THERMODYNAMICS OF REDUCTION PROCESSES (ELLINGHAM DIAGRAM)

The extraction of metals from their oxides using carbon or other metals, and by thermal decomposition, involves a number of points which merit detailed discussion.

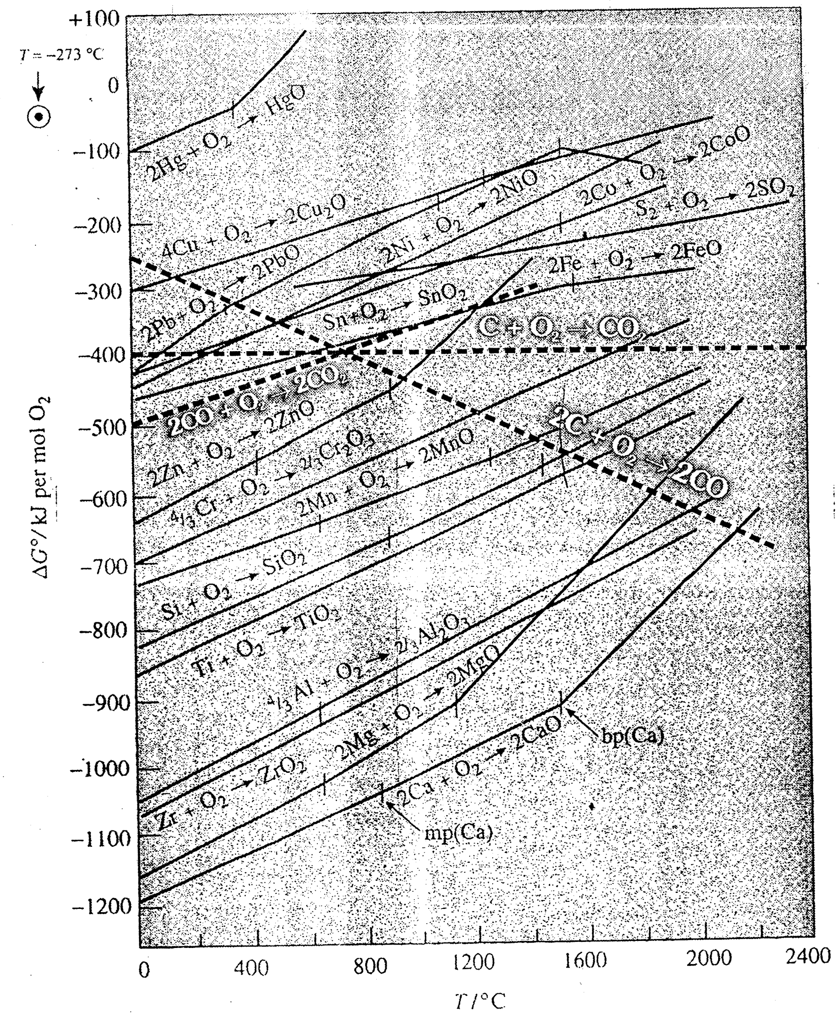
For a spontaneous reaction, the free energy change ΔG must be negative.

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

ΔH is the enthalpy change during the reaction, T is the absolute temperature, and ΔS is the change in entropy during the reaction. Consider a reaction such as the formation of an oxide:

$$M + O_2 \rightarrow MO$$

Dioxygen is used up in the course of this reaction. Gases have a more random structure (less ordered) than liquids or solids. Consequently gases have a higher entropy than liquids or solids. In this reaction S the entropy or randomness decreases, the hence ΔS is negative. Thus if the temperature is raised then $T\Delta S$ becomes more negative. Since $T\Delta S$ is subtracted in the equation, then ΔG becomes less negative. Thus the free energy changed (ΔG) valuc increases with an increase of temperature.



The free energy changes that occur when one gram molecule of a common reactant (in this case dioxygen) is used may be plotted graphically against temperature for a number of reactions of metals of their oxides. This graph is shown in figure and is called an Ellingham diagram (for oxides). Similar diagrams can be produced for one gram molecule of sulphur, giving an Ellingham diagram for sulphides, and similarly for halides.

The Ellingham diagram for oxides shows several important features:

(a) In the graph for metal oxide all slope upwards, because the free energy change increases with an increase of temperature as discussed above.

(b) The free energy changes for all follows a straight line unless the materials or metal get vaporize.

(c) When the temperature is raised, a point will be reached where the graph crosses the $\Delta G = 0$ line and the oxide becomes unstable, and should decompose into the metal and dioxygen.

(d) Any metal (M_1) will reduce the oxide of other metals (M_2) (which lie above it in the Ellingham diagram) because the free energy will become more negative by an amount equal to the different between the two graphs at that particular temperature.

$$M_1 + M_2O \longrightarrow M_2 + M_1O \; ; [\Delta G = -ve] \text{ overall}$$

VIII
Fe Co Ni
Ferous } → platinum

Tc, Pm
Synthetic element
90 naturally occuring

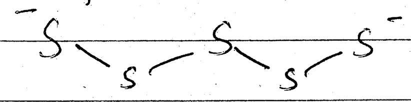
★ Chalcopyrite

$CuFeS_2$
$\downarrow$
$\underbrace{Cu_2Fe_2S_4}$
$\downarrow$
$Cu_2S + Fe_2S_3$
$\downarrow$
$FeS + FeS_2$ → Per sulphide

$(Cu^{+})_2S^{2-} / Fe^{+2}S^{2-} / Fe^{+2} / \bar{S}-\bar{S}$

~~Hf~~ ~~Ta~~ Ir

Pentasulphide ion



METALLURGY

METAL EXTRACTION

- Various compounds and forms of metal present in earth crust are called minerals
- Minerals from which extraction of metal is chemically convenient and economically cheap They are called ores
- All ores are minerals but all minerals are not ores
- Composition Of Earth Crust

  O, Si, Al, Fe, Ca, Mg, Na, K, Ti, H

Universe : H_2
Atmosphere: N_2

- Ores : Malachite $CuCO_3 \cdot Cu(OH)_2$
  basic copper carbonate

Types Of Ore

(1) Native Ore

- Ores in which metal is present in elemental form They are called native ores Rh Os ~~(traces)~~ Cu, Ag, Hg (traces)

~~(2)~~ - Gold, platinum, Pd, ~~Os~~, Ir, etc. are present in native form
- (Cu, Hg, Ag) ~~traces~~ small amount
- Nuggets, oriferrousquartz, etc. are gold
- Metal in its oxidation state 0

- Sandy and rocky particles present in ore are called gangue or matrix

CONCENTRATION
Of ORE

~~(Metal Extr~~

1. Levigation
2. Magnetic seperation
3. froth floatation
4. Leaching

B) Reduction of ore.

I) Calcination
II) Roasting

1. Carbon reduction
2. Reduction by Mg/Al
3. Self reduction
4. Metal displacement rxn.
5. Electrolytic redn.

C) Refining of metal

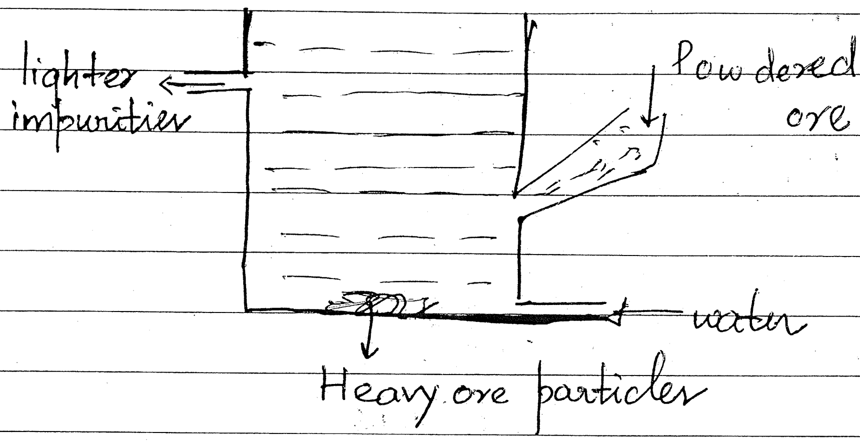
(1) Liquation
(2) distillation
(3) Vapour phase refining
~~(4) Mond's process~~
(4) Besserization
(5) Electrolytic refining
(6) Poling
(7) Zone refining

ORE $\xrightarrow{\text{seperation}}$ Concentrated Ore $\longrightarrow$ Metal $\longrightarrow$ Pure metal

(A) CONCENTRATION Of ORE

(a) ◦ Levigation

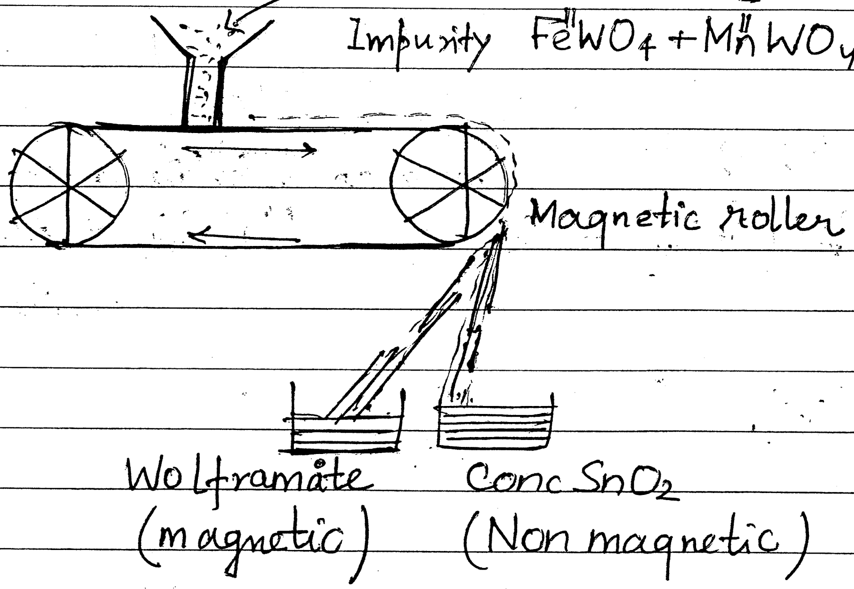
Levigation is just hydraulic washing used to seperate heavy ore particles from lighter silicious impurities



◦ gravity seperation ~~similar~~
◦ ~~were~~ in case of diff in densities of ore and impurities

(b) Magnetic seperation

Ore: Casserite SnO_2
Impurity $Fe^{II}WO_4 + Mn^{II}WO_4$ (Wolframite)
WO_4^{2-}



- White bauxite contains silica as impurity

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(c) Leaching

exp1 : for red bauxite (Baeyer's process)
(main impurity Fe_2O_3)

- Seeding agent

$$Al_2O_3 + Fe_2O_3 \xrightarrow{\text{Conc. NaOH/KOH}} Fe_2O_3 + 2Na[Al(OH)_4]$$

$Na[Al(OH)_4]$ sol^n | Fe_2O_3 residue

$$Al(OH)_3 + \underset{\text{excess}}{NaOH} \underset{\substack{\text{(i) } CO_2 \\ \text{(ii) Excess water ([NaOH]}\downarrow) \\ \text{(iii) fresh } Al(OH)_3}}{\overset{\text{Conc Ex NaOH}}{\rightleftharpoons}} Na[Al(OH)_4]$$

seeding agent. ← (iii) fresh $Al(OH)_3$
(used to initiate backward rxn)

$$2Na[Al(OH)_4] + CO_2 \longrightarrow Na_2CO_3 + \underset{\text{white gelatinous ppt}}{Al(OH)_3\downarrow}$$

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

- method used when one of ores or gangue sensitive to particular chemical

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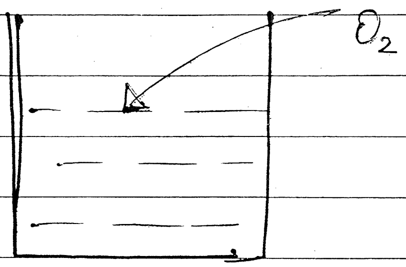
exp2: Leaching
~~ex~~ Au/Ag



Slurry "Au"/OH^-
NaCN

$4e^- + O_2 + 2H_2O \longrightarrow 4OH^-$
$4 \times [Au \longrightarrow Au^+ + e^-]$

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

$4Au + 8CN^- + O_2 + 2H_2O \longrightarrow 4OH^- + 4[Au(CN)_2]^-$ ($\Delta G = -ve$
sol^n

- O_2 oxidise gold due to formation of stable gold complex
- $Ag_2S + 4CN^- \rightleftharpoons 2[Ag(CN)_2]^- + S^{2-}$ (Non spontaneous without oxidation)

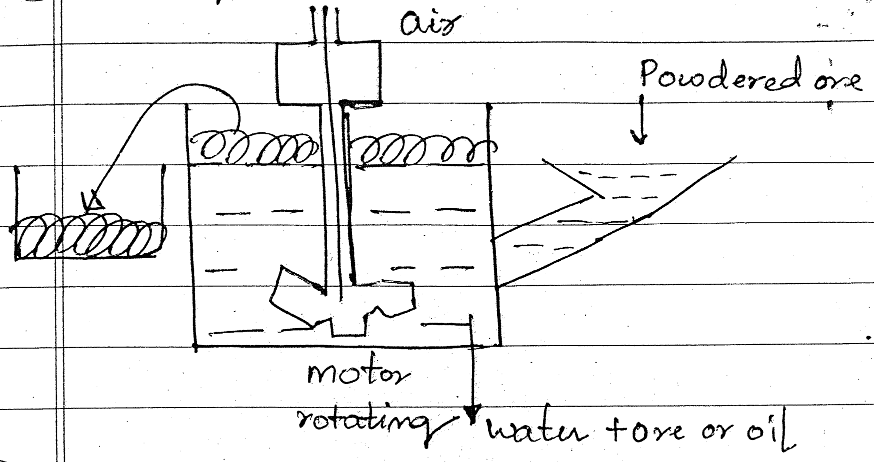
$$S^{2-} \xrightarrow{O_2/OH^-} SO_4^{2-} + S$$

Le Chatelier (Reaction proceeds forward on oxidation of sulphur)

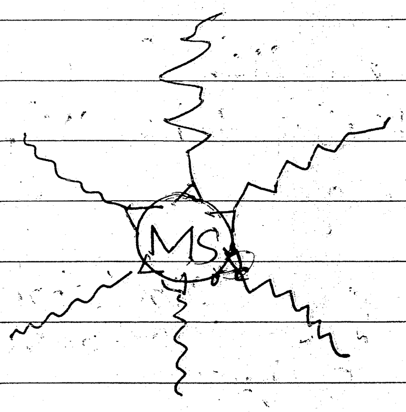
Ex III
all

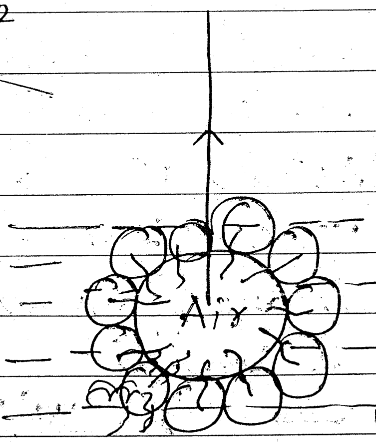
$IA, (NH_4)_2S$ Soluble

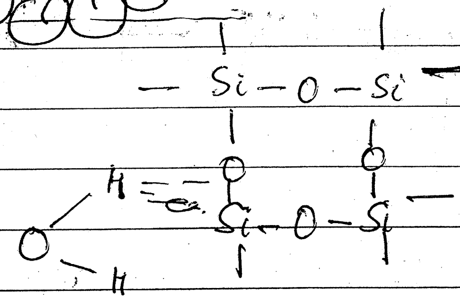
(4) Froth floatation

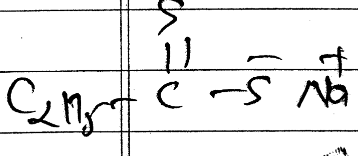


~~$\circ\ Cu_2S + CuCO_3 \cdot Cu(OH)_2 \downarrow K_2S$~~





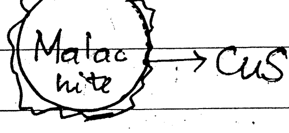




→ ∘ $PbS + ZnS$
(impurity)

$ZnS + 4KCN \longrightarrow K_2[Zn(CN)_4] + K_2S$
(depresent) sol soluble

→ ∘ $Cu_2S + CuCO_3 \cdot Cu(OH)_2$
$\downarrow K_2S$ (activator)



Cohesive force
unstable

frother, collector
to increase
life of surface tension

Silical impurities has greater tendency for water and sulphide particles for oil

- Froth floatation is applied for conc. of sulphide ores at
This method is based on adsorption A surface phenomena
- It is observed that sulphide particles have more affinity for oil but silicates have more affinity for water.
- In froth floatation process powdered ore is compressed with agitate air in mixture of oil and water
- Some other additives are required for eg anniline, cresol used as froth stabiliser
- Sodium ethyl xanthate used as collector because it help to collect sulphide ore on surface of air bubble
- When galena is concentrate by froth floatation method NaCN is added as depressent because it form soluble complex with ZnS
- When two sulphide ores are present, then one is seperated from other by adjusting proportion of oil and water
- When chalcocyste contain impurity as malachite Na_2S added as activator to increase ability for froth formation by malachite (due to formation of CuS coating on surface of malachite powder)
- During froth floatation of ZnS copper sulphate used as activator
- frother and collector both have polar and non-polar part
Oil is a good frother but poor collector Sodium ethyl xanthate is a good collector but poor frother
Small Organic chain and unable to break hydrogen bonding in water

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Processes Before

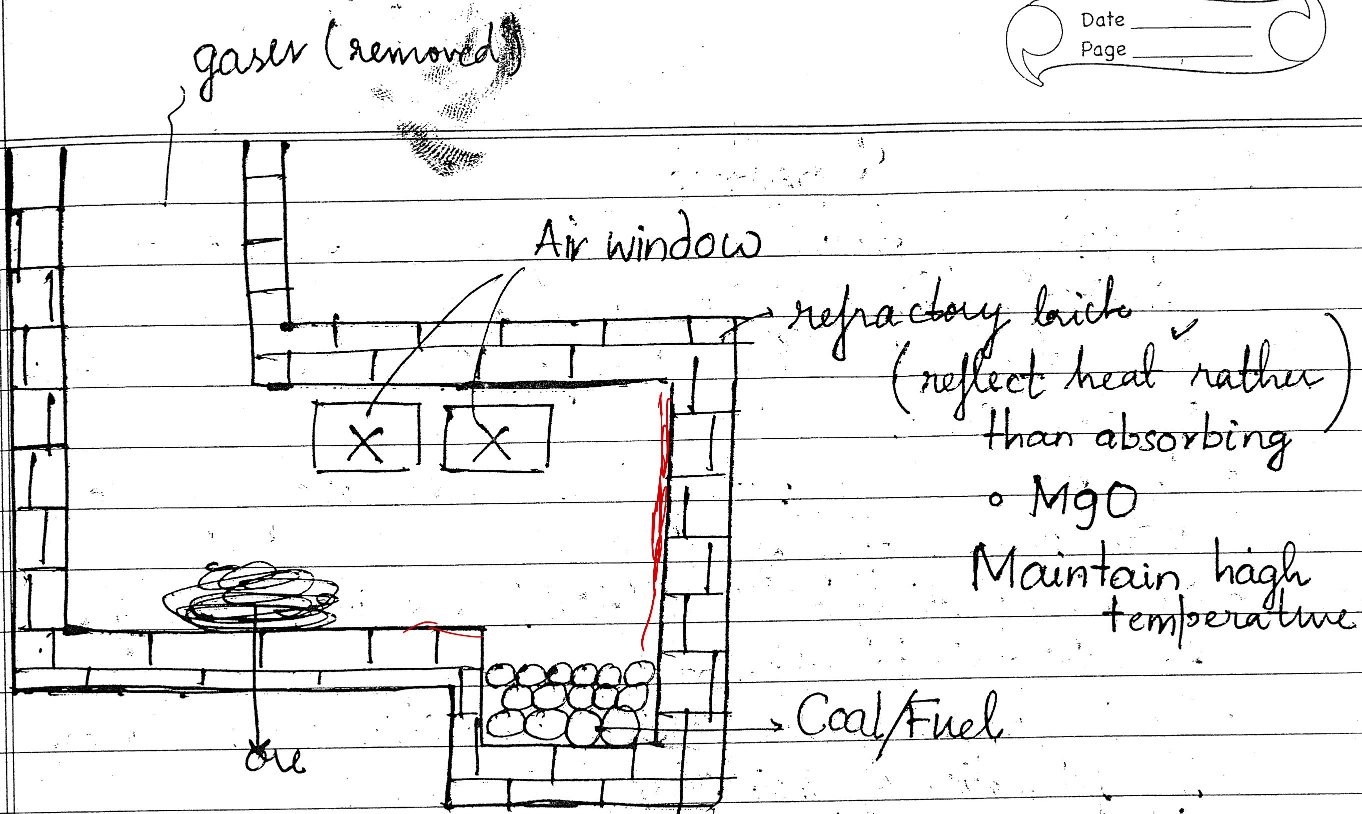
(I) CALCINATION

$$CaCO_{3(s)} \xrightarrow{\Delta} CaO + CO_2$$

(~~Melt first~~ Decompose first before melting)

- Calcination is process of heating ore in limited supply or absence of oxygen
- Process is completed in ~~river~~ revarberratory furnace
- Calcination is used for the conversion of carbonates, sulphate, nitrate, hydroxide ores to oxide ores
- Actually calcination is thermal decomposition of this type of ores
- During calcination ore is ~~maintained~~ heated below melting pt to maintain porocity of ore
- Volatile impurities and moisture removed during calcination
- Some other impurities like elimental sulphur, arsenic sublimate during calcination

Note that process not in equilibrium   Azu (blue)



Revorbaratory furnace

→ Malachite : $Cu(OH)_2 \cdot CuCO_3$ (green) $\xrightarrow{\Delta}$ $2CuO + CO_2 + H_2O$ (black)

→ Azurite (blue) $Cu(OH)_2 \cdot 2CuCO_3 \xrightarrow{\Delta} 3CuO$ (black) $+ 2CO_2 + H_2O$

→ Anglesite $PbSO_4$ (white) $\xrightarrow{\Delta}$ PbO (yellow) $+ SO_2 + \frac{1}{2}O_2$

→ Dolomite $CaCO_3 \cdot MgCO_3 \xrightarrow{\Delta} CaO + MgO + 2CO_2$

→ Calamine $ZnCO_3 \xrightarrow{\Delta} ZnO$ Hot yellow, Cold white

→ Cerrusite $PbCO_3 \xrightarrow{\Delta} PbO + CO_2$

→ limonite $Fe_2O_3 \cdot 3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O$

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

mix. of hydroxide and oxide ores just like bauxite

∘ $Ca(NO_3)_2 \xrightarrow{\Delta} CaO + 2NO_2 + \frac{1}{2}O_2$

Norweigen salt petre

$CO_2 + H_2O$

(I) ROASTING.

- Roasting is process of heating ore in excess ~~absence or limited~~ supply of oxygen.
- This method is mostly used for conversion of sulphide ores to oxide ores
- The process is completely in riverbarratory furnace with excess supply of oxygen
- During roasting ore is heated below its melting to maintain porocity of ore
- During roasting non volatile impurities are removed by formation of their oxide
- Moisture and volatile impurities removed during roasting
- Less reactive metals like mercury, silver, gold etc produce metal when their oxide are heated

In anhydrous form Cu^+ stable

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

  $PbS + 2O_2 \longrightarrow PbSO_4$
- $Cu_2S + \frac{3}{2}O_2 \rightarrow Cu_2O + SO_2$
- $ZnS + \frac{3}{2}O_2 \longrightarrow ZnO + SO_2 \uparrow$
- $HgS + \frac{3}{2}O_2 \longrightarrow HgO + SO_2 \uparrow$

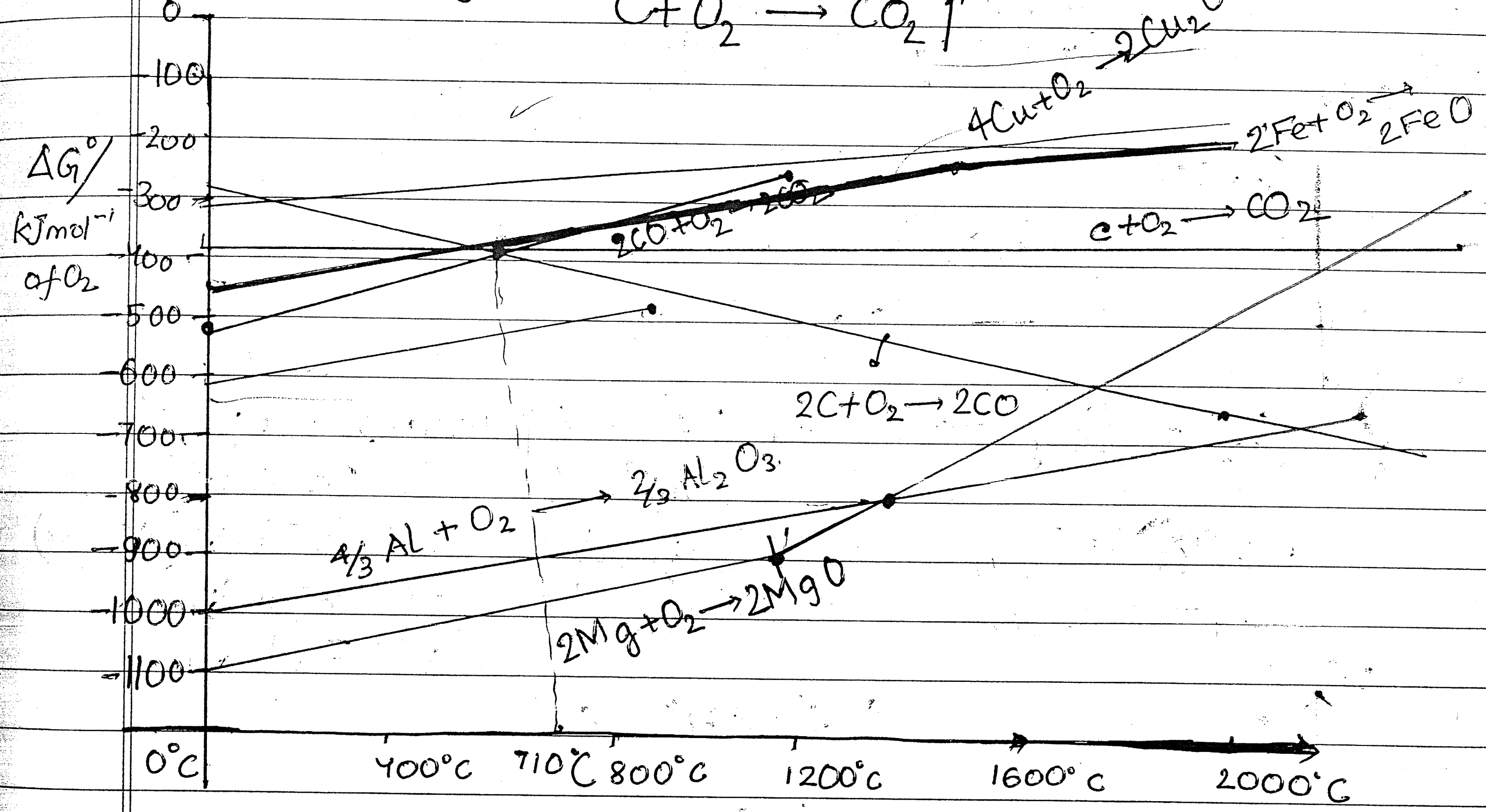
  $HgO \xrightarrow{\Delta} Hg + \frac{1}{2}O_2$

2 Race

• ELLINGHAM DIAGRAM Draw

- $ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$
  (always calcination)
- Roasting of chlorine ~~does not~~ take place
- Non volatile impurities

Non volatile
$$\begin{cases} Sb_2S_3 + O_2 \xrightarrow{\Delta} Sb_2O_5\uparrow + SO_2\uparrow \\ As_2S_3 + O_2 \xrightarrow{\Delta} As_2O_5\uparrow + SO_2\uparrow \\ C + O_2 \longrightarrow CO_2\uparrow \end{cases}$$



Au Ag Al Pb Sn Zn Fe Cu
Mg

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$Au^{+} > Al^{3+}$ (oxidising agent)

(B) Reduction Of Ore

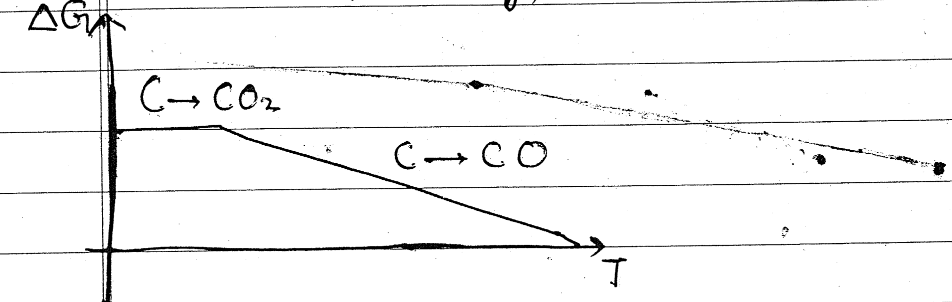
Q Below 710°C carbon mo~~o~~nonoxide is better reducing agent than carbon but reverse is true above 710°C Explain

A

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}$$

water

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$$

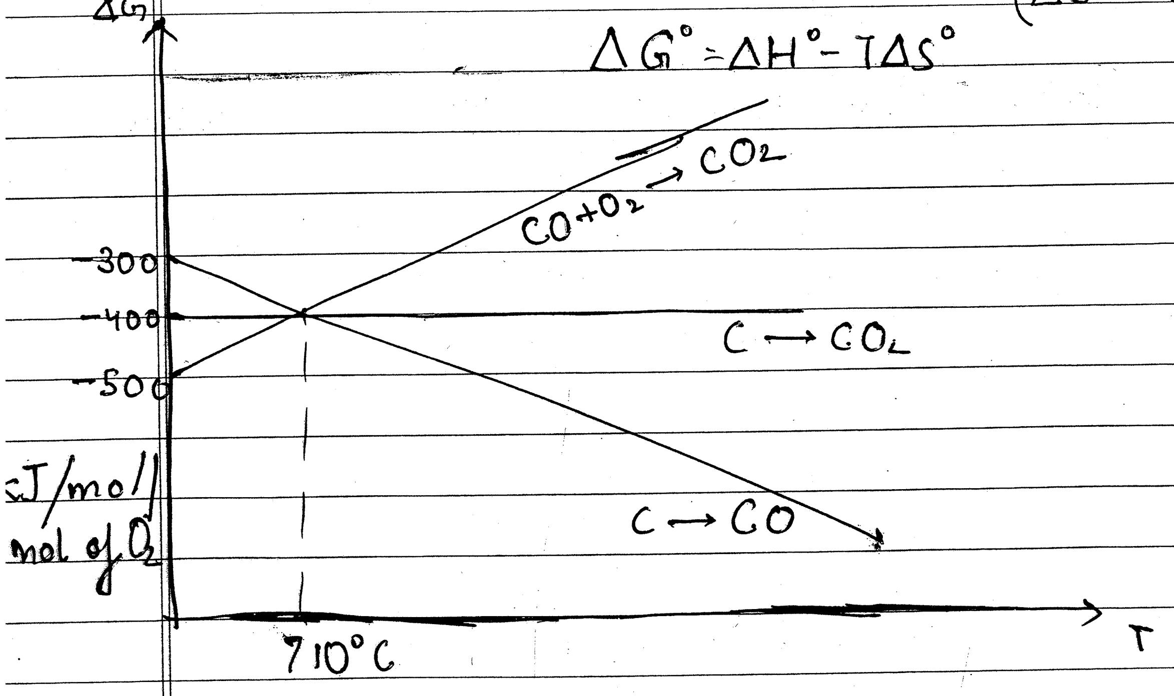


$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta G^{\circ} = -400\,kJ/mol$
$\Delta S^{\circ} \approx 0$ (2kJ/mol)

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

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

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



(2 Diagram)

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* ○ $2M_{(s)} + O_{2(g)} \longrightarrow 2MO_{(s)}$ $\Delta G^\circ = -ve$

($\Delta S^\circ = -ve$)

$\boxed{\Delta G^\circ = \Delta H - T\Delta S}$

$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$ $\Delta G = -ve$

Aluminothermite process

○ $MgO_{(s)} + C_{(s)} \xrightleftharpoons{\text{above } t^\circ C} \underbrace{Mg_{(g)} + CO_{(g)}}$

$\downarrow$ rapid cooling by He/Ne

$Mg_{(s)} + CO_{(g)} \uparrow$

by rapid cooling process becomes irreversible
Hence $Mg_{(s)}$ formed

○ Ellingham diagram is graph of ΔG° vs temperature for rxn of metals with 1 mole O_2

○ Diff metals have diff affinity for oxygen so starting pts diff in Ellingham diagram

○ Reactive metals on lower side and less reactive on upper side

○ Lines of metal in ellingham diagram have upward displacement because oxide formation rxn is not entropy supported *

○ Sharp changes in line of metal indicate phase transition (shown by cuts)

○ Metal placed lower side in Ellingham diagram can be used for ~~redu~~ extraction of metal placed upper side in ellingham diagram

○ Theoretically all metal oxide decompose at suitable temperature to produce metal but practically this method is used for extraction of metal placed upper side in Ellingham diagram (T_{max} is suitable)

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- C is very versatile reducing agent in metallury because of downward displacement of line of carbon
- Ellingham diagram drawn for reversible changes However in blast furnaces irreversible changes may occur which may not be related by ellingham diagram

① Reduction by Al/Mg

Al

$Fe_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Fe$ ($\Delta H = -ve$)

Commercial extraction

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

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

$3NbO + 2Al \longrightarrow Al_2O_3 + 3Nb$

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

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

- Mg: initiator
- Calcination $3MnO_2 \longrightarrow Mn_3O_4 + O_2$
  Pyrolusite

Ignitor: $Mg + BaO_2 / NaNO_3$ or KNO_3 or $KClO_3$

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

$NaNO_3 \xrightarrow{\Delta} NaNO_2 + \frac{1}{2}O_2$ (leaves O_2)

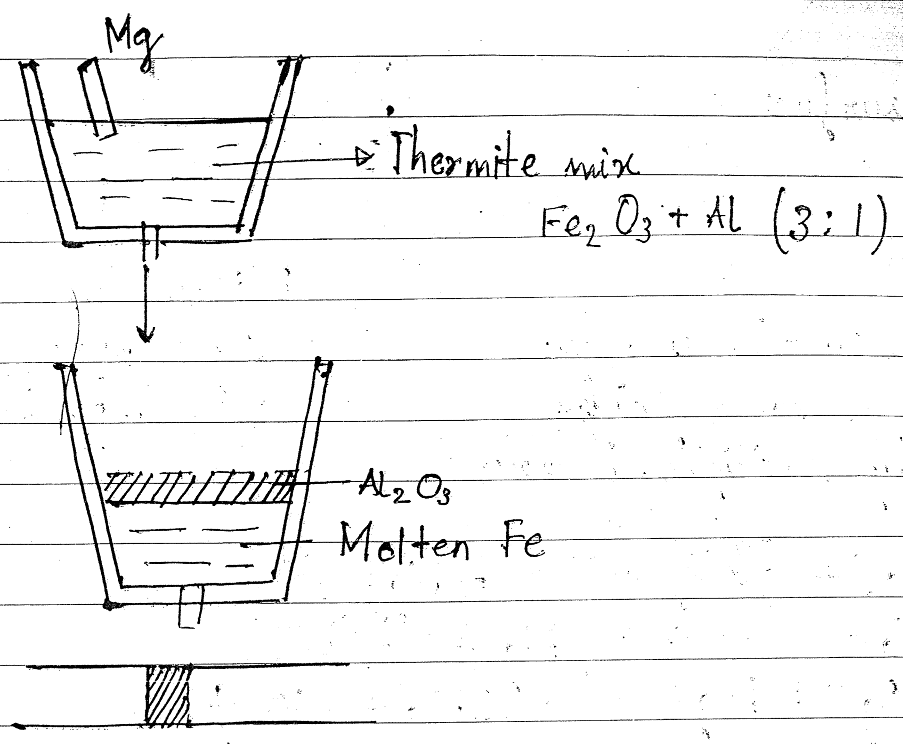
$BaO_2 \xrightarrow{\Delta} BaO + \frac{1}{2}O_2$

- by magnesium (has great affinity for chloride)

$TiCl_4 + Mg \longrightarrow 2MgCl_2 + Ti$

Kroll ~~Van Arkel~~ process

Ellingham diagram limitations



SELF REDUCTION METHOD

- Pyrometallurgy: Using heat
- Electrometallury: electricity
- Hydrometallury: displacement rxn in water

→ River barratory furnace

→ Self reduction method is applicable for extracting of metals which exist in form of sulphide ores and placed ~~above~~ above sulphur in ellingham diagram.

→ $PbS + \frac{3}{2}O_2 \xrightarrow[\text{excess of } O_2]{\Delta} PbO + SO_2$ (not in molten form)

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

$2PbO + PbS \xrightarrow[\text{high temp (abs of } O_2)]{\Delta} 3Pb + SO_2\uparrow$ (molten form homogenous phase)

$PbSO_4 + PbS \xrightarrow{\Delta} 2Pb + 2SO_2\uparrow$ (extraction complete)

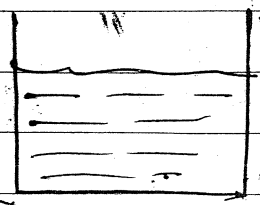
$Cu_2S + \frac{3}{2}O_2 \xrightarrow[\text{excess } O_2]{\Delta \text{ with}} Cu_2O + SO_2\uparrow$

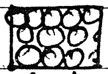
$Cu_2S + 2Cu_2O \xrightarrow[O_2/\text{High temp}]{\text{absence of}} 6Cu + SO_2\uparrow$

Q NCERT
Metallurgy easy in
'molten form

$SO_3 \xrightarrow{750\,C} SO_2$

Blisters on surface



- 

bubbles of SO_2

- Reaction continues after seperating in sand flask. and finally solidifies. Bubbles

Blister Cu
98% pure
2% impurity (Main Cu_2O)

- $HgS + \frac{3}{2}O_2 \longrightarrow HgO + SO_2$

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

  $2HgO + HgS \xrightarrow{\Delta} 3Hg + SO_2\uparrow$

- In excess of O_2, see ΔG of oxides

$CO_2 + C \longrightarrow 2CO$
$\Delta H = +ve$
172 kJ/mol

③ Carbon Reduction Method

eg Extraction of Fe from Haematite

$\cancel{\boxed{CaO}}$

Combustion Zone

$C + O_2 \longrightarrow CO_2$ $\Delta H = -ve$ (forms at high temp due to excess supply of oxyg

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

(Temp decreases going upward

Reduction Zone

$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$
(spongy iron)

Slag formation Zone

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

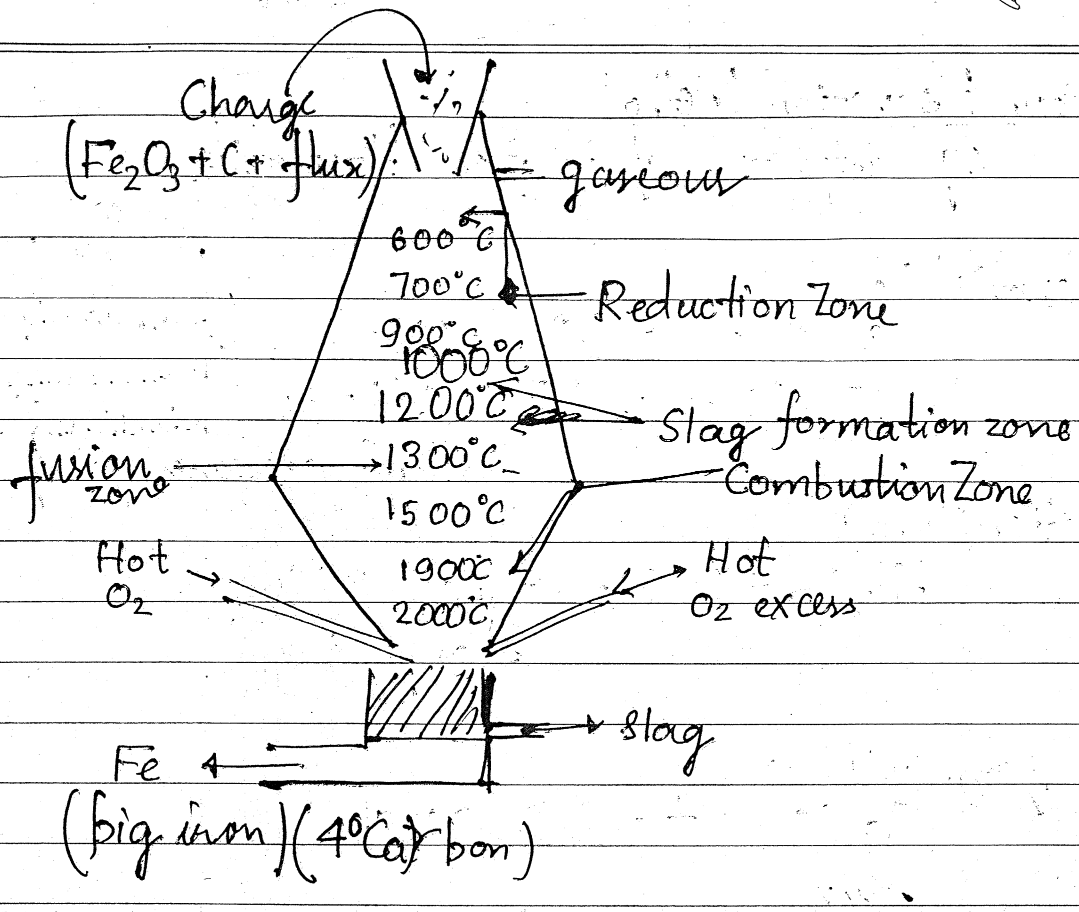
$SiO_2 + CaO \xrightarrow{\Delta} CaSiO_3$
(acidic impurity) (basic flux) (slag)

- $Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$ (starts at 750°C)
- $MnO_2 + 2C \longrightarrow Mn + 2CO$

$SiO_2 + 2C \longrightarrow Si + 2CO$ → starts at 1400°C

$P_4O_{10} + 10C \longrightarrow 4P + 10CO$

(impurities)



- Extraction of iron from haematite is best example of carbon reduction method
- In blast furnace haematite, carbon and flux act as charge
- Flux is substance added according to nature of impurity in ore
- SiO_2 act as acidic flux and CaO/ $CaCO_3$ / $MgCO_3$ act as basic flux
- flux combined with impurity to produce slag
- Major amt of haematite is reduced by carbon monoxide
- after reduction of haematite spongy iron produced in reduction zone
- MP of pure iron is approximate 1535°C but in blast furnace it is molten at merely 1300°C due to presence of impurity

Metal ion $\longrightarrow$ metal

Deciding factor for type of process

Ex2

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- Iron obtained from blast furnace is called pig iron which contain almost 95% iron + 4% Carbon and small amt of Mn, Si, P, & etc.
- When pig iron is moulded with scrap iron it produce cast iron in which percentage of carbon is nearly same as in pig iron (slightly less)
- Temp decreases ~~on~~ as $CO_2 + C \longrightarrow 2CO \quad \Delta H = +ve$

(4) METAL DISPLACEMENT IN WATER

Q $Au + KCN_{Aq} \xrightarrow{Air} Product\text{-}1_{Aq}$

$Product\ 1_{aq} + Zn \longrightarrow Product\ 2_{Aq} + Au$

$\longrightarrow$ Product (1) and (2) are respectively

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

~~Li, K, Na, Ca~~

Pig Iron C content > Cast Iron C content

Li
Na
K
Mg
Al
Ca
Zn
Fe
Cd
Sn
Pb
H
Cu
Hg
Ag
Pt
Au

$\downarrow$ Increasing SRP

Down cell.

pyrene

Mac Aurther forest cyanide process

Hydrometallury

$$4Au + O_2 + 8\bar{C}N + 4H_2O \xrightleftharpoons{\text{leaching}} 4[Au(CN)_2]^-_{aq} + 8OH^-$$

$$4[Au(CN)_2]_{Aq} + 2Zn_{(s)} \xrightarrow[\text{displacement in water}]{\text{Metal}} 4Au\downarrow + 2[Zn(CN)_4]^{2-}_{aq}$$

dark ppt amorphous

$$Ag_2S + 4\bar{C}N \xrightleftharpoons{\text{Leaching}} 2[Ag(CN)_2]^- + S^{2-}$$

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

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

dark ppt amorphous

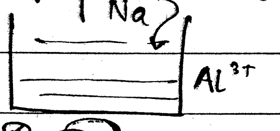
The metal ppt is black in colour since it is amorphous and proper packing not done However on slight heating then cooling, the lustre appears

Q Extraction of reactive metals (eg – Na, Mg, Ca, K) is done by

(A) Carbon reduction method
(B) Metal displacement in water
(C) Electrolysis of Aq salt
~~(D)~~ Molten salt electrolysis

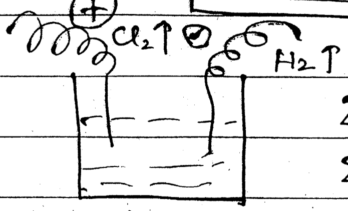
(A) At high temp, carbides are formed.

(B)



Na gives first electron to H^+

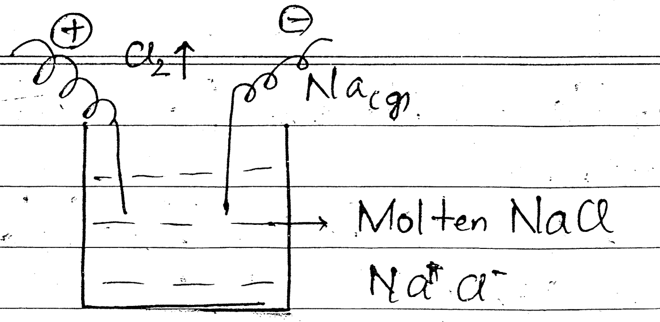
(C)



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

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

NaCl



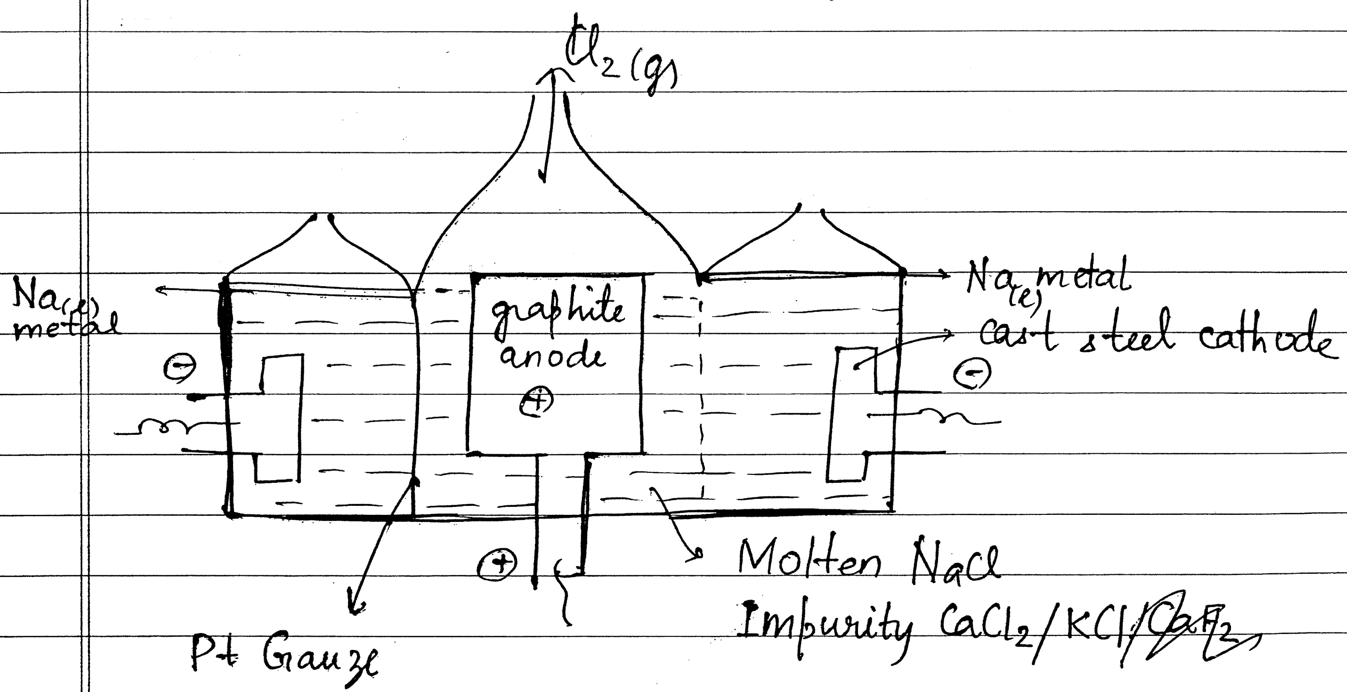
NaCl (MP) 800°C
Na (BP) ≈ 750°C

To collect $Na_{(s)}$ is nearly impossible even in inert atmosphere (rxn with components)

- Extraction of reactive metals is not possible by carbon reduction metal because reactive metals easily react with carbon to form carbides
- Metal displacement in water not possible for reactive metals bcoz they easily react with ~~metal~~ water and evolve H_2
- not poss by Electrolysis of aq salt because H_2 evolved at cathode
- ~~Re~~ They are extracted by molten salt electrolysis

Electrometallurgy

DOWN CELL (Na extraction)



$\ominus$ $2Na^+ + 2e^- \longrightarrow 2Na$

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

Race 2

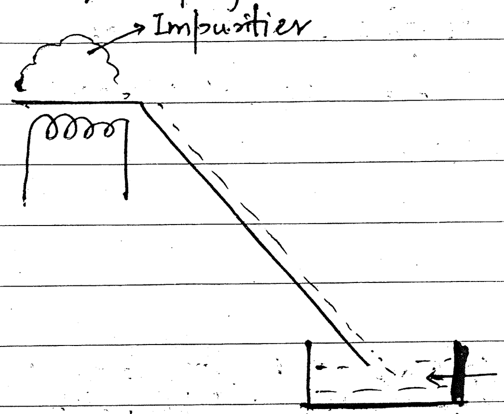
- Extraction of Na completed in Down Cell using molten NaCl as electrolyte
- $CaCl_2 + KCl$ added as impurity (flux) to decrease Mp of electrolytic mixture
- Fire which is caused by reactive metals can be extinguished by spray of CCl_4 (pyrene : high V.D. (vapour density) settles on metal) It is non combustible

→ Pt gauze used so that less amount of Na shifts into middle chamber and reacts with Cl_2. Also it is possible that sodium forms a conducting layer b/w cathode and anode and rxn stops

Department C Refining of Metal

① Liquation/Liquification

hearth
(small furnace)



~~This mol~~ Liquation method is used for refining on metals which have low melting pt as compared to impurities The process is completed in sloping hearth
This method is used for refining of Sn, Pb, Bi etc. (low melting metals)

② Distillation

Distillation method based on diff in BP. Metals which have low bP and contain major impurity of elements which have high bp They can bee seperated by distillation (fractional distillation) Repeated cooling upto 800°C

BP of Zn : 905°C

Impure Zn (Spelter) $\xrightarrow[850-950]{\Delta}$ $Zn_{(g)} + Cd_{(g)}$ → $Cd_{(g)}$; $Zn_{(s)}$ pure

→ Fe + Pb (Impurity)

Impurity
Fe BP : ~~3000~~°C 2750°C
Pb BP : ~~1600~~°C 1751°C
Cd BP : ~~700~~°C 765°C

Extend of metallic bonding depends on no. of unpaired $\bar{e}$

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(3) Vapour Phase Refining

Vapour phase refining differ from distillation because in this method metal is seperated from impurities by formation of their volatile compounds

Volatile compounds decompose at suitable temp to obtain pure metal

(I) Mond's process

$$\text{Impure Ni} \xrightarrow[50-60^\circ C]{\Delta \text{ with } CO} [Ni(CO)_4]\uparrow \xrightarrow[\text{high temp} \approx 250^\circ C]{\text{decompose at}} \underset{\text{pure}}{Ni} + 4CO\uparrow$$

$\hookrightarrow$ Impurity

(II) Van Aurakal method

$$\underset{\text{(impure)}}{Ti} + 2I_2 \xrightarrow{\Delta} TiI_4\uparrow \xrightarrow[\Delta]{\text{decom}} \underset{\text{pure}}{Ti} + 2I_2$$

$\hookrightarrow$ Impurity

(Same rxn for Ti, Zr, Hf)

$$BI_3 \xrightarrow{\Delta} B + \frac{3}{2} I_2$$

CO is reactant

The impurities do not form complexes at these temperatures and or their complexes do not decompose

- Ti^{+4} ion

Iodine used due to its high polarisability. Hence covalent character dominant Low bp

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(4) Bessemerization

• This method is based on knowledge of Ellingham diagram

• ~~Metal which have less affi~~ This method is used when metal have less affinity for oxygen as compared to impurity

• Refining of pig iron by bessemerization is an important example because impurities present in iron easily form oxide as compared to iron

Molten pig iron

affinity for O_2 $Si > Mn > P > C > Fe$ (at 1500°C)

$Si + O_2 \longrightarrow SiO_2$

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

$MnO + SiO_2 \longrightarrow MnSiO_3$

[Accordingly on relative amount of MnO and SiO_2 coating done

MnO excess $\longrightarrow SiO_2$

SiO_2 excess $\longrightarrow MgO$

Currently SiO_2 in excess (R and D)

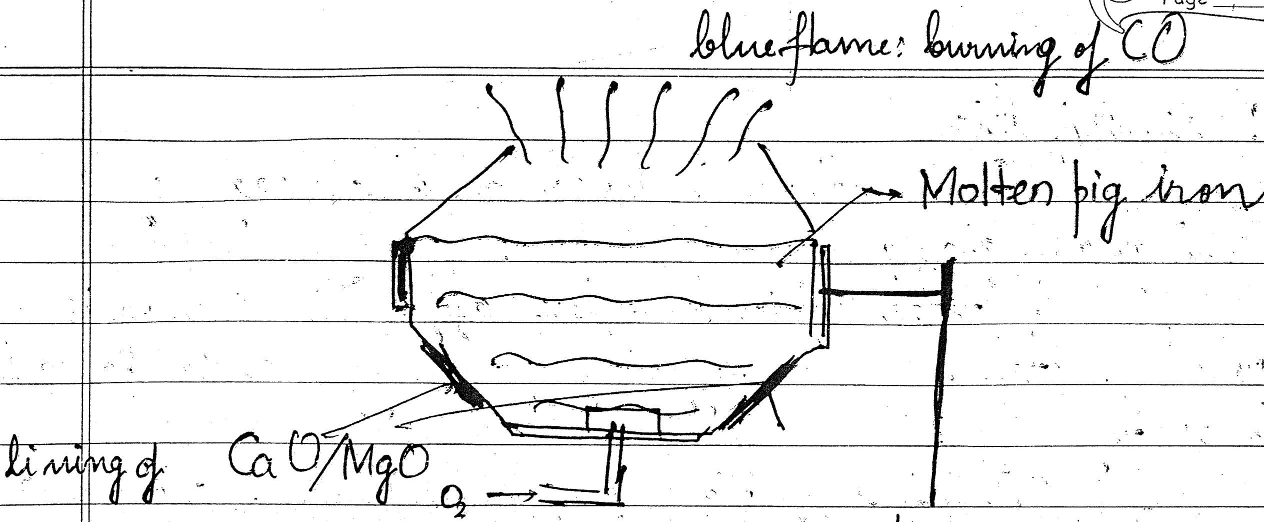
$MgO + SiO_2 \longrightarrow MgSiO_3$

$P + O_2 \longrightarrow P_4O_{10}$

$P_4O_{10} + 6CaO \longrightarrow Ca_3(PO_4)_2$

(Thomas slag

Usually sold to fertilizer plants)



Bessemer Convertor
(due to apple shaped)

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

burn with blue flame

In Bessemer convertor after oxidation of all impurities present in pig iron ~~ca~~ wrought iron is produced
It is most pure form of iron and contain 0.2-0.4% carbon as impurity
To prepare steel calculated amount of spegilion (alloy of Fe, Mn and C) is added to prepare steel

- The oxygen is supplied at intervals of 3 min, 5 min, 10 min in increasing order so that there is competition and only reactive metals react with oxygen
- The intervals are gradually increased as amt of impurity decreases
- The flame of CO tells about extent of conversion

Race 27, 29

Electron affinity
Electronegativity

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Poling

- Poling metal is used for refining of metal which contain impurity of same metal oxide
- Hydro carbon produced from destructive distillation of green charcoal act as reducing agent for metal oxide
- for eg this method is used for refining of Cu and Sn
- The metal must be above carbon

destructive distillation (heating in absence of O_2)

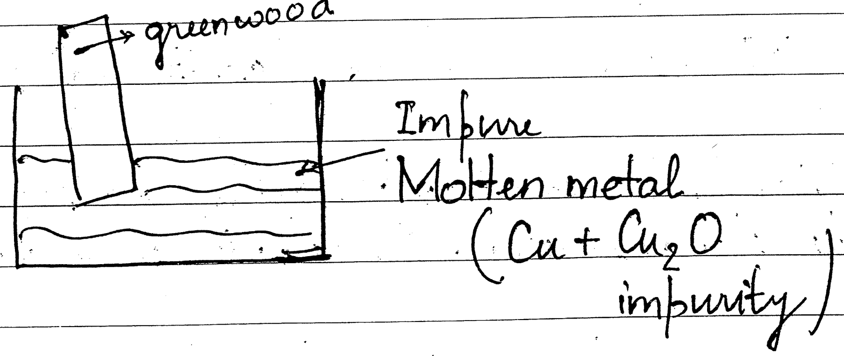
The hydrocarbons on heating produce C/CO/CH_4 which and other hydrocarbons all act as reducing agent

In Cu

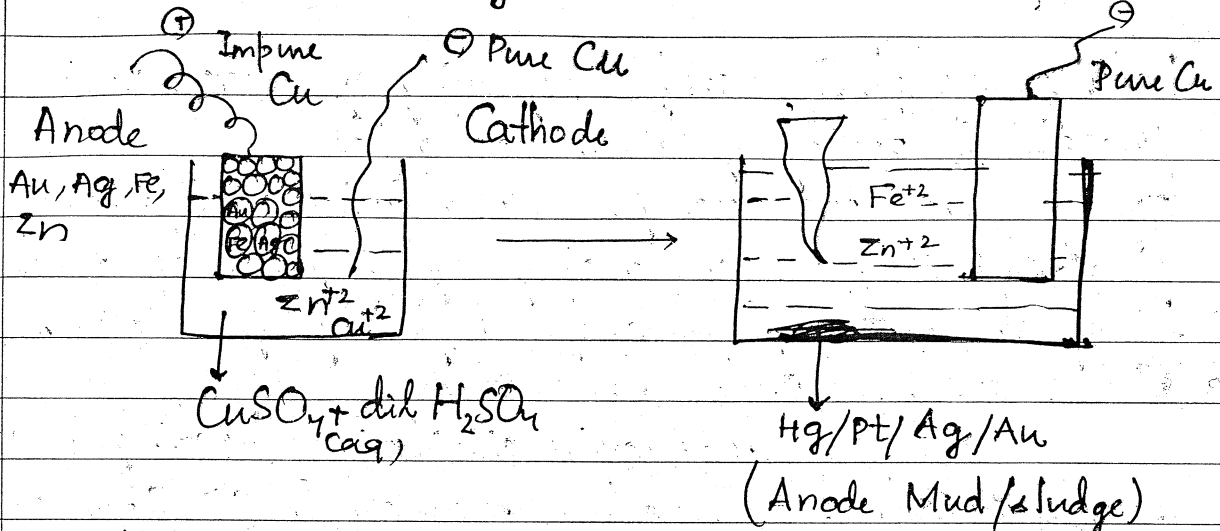
$$3Cu_2O + CH_4 \longrightarrow 2H_2O\uparrow + CO\uparrow + \underline{\underline{6Cu}}$$

In Sn

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



⑥ ELECTROLYTIC Refining



$H^+ \quad OH^-$

$H^+ \quad SO_4^{2-}$

$Cu^{+2} \quad SO_4^{2-}$

Zn^{+2}

⊕ $Zn \longrightarrow Zn^{+2} + 2e^-$ (1^{st} round)

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

⊖ $Cu^{+2} + 2e^- \longrightarrow Cu$ (continued)

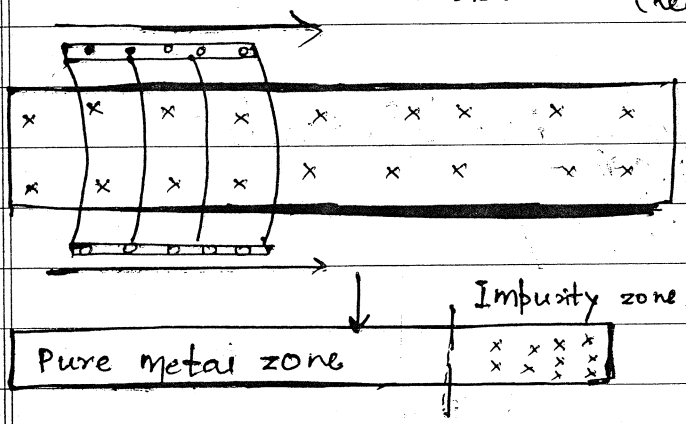
The elements above copper oxidise and remain in sol^n while elements below it deposit as anode mud

lead ⟶ battery

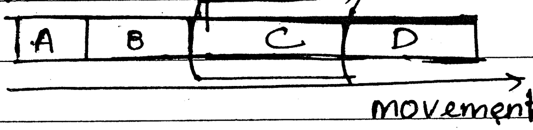
SCUM

(7) Zone refining

- It is based on the fact that impurities have more solubility in molten form of metal as compared to pure metal
- Process is completed by fractional crystallisation
- This method gives ultra purity in metallurgy so that it is reqd ~~when~~ in case of refining of metals used in semiconductors or diodes transistors (arsenic, silicon, germanium etc) ~~(lead)~~ → ~~ba~~ gallium, indium, boron



The heated melts part A, semisolid B, melting C, D solid



fractional crystallisation as one part melts and then ~~freezes~~ solidifies

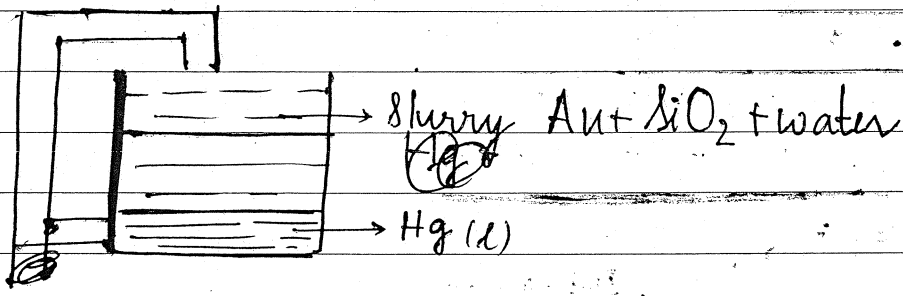
Quartz along with gold
auriferrous quartz

INDIVIDUAL METALLURY
GOLD

extraction of ~~A~~ GOLD from alluvial sand or oriferrous quartz

No amalgam (Fe, Pt)

(A) Amalgamation



$$\text{Hg - Au alloy} \xrightarrow{\Delta} \begin{cases} Hg_{(g)} \xrightarrow{\text{cooling}} Hg_{(l)} \\ Au_{(s)} \end{cases}$$

(B) Cyanide process
→ Hydrometallury / Mac Aurther forest cyanide process
(remaining gold in slurry)

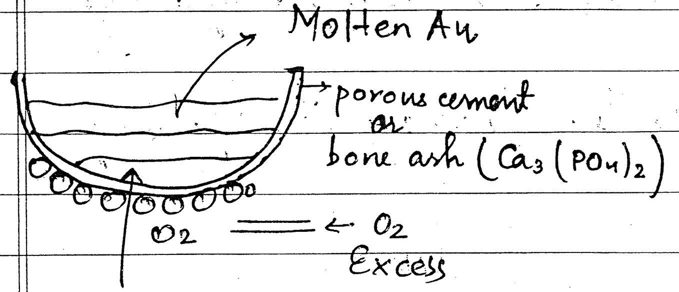
$$4Au + O_2 + 8CN^- + 2H_2O \xrightarrow{\text{leaching}} 4[Au(CN)_2]^- + 4OH^-$$
sol^n

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

$$\underset{\text{(dark powder)}}{Au + Zn} \xrightarrow{NaNO_3, \Delta} \underset{\text{(crude metallic)}}{Au + ZnO}$$
→ scum

Mercury does Not amalgam with Fe, Pt

(C) Refining of metal
(I) Cuplation



$$Pb + \frac{1}{2}O_2 \xrightarrow[1600^\circ c]{\Delta} PbO \uparrow$$

$$Cu + \frac{1}{2}O_2 \longrightarrow CuO$$
(excess O_2)

$$Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$$

$$CuO + B_2O_3 \longrightarrow \underset{\text{blue slag}}{Cu(BO_2)_2}$$

sodium borate and blue slag float and are seperated similarly with other oxides

(II) Electrolytic refining

Anode: Impure Au
Cathode: Pure Au
Electrolyte $H[AuCl_4]_{aq} + HCl_{aq}$

Rxn : $AuCl_4^- \longrightarrow Au + 4Cl^-$

- Gold particle present in its native form in their ores so that mercury is used to extract gold particles
- Gold is seperated from amalgam by distillation method
- 70–80% gold present in slurry is extracted by amalgamation and remaining amt of particles extracted by cyanide process
- Amorphous gold obtained by hydrometallurgy is heated with $NaNO_3$ to remove impurity of Zn because Zn form ZnO when heated with $NaNO_3$
- after removal of Zn, crude metallic Au is obtained
- Lead present in gold is removed by cuplation

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- Couple is a cup shaped crucible (silicious) which is made by bone ash or porous cement
- Other metal oxides are removed on addition of borax (acidic flux)
- Purity of gold is increased by electrolytic refining

5 Solubility ptr
Pg 2

Extraction of Ag from Argentite (Ag_2S)

(A) Concentration of Ore by froth floatation

(B) ~~Reduction~~

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

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

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

dark ppt

• $Ag + Zn \xrightarrow{NaNO_3,\ \Delta} Ag + ZnO$ (scum)

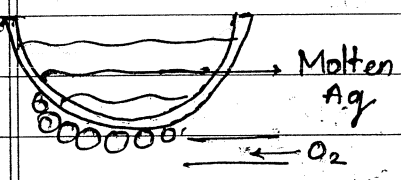
(dark powder) (Crude metallic)

Zn impurity from forest cyanide process

(C) Refining of metal

(I) Cuplation

$$Pb + \frac{1}{2}O_2 \xrightarrow[\approx 1600^\circ C]{\Delta} PbO \uparrow$$



$$Cu + \frac{1}{2}O_2 \longrightarrow CuO$$

$$Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$$

$$CuO + B_2O_3 \longrightarrow Cu(BO_2)_{2n}$$

blue sol

Silver has more lead impurity than gold

Extended cupalation

(II) Electrolytic refining

Anode: Impure Ag

Cathode Pure Ag

Electrolyte: $AgNO_{3aq} + HNO_{3aq}$

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(3) Extraction of Al from Bauxite $AlO_n(OH)_{3-2n}$

(A) Concentration of ore
(I) Leaching by NaOH (Baeyer's process)
(for red bauxite)

(II) Hall's process
(Red Bauxite)

$$Al_2O_3 + Fe_2O_3 + Na_2CO_3 \xrightarrow[\text{fused at high temp}]{\Delta} \underbrace{\underset{\text{amphoteric}}{Al_2O_3} + \underset{\text{basic}}{Fe_2O_3} + \underset{\text{basic}}{Na_2O}}_{2NaAlO_2 + Fe_2O_3} + CO_2\uparrow$$

$$NaAlO_2 + Fe_2O_3 \xrightarrow{\text{water}} \underset{\text{residue}}{Fe_2O_3} + \underset{\text{sol}^n}{Na[Al(OH)_4]}$$

$$2Na[Al(OH)_4] + CO_2 \longrightarrow Na_2CO_3 + \underset{\text{white ppt}}{Al(OH)_3\downarrow} + H_2O$$

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

- Na_2CO_3 does not decompose rather aluminium and iron carbonate formed which decompose (fusion)

MP ↓ Al_2O_3 : corundum

Conductivity ↑

1–9

BiOBr insoluble.

(II) Serpak's method

$$\underset{\text{(main imp)}}{\underset{\text{(white bauxite)}}{Al_2O_3}} + SiO_2 + 5C + N_2 \xrightarrow[1800^\circ C - 2000^\circ C]{1800^\circ C - 2000^\circ C} 5CO\uparrow + Si\uparrow + 2AlN_{(s)}$$

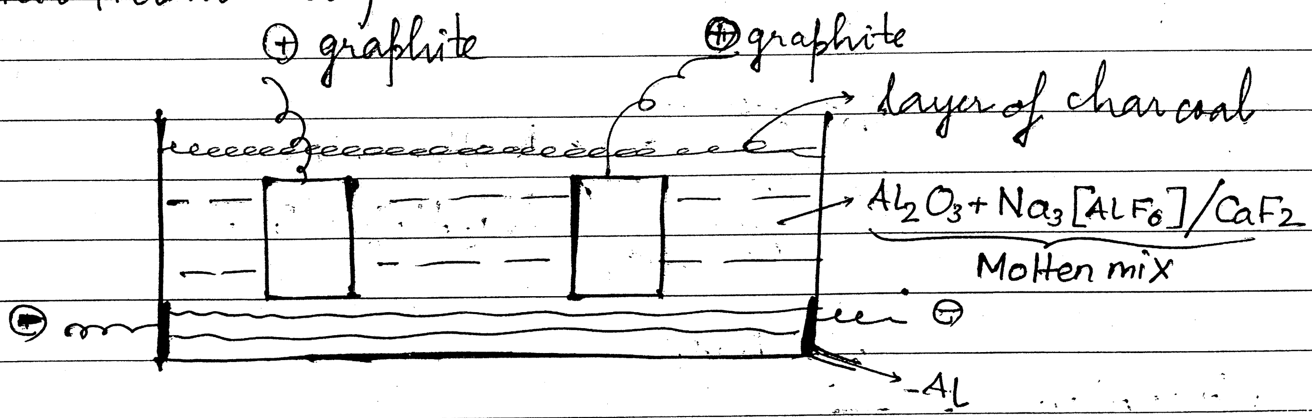
[Difficult to recover from Al_4C_3]

$$AlN_{(s)} + 3H_2O \xrightarrow{\text{hydrolysis}} \underset{\text{white ppt}}{Al(OH)_3\downarrow} + NH_3\uparrow$$

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

(B) Reduction of Ore

- By electrolytic method (Hall Heroult cell)



$$Al_2O_3 \longrightarrow 2Al^{3+} + 3O^{2-}$$

500g C/kg of alumina

(+) $3O^{2-} \longrightarrow 6e^- + 3/2\, O_2$

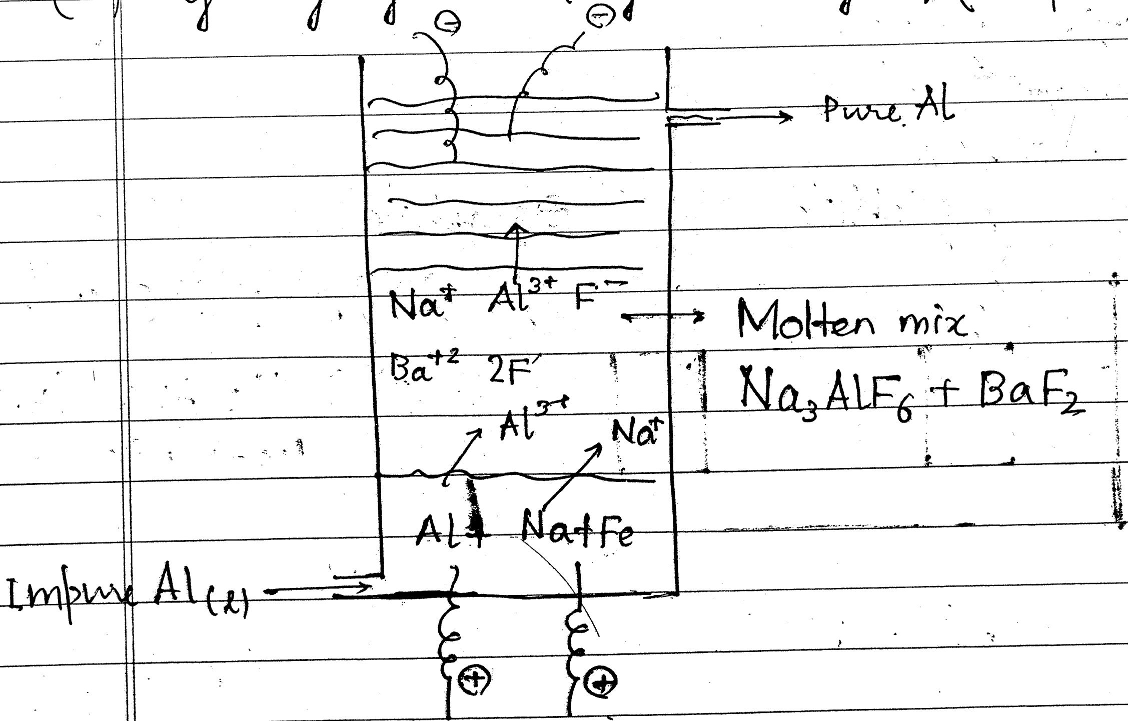
$C + O_2 \longrightarrow CO/CO_2$

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

Smelting (Melting with formation of slag) (Using C)

- Extraction of Al done by electrolysis since it is passive in nature
- Graphite coating done on four surfaces

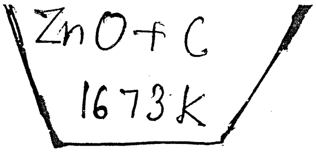
(C) Refining of metal (by Electrolysis) (Hoop's cell)



$\oplus$ $Na \longrightarrow Na^+ + e^-$

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

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



Imp note

(1) Extraction of aluminium by electrolytic method in Hall Heroult cell

(2) In Hall Heroult cell graphite anode and layer of graphite act as cathode

(3) Molten mixture of Al_2O_3 and Na_3AlF_6/CaF_2 or both used as electrolyte

(4) Na_3AlF_6 and CaF_2 added to improve electrical conductance of electrolyte and make the melting pt of mixture low (flux)

(5) Graphite anode are rapidly consumed due to formation of CO and CO_2

(6) Layer of charcoal prevent loss of heat radiation and ~~no shi~~ prevent lustre of molten mixture

It also prevents combustion of graphite electrodes from atmospheric oxygen

(7) During refining of aluminium middle layer which act as electrolyte contain cryolite and BaF_2

BaF_2 required to maintain density of middle layer (relatio)

Exercise ✓
Intext ✓

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(4) Extraction of Zn from ZnS / $ZnCO_3$

(A) Concentration of Ore

ZnS (froth floatation)
$ZnCO_3$ (gravity seperation)

(B) Reduction of Ore

(I) Roasting / Calcination

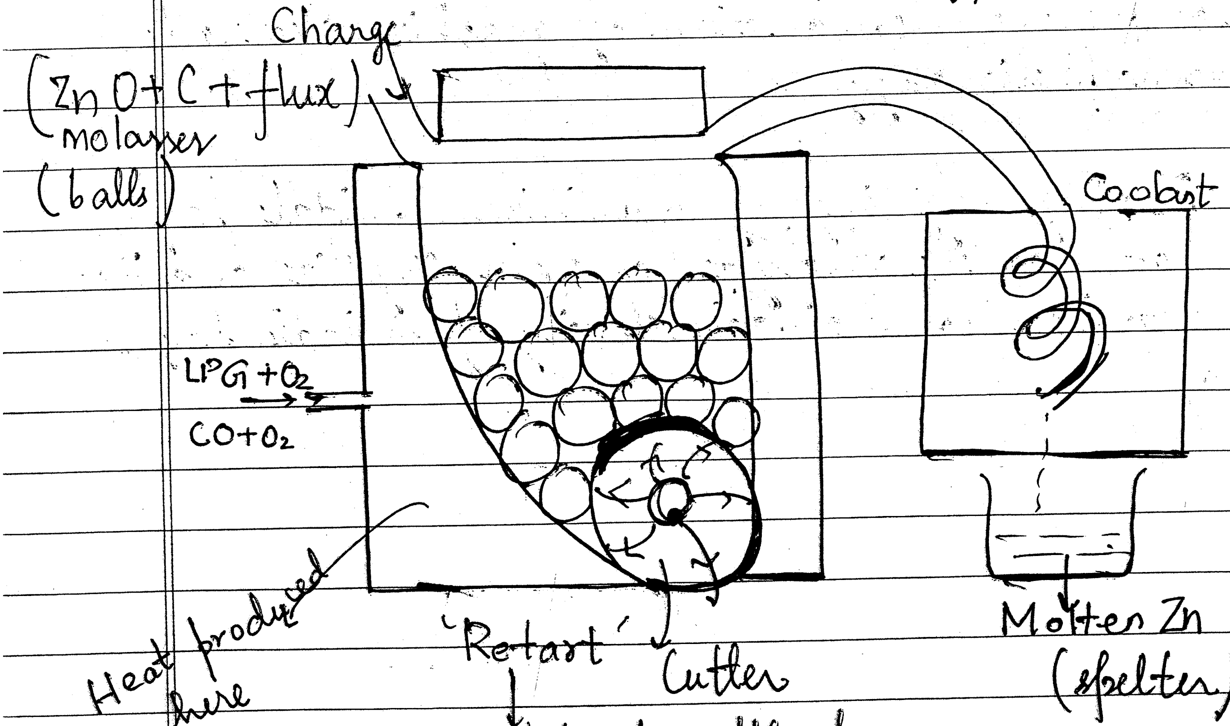
$$ZnS + \frac{3}{2}O_2 \longrightarrow ZnO + SO_2\uparrow$$

Calcination

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2\uparrow$$

(II) Reduction of ZnO (By carbon reduction (smelting))

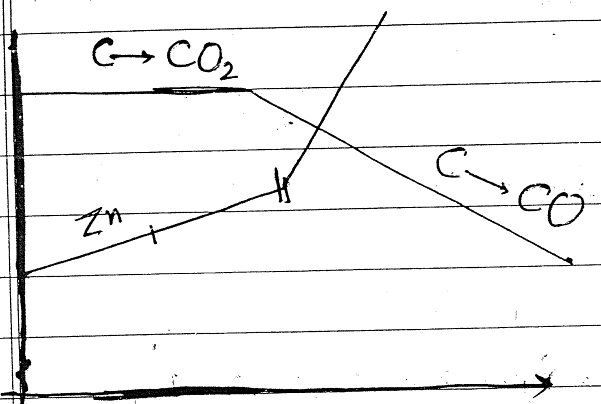
$$ZnO + C \xrightarrow{1673K} Zn_{(g)} + CO_{(g)}$$



- a type of muffle furnance
  no flame in main part
  boundary heated

ZnS ~~used~~ froth floation $CuSO_4$ used since ZnS dissolves in ethyl zanthate Hence to prevent loss $CuSO_4$ added which does sulphide coating on surface and prevents loss of metal

K_{sp} CuS $\ll$ K_{sp} ZnS



(C) Refining of Zn:—

(I) distillation

(II) Electrolytic refining

Anode: Impure Zn

Cathode Strip of Al (Initiation better)

Electrolyte $ZnSO_{4(aq)} + H_2SO_{4(aq)}$

Imp pts

(1) ~~For~~ During froth floatation process of ZnS, $CuSO_4$ used as activator because in the presence of sodium ethyl zanthate some of Zn^{+2} dissolve. But Cu^{+2} produces coating of CuS on surface.

(2) from ellingham diagram it is observed that carbon is better reducing agent for reduction of ZnO

(3) When ZnO is reduced by carbon, is higher than the boiling pt of Zn so that zinc is obtained in gaseous form collected at top of retart.

(4) Partial fusion of ZnO with carbon in retart furnace is called sintering

• Opposite to grinding

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(5) Extract of Pb from galena

(A) Conc of ore
PbS = by froth floatation

NaCN: depressant

(B) Reduction of Ore
(i) Self reduction (for high grade galena)
less silica

Roasting
$$PbS + \frac{3}{2}O_2 \xrightarrow{\Delta} PbO + SO_2$$
excess
$$PbS + 2O_2 \xrightarrow{\Delta} PbSO_4$$
excess

$$PbS + 2PbO \xrightarrow[\text{high temp}]{\Delta} 3Pb + SO_2\uparrow$$
$$PbSO_4 + PbS \xrightarrow{\Delta} 2Pb + 2SO_2\uparrow$$

After this the air window is opened for limited supply for oxidation Zn, Fe etc.
In this process, lead becomes soft (softening)
(scum formation)

(II) ~~H~~ Carbon reduction (for low grade galena)
SiO_2

(a) Roasting with lime

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

~~Before~~ ~~Red~~
Red

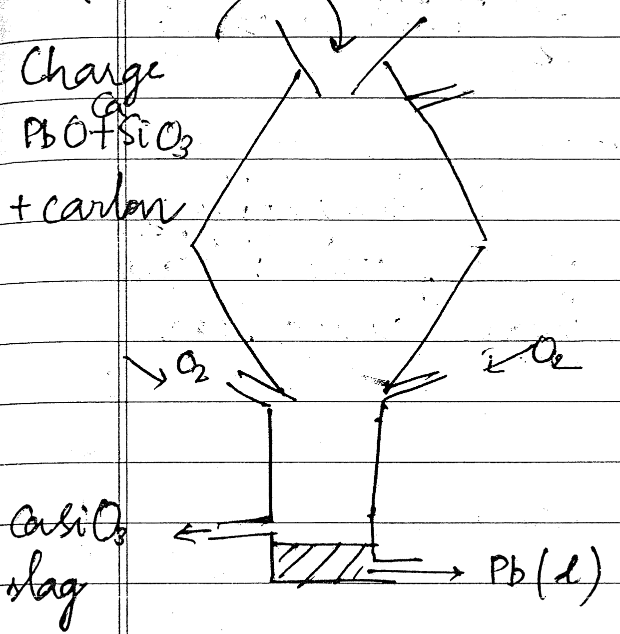
$$(PbO + SiO_2) \longrightarrow PbSiO_3 \quad X$$
$$\underbrace{CaO}_{\text{strong}} + SiO_2 \longrightarrow CaSiO_3$$

final product

it occurs before also but ~~.....~~ independent of initial (equilibrium)

*◦ (Silicates : No carbon reduction)
Difficult & self reduction
silicites formed

(b) Carbon reduction in blast furnace (smelting)



$PbO + CO \longrightarrow Pb + CO_2 \uparrow$
$PbO + C \longrightarrow Pb + CO \uparrow$

- Carbon reduction used
- Not self reduction
  $CaSiO_3$* impurities

- No flux
  already done with lime

- $T \approx 1000°C$
  ~~(1000~~

(c) Refining
(I) liquation
(II) electrolytic refining (Important)
Impure Pb: Anode.
Pure Pb: Cathode
Electrolyte: $Pb[SiF_6]_{aq} + H_2SiF_{6(aq)}$

- $PbSO_4$ could not be used (insoluble)
- $Pb(NO_3)_2$ could not be used. HNO_3 oxidising.
  Pb(electrode) dissolves
- Hence overall $Pb[SiF_6]$ soluble and H_2SiF_6 does not react with electrodes

Zn, Pb immiscible

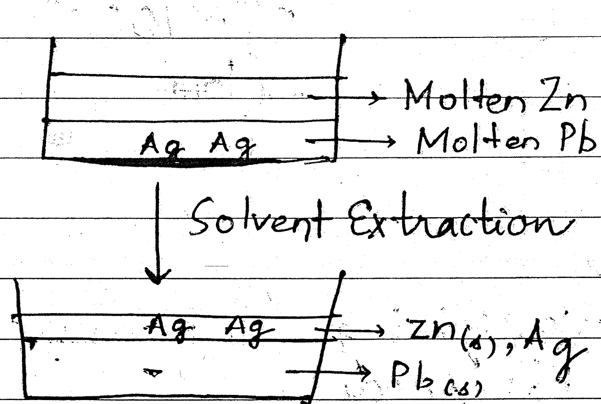
(i) During extraction of Pb from low grade ore lime is req'd to prevent formation of $PbSiO_3$ because more basic CaO react with SiO_2

ii) Lead obtained by self reduction or carbon reduction method is heated with limited supply of oxygen to prevent impurity of some other metals which have more affinity for oxygen (called lead softening)

Desilverization of argentiferrous lead

Two diff methods

(I) Park's method



→ Silver has more solubility in Zn

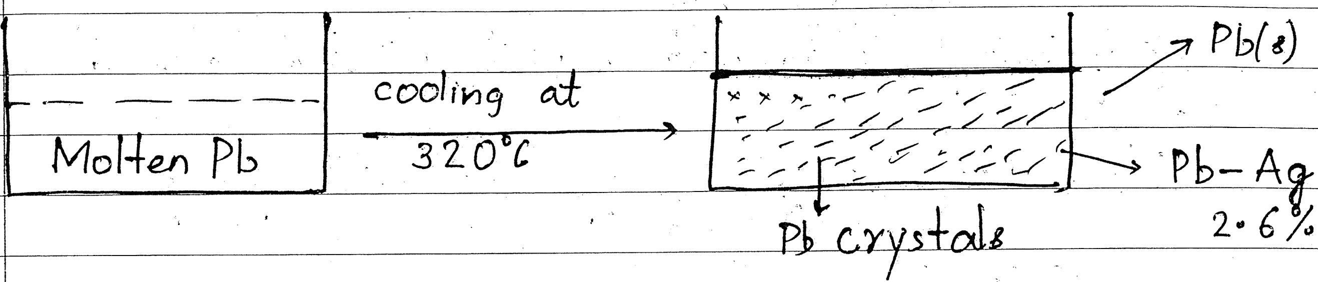
→ After this electrolytic refining

Do not relate solubility of metal

~~Ex01 1-20~~
Ex01 1-20

(2) Patinson process

Pure Pb (MP : 327°C)
Pb- Ag alloy (MP 303°C)
(2.6%)
(Eutectic mix) (fixed MP)



(6) Extraction of Sn from Casserite
(A) Concentration of ore by magnetic seperation
(B) Reduction of ore (Carbon reduction)
smelting

$SnO_2 + 2CO \longrightarrow Sn + 2CO_2$] Temp ≈ 1000°C
$SnO_2 + 2C \longrightarrow Sn + 2CO\uparrow$ → Higher

(C) Refining of metal
(I) Polling
(II) Liquation
special* case (III) Electrolytic refining (conductive)
$SnSO_{4(Aq)} + H_2SO_{4(aq)}$ (less)
Specific (In case of ~~direction~~ op from not answer)
o When SnO_2 contain Cu and Fe sulphides are impurity partial roasting is reqd to convert them in soluble sulphates

$Cu_2S + CuS + FeS \xrightarrow[\text{partial roasting controlled}]{\text{limited or}} CuSO_4 + FeSO_4$

$Fe_3^\circ C^\circ$

★ Cast iron less brittle than pig iron

wrought iron soft

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(7) Extraction of Fe from Haematite (Fe_2O_3)

(A) Concentration of Ore

(I) Magnetic seperation

(2) gravity seperation

(B) Reduction of Ore

(I) Roasting

Roasting of ore done to convert all iron ores to Fe_2O_3

This is because FeO (more basic) may react with gangue

$$\left.\begin{array}{l} Fe(OH)_3 \\ FeCO_3 \\ FeS \\ FeO \end{array}\right\} \xrightarrow[\text{excess } O_2]{\text{Roasting}} Fe_2O_3 + \begin{array}{l} SO_2\uparrow \\ CO_2\uparrow \\ H_2O\uparrow \end{array}$$

(II) Carbon reduction in blast furnace (smelting)

White cast iron (Carbon: graphite)

Grey cast iron ($Fe_3^\circ C^\circ$: Cementite)

(C) Refining of metal

(I) Bessemerization (oxidation of impurity by O_2)

(II) Puddling (oxidation by Fe_2O_3)

- The slag prevents reoxidation of molten iron on surface

★ Red^n Zone

$$Fe_2O_3 \xrightarrow[CO]{} Fe_3O_4 \longrightarrow FeO \xrightarrow{CO} Fe$$

✓ Manganese steel hard (Mn 5 unpaired e^-, Cross linked) — better metallic bonding

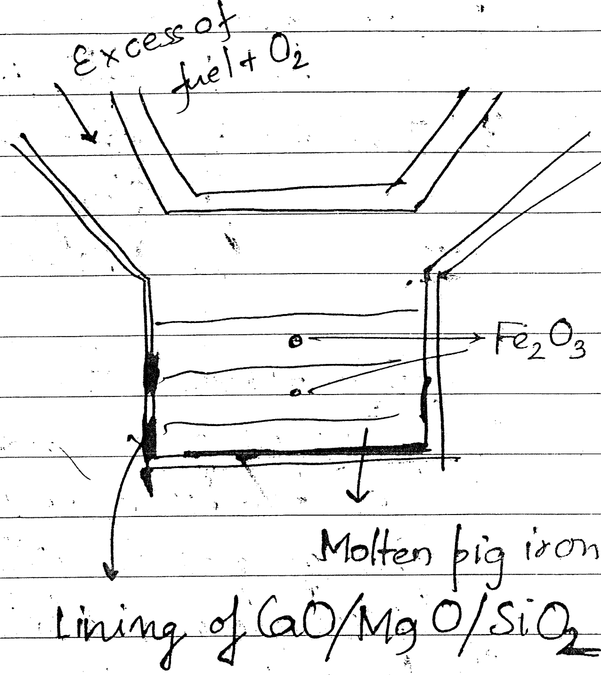
Fe_3N non stoichiometric

Fe — Mn — Fe, Fe, Fe, Fe

Prepartion of steel

(i) Bessemerization
(ii) Open Hearth process / puddling
(Fe_2O_3 pieces in pig iron)

(affinity for O_2 in pig iron
$Si > Mn > P > C > Fe$)



$3Si + 2Fe_2O_3 \longrightarrow 3SiO_2 + 4Fe$
$3Mn + Fe_2O_3 \longrightarrow 3MnO + 2Fe$
$MnO + SiO_2 \longrightarrow MnSiO_3$
$Fe_2O_3 + P \longrightarrow P_4O_{10} + 2Fe$
$3C + Fe_2O_3 \longrightarrow 2Fe + 3CO\downarrow$

- BaO although more basic not used because of its lower mp
- Fe_2O_3 added just for oxidation of impurity

After oxidation of impurity spegilision added.

(3) Electric furnace process
Same as Open Hearth process but electricity is used for heating

(4) LD process
LD process is most modern method to prepare high grade steel. In this process impurities are oxidised by pure O_2 in specially designed convertor.
After the oxidation of impurities calculated amt of spigielin is added

P 990. Scum - Ti Mg

(Otherwise Fe_3N formed from air)

Note:

(1) Haematite is oxide ore still roasting is applied to convert $FeCO_3$, FeS, FeO to Fe_2O_3

(2) Iron obtained from blast furnace is pig iron. It is converted to cast iron by melting with scrap iron.

(3) There are two types of cast iron
(a) Grey cast iron (Carbon in form of graphite)
(b) White cast iron (Carbon in form of cementite Fe_3C)

Heat treatment

(i) Quenching or hardening: Steel is heated to red hot temperature and is then cooled suddenly by plunging into either cold water or oil. It makes steel hard and brittle

(ii) Annealing: The steel is heated to red hot temperature and then cooled slowly. It makes steel soft

(iii) Tempering: If Quenched steel is heated to temperature b/w 500 to 575 K and then cooled slowly, it becomes quite hard but brittleness disappears

Surface treatment

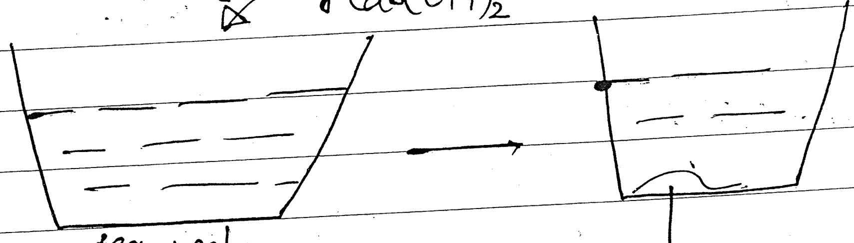
(i) Nitriding: Process of heating steel at 1000K in an atmosphere of NH_3. This gives hard coating of iron nitride on surface

(ii) Case hardening: Process of giving a thin coating of hardened steel by heating steel in contact with charcoal followed by quenching in oil

(8) Extraction of Mg by Dow's Sea Water process
sea water contain Mg as $Mg^{+2} = 0.13\%$

(A) seperation of Mg^{+2} from sea water

$Ca(OH)_2$



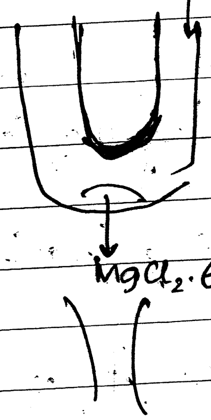
$Mg(OH)_2 + 2HCl\ aq \longrightarrow \underset{sol^n}{MgCl_2\ aq} + H_2O$

$MgCl_2\ aq \xrightarrow{cooling} MgCl_2 \cdot 6H_2O(l)$

MP
MgO ($\approx$ 1200°C) Cost red^n
$MgCl_2$ ($\approx$ 700°C)

(B) Preparation of anhydrous $MgCl_2$ | Calcination with dry HCl

$MgCl_2 \cdot 6H_2O \xrightarrow[dry\ HCl]{\Delta\ with} \underset{anhy}{MgCl_{2}(s)} + 6H_2O \uparrow$



[$Mg(OH)_2 \xrightarrow{HCl} MgCl_2$]

[excess HCl HCl (weak acid)]

(c) Electrolysis of molten $MgCl_2$

$$MgCl_2 \xrightarrow[\text{elec}]{\text{molten salt}} Mg^{+2} + 2Cl^-$$ (Iron pot Cathode)

(Impurity $KCl/CaCl_2$)
Decrease MP
Increase conductivity

(−) $Mg^{+2} + 2e^- \longrightarrow Mg$
(+) $2Cl^- \longrightarrow Cl_2 + 2e^-$

☆ $MgCl_2 \cdot 6H_2O \xrightarrow{\Delta} \underbrace{MgCl_2 - MgO}_{\text{high temp (high cost)}}$

same problem wid
$AlCl_3 \cdot 6H_2O$
$SnCl_2 \cdot 2H_2O$
$FeCl_3 \cdot 6H_2O$
$BeCl_2 \cdot 2H_2O$
$CuCl_2 \cdot 2H_2O$

- $Mg^{+2} + H_2O \xrightarrow[\text{hydrolysis}]{} Mg(OH)_2$ (weak base)
  $\downarrow \Delta$
  $\underbrace{MgO}_{\text{high mp}}$
- Mg^{+2} seperated from sea water by formation of insoluble hydroxide (All metal hydroxides are water ins. except IA & Ca, Sr, Ba)
- Anhydrous $MgCl_2$ prepared by heating $MgCl_2 \cdot 6H_2O$ with excess current of dry HCl
- When $MgCl_2 \cdot 6H_2O$ is directly heated it produce $MgCl_2$ with impurity of MgO due to hydrolysis of Mg^{+2}
Similar problem is observed for other metal chlorides
-

- Mg obtained by molten salt electrolysis (electrometallurgy)
Impurity of KCl and $CaCl_2$ added to reduce mp and to improve electrical conductance
$MgCl_2$ (covalent)

Piogeon process

$$MgCO_3 \cdot CaCO_3 \xrightarrow{\Delta} CaO \cdot MgO + 2CO_2$$

$$CaO \cdot MgO + \underbrace{Fe\text{-}Si}_{\text{used since its bp is high}} \xrightarrow{\Delta} Mg\uparrow + CaSiO_3 + Fe$$

Water Cu^{+2}
Non aq. Cu^{+1}

Pg 301
2nd para row

Pyrometallury

copper ore

Extraction of Cu from Chalcopyrite ($CuFeS_2$)

(Max availability)

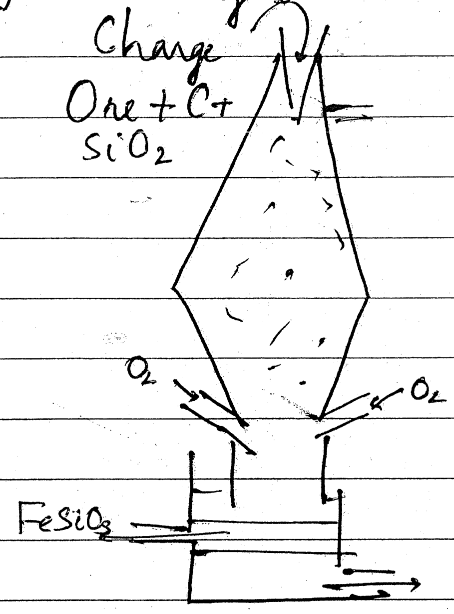
(A) Concentration of ore by froth floation
(B) Reduction of Ore
(A) Partial roasting

$$CuFeS_2 + O_2 \xrightarrow[\text{roasting}]{\text{partial}} Cu_2S + FeO + SO_2 \uparrow$$

(not to convert $Cu \rightarrow Cu_2O$)

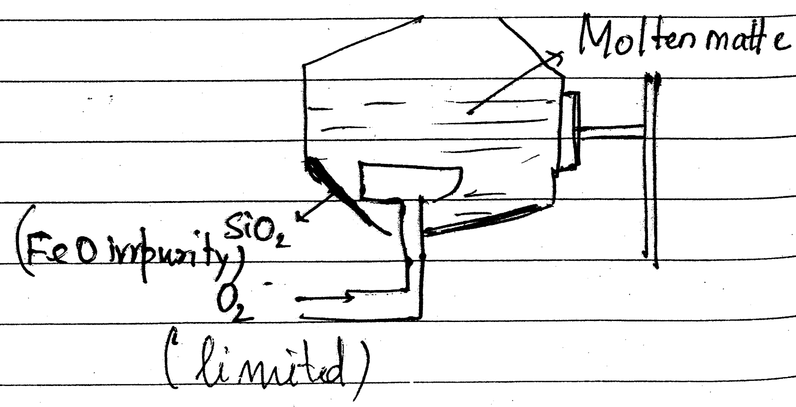
(Bi) Smelting in blast furnace

small amount of FeS converted into FeO



Matte Cu_2S + (small FeO FeS)

iii) Self reduction (Bessemerization)



Saum : Fan slag (Silicates, large quantity)
(Oxide) : Metal oxide does not dissolve in metal

~~Au + Zn~~ $\xrightarrow{N}$

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

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

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

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

(Blister Cu)
(98% pure)

(C) Refining of Metal
(I) Poling (II) Electrolytic refining
$CuSO_4 + H_2SO_4$

(Large silica impurity)

NCERT — Low grade Cu ore

hydro metallurgy

(I) Leaching by

$$Cu_2O / CuCO_3 \cdot Cu(OH)_2 \xrightarrow[\text{Bacteria}]{\text{dil } H_2SO_4 /} Cu^{+2}_{aq}$$

$CuSO_4 \cdot 5H_2O_{(s)}$

(II) Metal displacement

$$Cu^{2+}_{Aq} + Fe \text{ or } H_{2(g)} \xrightarrow{\text{by } Fe/H_2} Cu + Fe^{+2} \text{ or } 2H^+$$

scrap iron

JEE

$$Cu_2S + 2Cu_2O \xrightarrow{\Delta} 6Cu + SO_2 \uparrow$$

$$Cu_2S + 2CuO \xrightarrow{\Delta} 4Cu + SO_2 \uparrow$$

$$Cu_2S + CuSO_4 \xrightarrow{\Delta} 3Cu + 2SO_2 \uparrow$$

decompose to Cu_2O

$$2CuO \xrightarrow{\approx 1100^\circ C} Cu_2O + \frac{1}{2}O_2$$

all sulphates

$CaSO_4$ (ss)

$NaHCO_3$ (ss)

- Carbon reduction $MO + C \longrightarrow M + CO$
- Smelting Slag formation with melting