METALLURGY

Metallurgy

Introduction :

The	compound of a metal found in nature provide the second approximative autorated	e is ca	Illed a mineral. The minerals from which metal can be		
	lesired materials known as gangue. So	are ca o all m	inerals are not ores but all ores are minerals. Ores may		
be	classified mainly into following four classified	sses.			
	 (a) Native ores : They contain the met (b) Oxidised ores : These ores c subpates and silicates) of metals 	tal in fr onsist	ee state. Silver, gold, platinum etc, occur as native ores. of oxides or oxysalts (e.g. carbonates, phosphates,		
	(c) Sulphurised ores : These ores consist	onsist o of halio	of sulphides of metals like iron, lead, zinc, mercury etc. des of metals.		
Important of	ore :				
1.	Oxide ore :				
	(i) Haematite $\rightarrow Fe_2O_3$		(ii) Bauxite $\rightarrow AIO_X(OH)_{3-2x}$ (Major ore of AI)		
***	(iii) Cassiterite or tin stone \rightarrow SnO ₂ (Black Tin = 60 - 70% SnO ₂)		(iv) Zincite = ZnO_2		
2.	Carbonate ore :				
	(i) Lime stone \rightarrow CaCO ₃		(ii) Dolomite \rightarrow CaCO ₃ .MgCO ₃		
***	(iii) Calamine \rightarrow ZnCO ₃		(iv) Siderite \rightarrow FeCO ₃		
**	(v) Cerussite $\rightarrow PbCO_3$		(vi) Malachite \rightarrow CuCO ₃ .Cu(OH) ₂		
	(vii) Azurite \rightarrow 2CuCO ₃ .Cu(OH) ₂				
3.	Sulphate ore :				
	$Epsom \ salt \to MgSO_4.7H_2O$				
4.	Silicate ore :				
_	$Feldspar \to KAlSi_3O_8$				
5.	Sulphurised ore :	lood			
	(i) Iron pyrites > EoS				
	(ii) Zinc Blende \rightarrow ZnS		(ii) Calcha \rightarrow 1 bC		
	(iii) Zine biende \rightarrow 2ns (v) Copper diance \rightarrow Cu.S		(v) Copper pyrite or chalcopyrite \rightarrow CuFeS.		
6	Halide ore				
•••	(i) Horn silver \rightarrow AgCl	**	(ii) Carnallite \rightarrow KCI.MgCI.6H ₂ O		
	(iii) Fluorspar $\rightarrow CaF_{a}$		(iv) Sylvine \rightarrow KCl		
	(v) Cryolite $\rightarrow Na_{a}AIF_{a}$				
Note :	Mg obtained from both sea water & ea	arth cru	ust.		
	Solved Examples —				
Example-1 Solution	Which metals are supposed to occur i Elements below hydrogen in the elect	in the r rocher	native state in nature ? nical series like Cu, Ag, Au etc, exist native ores.		
Example-2	Match the ores listed in Column-I with	their c	correct chemical formula listed in Column-II.		
	(A) Cassiterite (p)	FeCO ₃		

Column I		Columi
(A) Cassiterite	(p)	FeCO₃
(B) Siderite	(q)	SnO ₂
(C) Cerussite	(r)	$PbSO_4$
(D) Anglesite	(s)	$PbCO_{3}$

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Solution SnO₂ is called as cassiterite or tin stone, FeCO₃ is called as siderite, PbCO₃ is called as cerussite and PbSO₄ is called anglesite. So correct match is (A) \rightarrow (q), (B) \rightarrow (p), (C) \rightarrow (s) and (D) \rightarrow (r).

Metallurgy :

The scientific and technological process used for the extraction/isolation of the metal from its ore is called as metallurgy.

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.



1. Physical Method :

- (A) **Crushing and Grinding :** The ore is first crushed by jaw crushers and ground to a powder (pulverisation of the ore) in equipments like ball mills and stamp mills.
- (B) Concentration : The removal of unwanted useless impurities from the ore is called dressing, concentration or benefaction of ore.

It involves several steps and selection of these steps depends upon the difference in physical properties of the compound of metal and that of gangue. Some of the important procedures are described below.

(i) Hydrolytic washing :

Gravity separation or "Levigation". Based on the difference in the densities of the gangue and ore particle.

Generally used for the concentration of oxide & native ore.

(ii) Electromagnetic sepration :

Based on difference in magnetic properties of mineral and gangue particle.



Electromagnetic separation

- (a) Chromite ore [FeO.Cr₂O₃] is seprated from non magnetic silicious impurities.
- (b) Cassiterite ore $[SnO_2]$ is seprated from magnetic wolframite $[FeWO_4 + MnWO_4]$

(iii) Froth floatation process :

Generally used for concentration of low grade sulphide ore PbS, ZnS, Cu₂S, CuFeS₂

Principle :

Based on fact that mineral & gangue particles have different wettability in water and oil (pine oil used)

Mineral particle \rightarrow are wetted by oil.

Gangue particle \rightarrow Wetted by water.

Reagents Used :

(i) Frothers :

These form stable froth which rises to the top of the flotation cell.

Oil like pine oil, comphor oil are used in small quantities.

Main Function of :

Frother \rightarrow Stick to ore & then take it to rise upto the top.

Stabilizer \rightarrow To stabilize the froth, froth stabilizer like [cresol & aniline] are added.

(ii) Collector :

K⁺ or Na⁺ ethyl xanthates (ROCS₂⁻M⁺) (R = alkyl,M⁺ = Na⁺, K⁺) are used as collectors. Which collect or attract mineral partical and make them water repellant.

Main Function : Make the ore hydrophobic.

(iii) Activating & Depressing agents :

In <u>PbS + ZnS + FeS₂</u> mixture <u>NaCN + Na₂CO₃</u> is used to depress the floation properties of ZnS & FeS₂.

 $ZnS + CN^{-} \longrightarrow [Zn(CN)_{4}]^{2-}$

 $\operatorname{FeS}_2 + \operatorname{CN}_{-} \longrightarrow [\operatorname{Fe}(\operatorname{CN})_6]^{4-}$

CuSO₄ is then added which is activating for ZnS as Cu forms more stable complexing with CN⁻ than Zn²⁺



Froth floatation process

Solved Examples

- **Example-3** How does NaCN act as a depressant in preventing ZnS from forming the froth?
- **Solution** NaCN reacts with ZnS and forms a layer of $Na_2[Zn(CN)_4]$ complex on the surface of ZnS and thus prevents it from the formation of froth.
- **Example-4** What is the role of stabiliser in froth floatation process ?

Solution Froth can last for a longer period in presence of stabiliser.

2. Chemical Method :

(4) Leaching :

Used when ore is soluble in some suitable solvent like \rightarrow acid, base & suitable chemical reagent.

- Ex. (a) Leaching of alumina from bauxite.
 - (b) Extraction of Ag & Au from their ores in the complex form by treatment with NaCN & KCN.
 - (c) Treatment of low grade Cu ores with conc. H₂SO₄.

(C) Extraction of crude metal from concentrated ore :

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.
- (i) 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 + CO₂

 $ZnCO_3$ (calamine) \longrightarrow $ZnO + CO_2$

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

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

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

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

 AI_2O_3 . $2H_2O$ (bauxite) $\xrightarrow{\Delta} AI_2O_3$ (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 :

Generally used for sulphide ore.

Process : Concentrated ore is strongly heated in excess of air or O₂ below its metling point.

(a) Roasting at moderate temperature :

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

 $2ZnS + 2O_2 \xrightarrow{\Lambda} 2ZnO + 2SO_2$

If temperature is low (500°C) & concentration of SO₂ is high sulphate are produced.

 $PbS + 2O_2 \xrightarrow{\Delta} PbSO_4$

 $ZnS + 2O_2 \xrightarrow{\Delta} ZnSO_4$

(b) Roasting at High temperature :

Self reduction / auto reduction / air reduction :

Sulphide ore of Cu, Pb, Hg & Sb when strongly heated in free supply of air, directly reduced to the metal this known as self reduction.

 Cu_2S (Copper glance) + $O_2 \longrightarrow 2Cu + SO_2$

PbS (Gelena) + $O_2 \longrightarrow Pb + SO_2$

HgS (Cinabar) + $O_2 \longrightarrow$ Hg + S O_2

Important Points

1. It remove impurities of As as As_2O_3 , sulphur as SO_2 , P as P_4O_{10} & Sb as Sb_2O_3

4M (M = As, Sb) + $3O_2 \longrightarrow 2M_2O_3^{\uparrow}$

$$S + O_2 \longrightarrow SO_2^{\uparrow}$$

 $P_4 + 4O_2 \longrightarrow P_4O_{10}^{\uparrow}$

2. Impurities of CuS & FeS in SnO₂ converted to CuSO₄ & FeSO₄

 $CuS + 2O_2 \xrightarrow{\Delta} CuSO_4$

 $FeS + 2O_2 \xrightarrow{\Delta} FeSO_4$

Note : Calcination & Roasting carried out in a reverberatory furnace.

Smelting :

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

The principle of slag formation is essentially the following :

Removal of unwanted basic and acidic oxides: For example, FeO is the impurity in extraction of Cu from copper pyrite.

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.

 $CaCO_{3} \longrightarrow CaO + CO_{2}$ $CaO + SiO_{2} \longrightarrow CaSiO_{3} \text{ (fusible slag)}$ $6CaO + P_{4}O_{10} \longrightarrow 2Ca_{3}(PO_{4})_{2} \text{ (fusible slag - Thomas slag)}$

Properties of a slag :

(i) Slag is a fusible mass.

(ii) It has low melting point.

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

Type of flux : Fluxes 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 the basic impurity like CaO, FeO, MgO etc. The acidic flux combines with the basic impurity and forms a slag.

(b) Basic flux : It is a basic oxide (i.e., oxide of a metal) like CaO (obtained from lime stone, CaCO₃), MgO (from magnesite, MgCO₃), haematite (Fe₂O₃) etc. It is used to remove the acidic impurity like SiO₂, P_2O_5 etc. The basic flux combines with the acidic impurity and forms 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.

Reduction of a Metal Oxide

- (1) Reduction with Carbon : $PbO + C \longrightarrow Pb + CO$ $2Fe_2O_3 + 3C \longrightarrow 4Fe + 3CO_2$
- *** $ZnO + C \xrightarrow{1200^{\circ}C} Zn + CO$ (Extraction of Zn)
- *** $SnO_2 + 2C \xrightarrow{1200^{\circ}C} Sn + 2CO$
- (2) Reduction with CO :

 $Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$

 $Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$

Reduction with C & CO is carried out in blast furnace.

Redution with AI : GoldSchmidt or Aluminothermic process : Metallic oxide of Cr & Mn reduced by AI & this reaction is known as thermite reaction.



Reduction of Cr₂O₃ by Al-powder (Aluminothermic process).

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

(i)
$$\operatorname{Cr}_2O_3 + \operatorname{Al} \longrightarrow 2\operatorname{Cr}(\ell) + \operatorname{Al}_2O_3$$

(ii)
$$3Mn_3O_4 + 8AI \longrightarrow 4Al_2O_3 + 9Mn$$

(iii)
$$2AI + Fe_2O_3 \longrightarrow Al_2O_3 + 2Fe$$

(iv)
$$B_2O_2 + 2AI \longrightarrow 2B + AI_2O_2$$

(4) Redution by Mg & Na :

(i)
$$\text{TiCl}_{4} + 2\text{Mg} \xrightarrow[1000^{\circ}-1150^{\circ}\text{C}]{} \text{Ti} + 2\text{MgCl}_{2}$$

(ii)
$$\text{TiCl}_4 + 4\text{Na} \xrightarrow{\text{Kroll process}} \text{Ti} + 4\text{NaCl}$$

(5) Self reduction or auto reduction or air reduction :

Sulphide ore of some of the metal like Hg, Cu, Pb & Sb, when heated in air some part of these ore change into oxide or sulphate, then that part react with remaing part of sulphide ore to give its metal & sulphur dioxide.

This process is known as self reduction.

Ex. (i)(a) $2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$

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

- (b) $PbS + 2O_2 \longrightarrow PbSO_4$ $PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2$
- (ii) $2HgS + 3O_2 \longrightarrow 2HgO + 2SO_2$ $2HgO + HgS \longrightarrow 3Hg + SO_2$

(6) Electrolytic Reduction :

Electrolytic reduction is an expensive method than chemical method, that's why generally we do not use this method.

But when very high pure metal is required then we use this method.

This method is also used for highly reactive metal.

(i) Electrolyric reduction in aqueous solution :

This method is used when product does not react with water. Electrolytic reduction of Cu & Zn from their sulphates.

- (ii) **In other solvents :** Flourine react with water so it is produced by electrolysis of KHF₂ dissolved in anhydrous HF.
- (iii) **In fused metal :** When produced metal react with water, then metal is extracted from fused melt of their ionic salt.
- Eg. (i) Al is extracted from electrolysis of fused mixture of Al₂O₃ and cryolite (Na₃AlF₆).
 (ii) Extraction of Na by electrolysis of fused NaCl.

Note : In this electrolysis CaCl₂ is added as impurity to lower the melting point from 800°C to 500°C.

(i) Hydro Metallurgy :

When metal can be extracted using solution without any heating or without any electrolysis then operation is known as hydrometallurgy.

Basic Step

(i) Dissolution of the valuable metal in aqueous solution.

(ii) Purification of leach solution.

(iii) Recovery of metal from purified solution.

Ex. Extraction of Ag & Au :

Metallic Ag dissolved in NaCN from ore of Ag & then precipitated with the help of Zn.

 $AgS(s) + 4CN^{-} \longrightarrow 2[Ag(CN)_{2}^{-}](aq) + S^{2-}$

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

(ii) Pyrometallurgy :

If furnace are used and ore are heated to extract metal then it is called pyrometallurgy.

Electrochemical principles of metallurgy :

Electrolytic reduction can be regarded as a technique for driving a reduction by coupling it through electrodes and external circuit 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 electrode potential of the redox coupled formed in the system.

Hence, the total Gibb's energy of the coupled internal and external process is

 $\Delta G + \Delta G$ (external) = $\Delta G - nFE_{ext}$

If the potential difference of the external source exceeds

$$E_{ext} = -\frac{\Delta G}{nF}$$

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^0 values corresponds to a positive E^0 and consequently negative ΔG^0 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.,

$$Cu^{2+}(aq) + Fe(s) \longrightarrow Cu(s) + Fe^{2+}(aq)$$

In simple electrolysis, the M^{n+} ions are discharged at negative electrodes (cathodes)and deposited there. Precautions are taken considering the reactivity of the metal produced and suitable materials are used as electrodes. Sometimes a flux is added for making the molten mass more conducting.

Hydrometallurgy : The processing of ores and minerals as well as metals and their compounds at relatively low, often ambient temperatures employing 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 low grade ore it is leached out using acid and bacteria. The solution containing Cu^{2+} is treated with scrap iron or H_2 .

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

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 leach solution and 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 :

(A) Extraction of Ag and Au : Metals like Au and Ag can be precipitated for their salt solution by electropositive metals for example, Zn.

Metallic Ag is dissolved from its ore in dilute NaCN solution, and the solute so obtained is treated with scrap Zn when Ag is precipitated. Air is blown into the solution oxidize Na_2S . Leaching the metals like silver, gold with CN^- is an oxidation reaction (Ag \rightarrow Ag⁺ or Au \rightarrow Au⁺)

 $\begin{array}{l} \text{Ag}_2\text{S}(\text{s}) + 4\text{CN}^-(\text{aq}) \longrightarrow 2 \left[\text{Ag}(\text{CN})_2\right]^-(\text{aq}) + \text{S}^{2-}(\text{aq}) \\ 2[\text{Ag}(\text{CN})_2]^-(\text{aq}) + \text{Zn}(\text{s}) \longrightarrow \left[\text{Zn}(\text{CN})_4\right]^{2-}(\text{aq}) + 2\text{Ag}(\text{s}) \\ 4\text{Au}(\text{s}) + 8 \text{CN}^-(\text{aq}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{I}) \longrightarrow 4 \left[\text{Au}(\text{CN})_2\right]^-(\text{aq}) + 4\text{OH}^-(\text{aq}) \\ 2[\text{Au}(\text{CN})_2]^-(\text{aq}) + \text{Zn}(\text{s}) \longrightarrow \left[\text{Zn}(\text{CN})_4\right]^{2-}(\text{aq}) + 2\text{Au}(\text{s}) \end{array}$

Here Zn acts as reducing agent.

(B) Extraction of Aluminium : It involves the following processes

(a) Purification of bauxite :

(1) Leaching of Alumina from bauxite :

If Fe_2O_3 is main impurity (red bauxite) \rightarrow Bayer's/Hall's

If SiO_2 is main impurity (white bauxite) \rightarrow Serpeck's process.

(i) Bayer's process : Red Bauxite + SiO₂ + Iron oxide + TiO₂

conc. NaOH solution

 $[Al(OH)_4]^-$ and SiO₂ will go into solution phase & Fe₂O₃ & TiO₂ remain undissolve.

Filter & pass

$$\downarrow$$
 $CO_2(g) (WA)$
 $AI(OH_3)\downarrow$
 \downarrow Δ , 1473 K
 $AI_2O_3(s)$
 $Alumina$
(ii) Hall's Process :

Red bauxite + SiO₂ + Fe₂O₃ Fuse with \checkmark Na₂CO₃ NaAlO₂ (soluble) \downarrow CO₂(g), 60°C Al(OH)₃ \downarrow \downarrow 1473, K Al₂O₃

(iii) Serpeck's process :

Used for white bauxite containg silica as impurities.

$$\begin{array}{l} \operatorname{Al}_2\operatorname{O}_3 + \operatorname{N}_2 + & \xrightarrow{\Delta} & \operatorname{Coke} \operatorname{AIN} + \operatorname{CO}^{\uparrow} \\ & \xrightarrow{+\operatorname{H}_2\operatorname{O}} & \operatorname{Al}(\operatorname{OH})_3 + \operatorname{NH}_3^{\uparrow} \\ & \xrightarrow{-1473 \text{ K, } \Delta} & \operatorname{Al}_2\operatorname{O}_3 \text{ (pure)} \end{array}$$

(2) Electrolytic reduction [Hall-Heroult process] :

Electrolysis of fused Al_2O_3 is difficult as its MP is very high (2323 K) & It is bed conductor of electricity in fused state.

So Al₂O₃ is mixed with Na₃AlF₆ or CaF₂. Which lowers the MP (1173 K) & make alumina conducting.



Note : During electrolytic reduction of aluminum, the carbon anodes are replaced from time to time because oxygen liberated at the carbon anodes react with anode to form CO & CO₂.

Electrolytic refining of AI :

	Hoop's process : For electrolytic refining of AI, Hoop's process is used.							
	Anode	\Rightarrow	Impure Al	-				
	Cathode	e ⇒	Pure Al					
	Electrol	yte ⇒	Fused salt of A	Aluminium	n Fluoride			
Note :T	Note : The fused material remain in three different layer & remain separated because all the layer have different						different	
	density.							
	Anode	node \Rightarrow Al(melt) \longrightarrow Al ³⁺ + 3e ⁻						
	Cathode \Rightarrow Al ³⁺ + 3e ⁻ \longrightarrow Al							
	From anode (bottom layer), AI passes into solution as Al3+ ions and then from solution (middle layer)						dle layer)	
	these Al ³⁺ ion pass to cathode (top layer) and get reduced to pure metal.							
	Extract	ion of Na : Th	ne fused mixture	e of NaC	I and CaCl ₂ is t	aken in Down	's cell which co	onsists of
	circular	iron cathode a	ind carbon ano	de. On p	assing the elect	ric current the	following reacti	ions take
	place :							
	Ionisation of NaCl : NaCl = Na ⁺ + Cl ⁻							
	Collection of Na at cathode : $Na^+ + e^- \rightarrow Na(Reduction)$.							
	Collection of Cl_2 at anode : $Cl^- + e^- \rightarrow Cl$ (Oxidation), $Cl + Cl \rightarrow Cl_2$.							
	Na can	also be obtaine	d by electrolysir	ng molten	NaOH in Castne	er's cell.		
		olved Ex	amples —					
Evamn	lo-5		rities present in	Rauvita a	ro ·			
Lvamp	16-0	(A) CuO		(B) ZnC)	(C) Fe ₂ O ₃	(D) S	biO ₂
Solutio	c) C) Red Bauxite contains Fe_2O_3 as impurity. (D) white Bauxite contains SiO_2 as impurity.				ty.			
		mereiore, (C)	and (D) are con		15.			
Examp Solutio	 Which metals are generally extracted by the electrolytic reduction and why? Sodium, aluminium, magnesium etc. are extracted by the electrolytic reduction of their fused salts because being more reactive and electropositive elements they themselves acts as strong reducing agents. Hence they can not be extracted by any of the chemical methods. 				eir fused as strong			

THERMODYNAMICS OF EXTRACTION : ELLINGHAM DIAGRAM OF A METAL Ellingham Diagram



Thermodynamic of extraction :

For a Proces to be spontaneous ΔG must be negative.

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

(i) $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \Rightarrow \Delta S = +ve$
 $T^{\uparrow} \Rightarrow T\Delta S^{\uparrow} \Delta G^{\downarrow}$
(ii) $C(s) + O_2(g) \longrightarrow CO_2(g) \Delta S = 0$
 $T^{\uparrow} \Rightarrow T\Delta S = 0 \Rightarrow \Delta G$ Constant
(iii) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g) \Delta S = -ve$
 $T^{\uparrow} \Rightarrow T\Delta S^{\downarrow} \Rightarrow \Delta G^{\uparrow}$
 $\Delta G^{=0} \qquad \Delta G^{=0$

$$\begin{array}{ll} XM(s) + \frac{Y}{2} \, O_{_2}(g) \longrightarrow M_{_X}O_{_Y}(s) \\ \text{number of gaseous moles decreae with progress of reaction.} \\ As & \Delta S = -ve & \text{If } T\uparrow \Rightarrow \Delta G\uparrow \end{array}$$

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Important Points

- (1) Below 710°C, CO is better reducing agent than C.
- (2) All the graphs are upgrowing and on increasing temperature, ΔG of formation of metal oxide become less negative, while on increasing temperature, ΔG of C \longrightarrow CO reaction become more negative SO, C can reduce any metal from their metal oxide.
- (3) Temperature above which ΔG of formation of metal oxide become positive, metal oxide become unstable & it decomposes into metal & oxygen.
- (4) Theoritically, all metal oxide can be decomposed to give metal & oxygen, if suficiently high temperature is applied.
- (5) When plot of one metal oxide is below the others then former metal is capable of reducing the later metal oxide into their metal.

Some important result

- (1) All the three oxidation graph of carbon system are above the oxidation graph of ZnO upto temperature 1000°C. At this temperature C is thermodynamically capable of reducing ZnO to Zn. So C is better reducing agent for ZnO to Zn than CO.
- (2) Below 1500°C temperature, the graph of MgO lies below the graph of Al_2O_3 , so below this temperature AI cannot reduce MgO, but above this temperature graph of Al_2O_3 shifts below the graph of MgO so above 1500°C, AI can reduce MgO.



Solved Examples -

Example-7	The reaction $\operatorname{Cr}_2 \operatorname{O}_3 + 2\operatorname{Al} \longrightarrow \operatorname{Al}_2 \operatorname{O}_3 + 2\operatorname{Cr}$ ($\Delta \operatorname{G}^0 = -421 \text{ kJ}$) is thermodynamically
	feasible as is apparent from the Gibb's energy value. Why does it not take place at room temperature ?
Solution	Certain amount of activation energy is essential even for such reactions which are thermodynamically feasible, therefore heating is required.
Example-8	Is it true that under certain conditions, Mg can reduce AI_2O_3 and AI can reduce MgO? What are those conditions ?
Solution	Below 1350°C Mg can reduce AI_2O_3 and above 1350°C. Al can reduce MgO as evident from the Ellingham diagram.

Metallurgy of Some Important Metals

1. Extraction of iron (Fe)

Ore: Haematite



Oxide ores of iron, after concentration through calcination / roasting in reverberatory furnace (to remove water, to decompose carbonates and to oxidise sulphides) are mixed with lime stone and coke and fed into a Blast furnace from its top with the help of a cup and cone arrangement. Here, the oxide is reduced to the metal.

Thermodynamics helps us to understand how coke reduces the oxide and why this furnace is chosen. One of the main reduction steps in this process is :

$$FeO(s) + C(s) \longrightarrow Fe(s/l) + CO(g)$$
(11)

It can be seen as a couple of two simpler reactions. In one, the reduction of FeO is taking place and in the other, C is being oxidised to CO :

When both the reactions take place to yield the equation (10), the net Gibbs energy change becomes:

Naturally, the resultant reaction will take place when the right hand side in equation (14) is negative. In ΔG^{0} vs T plot representing reaction (12), the plot goes upward and that representing the change C CO (C,CO) goes downward. At temperatures above 1073K (approx.), the C,CO line comes below the Fe,FeO line

 $[\Delta G_{(C, CO)} < \Delta G_{(Fe, FeO)}]$. So in this range, coke will be reducing the FeO and will itself be oxidised to CO. In a similar way the reduction of Fe₃O₄ and Fe₂O₃ at relatively lower temperatures by CO can be explained on the basis of lower lying points of intersection of their curves with the CO, CO₂ curve in the given figure.

In the Blast furnace, reduction of iron oxides takes place in different temperature ranges. Hot air is blown from the bottom of the furnace and coke is burnt to give temperature upto about 2200K in the

lower portion itself. The burning of coke therefore supplies most of the heat required in the process. The CO and heat moves to upper part of the furnace. In upper part, the temperature is lower and the iron oxides (Fe_2O_3 and Fe_3O_4) coming from the top are reduced in steps to FeO.



Reactions involved : The reactions proceed in several stages at different temperatures. Since the air passes through in a few seconds, the individual reactions does not reach equilibrium.

At 500 – 800 K (lower temperature range in the blast furnace)

$$3 \operatorname{Fe}_2 \operatorname{O}_3 + \operatorname{CO} \longrightarrow 2 \operatorname{Fe}_3 \operatorname{O}_4 + \operatorname{CO}_2$$

$$\operatorname{Fe}_3 \operatorname{O}_4 + \operatorname{CO} \longrightarrow 3\operatorname{Fe} + 4 \operatorname{CO}_2$$

$$\operatorname{Fe}_2 \operatorname{O}_3 + \operatorname{CO} \longrightarrow 2\operatorname{FeO} + \operatorname{CO}_2$$

At 900 – 1500 K (higher temperature range in the blast furnace):

С

+
$$CO_2 \longrightarrow 2 CO$$
; FeO + CO \longrightarrow Fe + CO_2

Limestone is also decomposed tom CaO which removes silicate impurity of the ore as slag. The slag is in molten state and separates out from iron.

$$CaCO_3 \longrightarrow CaO + CO_2$$
; $CaO + SiO_2 \longrightarrow CaSiO_3$

Note : (1) CaSiO₃ is used in cement industry or used in making building material.

(2) Slag CaSiO₃ is lighter than molten Iron, get collected above it and protect iron from oxidation.

<u>**Pig Iron</u>** : Iron obtained from blast furnance contain 4%C & smaller amount of impurities of S , P , Si , Mn.</u>

<u>Cast Iron</u>: Made by melting pig iron with scarp iron & coke & blast of hot air is passed through the molten mass. Contain about 3% carbon.

<u>Wrought Iron</u>: Purest form of iron prepared from cast iron by oxidising impurities in a reverbertory furnance lined with haematite. It have carbon about 0.1 to 0.21%

Note : (1) In steel making pure O_2 is poured into molten metal where all impurities are converted to oxides then

forming slag (basic oxygen) .

- (2) Steel making process, from iron is an oxidation process.
- (3) In production of steel from haematite ore involve first reduction & oxidation chemical process.

2. Extraction of Copper

 (i) From Cuprous oxide Sulphide ore are roasted to give oxide.
 2 Cu₂S + 3O₂ → 2Cu₂O + 2SO₂ As Cu₂O line in ∆G V/s T graph is almost at top. so it is easily reduce to metal by heating with coke. Cu₂O + C → 2 Cu + CO

(ii) From Copper Glance/ Copper Pyrite [self reduction]

Ore + flux $\xrightarrow{\text{Heated in}}$ Slag + copper matte $\xrightarrow{\text{"reverberatory}}$ furnace" [CuFeS₂] FeSiO₃ [Cu₂S + FeS] (i) 2 CuFeS₂ + 4O₂ \rightarrow Cu₂S + 2FeO + 3SO₂. (ii) Cu₂S + FeO + SiO₂ \rightarrow FeSiO₃ + Cu₂S Fusible slag Matte



Reverberatory furnace

* Chemical composition of matte = (Mostly Cu₂S + some FeS)

 $\begin{bmatrix} Copper & matte \\ + & \\ SiO_2 \end{bmatrix} \xrightarrow{Bessemer convertor} Cu$ $2 \text{ FeS} + 3O_2 \rightarrow 2 \text{ Fe} + 2 \text{ SO}_2 ,$ $FeO + SiO_2 \rightarrow FeSiO_3 \text{ [Slag]}$ $Cu_2S + 3O_2 \rightarrow 2 \text{ Cu}_2O + 2 \text{ SO}_2$ $2 \text{ Cu}_2O + \text{Cu}_2S \rightarrow 6 \text{ Cu} + SO_2 \text{ [Self Reduction]}$



Bessemer convertor

Note : Solidified copper has blistered appaerance due to evolution of SO₂ so called as blister copper.

(iii) From Low Grade Ore

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⇒ From low grade ore , Cu is extracted by hydrometallurgy. (leaching)

(a) Low grade ore of Cu

Cu<sub>2</sub>O (Cuprite)

Cu<sub>2</sub>S [Copper glance] + \xrightarrow{dil. H_2SO_4} CuSO<sub>4</sub>

Cu(OH)<sub>2</sub> . CuCO<sub>3</sub> (Malachite)

(b) CuSO<sub>4</sub> \longrightarrow Cu

(i) Electrolysing or(ii) Metal displacement with Fe

Electrolytic Refining [Cu is purified by electro refining]

Anode ⇒ impure Cu & cathode = pure Cu.

Electrolyte ⇒ aqueous solution of CuSO<sub>4</sub> :
```



The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper. For the purpose of heating, the oxide is made into brickettes with coke and clay.

 $ZnO + C \xrightarrow{Coke, 1673 K} Zn + CO$

The metal is distilled off and collected by rapid chilling.

Note :

ZnO may be reduced by carbon monoxide at 1473 K (i.e. 1200° C) in smelter. The reaction is reversible, and the high temperature is required to move the equilibrium to the right. At this temperature the Zn is gaseous. If the gaseous mixture of Zn and CO₂ was simply removed fom

the furnace and cooled, then reoxidation of Zn would occur. Thus the zinc powder obtained would contain large amounts of ZnO.



5. Extraction of tin from cassiterite (SnO₂)

- (i) Washing with water \Rightarrow To remove silicious impurities.
- (ii) Electromagnetic sepration \Rightarrow To remove magnetic impurity of wolframite.

(iii) Roasting

(a) To remove volatile impurities S as SO_2 As as AS_2O_3 and Sb as Sb_2O_3 .

(b) ore contain impurites of CuS & FeS which are $CuS + 2O_2 \longrightarrow CuSO_4$, FeS + $2O_2 \longrightarrow FeSO_4$ converted to their sulphate

- (iv) Leaching \rightarrow CuSO & FeSO₄ dissolve in water.
- (v) Washing \rightarrow Ore is washed with running water. obtained orecontain 60-70% SnO₂ & called as Black Tin.
- (vi) Smelting : SnO_2 is reduced by Carbon.

Product contain traces of Fe which is removed by passing air through molten mixture. SnO_a + C \longrightarrow Sn + CO

$$SnO_2 + C \longrightarrow Sn + C$$

 $2Fe + O_2 \longrightarrow 2FeO$

Tin Stone



6. Extraction of Magnesium :

(i) From Carnallite :

The ore is dehydrated in a current of hydrogen chloride and the mixture of fused chlorides is electrolysed.

(ii) From Sea water (Dow's process) :

Sea water contains 0.13% magnesium as chloride and sulphate. It involves following steps.

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaCl_2$$

(b) Preparation of hexahydrated magnesium chloride : $Mg(OH)_2 + 2HCI(aq) \longrightarrow MgCI_2 + 2H_2O$

The solution on concentration and crystallisation gives the crystals of MgCl₂.6H₂O

(c) Preparation of anhydrous magnesium chloride :

 $MgCl_{2}. \ 6H_{2}O \xrightarrow{\Delta \ (calcination)}{Dry \ HCl(g)} MgCl_{2} + 6H_{2}O$

It is not made anhydrous by simple heating because it gets hydrolysed

MgCl₂. $6H_2O \xrightarrow{\Delta} MgO + 5H_2O + 2HCl$

(d) Electrolysis of fused anhydrous MgCl₂:

Magnesium chloride obtained by any of the above methods is fused and mixed with sodium chloride and calcium chloride in the temperature range of 973 - 1023 K. The molten mixture is electrolysed. Magnesium is liberated at the cathode (iron pot) and chlorine is evolved at graphite anode.



At cathode : $Mg^{2+} + 2e^{-} \longrightarrow Mg(99\% \text{ pure})$;

At anode : $2CI^{-} \longrightarrow CI_{2} + 2e^{-}$

A stream of coal gas is passed through the pot to prevent oxidation of magnesium metal. The magnesium obtained in liquid state is purified by distillation under reduced pressure. (1 mm of Hg at 873 K).

7. Extraction of gold and silver (MacArthur-Forrest cyanide process) :



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8. Extraction of Gold & Silver

MacArthur-forrest Cyanide process

(A) From native ore :

(i) Complex formation with CN⁻ in presence of air

 $Ag + CN^{-} + O_2 \longrightarrow [Ag(CN)_2]^{-} (aq)$

In this process, air is used which oxidises metal M(Ag/Au) to $M^{+}(Ag^{+}/Au^{+})$ which form complex with CN^{-} ion.

(ii) Metal displacement with Zn

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

This is leaching (Hydro Meltallurgy) process.

(B) From Argentite ore

Extraction of Ag from Argentite ore by dissolving in NaCN and then using metal displacement is leaching process, which is an example of hydrometallurgy.

 Ag_2S (conc. ore) + 2 NaCN \rightarrow 2AgCN + Na₂S

Role of air : As $Ag_2S \& AgCN$ are in equilibrium , air oxidise

Na₂S to Na₂SO₄ & shift the equilibrium right.

 $4 \text{ Na}_2\text{S} + 5\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Na}_2\text{SO}_4 + 4 \text{ NaOH} + 2\text{S}$

AgCN + NaCN \rightarrow Na [Ag(CN)₂] " soluble complex "

2 Na $[Ag(CN)_2]$ + Zn $[dust] \rightarrow 2 Ag + Na [Zn (CN)_4]$

9. Extraction of Mercury



Purification or Refining of Metal Physical Method :

(1) Liquiation Process :

Based on difference in melting point of metal and impurity. This process is used for purification of those metal which have low melting point than each of impurities associated with metal.

Used for Purification of

(i) Impure tin metal (ii) Impure zinc (spelter)

Spelter \Rightarrow 97 % to 98 % zinc is known as spelter.

(iii) For removing Pb from Zn – Ag alloy.

(2) Fractional Distillation process

Used for purifying those metal which are easily volatile, while impurities present in it are not used for purifying Zn, Cd & Hg.

(3) Zone refining of metal

Principle : Based on principle that an impure molten metal on gradually celling will deposit crystal of pure metal while the impurity will be left in the remaining part of molten metal.

*This method is used when metal is required in very high purity.

Mainly used for purification of Si & Ge.



Note : High purity of metal can be obtained by zone refing method , if impurities have lower melting point.

(4) Chromatographic method

Principle : Based on the principle of adsorption. *Different component of a mixture are differently adsorbed on an adsorbent.



Fig. Schematic diagrams showing column chromatography

Chemical Method

(1) Oxidative Refining

Used when impurities present in metal are easily oxidised by oxygen. Mainly used for refining \Rightarrow Pb , Ag , Cu , Fe In this method , molten impure metal is subjected to oxidation. (i) Bessemerisation [Purification of Iron]

Mainly used for manufacture of steel from cast iron.
Haematite ore Sentence in Pachatemin pig iron
$$\frac{O_{2}}{Oudetion}$$
 steel
P is also oxidise to P₂O₁₀ (*P*)
P₄ (*P*) + 5O₂ → P₂O₁₀ (*P*)
6 CaO (g) + P₂O₁₀ (*P*) → 2 Ca₃ (PO₂)₂ (*P*)
Thomas Slag
Which is used as fertilizer.
(i) Cupellation (Removal of lead)
Mainly used to remove Pb from Ag or Au.
Poling Process
This method is used for purification of those impure metal which contain their own oxide as one of the
impurities.
Eg. (a) Purification of Cu.(b) Purification of impure Tin.
Electrolytic refining
Metal, Cu., Ni & Al refined electrolytically.
The anode mud obtained in the electrolytic refining has
Electrolytic refining Anode Mud
(i) Lead Ag, Au, Sb, Cu.
(ii) Cu Ag, Au, Pt.
(iii) Ag Au, Pt.
(a) Extraction of Nickel [Mond's Process]
Used for purification (refining) of Ni.
Ni form complex with Co. [Ni(CO)], which volatilized
[BP=43°] & then decompose at 200°C in Ni & CO.
Ni_{log} + 4 CO $\xrightarrow{00°C} \rightarrow Ni + 4 CO.$
readily volatile
(BP=43°] & then decompose at 200°C in Ni & CO.
Ni_{log} + 4 CO $\xrightarrow{00°C} \rightarrow Ni + 4 CO.$
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readily volatile
(BP=43°] & then decompose at 200°C in Ni & CO.
Ni_{log} + 4 CO $\xrightarrow{00°C} \rightarrow Ni + 4 CO.$
Tungater Flamment Ti + 21₂

Example-11	Sketch an electrolytic cell suitable for electroplating a silver spoon. Describe the electrode and				
	the electrolyte. Label the anode and cathode, and indicate the direction of electron and ion flow.				
	Write balanced equations for the anode and cathode half reaction.				
Solution	Anode : $Ag(s) \longrightarrow Ag^{+}(aq) + e^{-}$				
	Cathode : Ag ⁺ (aq) + e ⁻ \longrightarrow Ag(s)				

The overall reaction is transfer of Ag metal from silver anode to the silver spoon.



KROLL'S PROCESS :

 $\begin{array}{l} \text{TiCI}_{_{4}} + 2 \text{ Mg} & \xrightarrow{1000-150^{\circ}\text{C}} \text{Ti} + 2 \text{ MgCI}_{_{2}} \text{ (Kroll's process)} \\ \text{TiCI}_{_{4}} + 4 \text{ Na} & \xrightarrow{\text{under atmosphere of Ar}} \text{Ti} + 4 \text{ NaCI (Imperial metal industries (IMI) process)} \end{array}$

NaCl is leached with H_2O . Ti is in the form of small granules. These can be fabricated into metal parts using "powder forming" techniques and sintering in an inert atmosphere. Zr is also produced by Kroll's process.

VAPOR PHASE REFINING :

(i) Extraction of Nickel (Mond's process) :

Nickel is extracted from sulfide ore by roasting followed by reduction with carbon, but the process is complicated by the fact that nickel is found in association with other metals. The refining is rather unusual, for nickel forms a complex with carbon monoxide tetracarbonylnickel (O) [Ni(CO)₄]. This substance is molecular in molecular in structure and readily volatilized (boiling point 43°C). It is made by heating nickel powder to 50°C, in a stream of CO and then decomposed at 200°C. Any impurity in the nickel sample remains in the solid state and the gas is heated to 230°C, when it decomposes, giving pure metal and CO, which is recycled. Ni(CO)₄ is gaseous and may be produced by warming nickel with CO at 50°C.

 $H_0O(g) + C \longrightarrow CO(g) + H_0$

The sequence of reaction is

$$Ni(s) + 4 CO(s) \xrightarrow{50^{\circ}C} [Ni(CO_4)] (g)$$
$$[Ni (CO)_4](g) \xrightarrow{200^{\circ}C} Ni + 4CO(g)$$

(ii) Van Arkel–De Boer process :

Small amounts of very pure metals (Ti, Zr, or Bi) can be produced by this method. This process is based on the fact that iodides are the least stable of the halides. The impure element is heated with iodine, producing a volatile iodide, Til_4 , Zrl_4 , or Bil₃. These are decomposed by passing the gas over an electrically heated filament of tungsten or tantalum that is white hot. The element is deposited on the filament and the iodine is recycled. As more metal is deposited on the filament, it conducts electricity better. Thus, more electric current must be passed to keep it white hot. Thus the filament grows fatter and eventually the metal is recovered. The tungsten core is distilled out of the center and a small amount of high purity metal is obtained.

Impure Ti + 2I₂
$$\xrightarrow{50-250^{\circ}C}$$
 TiI₄ $\xrightarrow{1400^{\circ}C}$ Ti + 2I₂
Tungsten filament

The method is very expensive and is employed for the preparation of very pure metal for specific use.

(iii) Parke's process :

The removal of the impurities of Ag from the commercial **lead** is called desilverisation of lead and is done by **Parke's process**. Thus, Parke's process is the desilverisation of lead. In Parke's process, the commercial lead, which contains Ag as impurities, is melted in iron pots and 1% of Zn is added to it. The molten mass is thoroughly agitated. Since Ag is about 300

times more soluble in Zn than in Pb, most of the Ag present in the commercial lead as impurity mixes with Zn, to form Zn–Ag alloy. When the whole is cooled, two layers are obtained. The upper layer contains Zn–Ag alloy in the solid state, while the lower layer has lead in the molten state. This lead contains only 0.0004% of Ag and hence is almost pure. Lead obtained after removing most of Ag from it (desilverisation of lead) by Parke's process, is called desilverised lead. This lead contains the impurities of metals like Zn, Au, Sb etc. These metal impurities are removed from desilverised lead by **Bett's electrolytic process**.

Zn–Ag alloy, formed in the upper layer, is skimmed off from the surface of the molten lead by perforate ladles. This alloy contains lead as impurity. This impurity of Pb is removed from the alloy by **liquation process**, in which Zn–Ag alloy is heated in a slopping furnace, when the impurity of Pb melts and hence drains away from the solid alloy. Thus purified Zn–Ag is obtained. Now Ag can be obtained from this purified Zn–Ag alloy by **distillation process**, in which the alloy is heated strongly in presence of little carbon in a fire–clay retort. Zn, being more volatile, distills off while Ag remains in the retort, carbon used in the process reuses the oxide of Zn, if formed. Ag obtained from Zn–Ag alloy is contaminated with a little of Pb as impurity. This impurity of Pb placed in a cupel (cupel is a boat–shaped) dish made of bone ash which is porous in nature) in a reverberatory furnace and heated in the presence of air. By doing so, lead (impurity) is oxidised to PbO(litharge) which volatilises and pure Ag is left behind in the cupel. Last traces of PbO are absorbed by the porous mass of the cupel.

(iv) **Pudding process :** This process is used for the manufacture of wrought iron from cast iron. We know that cast iron contains the impurities of C, S, Si, Mn and P. When these impurities are removed from cast iron, we get wrought iron. In this process the impurities are oxidised to their oxides not by blast of air but by the haematite (Fe_2O_3) lining of the furnace.

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

- 1. At a site, low grade copper ores are available and zinc and iron scraps are also available. Which of the two scraps would be more suitable for reducing the leached copper ore and why?
- **Sol.** Since zinc lies above iron in electrochemical series, it is more reactive than iron. As a result, if zinc scraps are used the reduction will be faster. However, zinc is a coastiler metal than iron. Therefore, it will be advisable and advantageous to use iron scraps.
- 2. A metal is extracted from its sulphide ore and the process of extraction involves the following steps. Metal sulphide $\xrightarrow{(A)}$ Concentrated ore $\xrightarrow{(B)}$ Matte $\xrightarrow{(C)}$ Impure metal $\xrightarrow{(D)}$ Pure metal Identify the steps (A), (B), (C) and (D).
- **Sol.** (A) Froth floatation process. Sulphide ores are concentrated by froth-floatation process. (B) Roasting. Metal sulphides are roasted to convert into metal oxide and to remove impurities. In roasting; $2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$.

$$2\text{FeS} + 3\text{O}_2 \longrightarrow 2\text{FeO} + 2\text{SO}_2.$$

$$2\text{Cu}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{Cu}_2\text{O} + 2\text{SO}_2.$$

$$\text{FeO} + \text{SiO}_2 \longrightarrow \text{FeSiO}_2.$$

(C) Bessemerisation / self reduction. Reduction of metal oxide by its sulphide takes place in Bessemer converter.

In Bessemerisation ; $2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$ (self - reduction) (D) Electro-refining. Pure metal is obtained at cathode. ; $M^{n+} + n e^- \longrightarrow m$

- Write chemical equations for metallurgical processes to represent :
 (i) roasting of galena (PbS) in limited supply of air at moderate temperature.
 (ii) reduction of Cu₂O using coke as a reducing agent.
- (iii) deposition of pure silver from an aqueous solution of Ag⁺. **Sol.** (i) 2PbS + 30, \rightarrow 2PbO + 2SO, : PbS + 2O, \rightarrow PbSO,

(ii)
$$Cu_{2}O + C \longrightarrow 2Cu + CO$$
 (iii) $Aq^{+} + e^{-} \xrightarrow{(Electrolysis)} Aq \downarrow$ (at cathode)

4. Using data given below, predict whether the reduction of MgO with C is spontaneous or not at 1500°C. $2 C + O_2 \longrightarrow 2 CO$ $\Delta G^{\circ} \approx -530 \text{ kJ}$

 $2 \text{ MgO} \longrightarrow 2 \text{ Mg} + \text{O}_2 \quad \Delta \text{G}^\circ \approx + 730 \text{ kJ}$

or

Sol. The positive value of ΔG° indicates that the reduction of MgO with C dose not occur to a significant extent at 1500°C.

$2 \text{ C} + \text{O}_2 \longrightarrow 2 \text{ CO}$	$\Delta G^{\circ} \approx -530 \text{ kJ}$
$2 \text{ MgO} \longrightarrow 2 \text{ Mg} + \text{O}_2$	$\Delta G^{\circ} \approx$ + 730 kJ
$2 \text{ MgO} + 2\text{C} \longrightarrow 2\text{Mg} + 2\text{CO}$	
$MgO + C \longrightarrow Mg + CO$	ΔG° positive value.

- 5. Sea water $\xrightarrow{(A)} Mg(OH)_2 \xrightarrow{(B)} Mg CI_2$. $6H_2O \xrightarrow{(C)} MgCI_2 \xrightarrow{(D)} Mg + CI_2^{\uparrow}$ Identify the reagents and processes (A) to (D) and give the name of this process.
- **Sol.** MgCl₂ (from sea water) + Ca(OH)₂ (A) \rightarrow Mg(OH)₂ + CaCl₂ ; Mg(OH)₂ + 2HCl (B) \rightarrow MgCl₂ (aq.) + 2H₂O

Crystallisation of MgCl₂(aq) yields MgCl₂.6H₂O

$$\begin{array}{c|c} \mathsf{MgCl}_2 \ \mathsf{6H}_2 \mathsf{O} & \xrightarrow{\mathsf{Calcination} \ (\mathsf{C})} & \mathsf{MgCl}_2 + \mathsf{6H}_2 \mathsf{O} \\ \hline & & & & & & \\ \mathsf{MgCl}_2(\ell) & \xrightarrow{\mathsf{Electrolysis}(\mathsf{D})} & \mathsf{Mg}^{2+} & + & 2\mathsf{Cl}^- \\ & & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\$$

Name of the process is Dow's process.

6. Convert magnesite into anhydrous MgCl₂.

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Sol.	$Mg CO_3 \xrightarrow{\Delta} MgO + CO_2. ;$	MgO +	$C + CI_2 \longrightarrow Mg$	$CI_2 + CO$	
7. Sol.	Which is not the correct process-mineral matching in metallurgical extraction.(A) Leaching : silver(B) Zone refining: lead.(C) Liquation : tin(D) Van Arkel: ZrLead is purified by Electro-refining. Zone refining is used for the purification of Si and Ge.Therefore, (B) option is correct.				
8. Sol.	Tin stone, an oxide or of tin is amphoteric in nature. Explain. Tin stone is cassiterite i.e. SnO_2 . SnO_2 dissolves in acid and alkali both, hence amphoteric oxide. $SnO_2 + 4HCI SnCI_4 + 2H_2O$: $SnO_2 + 2NaOH Na_2SnO_3 + H_2O$				
9.	Select the incorrect statement. (A) In the Bayer's AI_2O_3 goes in to solution as soluble $[AI(OH)_4]^-$ while other basic oxides as TiO_2 and Fe_2O_3 remain insoluble (B) Extraction of zinc from zinc blende is achieved by roasting followed by reduction with carbon. (C) The methods chiefly used for the extraction of lead and tin are respectively carbon reduction and electrolytic reduction.				
Sol.	Lead \rightarrow self reduction; 2PbO + PbS \longrightarrow 3Pb + SO ₂ Tin \rightarrow carbon reduction, SnO ₂ + 2C \longrightarrow Sn + 2CO Therefore, (C) option is correct.				
10. Sol.	Which of the following is not an ore of iron ? (A) limonite (B) cassiterite SnO_2 , cassiterite is an ore of tin. Therefore, (B) option is correct.	(C) mag	gnetite	(D) none of these	
11.	In the extraction of copper from sulphide ore the (A) FeS (B) CO	metal is (C) Cu ₂	formed by reduc S	ction of Cu ₂ O with : (D) SO ₂	
Sol.	$2Cu_2O + Cu_2S \xrightarrow{\Delta} 6Cu + SO_2$. Therefore, (C) option is correct.				
12. Sol.	Which of the following is a carbonate ore ? (A) pyrolusite (B) malachite $CuCO_3.Cu(OH)_2 \longrightarrow$ Malachite. Therefore, (B) option is correct.	(C) dias	pore	(D) cassiterite	
13. Ans. Sol.	Column-I and column-II contains four entries eventries of column-II. Each entry of column-I may of column-II. (A) Pb (B) Cu (C) Zn (D) Fe (pig iron) (A) q, r, s; (B) p, q, r, s; (C) q, r; (D) r; (A) 2PbS + 3O ₂ \longrightarrow 2PbO + 2SO ₂ (Roasting) PbS + PbO ₂ $\xrightarrow{\Delta}$ 2Pb + SO ₂ (Self-reduction (B) 2Cu ₂ S + 3O ₂ \longrightarrow 2Cu ₂ O + 2SO ₂ (Roasting) Cu ₂ S + 2Cu ₂ O $\xrightarrow{\Delta}$ 6Cu + SO ₂ (Self-reduction (C) 2ZnS + 3O ₂ \longrightarrow 2ZnO + 2SO ₂ (Roasting) ZnO + C $\xrightarrow{\Delta}$ Zn + CO (Carbon reduction) (D) Haematite ore is calcined.	ach. Ent y have th (p) (q) (r) (s)	ries of column-I ne matching with Column-II Bessemerisation Roasting Pyrometallurgy Self-reduction m d)	are to be matched with some n one or more than one entries n hethod	
	$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$				

 $\begin{array}{c} \operatorname{Fe_3O_4} + \operatorname{CO} & \xrightarrow{\Delta} & \operatorname{3FeO} + \operatorname{CO_2} \\ \operatorname{FeO} + \operatorname{CO} & \xrightarrow{\Delta} & \operatorname{Fe} + \operatorname{CO_2} \end{array}$