METAL EXTRACTION

Date

Various forms of metals or compounds present in earth's crust are called minerals and minerals from extraction of metal is chemically convenient and economically cheap are called ores.

Q. Which ore contain Cu & Fe both

A) Cuprite Cu_2O (Ruby Copper)
B) Chalcocite Cu_2S (copper glance)
C) Malachite $CuCO_3 \cdot Cu(OH)_2$
D) Chalcopyrite $\cdot CuFeS_2$ ✓

Type of Ores

→ Native Ore - less reactive metals or noble metals are present in elemental form.
For eg - Gold, Platinum, Osmium, Iridium, etc. Some amount of mercury and copper and silver also exist in elemental form.

Gold ores are called alluvial sand or ferrous quartz.

→ Combined Ore
Most of the metals exist in the form of compounds - They are called combined ores
For eg - oxides, sulphides, halides, oxo salt, etc

Haematite - Fe_2O_3 (Fe: III)
Magnetite - Fe_3O_4

$$Fe_2O_3 \cdot FeO$$

(Fe: III, Fe: II)

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Bauxite - $\underline{Al_2O_3 \cdot Al(OH)_3}$

3

$AlO_n(OH)_{3-2n}$

Malachite - $CuCO_3 \cdot Cu(OH)_2$ - green

Azurite - $2CuCO_3 \cdot Cu(OH)_2$ - blue

$CuFeS_2 \longrightarrow Cu_2Fe_2S_4$

I ↙ ↘

Cu_2S Fe_2S_3

II ↙ ↘

FeS FeS_2

Fe^{+2} $^-S-S^-$

ORE

↓ A] Concentration of Ore.

Concentrated Ore

↓ B] Reduction of Ore

$M^{n+} + ne^- \longrightarrow M$

C] Calcination

D] Roasting

Metal

↓ c] Refining of metal

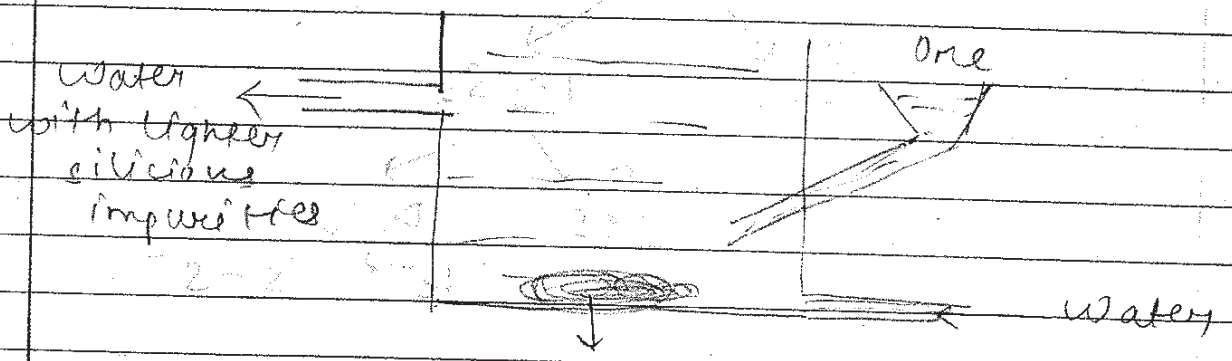
Pure Metal

Date

Concentration of Ore

1] Levigation -

Levigation is just hydraulic washing in which heavy ore particles are separated from lighter siliceous impurities by using water. It is also called gravity separation

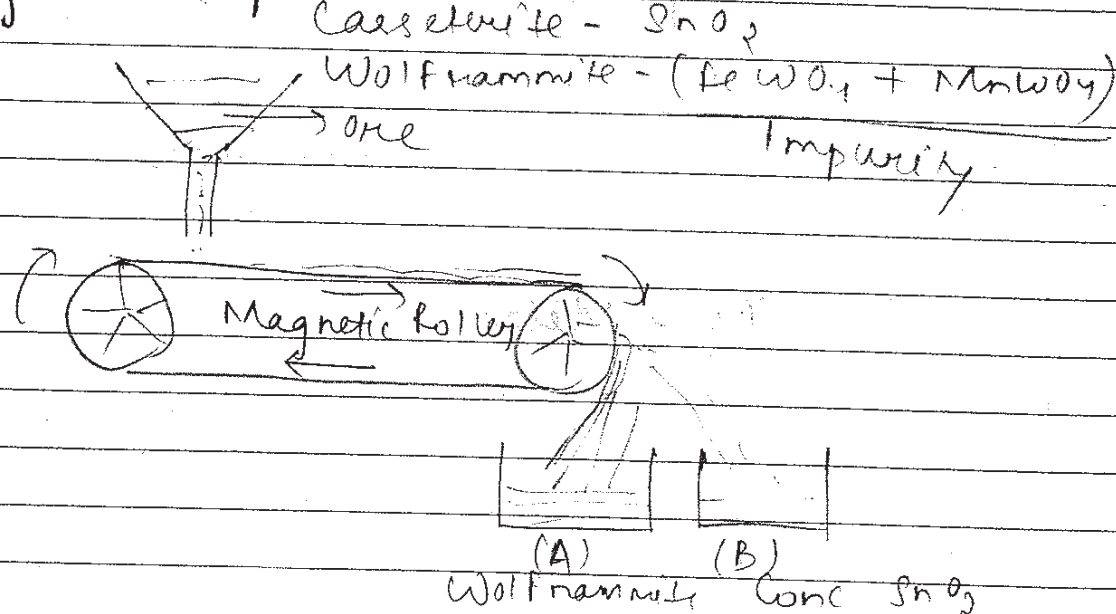


Cr - CrO_4^{2-}

Mo - MoO_4^{2-}

Wolframmate W - WO_4^{2-}

2] Magnetic Separation



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3] leaching

I] For red bauxite (Bayer's Process)

$Al_2O_3 + Fe_2O_3$

$\downarrow NaOH$ (conc)

$Na[Al(OH)_4]_{aq}$; $Fe_2O_3 \downarrow$ residue

$\downarrow CO_2$

$Al(OH)_3 \downarrow + Na_2CO_3\ aq.$

$\downarrow \Delta$

Al_2O_3

$Al_2O_3 + Fe_2O_3 + NaOH \longrightarrow Na[Al(OH)_4] + Fe_2O_3 \downarrow$

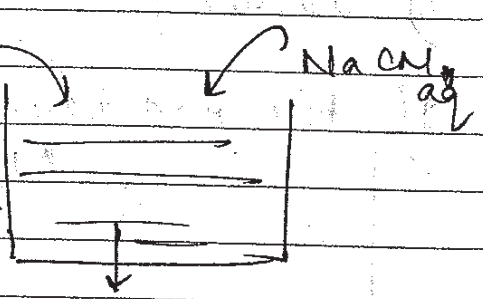
$Al(OH)_3 \downarrow$ gelatinous white $\xrightarrow[\text{(i) } CO_2 \text{ (ii) Excess } H_2O \text{ (iii) } Al(OH)_3 \text{ freshly prepared (seeding)}]{\text{conc. NaOH}}$ $Na[Al(OH)_4]_{aq}$ or $NaAlO_2 \cdot 2H_2O$

$2Na[Al(OH)_4] + CO_2 \longrightarrow Na_2CO_3\ (aq) + Al(OH)_3 \downarrow$

Date

i] Leaching of Gold

$4 \times [Au \rightleftharpoons Au^+ + e^-]$



$O_2 + 4H_2O + 4e^- \longrightarrow 2H_2O + 4OH^-$

$4Au + O_2 + 2H_2O \rightleftharpoons 4Au^+ + 4OH^-$

Water + fine powder of alluvial quartz

$4Au^+ + 8CN^- \longrightarrow 4[Au(CN)_2]^-$

$4Au + O_2 + 2H_2O + 8CN^- \longrightarrow 4[Au(CN)_2]^- + 4OH^-$

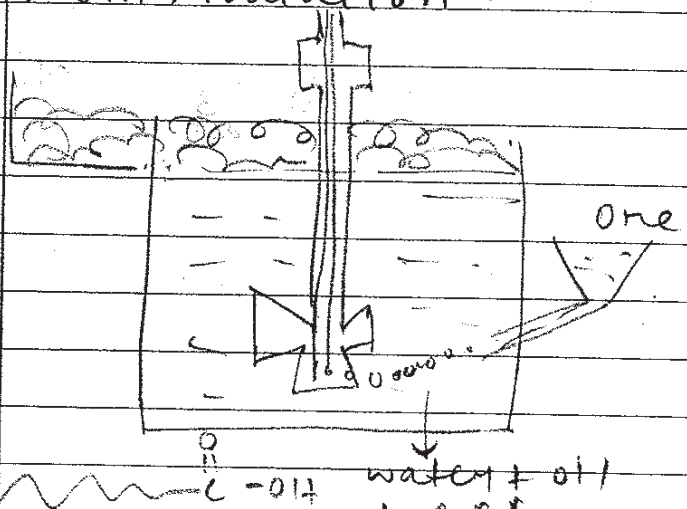
ii] Leaching of Ag -

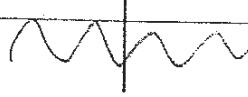
$4Ag + O_2 + 2H_2O + 8CN^- \longrightarrow 4[Ag(CN)_2]^- + 4OH^-$
(native)

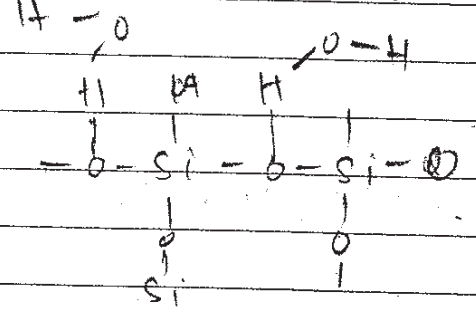
$Ag_2S + 4CN^- \xrightleftharpoons{OH^-} 2[Ag(CN)_2]^- + S^{2-}$

$S^{2-} \xrightarrow{O_2} SO_4^{2-} + (S)$

iv] Froth Floatation -







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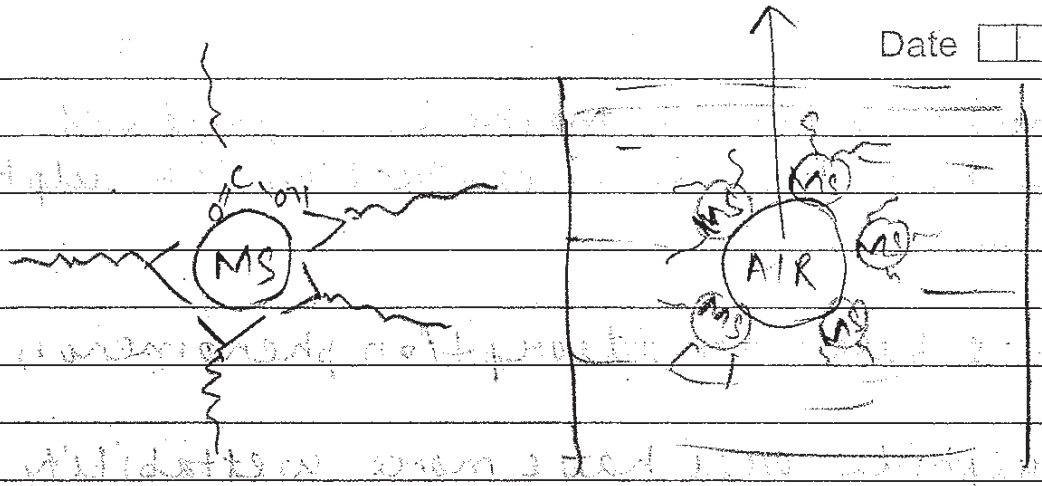
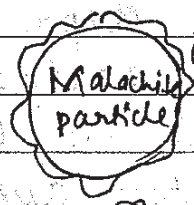


PbS + ZnS
(ORE) (Impurity)

$ZnS + 4CN^- \rightleftharpoons [Zn(CN)_4]^{2-}_{aq} + S^{2-}_{aq}$.
depressant.

$Cu_2S + CuCO_3 \cdot Cu(OH)_2 + K_2S$
(ORE) (Impurity) (activation)



$C_2H_5 - O - \underset{\underset{S}{\|}}{C} - S^{\ominus} Na^+$ (s)

Collection

Oil - Moderate collection but good frothing
Xanthate - Good collection but moderate frothing

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→ Froth floatation method is a physical method for the concentration of sulphide ores

→ It is based on adsorption phenomenon

→ Sulphide ores have more wettability by oil where silica and silicates have more wettability by water

→ During froth floatation process, powdered ore is agitated by compressed air in the mix. of oil and water

→ Sometimes other additives are also required. For eg,

A] Aniline or Cresol as a froth stabilizer
B] NaCN or KCN as a depressant
C] K_2S or Na_2S as a activator when malachite is present in chalcocite.
D] $CuSO_4$ as a activator during the froth floatation of ZnS.

→ Sodium ethyl xanthate used as a collector

→ When two sulphide ores are simultaneously present, one can be separated from other by using suitable depressant or by adjusting the proportion of oil and water

Date

CALCINATION

It is a process of heating ore in absence or limited supply of oxygen for the decomposition purpose.

It is mainly used for carbonate, sulphate, nitrate, hydroxide ores because they get converted to oxide ores on heating.

During calcination ore is heated below its melting because calcinated ore is porous ore which has large surface area.

During calcination, volatile impurities and moisture removed from ore and some other impurities are sublimated for eg. As, Sb, S, etc

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$

Calamine $ZnCO_3$ $\xrightarrow{\Delta}$ $ZnO + CO_2\uparrow$ (wild - white, hot - yellow)

Dolomite $MgCO_3 \cdot CaCO_3$ $\longrightarrow$ $CaO + MgO + 2CO_2\uparrow$ white

Azurite $2CuCO_3 \cdot Cu(OH)_2$ $\longrightarrow$ $2CuO + 2CO_2\uparrow + H_2O$ (black)

Malachite $2CuCO_3 \cdot Cu(OH)_2$ $\longrightarrow$ $2CuO + CO_2\uparrow + H_2O$ (black)

Cerussite $PbCO_3$ $\longrightarrow$ $PbO + CO_2\uparrow$

Anglesite $PbSO_4$ $\longrightarrow$ $PbO + SO_2\uparrow + \frac{1}{2}O_2$

Date

Magnesite ($MgCO_3$) $\xrightarrow{\Delta}$ $MgO + CO_2\uparrow$

$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$

ROASTING

Roasting is the process of heating ore in presence or excess supply of oxygen. This method is mainly used for sulphide ores to convert them into oxide ores.

During roasting, ore is heated below melting point.

During roasting, volatile impurities, moisture are removed from ore. Some other non volatile impurities are removed from ore by the formation of volatile oxides

$Sb_2S_3 + O_2 \longrightarrow Sb_4O_{10}\uparrow + SO_2\uparrow$

$As_2S_3 + O_2 \longrightarrow As_4O_{10}\uparrow + SO_2\uparrow$

$C + O_2 \longrightarrow CO_2\uparrow$

$S + O_2 \longrightarrow SO_2\uparrow$

Non-volatile impurity — Eg:

$PbS + \frac{3}{2}O_2 \longrightarrow PbO + SO_2\uparrow$

$PbS + 2O_2 \longrightarrow PbSO_4$

$ZnS + \frac{3}{2}O_2 \longrightarrow ZnSO_4 + SO_2\uparrow$

$ZnS + 2O_2 \longrightarrow ZnSO_4$

Date

$$Cu_2S + \frac{3}{2}O_2 \longrightarrow Cu_2O + SO_2\uparrow$$
(excess)

$$HgS + \frac{3}{2}O_2 \longrightarrow HgO + SO_2\uparrow$$
(excess)

$$HgO \xrightarrow{\Delta} Hg + \frac{1}{2}O_2$$

Reduction of Ore

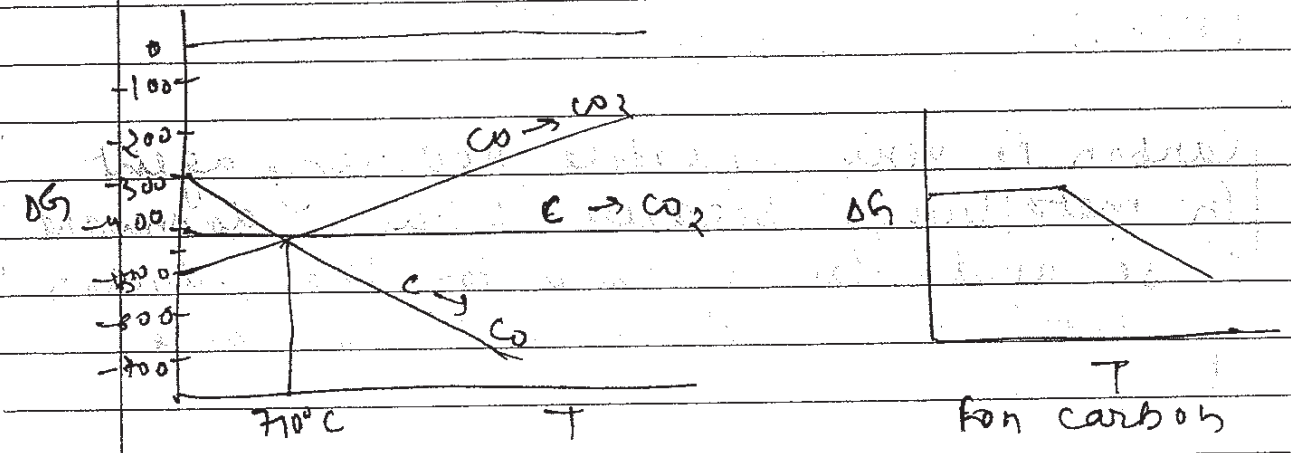
Q. Below 710°C, CO is better reducing agent as compared to C but reverse is true above 710°C. Explain.

I) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta G^\circ = -400$ kJ/mole ($\Delta S^\circ \approx 0$)

II) $2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$ $\Delta G^\circ = -500$ KJ/mol ($\Delta S^\circ = -ve$)

III) $2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{(g)}$ $\Delta G^\circ = -300$ KJ/mol ($\Delta S^\circ = +ve$)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$



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Ellingham Diagram

→ Ellingham Diagram is a graph of ΔG° v/s T for oxide formation rxn of metal with 1 mol O_2.

→ Upward displacement of line shows that when temperature is increased oxide formation tendency of metal decreases

→ Sharp changes in line show phase transition of metal

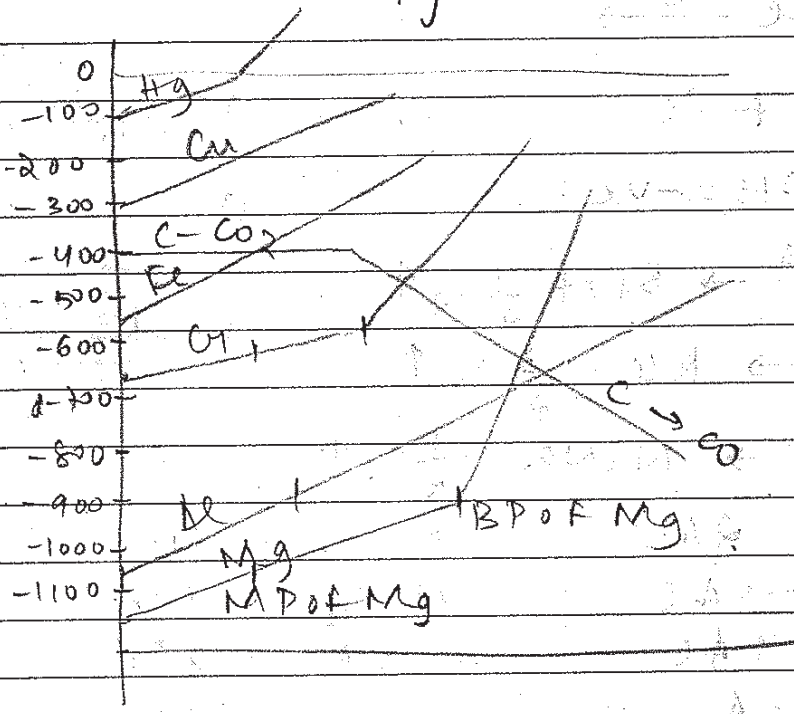
→ Theoritically, all metal oxides are decomposed to metal and oxygen at suitable temperature when ΔG° becomes +ve for oxide formation rxn.
~~Experimentally~~ Practically, it is possible for the oxide of gold, silver, mercury, etc.

→ Metal ~~displaced~~ placed on lower side in Ellingham Diagram can be used for the extraction of metal present in upper side in Ellingham diagram

→ Carbon is very versatile reducing agent in metallurgy because it has downward slope and can be used for the reduction of most of metal oxide at suitable temperature.

Date

→ If any metal contain impurities of other metal which is placed below it in Ellingham diagram can be removed by limited amount of oxygen.



$2M(g) + O_2(g) \longrightarrow 2MO(s)$ $\Delta G = -ve$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$Cr_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + 2Cr$ $\Delta G^\circ = -ve$

$MgO(s) + C(s) \xrightarrow{\approx 2000^\circ C} Mg(g) + CO(g)$

↓

Rapid cooling By inert gas

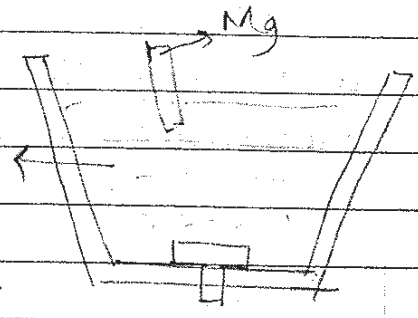
↓

Mg(s)

Date

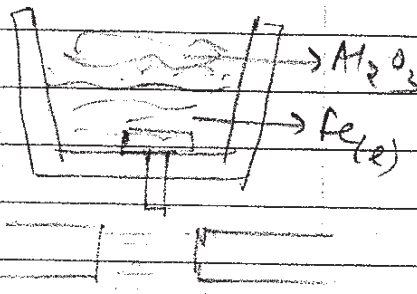
Reduction by Al/Mg

Thermite Process



$Fe_2O_3 + 2Al \xrightarrow{\Delta} Al_2O_3 + Fe$

($\Delta H = -ve$)



$BaO_2 \xrightarrow{\Delta} BaO + \frac{1}{2}O_2\uparrow$

$KClO_3 \xrightarrow{\Delta} KCl + \frac{3}{2}O_2\uparrow$

$NaNO_3 \longrightarrow NaNO_2 + \frac{1}{2}O_2\uparrow$

$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$

$3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn$

$3TiO_2 + 4Al \longrightarrow 2Al_2O_3 + 3Ti$

$3Nb_2O_5 + 10Al \longrightarrow 5Al_2O_3 + 6Nb$

$B_2O_3 + 2Al \longrightarrow Al_2O_3 + 2B$

Kroll's Process –

$TiCl_4 + 2Mg \longrightarrow 2MgCl_2 + Ti$

Self Reduction

Roasting

Eg-1

$2PbS + 3O_2(\text{excess}) \xrightarrow{\Delta} 2PbO + 2SO_2\uparrow$

$PbS + 2O_2 \longrightarrow PbSO_4$

Self Reduction

$2PbO + PbS \xrightarrow[\text{fusion}]{\Delta,\ \text{absence of } O_2} SO_2\uparrow + 3Pb$

$PbSO_4 + PbS \xrightarrow{\Delta} 2SO_2\uparrow + 2Pb$

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Eg2. $Cu_2S + \frac{3}{2}O_2 \xrightarrow[\text{excess } O_2]{\Delta} Cu_2O + SO_2 \uparrow$

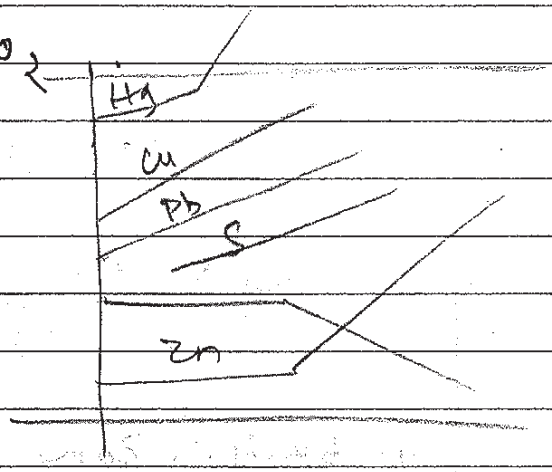
$2Cu_2O + Cu_2S \xrightarrow[\text{absence of } O_2]{\Delta} 6Cu + SO_2 \uparrow$

Blister Cu (98% pure) Main impurity - Cu_2O

Eg-3. $HgS + \frac{3}{2}O_2 \xrightarrow{\Delta} HgO + SO_2$

$2HgO + HgS \longrightarrow 3Hg + SO_2$

$HgO \xrightarrow{\Delta} Hg + \frac{1}{2}O_2$



→ Self reduction method is applicable for those metals which exist in the form of sulphide ores and their position in Ellingham diagram is above sulphur.

→ In this method, ore is roasted to convert it into oxide form and then roasted ore is heated with unroasted ore at high temperature to produce metal.
Reducing Agent → S^{2-}

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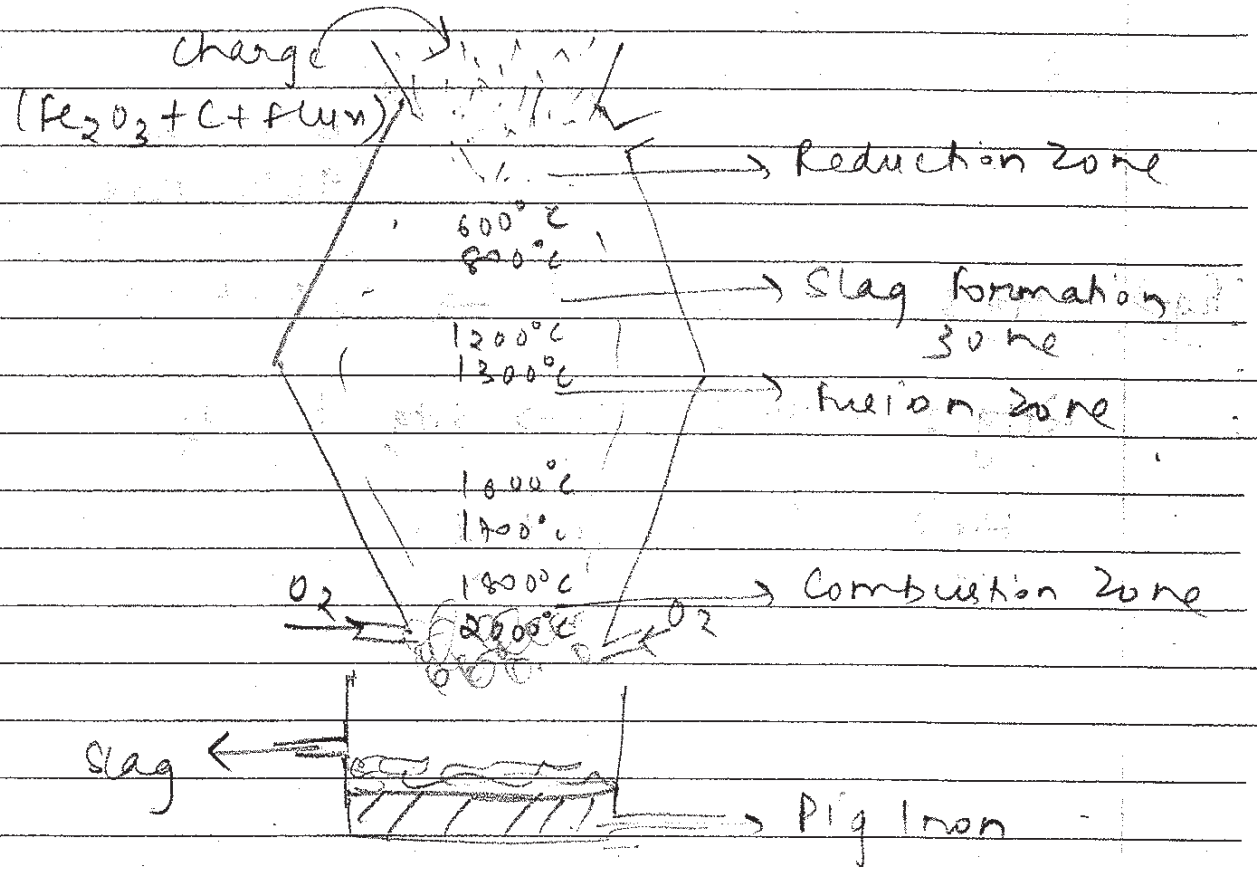
Carbon Reduction Method



Combustion Zone →

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = -ve$$

Above combustion zone ←

$$CO_2 + C \longrightarrow 2CO \qquad \Delta H = +ve$$

Reduction Zone →

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

(Fe_2O_3: Sponge Iron)

$$Fe_2O_3 \longrightarrow FeO \cdot Fe_2O_3 \longrightarrow FeO$$

($FeO \cdot Fe_2O_3$ = Fe_3O_4)

Slag formation Zone →

$$\underset{\text{flux}}{CaCO_3} \xrightarrow{\Delta} CaO + CO_2$$

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

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at high temp -

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO\uparrow$$

(Remaining)

$$MnO + C \xrightarrow{\Delta} Mn + CO\uparrow$$

$$SiO_2 + 2C \xrightarrow{\Delta} Si + 2CO\uparrow$$

$$P_4O_{10} + 10C \xrightarrow{\Delta} 4P + 10CO\uparrow$$

→ Reduction of haematite by C is best example of carbon reduction method

→ In blast furnace major amount of haematite is reduced by CO and converted into spongy iron in reduction zone.

→ In slag formation zone, flux combines with impurities and produce slag. Flux is a substance which is added in ore according to the nature of impurities.

→ Melting point of iron is approx. 1535°C but in blast furnace iron melts at 1300°C due to the presence of impurities

→ At high temperature, remaining amount of haematite is reduced by C.

→ Iron obtained from blast furnace is called pig iron which is almost 96% pure and contain ≈ 4% C as impurity

→ Very small amount of Si, P, S, Mn also present in pig iron

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→ Slag prevent oxidation of iron from atmospheric oxygen.

→ Due to high brittleness pig iron has no commercial uses.

→ On re-melting of pig iron with small amount of scrap iron produce cast iron

→ Impurities in cast iron are almost similar to pig iron but it has lots of commercial uses

→ Above process is also called smelting because molten product is formed along with slag.

4] Metal Displacement in Wakey

3. $Au \xrightarrow[(Air)]{NaCN\ aq.} (P)$

$(P) + Zn \longrightarrow (Q) + Au$

(P) and (Q) are resp

A] $[Au(CN)_2]^+$; $[Zn(CN)_4]^{2-}$

B] $[Au(CN)_2]^-$; $[Zn(CN)_4]^{2-}$

C] $[Au(CN)_4]^-$; $[Zn(CN)_4]^{2-}$

D] $[Au(CN)_2]^-$; $[Zn(CN)_6]^{4-}$

Date

$4Au + 8CN^- + O_2 + 2H_2O \xrightarrow{\text{leaching}} 4[Au(CN)_2]^-_{aq} + 4OH^-$

$4[Au(CN)_2]^- + 2Zn \xrightarrow[\text{water}]{\text{metal disp. in}} 2[Zn(CN)_4]^{2-} + 4Au\downarrow$

dark ppt
amorphous form

$2Ag_2S + 4CN^- \xrightarrow{\text{leaching}} 4[Ag(CN)_2]^-_{aq} + S^{2-}$

$\xrightarrow{H_2O_2/OH^-} SO_4^{2-}$

$+ S$

$4[Ag(CN)_2]^- + Zn \xrightarrow[\text{in water}]{\text{Metal disp.}} 2[Zn(CN)_4]^{2-} +$

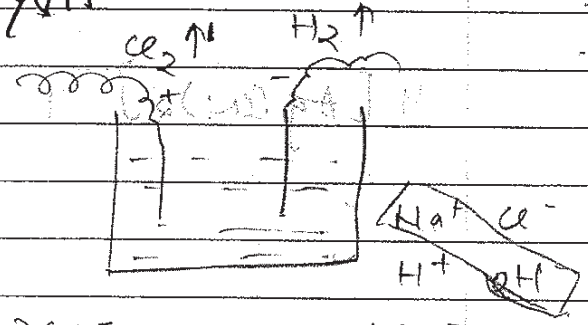
$4Ag\downarrow$
dark ppt

Li
K
Na
Mg
Al
Zn
Fe
Cd
Co
Ni
Sn
Pb
Cu
Hg
Ag
Pt
Au

Date

3. Which is best method for extraction of reactive metals (ie: Na, K, Ca, Mg, etc)

A] Carbon Reduction → Very high temp → Carbides formed
B] Metal displacement in water → It displaces H
C] Electrolysis of aq. salt
D] SHE Reduction
E] Molten Salt Electrolysis



$2Cl^- \longrightarrow Cl_2 + 2e^-$

$2H^+ + 2e^- \longrightarrow H_2\uparrow$

→ Extraction of reactive metals is not possible by carbon reduction because it is very difficult to reduce them by C and if they form under certain conditions, easily combine with C and produce carbides.

→ Metal displacement in water is not possible.. because all the metals react with water and produce H_2.

→ Aq. salt electrolysis produce H_2 at cathode rather than metal.

→ Extraction of reactive metals is best possible by fused salt electrolysis in the presence of suitable impurities

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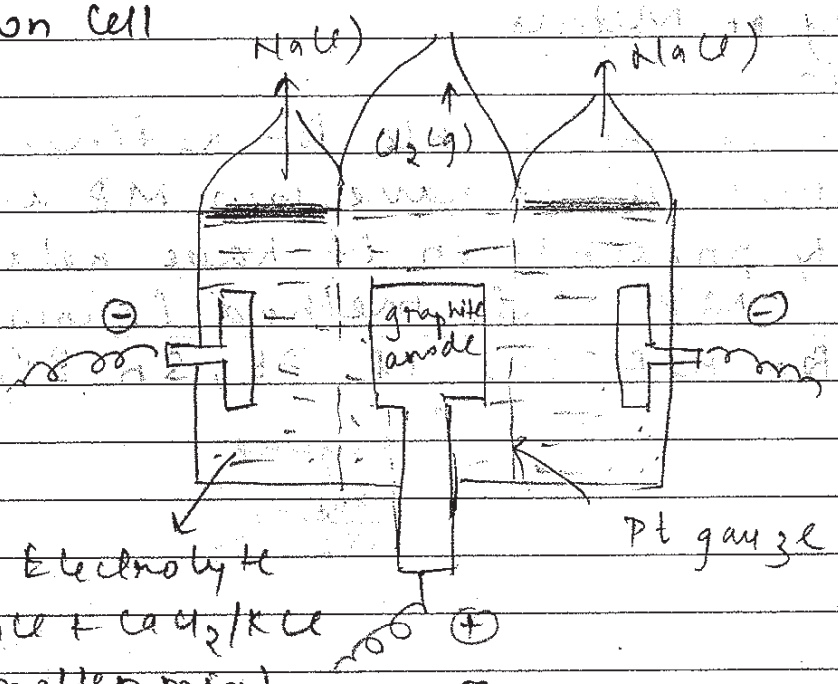
Down cell



⊕ $2Cl^- \longrightarrow Cl_2 + 2e^-$

⊖ $2Na^+ + 2e^- \longrightarrow 2Na(l)$

→ Sodium is extracted by fused salt electrolysis

→ Molten NaCl is used as an electrolyte alongwith the impurity of KCl or $CaCl_2$.

→ Impurity is added to decrease MP of electrolyte

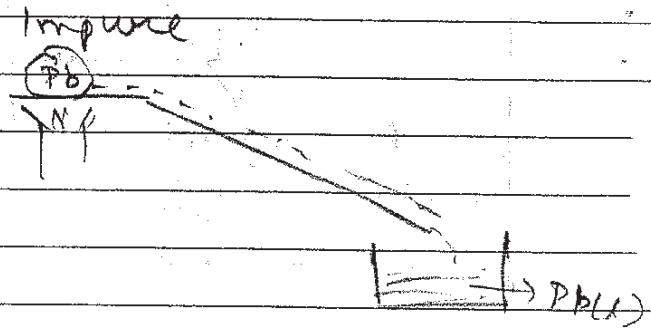
→ Fire which is caused by alkali metals can be extinguished by spray of CCl_4 (pyrine)

Date

Refining of Metals

I] Liquation

Liquation is applicable for refining of metals which have low MP and impurity present in it have relatively higher MP. This method is commercially used for refining of Pb, Sn, Bi, etc.



II] Distillation

Distillation method is based on diff. in BP of metal and impurities

Δ
Spelter (Impure - Zn) ——— above BP of Zn (BP of Zn ≈ 750°C)

Main Imp. - Fe, Pb

Zn(g) —cooling→ Zn(l)

→ Remaining metal Fe, Pb, ——

III] Vapour Phase Refining

Mond's Process -

$$Ni_{(Impure)} + 4CO \xrightarrow{50-60^\circ C} [Ni(CO)_4]\uparrow + Impurity$$

$$[Ni(CO)_4] \xrightarrow[\text{decompose}]{250^\circ C} Ni_{(pure)} + 4CO$$

Date

Van Arkel Method

$Ti + 2I_2 \xrightarrow{\Delta} TiI_4\uparrow + \text{impurity}$

(Impure)

$TiI_4 \xrightarrow{\text{decompose}} Ti + 2I_2$

(pure)

Same for Tl, 2H, Hf

$\left(BI_3 \xrightarrow{\Delta} B + \frac{3}{2}I_2\right)$

→ Vapour phase refining differs from distillation because in distillation, metal is separated from impurities by the vapourisation of metal but in vapour phase, metal is separated from impurities by formation of their volatile compound and metal is recovered by decomposition of that compound

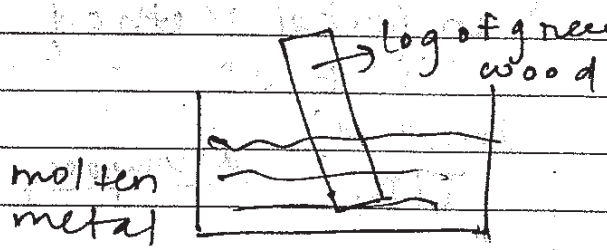
(iv) Polling

→ Polling method is applicable for the refining of metal in which oxide of metal is present as impurity.

→ Hydrocarbon / CO produced by destructive distillation of green charcoal or green wood act as reducing agent for metal oxide.

→ Refining of Cu and Sn is done by this method.

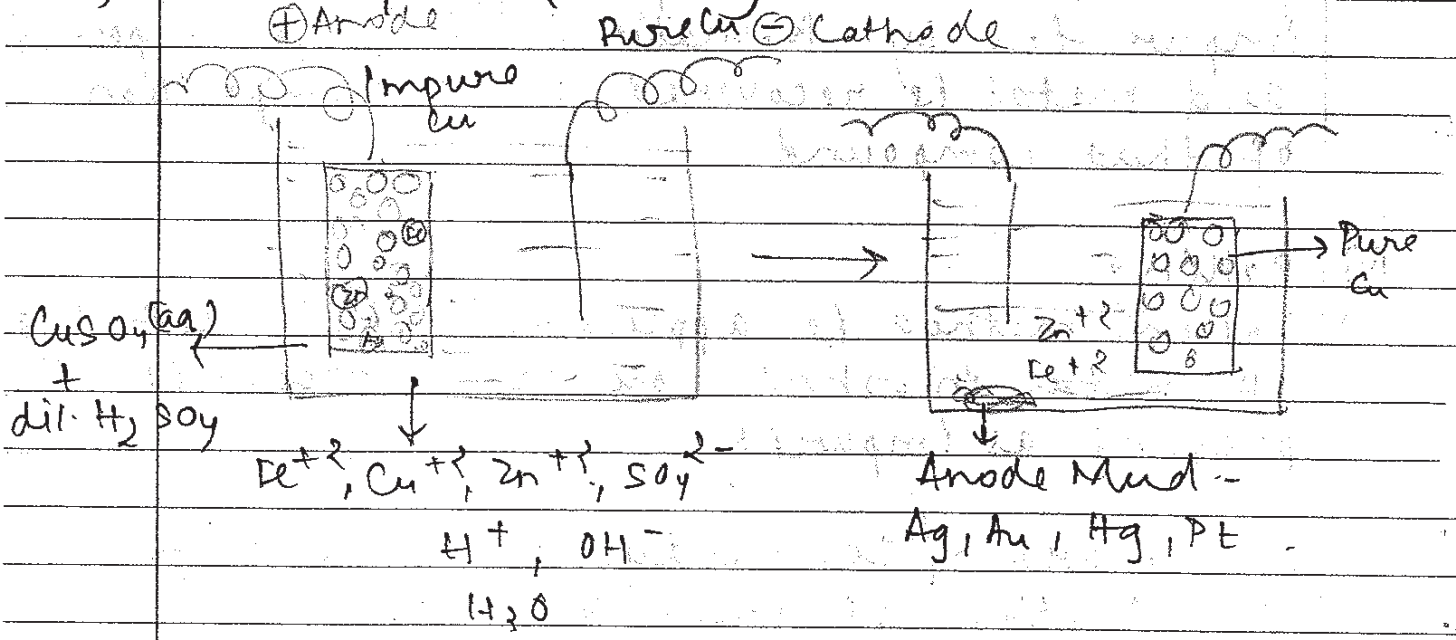
Date



$Cu_2O + CH_4 \longrightarrow Cu + H_2O + CO_2\uparrow$

$SnO_2 + CH_4 \longrightarrow Sn + H_2O + CO_2\uparrow$

5) Electrolytic Refining



⊕ $Zn \longrightarrow Zn^{2+} + 2e^-$

$Fe \longrightarrow Fe^{2+} + 2e^-$

$Cu \longrightarrow Cu^{2+} + 2e^-$

⊖ $Cu^{2+} + 2e^- \longrightarrow Cu$

Anode Mud - Antimony, Selenium, tellurium, silver, gold, platinum

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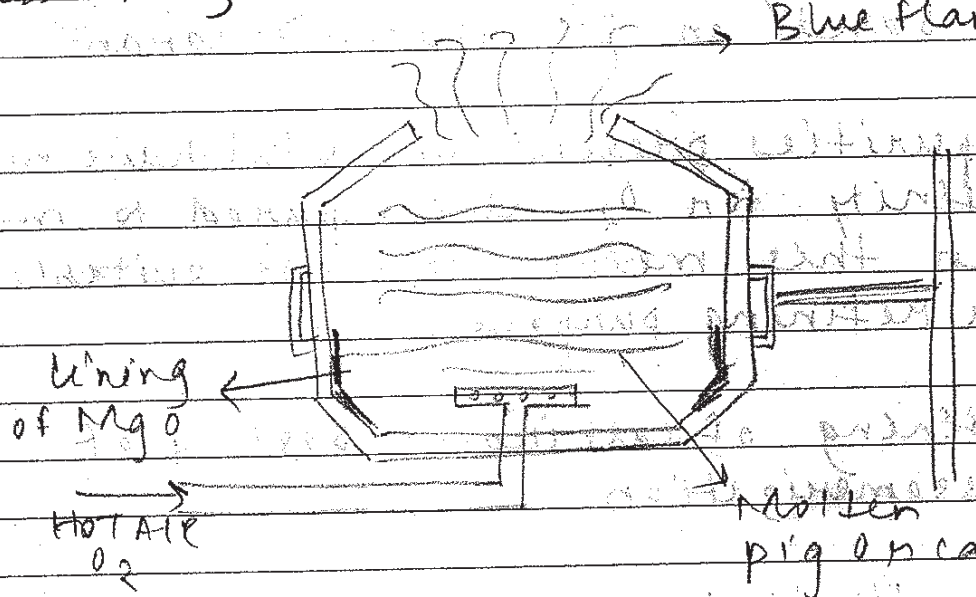
VI) Bessemerization



affinity for O_2 in molten iron :-
Si > Mn > P > C > Fe

$Si + O_2 \longrightarrow SiO_2$

$Mn + \frac{1}{2}O_2 \longrightarrow MnO$

$MnO + SiO_2 \longrightarrow MnSiO_3$ (Slag)

$P + O_2 \longrightarrow P_4O_{10} / P_4O_6$

$CaO + P_4O_{10} \longrightarrow Ca_3(PO_4)_2$ (Thomas Slag)

$C + \frac{1}{2}O_2 \longrightarrow CO\uparrow$

$Fe + O_2 \longrightarrow FeO$ (If any)

$FeO + C \longrightarrow Fe + CO\uparrow$

Specification - Fe + Mn + C

Date

→ Bessemerization process of refining is based on Ellingham Diagram

→ If impurities present in metal have more affinity for O_2 as compared to metal then this method is most suitable for refining purpose.

→ Refining of cast iron is best eg of bessemerization

→ When limited amount of O_2 is passed in molten pig iron, impurities are oxidised before iron and remove in the form of slag.

→ When blue flame at the top of the furnace ceases off, indicates completion of the oxidation of impurities

→ After the removal of impurities, wrought iron is produced

→ Wrought iron is the most pure form of iron. It contain ≈ 0.2% C as impurity

→ When calculated amount of spegiliseon (alloy of Fe, Mn, C) is added in molten wrought iron, steel is produced.

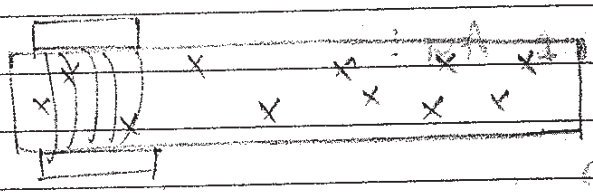
→ Steel is the most important commercial variety of iron in which % of C is almost 2%.

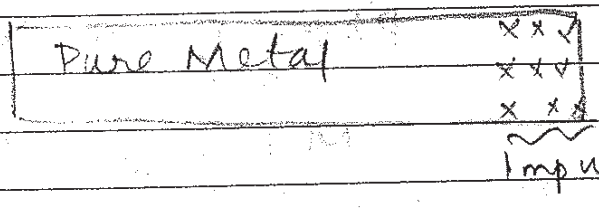
Date

Zone Refining

→ It is based on the fact that impurities have more solubility in molten form of metal as compared to solid or semi-solid form of metal.

→ This method is used to prepare ultra pure form of metal so that specially used to achieve highly pure form of the elements which are used in semiconductors.
Eg - Si, Ge, As, B, Ga, In

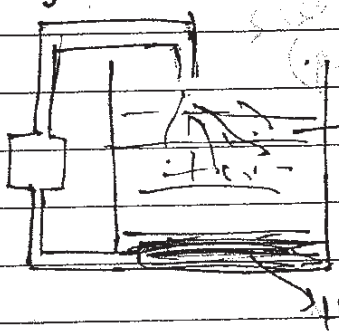




Individual Metallurgy

1] Extraction of gold from alluvial sand or auriferous quartz

A] Amalgamation



$Hg + Au\text{-}ore \rightarrow AuHg$
Amalgam

$AuHg \xrightarrow{\Delta} Hg(g) \xrightarrow{cool} Hg(l)$
$AuHg \xrightarrow{\Delta} Au(s)$

Date

B] Cyanide process -

Hydrometallurgy -

$$4Au + 8CN^- + O_2 + 2H_2O \longrightarrow 4[Au(CN)_2]^-_{aq} + 4OH^-$$

$$4[Au(CN)_2]^-_{aq} + Zn \xrightarrow[\text{disp.}]{\text{metal}} 2[Zn(CN)_4]^{2-} + 4Au\downarrow$$

dark ppt
(main imp = Zn)

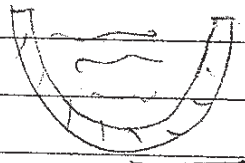
$$Au + Zn \xrightarrow[NaNO_3]{\Delta \text{ with}} Au + ZnO$$

(Imp) Crude metal (scum)

$$2NaNO_3 \longrightarrow Na_2O + N_2 + \frac{5}{2}O_2\uparrow$$

C] Refining of Au :-

(i) Cupellation.



$$Pb + \frac{1}{2}O_2 \longrightarrow PbO\uparrow$$

$$M + \frac{1}{2}O_2 \longrightarrow MO$$

excess O_2

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \xrightarrow{\text{high temp.}} 2NaBO_2 + B_2O_3$$

$$B_2O_3 + MO \longrightarrow M(BO_2)_2$$

(slag)

(ii) Electrolytic Refining

Anode - Impure Au

Cathode - Pure Au

Electrolyte - $H[AuCl_4]_{aq}$ + HCl_{aq}

Date

→ 70 - 80% Au present in slurry is extracted by amalgamation. Remaining amount of Au present in slurry is extracted by cyanide process.

→ Gold obtained by cyanide process is amorphous and contain Zn as a major impurity.

→ Zn is removed by fusion of amorphous gold with chile salt petre ($NaNO_3$).

→ Impurity of lead present in gold is removed by cupelation in the form of PbO

→ In the metallurgy of Au, borax is used as an acidic flux.

→ Purity of gold is increased by electrolytic refining.

2] Extraction of silver from Ag_2S :-

A] Concentration of Ore

(i) By froth floatation

(ii) By CN^- leaching

$$Ag_2S + 4CN^- \rightleftharpoons 2[Ag(CN)_2]^- + S^{2-}$$

$$S^{2-} \xrightarrow{O_2/OH^-} SO_4^{2-}$$

Date

B] Reduction of ore -

$$4[Ag(CN)_2]^-_{aq} + Zn \xrightarrow[disp.]{metal} 2[Zn(CN)_4]^{2-} + 4Ag\downarrow$$

dark ppt

(Main imp = Zn)

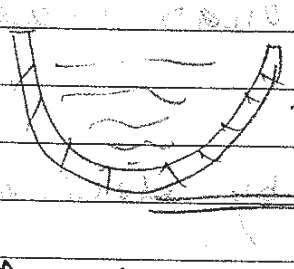
$$Ag + Zn \xrightarrow[HNO_3]{\Delta \text{ with}} Ag + ZnO$$

(Imp) (crude metal) (Scum)

$$2NaNO_3 \longrightarrow Na_2O + N_2 + \frac{5}{2}O_2\uparrow$$

C] Refining of Ag -

(i) Cupelation



$$Pb + \frac{1}{2}O_2 \longrightarrow PbO\uparrow$$

$$M + \frac{1}{2}O_2 \rightarrow MO$$

(ii) Electrolytic Refining

Anode - Impure Ag

Cathode - Pure Ag

Electrolyte - $AgNO_3 aq + HNO_3 aq$

3] Extraction of Al from Bauxite.

$AlO_n(OH)_{3-2n}$

A] Concentration of ore

(i) Bayer's process :- (for red bauxite)

Date

(ii) Hall's Process (Red Bauxite)

$Al_2O_3 + Fe_2O_3 + Na_2CO_3 \xrightarrow[\text{Fused}]{\Delta} CO_2\uparrow + \underset{\text{Basic}}{Na_2O} + Fe_2O_3 + \underset{\text{Amphoteric}}{Al_2O_3}$

(Basic + Amphoteric) ↓

$2NaAlO_2 + Fe_2O_3$

Residue

$NaAlO_2 + Fe_2O_3 \xrightarrow{\text{water}} \underset{\text{soln}}{Na[Al(OH)_4]aq} + \underset{\text{residue}}{Fe_2O_3\downarrow}$

$2Na[Al(OH)_4] + CO_2 \longrightarrow 2Al(OH)_3\downarrow + Na_2CO_3\,aq.$

$2Al(OH)_3 \xrightarrow{\Delta} \underset{\text{(white)}}{Al_2O_3} + 3H_2O\uparrow$

(iii) Serpeck's Method (white bauxite)

$Al_2O_3 + \underset{\text{(main imp.)}}{SiO_2} + 3C + N_2 \xrightarrow{\approx 2000^\circ C} 3CO\uparrow + 2\underset{(s)}{AlN}\downarrow$

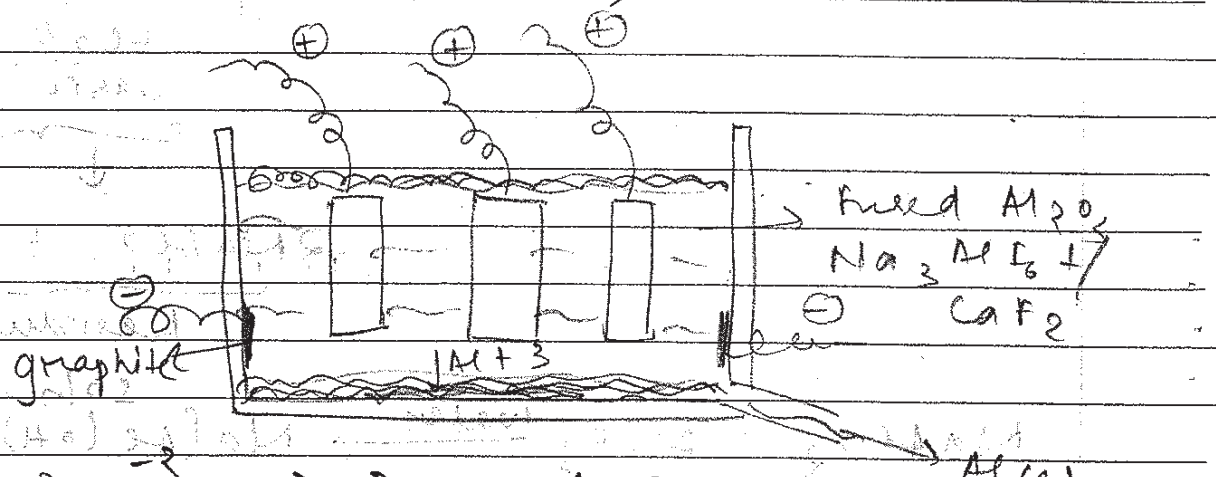
$Cl\uparrow$

$\underset{Al^{3+},\ N^{3-}}{AlN_{(s)}} + 3H_2O \longrightarrow Al(OH)_3\downarrow + NH_3\uparrow$

$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$

Date

B] Reduction of Ore :-
(Hall Heroult Cell)



$$3O^{-2} \longrightarrow \frac{3}{2}O_2 + 6e^-$$

$$C + O_2 \longrightarrow CO_2\uparrow / CO\uparrow$$

$$2Al^{+3} + 6e^- \longrightarrow Al(l)$$

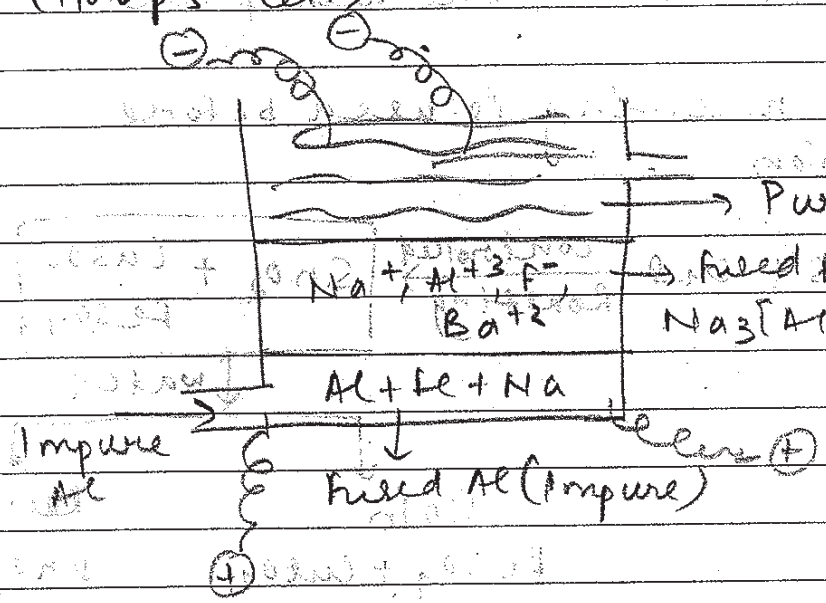
→ In Hall Heroult Cell, Al is obtained by the electrolysis of Al_2O_3 using cryolite and flourspar as impurity.

→ Impurity is added to decrease MP of electrolyte and enhance the electrical conductance

→ During the production of each kg of Al, 0.5 kg C is consumed of graphite anode.

Date

c] Refining of Al:-
(Hoop's cell)



⊕ $3Na \longrightarrow 3Na^+ + 3e^-$

$Al \longrightarrow Al^{3+} + 3e^-$

⊖ $Al^{+3} + 3e^- \longrightarrow Al$

4) Extraction of Sn from Cassetrite:-

A] Concentration of ore:-
By magnetic separation

B] Reduction of ore
(By carbon in blast furnace)

$SnO_2 + 2CO \xrightarrow{\Delta} Sn + 2CO_2\uparrow$

$SnO_2 + 2C \longrightarrow Sn + 2CO\uparrow$

(Main Imp. SnO_2)

C] Refining of metal

I] Polling

II] Liquation

Date

Consider when given in question

→ If Cu & Fe sulphides are also present in ORE

→ Controlled roasting is used before C-reduction

$SnO_2 + FeS + CuS \xrightarrow[\text{Roasting}]{\text{controlled}} \boxed{SnO_2 + CuSO_4 \; FeSO_4}$

↓ water

Soln	Residue
$FeSO_4 + CuSO_4$	$SnO_2 \downarrow$

5] Extraction of Zn from $ZnCO_3$ / ZnS

A) Concentration of ORE :-

I) Froth floatation for ZnS

II) Gravity separation for $ZnCO_3$

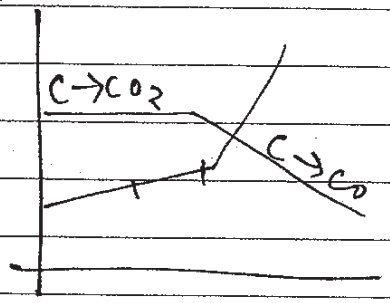
B] Reduction of ORE :-

I) Formation of oxide

$ZnS \xrightarrow[\text{by excess } O_2]{\text{Roasting}} ZnO + ZnSO_4 + SO_2 \uparrow$

$ZnCO_3 \xrightarrow{\text{Calcination}} ZnO + CO_2 \uparrow$

II) Reduction of ZnO :-



$ZnO_{(s)} + C_{(s)} \xrightarrow{1673\,K} Zn \uparrow_{(g)} + CO \uparrow_{(g)}$

Retort furnace →

See from sheet.

Fe_2O_3 - Red brown
Fe_3O_4 - Black
FeS_2 - Golden yellow Date

c) Refining of Zn :-

I) Distillation

II) Electrolytic Refining :-
Anode - Impure Al
Cathode - Al strip
Electrolyte - $ZnSO_4(aq) + H_2SO_4$

→ From Ellingham diagram, it is observed that C is better RA than CO for the reduction of ZnO.

→ From Ellingham diagram it is clear that temperature where ZnO is reduced to Zn by C is higher than the BP of Zn so that Zn is obtained in gaseous form.

→ During the process, ZnO is heated with C upto partial fusion (sintering) in Metort furnace.

6] Extraction of Fe from Haematite

A) Concentration of ORE
I) Magnetic Separation
II) Gravity Separation

B) Reduction of Ore
I) Roasting
Fe_2O_3
$FeO / FeS / FeCO_3 \xrightarrow[\text{excess } O_2]{\text{Roasting}} Fe_2O_3 + CO_2\uparrow + SO_2\uparrow$

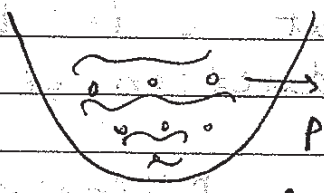
I) Smelting in Blast furnace :-
(Carbon Reduction)

C) Refining of Metal

I) Puddling :- (Open hearth process)
(Impurities are oxidised by Fe_2O_3)

$3Si + 2Fe_2O_3 \xrightarrow{\Delta} 3SiO_2 + 4Fe$

$3Mn + Fe_2O_3 \xrightarrow{\Delta} 3MnO + 2Fe$



$3MnO + 3SiO_2 \longrightarrow 3MnSiO_3$
(Slag)

$P + Fe_2O_3 \longrightarrow P_4O_{10} + Fe$

$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO\uparrow$

II) Bessemerization (Open h.

III) LD Process (Basic Oxygen Process) (BOP)
In this process impurities present in pig iron are oxidised by pure oxygen in a specially designed converter.
All the rxns are similar to bessemerization
It is best method to prepare high grade steel in short interval.

From the all the above methods of refining, wrought iron is produced which is finally converted to steel by the addition of specific.

slag formation alongwith molten pdt - Smelting

Date

7] Extraction of Cu from Chalcopyrite ($CuFeS_2$)

A) Concentration of ore -
By froth floatation

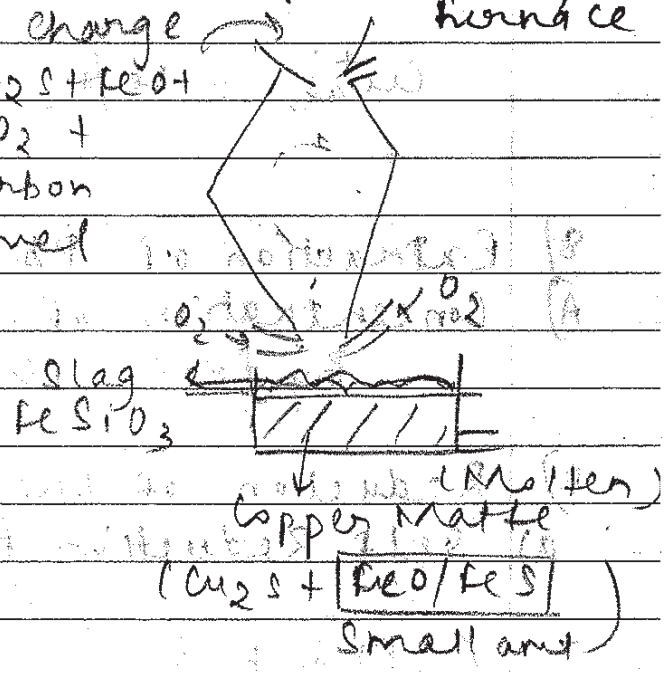
B) Reduction of ore -

I) Partial Roasting -

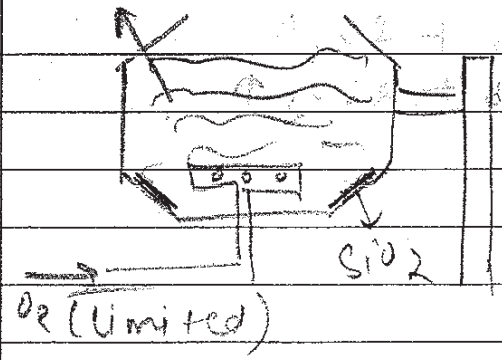
$2CuFeS_2 + 4O_2 \longrightarrow Cu_2S + 2FeO + 3SO_2$
(Limited)

II) Smelting in Blast furnace or Reverberatory furnace

$FeO + SiO_2 \xrightarrow{\Delta} FeSiO_3$
slag



III) Self Reduction in Bessemer Converter



$Cu_2S + \frac{3}{2}O_2 \longrightarrow Cu_2O + SO_2$

$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2\uparrow$

Blister Cu
(98% pure)
(main impurity - Cu_2O)

Date

C] Refining of Metal

I) Poling

II) Electrolytic Refining

NOTE :

Copper is also extracted by some low grade Cu ores by using leaching and metal displacement in water (hydrometallurgy)

$$Cu/Cu_2O/CuCO_3 \cdot Cu(OH)_2 \xrightarrow[\text{or } HNO_3]{\text{bacteria or conc. } H_2SO_4} Cu^{+2}_{aq}$$

$$Cu^{+2}_{aq} + Fe/H_2 \longrightarrow \underset{2H^+}{Fe^{+2}} + Cu\downarrow \quad \text{Reappt}$$

8] Extraction of Pb from PbS

A] Concentration of Ore -

By froth flotation

B] Reduction of Ore -

a) Self Reduction for high grade ~~ore~~ galena.

Excess O_2

$$PbS + \frac{3}{2}O_2 \longrightarrow PbO + SO_2\uparrow$$

$$PbS + 2O_2 \longrightarrow PbSO_4$$

No O_2

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

$$PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2\uparrow$$

Date

b) Carbon Reduction for low grade galena
(Main Impurity = SiO_2)

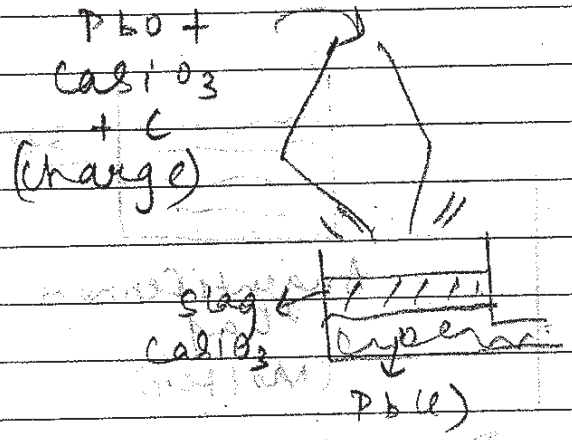
I] Roasting with lime

$$PbS + \frac{3}{2}O_2 \longrightarrow PbO + SO_2$$

$$(PbO + SiO_2 \longrightarrow PbSiO_3) \times X$$

$$CaO + SiO_2 \rightarrow CaSiO_3$$

II] Carbon Reduction in Blast furnace



$$PbO + CO \xrightarrow{\text{Main rxn}} Pb + CO_2\uparrow$$

$$PbO + C \xrightarrow[\text{temp.}]{\text{high}} Pb + CO\uparrow$$

c) Refing of Pb :-

I) Liquation

II) Electrolytic Refining

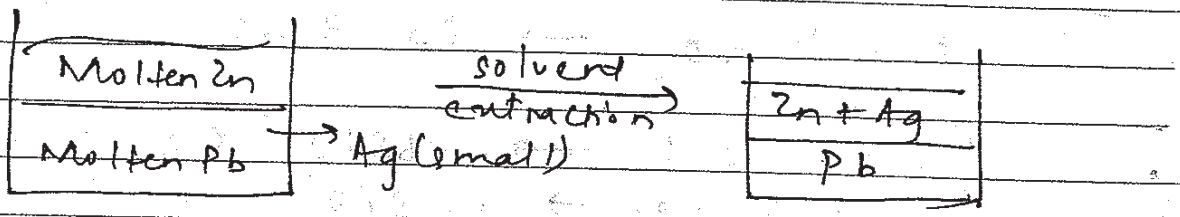
Anode - Impure Pb

Cathode - Pure Pb

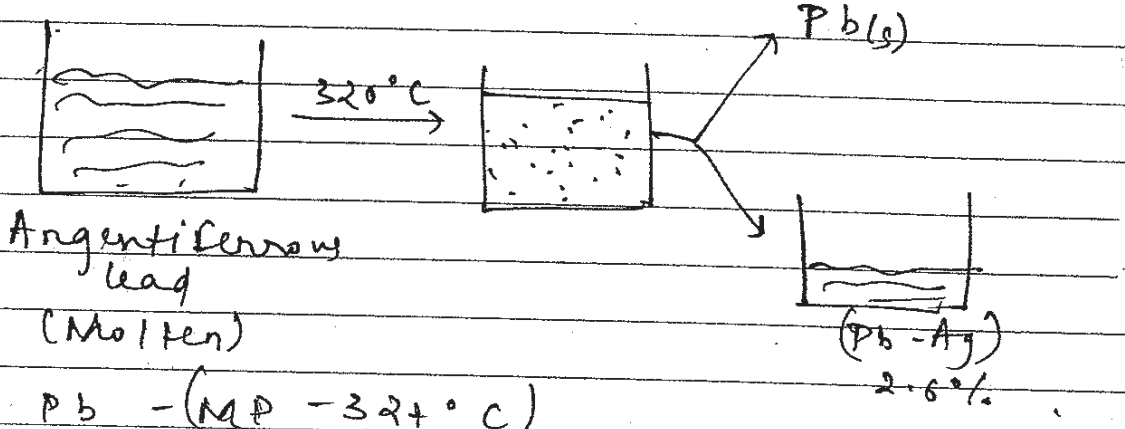
Electrolyte - $PbSiF_6(aq) + H_2SiF_6(aq)$

Desilverization of Argentiferrous lead -

I) Park's process -



II) Pattinson's Process -



Pure Pb - (MP - 327° C)

(Pb-Ag 2.6%) (MP = 303° C)

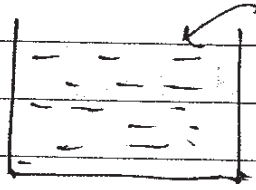
Alloy

Eutectic mix.

8) Extraction of Mg by Dow's sea water process :-

Sea water = 0.13% of Mg as Mg^{+2}

A] Separation of Mg^{+2} from sea water -



$Mg^{+2} + 2\,Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + Ca^{+2}$

white ppt.

Date

B) Preparation of anhydrous $MgCl_2$:

$$Mg(OH)_2 + 2HCl_{conc.} \longrightarrow MgCl_2\,aq + 2H_2O$$

$\downarrow$ crystallization

$$MgCl_2 \cdot 6H_2O(s)$$

$$MgCl_2 \cdot 6H_2O \xrightarrow[\Delta]{\Delta \text{ with excess } HCl(g)} MgCl_2 + 6H_2O\uparrow$$

(anhy.)

C) Extraction of Mg by fused $MgCl_2$ electrolysis

Electrolyte = $MgCl_2$ + $\underbrace{NaCl + CaCl_2}_{\text{impurity}}$

⊕ $2Cl^- \longrightarrow Cl_2 + 2e^-$

⊖ $Mg^{+2} + 2e^- \longrightarrow Mg$

NOTE :

→ All metal hydroxides are water insoluble except hydroxides of (I) A, $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$.

→ Mg is obtained by electrolysis of fused $MgCl_2$ using NaCl and $CaCl_2$ as impurity (to decrease MP of $MgCl_2$ and to increase electrical conductance of electrolyte).

8. Anhyd. $MgCl_2$ is not obtained by direct heating of $MgCl_2 \cdot 6H_2O$. Explain $MgCl_2 \cdot 6H_2O$ on direct heating does not produce pure $MgCl_2$ because of hydrolysis of Mg^{2+}. It also produce MgO in residue.

M1

Date

→ To prepare anhydrous $MgCl_2$, $MgCl_2 \cdot 6H_2O$ is heated with excess current of dry HCl.

→ The problem is also observed during the heating of hydrated halides of Be^{+2}, Mg^{+2}, $AlCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $SnCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$, etc

$$MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} MgCl_2 + Mg(OH)_2 + 2HCl$$

excess dry HCl

$$\downarrow \Delta$$

$$MgO + H_2O$$