WO_3 + 3H_2 \xrightarrow{\Delta} W + 3H_2O$	Used also for molybdenum
Aluminium	Al ₂ O ₃ · nH ₂ O (bauxite)	Electrolytic reduction (electrolysis) in molten cryolite. $Na_3[AlF_6].at\ 1000^\circ C.$ $2Al_2O_3 \xrightarrow{\Delta} 2Al + 3O_2$	
Sodium	NaCl (sea water)	Electrolysis of molten chlorides $2NaCl \xrightarrow{\Delta} 2Na + Cl_2$	Also for calcium, magnesium, and other active metals in group IA and IIA

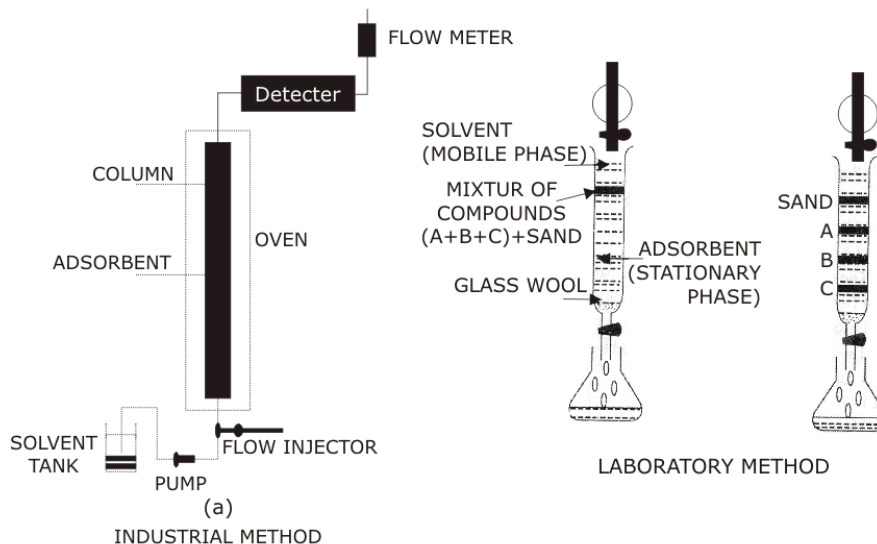
1.7 Refining of Crude Metals

	Methods	Metals purified
1.	Distillation	Zinc and mercury
2.	Electrolysis	<p>Copper, gold, silver, lead, zinc, aluminium Impure metal is made anode and the pure metal is cathode. The net result is the transfer of pure metal from anode to cathode.</p> 
3.	Liquation	<p>A low melting metal like tin can be made to flow on a sloping surface and thus separated from higher melting impurities.</p> 
4.	Zone refining	<p>Metal of high purity are obtained, Silicon, germanium, boron, gallium, indium are purified. (which are used in semiconductors) It is based on the fact that impurities are more soluble in the melt than in the pure metal.</p>
5.	Vapour phase refining	<p>In Mond process for the refining of nickel</p> $\underset{\text{impure}}{\text{Ni}} + 4\text{CO} \xrightarrow{80^\circ\text{C}} \text{Ni}(\text{CO})_4 \xrightarrow{200^\circ\text{C}} \underset{\text{pure}}{\text{Ni}} + 4\text{CO} \uparrow$ <p>In Van Arkel method for zirconium</p>

6. Chromatographic Method

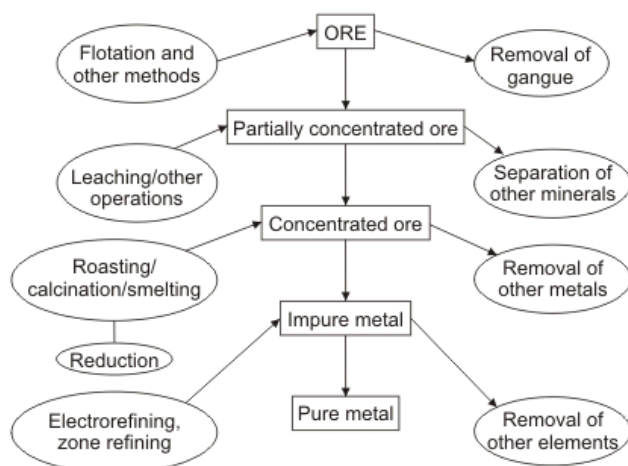


Based on the principle that the different components of a mixture are adsorbed to different extent on an adsorbent.



In a physical technique consists of two phases:-

- (i) Stationary phase (alumina, silica gel)
 - (ii) Mobile phase (Liquid, gas, supercritical fluid CO_2)
- This technique is especially suitable for such elements which are available in minute quantities and impurities are not very much different in chemical properties. [eg. Lanthanoids (rare earth metal) are purified by this technique using ion-exchange resins as adsorbent]



Factors Influencing the Choice of Extraction Process

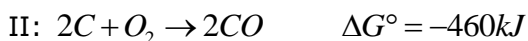
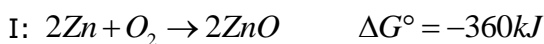
The type of process used commercially for any particular element depends on a number of factors:

- Is the element unreactive enough to exist in the free state?
- Are any of the compounds unstable to heat?
- Does the element exist as an ionic compound, and is the element stable in H₂O?
- Is there a cheap element above it in the ECS which can be sacrificed to displace it from solution?
- Does the element occur as sulphide ores which can be roasted, or oxide ores which can be reduced by carbon (which can be the cheapest) or by Al, Mg and Na (which can be still costlier).
- If all other methods fail, electrolysis is preferred (in aqueous solution which is the best to get metal of highest purity or in fused state which is again costlier).

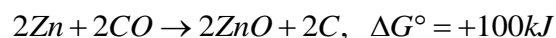
Thermodynamics of Extractive Metallurgy

It is interesting to think of the reduction of ZnO with C as involving a competition between Zn and C for O atoms.

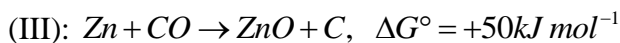
We consider following values at 1100°C for the oxidation of Zn and C:



(I)–(II) gives



Or



For reaction III, in which Zn reduces CO, ΔG° is positive indicating that this reduction is not spontaneous (in forward direction), but for the reaction IV with negative value of ΔG° , in which C reduces ZnO is spontaneous. (in forward direction).

Why must we carry out the reduction of ZnO with C at 1100°C? From an energy stand point it would certainly be more economical to carry it out at a lower temperature. The graphical representation of (**Ellingham diagram**) is useful tool to help answer such questions. The lines ($2C + O_2 \rightarrow 2CO$) and ($2Zn + O_2 \rightarrow 2ZnO$) cross at about 950°C. At about this temperature Zn and C have equal affinities for O atoms : ΔG° for reaction (IV) is zero. Above this temperature ΔG° is positive. To make reaction (IV) go essentially to completion we need a temperature somewhat in excess of 950°C.

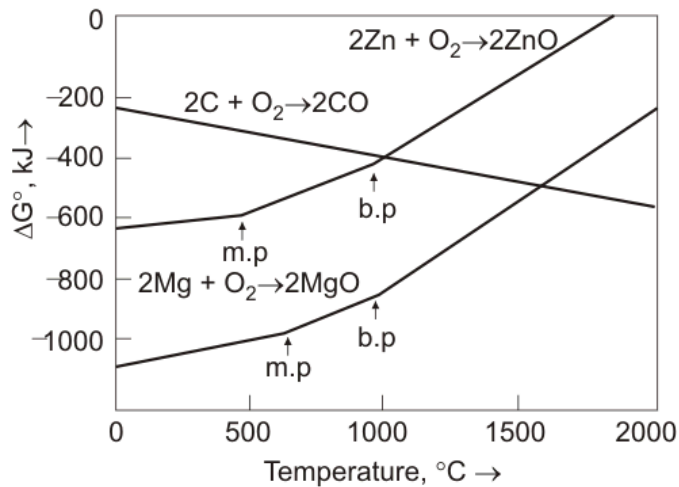


Fig: The points noted by arrows are the melting and boiling points of the metals zinc and magnesium. ΔG° as a function of temperature for some reactions of extractive metallurgy.

1.2 Extraction of Copper

Occurrence

Cuprite	Cu_2O
Malachite	$CuCO_3 \cdot Cu(OH)_2$
Azurite	$2CuCO_3 \cdot Cu(OH)_2$

Copper pyrites

Or

Chalco Pyrites $CuFeS_2$

Main source is copper pyrites. Some copper is also found in native state.

Pyrometallurgical Method (Dry Method)

Sulphide ore is converted into copper in following steps:

Step I: Concentration by Froth-Floatation process

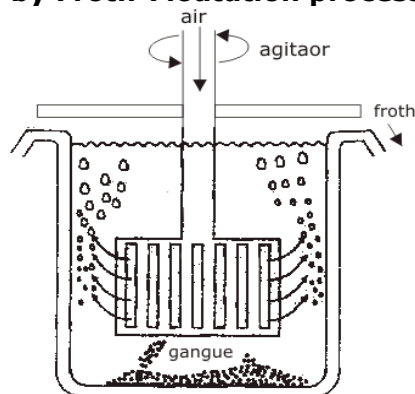
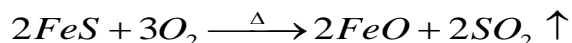


Fig: Concentration of an ore by floatation

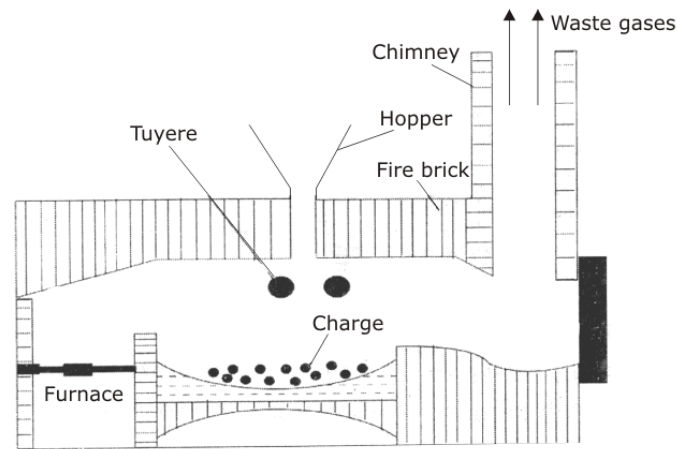
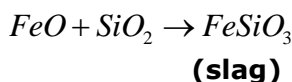
Powdered ore is suspended in water in a large vat, together with suitable additives, and the mixture is agitated with air. Particles of ore become attached to air bubbles, rise to the top of the vat, and are collected in the overflow froth. Particles of the undesired waste rock (gangue) fall to the bottom.

The success of this method depends on the use of proper additives—a material that will produce stable foam (frother) and a substance (collector) that coats the particles of ore but does not “wet” the particles to be rejected. Pine oil is widely used as a frother and sodium ethyl xanthate ($C_2H_5OCS_2Na$) as a collector.

Step II: Roasting is done in multiple hearth furnace. Volatile impurities are removed as thin oxide (As_2O_3, Sb_2O_3, P_2O_5). It also converts iron sulphide to iron oxide. The copper remains as the sulphide if the temperature is kept below $800^\circ C$.

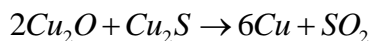
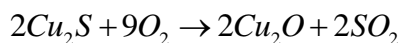


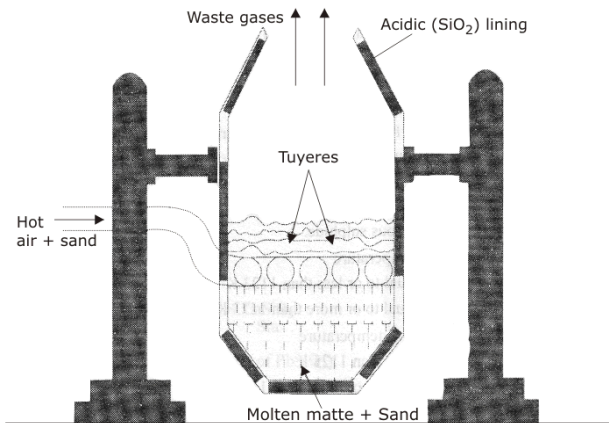
Step III: Smelting of the roasted ore is done in a furnace at $1400^\circ C$. In this furnace charge melts and separates into two layers. The bottom layer is copper-matte, consisting chiefly of the molten sulphides of copper and iron. The top layer is a silicate slag formed by the reaction of oxides of Fe, Ca, and Al with SiO_2 (which either is present in the ore or is added) and is removed.



Actually ore is heated in a reverberatory furnace after mixing with silica.

Step IV: Bessemerisation (or Converting) occurs in another furnace where air is blown through the molten copper matte. First, the remaining iron sulphide is converted to oxide (as in step II) followed by slag formation (as in step III). The slag is poured off and air is again blown through the furnace. Now the following reactions occur, yielding a product that is about 98 to 99% Cu.





The product of this step is called **Blister copper** because of frozen bubbles of SO_2 . It can be used where high purity is not required.

Step V: Electrorefining:

Anode	:	impure copper
Cathode	:	pure copper
Electrolyte	:	3.5% CuSO_4 + 15% H_2SO_4
Voltage	:	0.3 to 0.5 V
Temperature	:	50.55°C

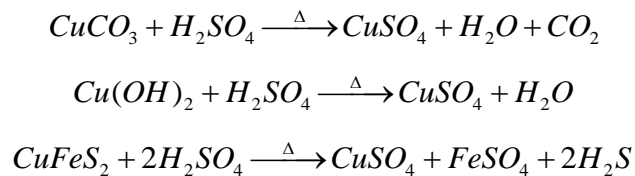
Cu from impure copper anode goes into solution and is deposited at the cathode:



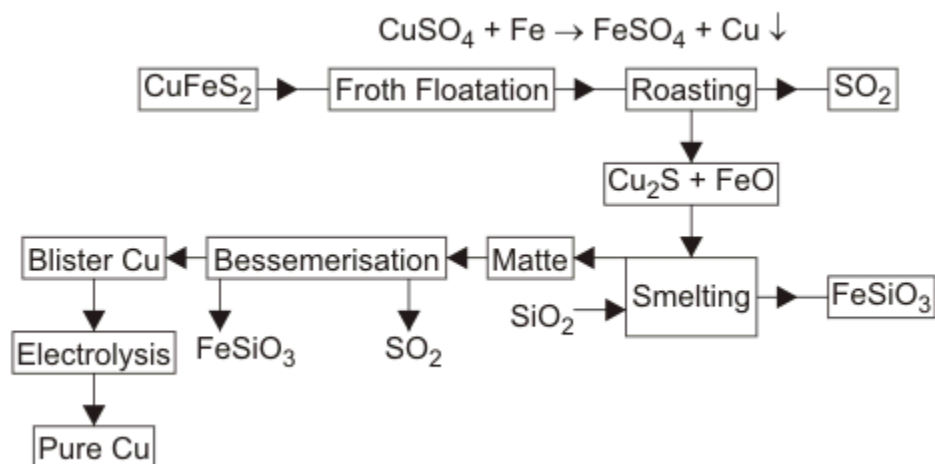
Anode-mud contains Au, Pt, Ag and other precious metals (noble metals).

Hydrometallurgical Process (Wet Process)

Step I: Leaching with H_2SO_4 converts salts into sulphates:



Step II: Electrochemical Displacement: Fe is above Cu in ECS, hence if Fe scrap is added to CuSO_4 solution, Cu is displaced:



1.3 Extraction of Magnesium

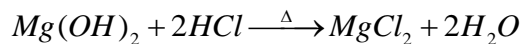
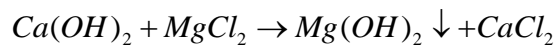
Occurrence

Magnesite	MgCO_3
Dolomite	$\text{MgCO}_3 \cdot \text{CaCO}_3$
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Sea water	Mg^{2+} as SO_4^{2-} and Cl^-
Carnallite	$\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$

Main sources are dolomite and sea water.

Dow Sea-Water Process

Sea water contains about 0.13% Mg^{2+} ions, and the extraction of Mg depends on the fact that $\text{Mg}(\text{OH})_2$ is very much less soluble than $\text{Ca}(\text{OH})_2$. Slaked lime, $\text{Ca}(\text{OH})_2$ is added to sea water, and calcium ions dissolve and $\text{Mg}(\text{OH})_2$ is precipitated. This is filtered off, treated with HCl to produce MgCl_2 , and electrolysed.



The process has been summarized in figures.

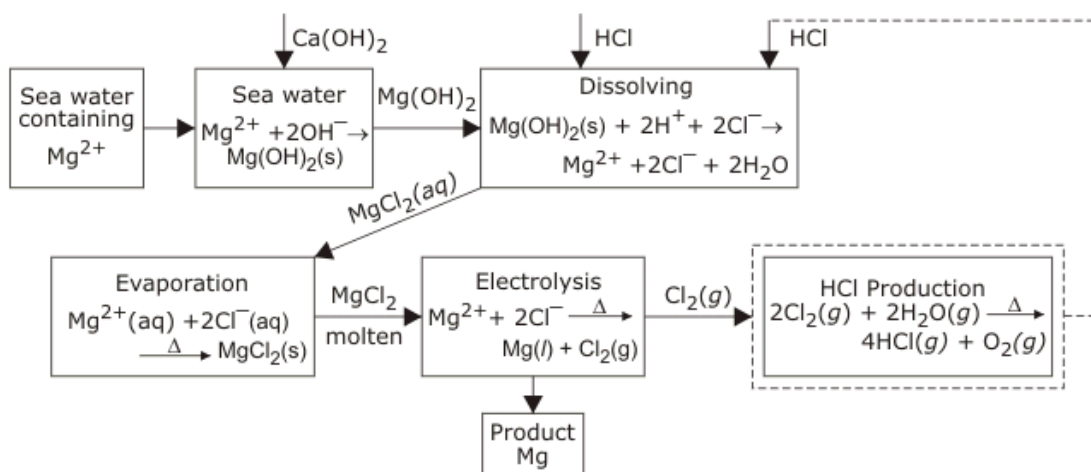


Fig: The Dow process for the production of Mg. The main reaction sequence is traced by solid arrows. Recycling of $Cl_2(g)$ is shown by broken arrows.

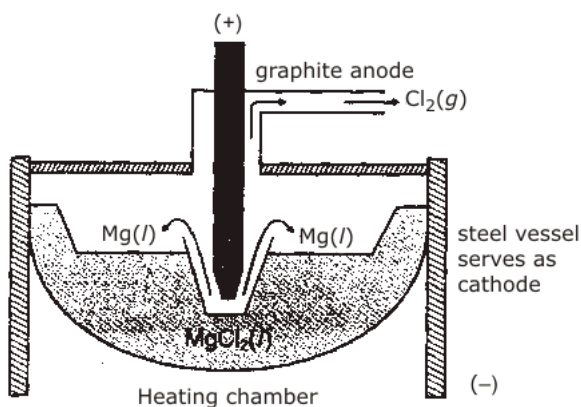


Fig: The electrolysis of molten $MgCl_2$

The actual electrolyte is a mixture of molten $NaCl$, $CaCl_2$ and $MgCl_2$. This mixture has a lower melting point and higher electrical conductivity than does $MgCl_2$ alone, but only Mg^{2+} is reduced under the conditions employed in the electrolysis.

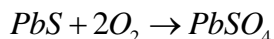
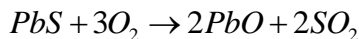
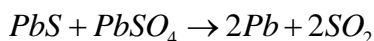
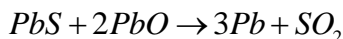


1.4 Extraction of Lead

Occurrence

Galena	:	PbS
Anglesite	:	$PbSO_4$
Cerussite	:	$PbCO_3$
Lanakite	:	$PbO \cdot PbSO_4$
Matlockite	:	$PbCl_2 \cdot PbO$

Main source is PbS .

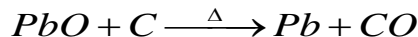
Reduction Method (Air Reduction Process)**Step I:** Concentration by froth flotation process.**Step II:** Roasting in a limited supply of air:**Step III:** Smelting is done along with step II. When 50% of the PbS has been oxidised, the air supply is cut off and the temperature is increased. PbS reduces PbO and PbSO₄ to Pb :

The metal contains a number of metallic impurities: Cu, Ag, Sn, As, Sb, Bi and Zn. These are removed by cooling to near the freezing point of Pb, when first Cu and then Zn containing most of the Ag and Au solidify (**Parke's method**). Preferential oxidation converts As, Sb and Sn to As₂O₃, Sb₂O₃ and SnO₂ which float on the surface of the molten metal and may be skimmed off.

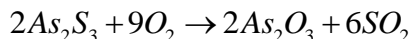
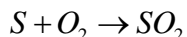
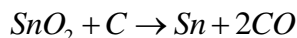
Further refining is done by electrolysis.

Carbon Reduction Process

Roasted ore as obtained in step II above is mixed with coke and melted.

**1.5 Extraction of Tin****Occurrence****Cassiterite (tin stone)** : SnO₂It contains FeWO₄ · MnWO₄ (Wolframite) as a magnetic impurity.**Step I: Concentration is done in stages:**

- **Electromagnetic separation:** To remove magnetic impurities(FeWO₄ · MnWO₄)
- **Gravity separation:** To remove gangue, ore is washed with current of water.
- **Roasting:** To remove volatile impurities as oxides:

**Step II: Reduction (Smelting):** Concentrated ore from step I is mixed with coal, lime stone and sand heated in a reverberatory furnace at 1200°-1300°C**Step III: Refining:** Sn obtained above has some SnO₂. It is refined by:

- (i) **Poling** process (molten tin is stirred with poles of green wood which reduce SnO₂ to Sn).
- (ii) **Liquation** (bars of tin are heated on the hearth of a reverberatory furnace when the readily fusible tin flows leaving the impurities like Fe, Cu, W, As etc. behind)

Step IV: Electro-refining

Cathode : Sheet of pure tin

Anode : blocks of impure tin

Electrolyte : tin sulphate (SnSO_4) in dil. H_2SO_4 and some phenol sulphonic acid
 Pure tin from the blocks (anode) is deposited at the cathode.

1.6 Extraction of Silver

Occurrence

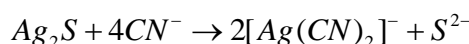
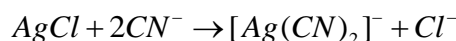
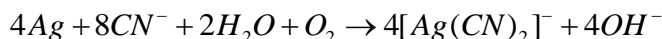
Argentite (silver glance) : Ag_2S
Horn silver (chlorargyrite) : AgCl
Argentiferrous galena : $\text{PbS} \cdot \text{Ag}_2\text{S}$
Pyragyrite or Rubysilver : $3 \text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$

Main source is argentite.

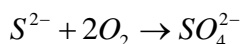
Cyanide Process

Step 1: Complexation of Ag/Ag₂S/AgCl

The powdered ore is treated with NaCN solution and O_2 is bubbled through the solution. Ag if any present in native state is oxidised to Ag^+ . Ag^+ is complexed by CN^- forming soluble $[\text{Ag}(\text{CN})_2]^-$

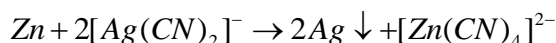


Last reaction is reversible due to very low solubility of Ag_2S in water. Air oxidizes S^{2-} to SO_4^{2-} , S and $\text{S}_2\text{O}_3^{2-}$



Step II: Precipitation of Ag

Zn is added to soluble $[\text{Ag}(\text{CN})_2]^-$ when Ag is displaced.



Step III: Refining by electrolysis

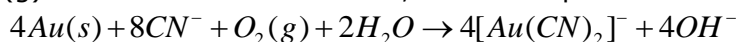
Cathode : pure Ag
 Anode : impure Ag
 Electrolyte : AgNO_3 (aq)

When electric current is passed, impure Ag (anode) is oxidised to Ag^+ and is deposited at pure Ag (cathode).

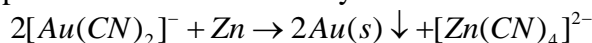
At anode: $\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$

At cathode: $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$

In case of gold, O_2 (g) oxidises free metal to Au^+ , which complexes with CN^-

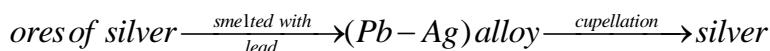


The pure metal is then displaced from the solution by an active metal.



Lead Process

This process depends upon the fact that when ores of silver are smelted down with lead, an alloy of lead and silver is formed; from this alloy lead is removed by oxidation.

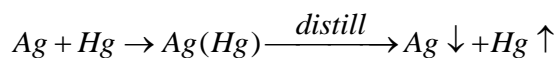
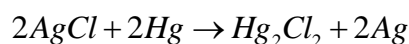
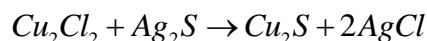
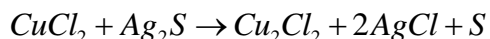
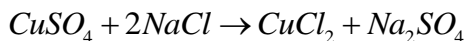


(Pb-Ag) alloy rich in silver: Cupellation process is used

(Pb-Ag) alloy poor in silver: Parke's or Pattinson process is used

Mexican Amalgamation Process

Mercury and magistral (burnt pyrites-sulphates and oxides of copper and iron) are added to the powdered mineral containing H_2O and $NaCl$. The mixture is kept for several days. Silver is formed in the amalgam form. On washing, drying and subsequent distillation, silver is obtained.



Desilverisation of Lead: When lead-silver alloy is poor in silver (such as argentiferous lead or galena), desilverisation of lead is affected by Parke's process. It depends upon the fact that:

- (i) When zinc is added to a melted alloy of silver and lead, zinc takes away silver from the alloy and itself forms an alloy with silver and not with lead
- (ii) Alloy of zinc and silver melts at a higher temperature than lead
- (iii) The alloy of silver and zinc is lighter than lead and forms two separate layers
- (iv) On distillation of silver and zinc, zinc separates.

Pattinson's Process

It depends upon the fact that the alloy of lead and silver containing less than 1.8 per cent of silver, melts at a lower temperature than pure lead. If this type of alloy is melted, and the melted alloy is allowed to cool, lead first separates and repeating the process, one becomes richer in silver. Further recovery is done by cupellation process.

1.7 Extraction of Aluminium

Occurrence

Bauxite	:	$Al_2O_3 \cdot 2H_2O$
Kaolin	:	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$
Cryolite	:	Na_3AlF_6
Felspar	:	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$
Corundum	:	Al_2O_3
Orthoclase	:	$KAlSi_3O_8$
Beryl	:	$Be_3Al_2Si_6O_{18}$

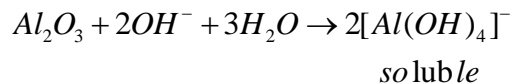
Main source is bauxite.

Felspar or orthoclase on weathering gives rise to porcelain-clay, China-clay or Kaolin.

Purification of Bauxite

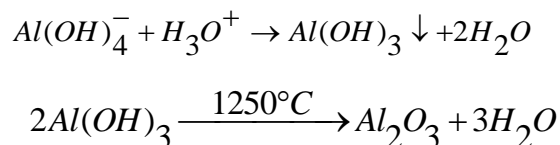
Baeyer's Process

Step I: Bauxite contains Fe_2O_3 and TiO_2 as impurities. Al_2O_3 is amphoteric and dissolves in $NaOH$. The other oxides are basic oxides and therefore insoluble in $NaOH$.

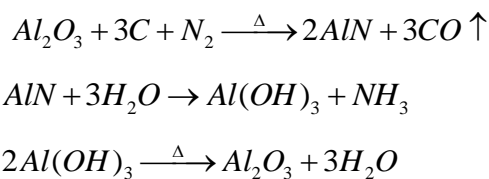


Insoluble oxides are removed by filtration

Step II: Soluble $[Al(OH)_4]^-$ is diluted and then acidified when $Al(OH)_3$ is precipitated which on ignition at $1250^\circ C$ gives pure alumina:



Serpeck's Process



Electrolysis of Al_2O_3 (Hall-Heroult Process)

Al is usually extracted by this process. Al_2O_3 is melted with cryolite $Na_3[AlF_6]$ and electrolysed in a graphite lined steel tank, which serves as cathode. The anodes are also made of graphite. The cell runs continuously and at intervals molten Al (m.p. $660^\circ C$) is drained from the bottom of the cell and more bauxite is added. Cryolite improves the electrical conductivity of the cell as Al_2O_3 is poor conductor. This also serves as an added impurity and lowers the m.p. of the mixture to about $950^\circ C$.

Al of 99.6 to 99.8% purity is obtained. Probable net reactions are.



Reduction at cathode:

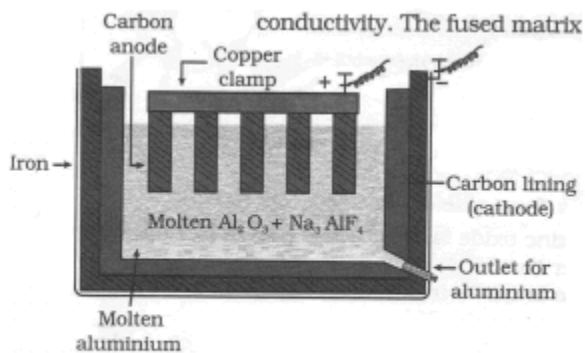
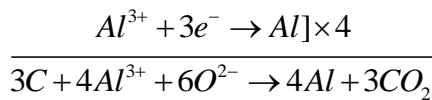
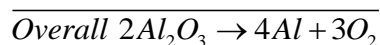
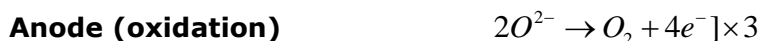
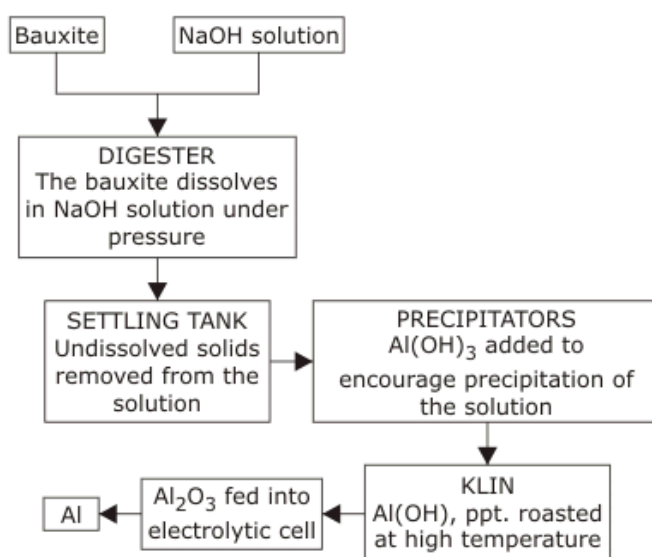


Fig. Electrolytic cell for the extraction of aluminium

Electrolysis cell for aluminium production. The cathode is a carbon lining in a steel tank. The anodes are also made of carbon. Liquid aluminium is denser than the electrolyte medium and collects at the bottom of the tank. A crust of frozen electrolyte forms at the top of the cell. Reaction can also be written as



Oxygen gas reacts with carbon anodes (at elevated temperature) to form CO



1.8 Extraction of Iron [Fe]

Occurrence

Haematite	:	Fe ₂ O ₃
Magnetite	:	Fe ₃ O ₄
Limonite	:	FeO(OH) or Fe ₂ O ₃ · 3H ₂ O
Siderite	:	FeCO ₃
Pyrites (fool's gold)	:	FeS ₂
Pyrrhotite	:	FeS
Ilmenite	:	FeTiO ₃

Oxide-ores are main source of iron.

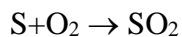
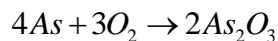
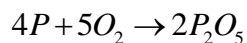
Carbon Reduction Method

Step I: Concentration by:

- Gravity separation method (which removes gangue)
- Magnetic separator (which enriches it by removing non-magnetic impurities)

Step II: Roasting is done:

- To decompose carbonates to Fe₂O₃ and also to remove moisture:
 $4FeCO_3 + O_2 \rightarrow 2Fe_2O_3 + 4CO_2$
- To oxide volatile impurities:



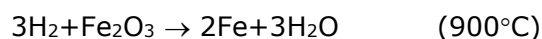
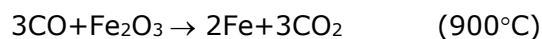
Step III: Reduction or Smelting:

It is done in a blast furnace, the reactions taking place in a blast furnace (along with working temperature) are:

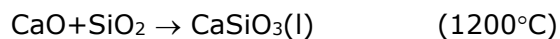
- Formation of reducing agents, principally CO(g) and H₂(g):



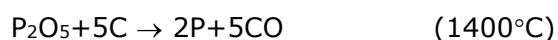
- Reduction of iron oxide:



- Slag formation to remove impurities from ore:

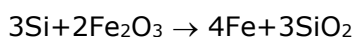
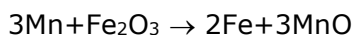
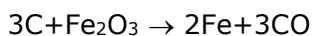


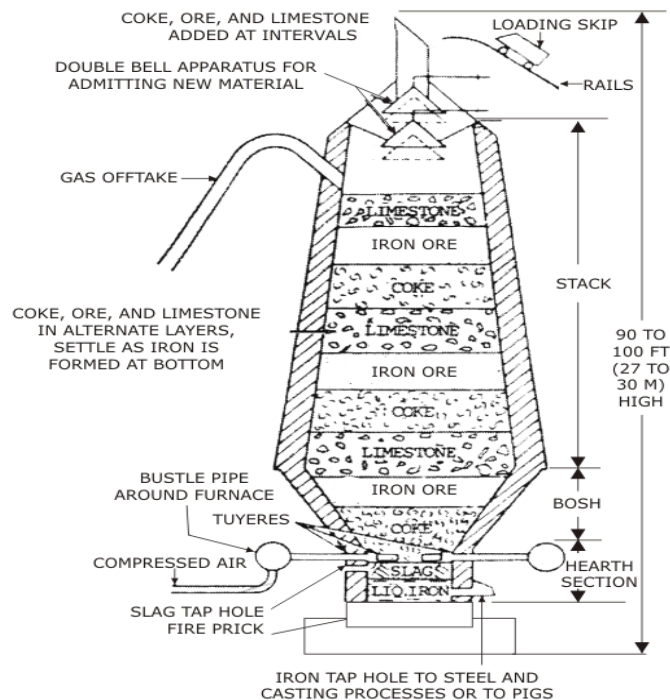
- Impurity formation in iron:



- Iron obtained from a blast furnace is called **pig iron**. It contains about 95% Fe, 4% C and varying quantities of other impurities. **Cast iron** can be obtained by pouring pig iron directly into molds of the desired shape. Cast iron is very hard and brittle and can be used where it will not be subjected to brittle and can be used where it will not be subjected to mechanical or thermal shock.

Wrought iron is prepared by "**Pudding process**" in which cast iron is fused in a reverberatory furnace, the hearth of which is lined with haematite. Reactions taking place are:

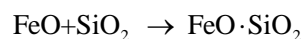
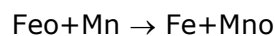
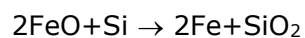
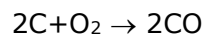




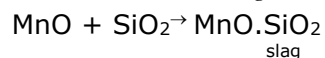
Iron ore, coke, and limestone are added at the top of the furnace, and hot air is introduced through the bottom. Maximum temperatures are attained near the bottom of the furnace where molten iron and slag are drained off.

- **Pig iron** is converted into steel by following changes:
 1. Reduce the carbon content from 3-4% in pig iron to 0-1.5% in steel.
 2. Remove, through slag formation, Si, Mn, and P (each present in pig iron to the extent of 1% or so), together with other minor impurities.
 3. Add alloying elements (such as Cr, Ni, Mn, V, Mo, and W) to give the steel its desired end properties.

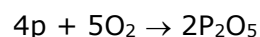
The most important method of steel making today is the **basic oxygen process (BOP)**. The process is carried out in a steel vessel with a refractory lining (usually made of dolomite, $\text{CaCO}_3 \cdot \text{MgCO}_3$). Oxygen gas at about 10 atm pressure and a stream of powdered limestone are fed through a water-cooled lance and discharged above the molten pig iron. The reactions that occur accomplish the first two objectives are:

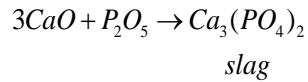


slag

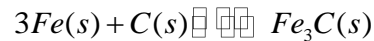


slag





The properties of steel depend on its chemical composition but also on heat treatment. At high temperatures, iron and carbon in steel combine to form iron carbide, Fe_3C , called **cementite**.



The forward reaction is endothermic, so that the formation of cementite is favoured at high temperatures. When steel containing cementite is cooled slowly, the above equilibrium shifts to the left, and the carbon separates as small particles of graphite, which give the steel a gray colour. If the steel is cooled rapidly, equilibrium is not attained and the carbon remains large in the form of cementite, Fe_3C . Steel containing cementite is light in colour, and is harder and more brittle than that containing graphite.

- Heating the steel to appropriate temperature for a short time and then cooling it rapidly in order to give it the desired mechanical properties is called **tempering**. In this way, the ratio of carbon present as graphite and as cementite can be varied within rather wider limits.

Table shows the composition, properties, and uses of various types of steel.

1.8 Types of Steel

Composition	Plain	Type-mass% High strength	stainless
C	1.35	0.25	0.03-1.2
Mn	1.65	1.65	1.0-10
P	0.04	0.04	0.04-0.06
S	0.05	0.05	0.03
Si	0.06	0.15-0.90	1-3
Ni	-	0.4-1.0	1.22
Cr	-	0.3-1.3	4.0-27
Others	Cu (0.2 – 0.6)	Cu (0.01-0.08)	-
Uses	Sheet products, Tools	Construction, Steel turbines	Kitchen utensils, razor blades