Ores Metallurgy

Grinding & pulverization

Major operations:

1) concentrated ores
2) Reduction of concentrated ore to crude oil.
3) Refining

Concentration

1) Hydraulic washing : based on gravitational force (↑ Density of gangue & ore)
For haematite Fe_2O_3, Cassiterite SnO_2.
Seperates due to density. Through water.

2) Magnetic seperation : based on magnetic & non mag property of ores or guangue.

For
- Chromite $(FeCrO_2)_2$, it is magnetic
  Siliceous impurities in it
- Wolframite $(FeWO_4)$, it is magnetic.
  Cassiterite impurities in it.
- Mixture of Rutile (TiO_2) (magnetic) and Chloroapatite ($CaCl_2 \cdot 3Ca_3(PO_4)_2$) (impurity non magnetic)

3) Froth floatation method
Based on different wetting props of ore and gangue by oil & water.
Ore is wetted by oil.
Gangue is wetted by water

For
- Sulphide ores mainly
  Eg Galena (PbS)

NaCN → depressant allows PbS to froth, ZnS remains inside

(*) Copper Pyride ($CuFeS_2$), Cu Glance (Cu_2S)
Zinc blende (ZnS)

eucalyptus oil, crude oil
frother's : Pine oil, ~~fatty acids, xanthates } toxic collectors~~
froth stabilizer : cresols, aniline.

Collectors: Ethyl xanthate, potassium ethyl xanthate, fatty acids help in enhancing the non wettability of mineral particles

Leaching

1) **Red Bauxite**: Fe_2O_3, TiO_2, SiO_2 : impurities.
↑ Bayer process
2) Low grade Red Bauxite: Hall process → Fe_2O_3 impurity.
3) White Bauxite : Serpeck : ~~White Phosphorous~~ more SiO_2

Bauxite extraction

BAYER PROCESS: Only for red bauxite.

Finely powdered bauxite containing Fe_2O_3, TiO_2, SiO_2 impurities

↓ calcination ($FeO \rightarrow Fe_2O_3$), organic matter removed

Calcined ore (Digested with 45% NaOH with at 150°C under 80 atm pressure)

↓ Filtration

- **Residue**: Fe_2O_3, TiO_2
- **Filtrate**: $NaAlO_2$, Na_2SiO_3

Freshly prepped $Al(OH)_3$, seeding agent, filtered

- **PPt** $Al(OH)_3$ ↓ 1000°C → **Pure Alumina** Al_2O_3
- **Filtrate**: $NaOH$, Na_2SiO_3

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HALL'S PROCESS

Crude bauxite at 1100°C reacts with Na_2CO_3, little $CaCO_3$ when $CaSiO_3$, Na_2SiO_3, $NaFeO_2$, etc form

$Al_2O_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2\uparrow$
$Fe_2O_3 + Na_2CO_3 \rightarrow 2NaFeO_2 + CO_2\uparrow$
$SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2\uparrow$
$CaO + SiO_2 \rightarrow CaSiO_3$

Then at 50–60°C, CO_2 is passed through $NaAlO_2$ solⁿ & produces thereby $Al(OH)_3$

$2NaAlO_2 + CO_2 + 3H_2O \rightarrow 2Al(OH)_3\downarrow + Na_2CO_3$
$2Al(OH)_2 \xrightarrow{1100°C} Al_2O_3 + 3H_2O\uparrow$

Serpeck's process

Bauxite with high silica percentage. In this, finely powdered bauxite is mixed with coke and the mix is heated at 1800°C in a current of N_2. The AlN thus obtained is reacted with hot and dil. NaOH to produce $NaAlO_2$ & excess AlN is hydrolysed to form $Al(OH)_3$

$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO\uparrow$
$SiO_2 + 2C \rightarrow Si\uparrow + 2CO\uparrow$
$AlN + NaOH \rightarrow NaAlO_2 + NH_3\uparrow$
$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3\downarrow + NaOH$
$AlN + 3H_2O \rightarrow Al(OH)_3\downarrow + NH_3\uparrow$
$2Al(OH)_3 \xrightarrow{1100°C} Al_2O_3 + 3H_2O$ (~~alumina~~)

IN NCERT: Bauxite contains SiO_2, Fe_2O_3, TiO_2 impurities. Concentration is carried out by digesting powdered ore with conc NaOH at 433–523K and 35–36 bar pressure.

$Al_2O_3(s) + 2NaOH(aq) + 3H_2O \rightarrow 2Na[Al(OH)_4]$ → leached

Alumenate is neutralised by passing CO_2 & hydrated Al_2O_3 ppted, induced by a fresh sample of Al_2O_3

$2NaAl(OH)_4 + CO_2 \rightarrow Al_2O_3 \cdot xH_2O + 2NaHCO_3$

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Sod silicate remains & hydrated alumina is obtained. $Al_2O_3 \cdot xH_2O \xrightarrow{1470K} Al_2O_3 + xH_2O$

The metals above Al in electrochemical series (more electropositive) do not require reducing agent, they are reduced by electrolytic reduction only.

Extraction of Ag and Au

Cyanide process /

Metals are leached out with dil NaCN or KCN in the presence of air (for O_2) from which metal is obtained later by replacement

1) $4M(s) + 8CN^-(aq) + 2H_2O(aq) + O_2(g) \rightarrow 4[M(CN)_2]^-(aq) + 4OH^-(aq)$, M = Ag or Au.

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

→ Ag : Silver Glance / Argentite Ag_2S Ruby silver $3Ag_2S \cdot Sb_2S_3$
Horn Silver: AgCl Ag Cu Glance / stromeyrite: $AgS \cdot Cu_2S$

Concentration: Crushed powder conc by froth floatation

Conc Ag_2S is then treated with 0.5% sol^n of NaCN in air.

$Ag_2S + 2NaCN \rightleftharpoons 2AgCN \downarrow + Na_2S$

$AgCN + NaCN \rightleftharpoons Na[Ag(CN)_2]$

$4Na_2S + 5O_2(air) + 2H_2O \rightleftharpoons 2Na_2SO_4 + 4NaOH + 2S$

Ppt: By reaction (2)

Electrolytic refining: Ag (metallic) thus obtained contains Zn, Cu, Au impurities. It is purified by electrolytic refining. Electrolytic bath contains $AgNO_3$ sol^n with 10% HNO_3. Ag (impure) at anode and thin sheets of pure Ag at cathode. Impurities like Zn & Cu go into sol^n and Au settles under Anode as Anode mud

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Au: Found in native state, mixed with quartz in rocks or scattered in sand. Also as sulphide, telluride or arsenosulphide. Ores: i) Calaverite ($AuTe_2$), Sylvanite ($AuAgTe_4$)

Extraction: After conc by froth floatation ore of Au is put in large vats made of wood or cement having perforated false bottoms with coconut matting. Extraction by rxn (1) and (2)

Isolation of metals from conc ore, involves 2 major steps:
1) conversion to oxide
2) Reduction to metal:

conversion to oxide: → volatile parts of metal ores escape leaving behind oxide.

Calcination: substances are heated without air.

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

$Fe_2O_3 \cdot xH_2O \xrightarrow{\Delta} Fe_2O_3$

$CaCO_3, MgCO_3 \rightarrow CaO, MgO$

$Al_2O_3 \cdot 2H_2O \rightarrow Al_2O_3 + 2H_2O$

Roasting: process in which ore is heated strongly in presence of air, at temp below the M.P of ore. Usually done in reverberatory furnace or blast furnace

$ZnS + O_2 \xrightarrow{\Delta} ZnO + SO_2$

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

$Cu_2S + O_2 \xrightarrow{\Delta} Cu_2O$ (Cu glance)

(Autoreduction & self reduction process)
(Cu, Hg, Pb,) sulphides of these metals are reduced without any other RA as they undergo self reduction

$HgS + O_2 \rightarrow Hg + SO_2$

→ Cu from low grade ores by electrolytic:
$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$

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$Cu_2S + O_2 \longrightarrow Cu_2O + SO_2$
$Cu_2O + Cu_2S \longrightarrow Cu + SO_2$ } self reduction.

↳ blister copper, as it solidifies and SO_2 hidden in it escapes out, producing blisters on its surfaces

~~PbS + O~~$_2$ $PbO + PbS \longrightarrow Pb + SO_2$ (1)

(or)
$PbS + O_2 \longrightarrow PbSO_4$
$PbSO_4 + PbS \longrightarrow Pb + SO_2$

If conc ore containing non-metallic impurities like As, Sb, S, P, they convert into volatile gases in roasting

$As + O_2 \longrightarrow As_2O_3$
$Sb + O_2 \longrightarrow Sb_2O_3$
$S + O_2 \longrightarrow SO_2$
$P_4 + 5O_2 \longrightarrow P_4O_{10}$ ↑

Reduction of roasted or calcinated ore to metal

→ Chemical reduction → Ellingham diagram
→ Auto / Self reduction → above.
→ Electrolytic.

Electrolytic reduction

When chemical reduction method is Not Applicable, electrolytic reduction is done. It is of 2 types:
1) Reduction at high temp in the absence of water: molten electrolyte is used
2) Using water, hydrometallurgy

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→ Cat. $Al^{3+}(melt) + 3e^- \longrightarrow Al(l)$

An. $C(s) + O^{2-}(melt) \longrightarrow CO(g) + 2e^-$

$C(s) + 2O^{2-}(melt) \longrightarrow CO_2(g) + 4e^-$

Reduction at H.T is mainly used for alkali & alkaline earth metals

→ ~~Extraction~~ Reduction of Al from alumina

20% Al_2O_3, 60% Cryolite Na_3AlF_6, 20% Flourspar: CaF_2

are taken in an iron tank with carbon lining that act as a cathode. A graphite rod hanging at the top acts as anode. Cryolite & flourspar purify alumina, which increase conductivity of alumina and reduce melting pt to 1140K.

This process is Hall-Heroult process.

Reduction by RA

Ellingam Diagram.

Note drawbacks and make diagram.

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

$\frac{4}{x}M + O_2 \longrightarrow \frac{2}{x}M_2O_x$

(O_2: conc = 1)

$\Delta G = \Delta G^\circ + RT\ln Q$

we take rxn at eqb, so $Q = \frac{1}{[O_2]} = 1$.

$\Rightarrow \Delta G = \Delta G^\circ$

The graph is Ellingam diagram b/w ΔG & ΔG°

Van Arkel also for $BI_3 \xrightarrow{W,heat} 2B + 3I_2$

In the diagram, upon a given temp, the slope of line suddenly increases as it is the melting pt of metal. ∴ ΔS reduces (reactant is liquid) & was already negative. so $-T\Delta S > 0$ and increases so ~~tan~~ slope increases.

Refining

a) Distillation : for low boiling metals like Hg, Zn, Cd.

b) Liquation : for low melting metals, Bi, Sn, Pb, Hg

c) Zone refining / fractional crystallization : Based on solubility of impurities (Greater in molten than solid state)
eg Ge, Si, Ga, In, B

d) Electrolytic refining
Cu, Ag, Zn, Sn, Pb, Cr

e) Vapour phase : a) metal should form volatile compound
b) volatile compound should be decomposable
Mond process : Temp of volatile < temp of decomposition
filiment growth method. eg. $Ni + 4CO \xrightarrow{330-350} Ni(CO)_4$
$Ni(CO)_4 \xrightarrow{450-470K} Ni + 4CO$

f) Van Arkel method (Ti & Zr): Only those metals are purified with MP > 1800°C : $Zr + 2I_2 \longrightarrow ZrI_4 \uparrow$
On tungsten filament now : $ZrI_4 \xrightarrow[1800K,\ W]{} Zr + 2I_2$

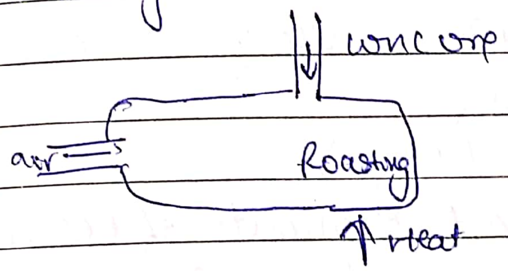
Kroll's process .....

g) Chromatography (done later)

Extraction of Cu:
from Copper pyrites ($CuFeS_2$)

1) Concentration of Ore by Froth floatation :— In sod ethyl xanthate and pine oil. Froth is collected & dried when conc ore is obtained with 25-30% Cu.

2) Roasting in reverberatory flask



In roasting, volatile impurities are removed.

$S + O_2 \rightarrow SO_2\uparrow$, $P_4 + O_2 \rightarrow P_4O_{10}$

$As + O_2 \rightarrow As_2O_3$, $Sb + O_2 \rightarrow Sb_2O_3$

$Cu_2S + Fe_2S_3 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$

as Fe is more electropositive than Cu, it gets oxidized preferentially first, & Cu_2S remains unaffected

$FeS + O_2 \rightarrow FeO$

If any Cu_2O is formed it also reacts with unaffected FeS and gives back Cu_2S

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

$Cu_2O + FeS \rightarrow Cu_2S + FeO$.

3) Smelting in blast furnace : material required.

→ Roasted ore → lime stone (to remove exc silica) → Coke (fuel) → Silica (flux).

On the top: $Cu_2S + O_2 \rightarrow Cu_2O + SO_2\uparrow$

$Cu_2O + FeS \rightarrow Cu_2S + FeO$ → high M.P.

So flux is added : SiO_2 : acidic flux.

$FeO + SiO_2 \rightarrow FeSiO_3$ (slag)

Parallel: $FeS + O_2 \rightarrow FeO + SO_2$

Bessemerization :

Material: molten Cu_2S (more) + FeS (less) / from previous steps) ↓ copper matte.

In furnace, Bessemer converter is used.

In Bessemirization, SiO_2 is added from ext source

$FeS + O_2 \rightarrow FeO + SO_2$

$FeO + SiO_2 \rightarrow FeSiO_3$ (slag)

Green flame is observed at mouth of Bessemer converter indicating Fe as FeO. Dissapearance of green flame indicates the slag formation is complete. The air blasting is then stopped & slag is removed.

Again air blasting is restart for partially roasting before self reduction till $\frac{2}{3}$ rd $Cu_2S \rightarrow Cu_2O$

After this only heating is continued for self reduction process.

$Cu_2S + 3/2 O_2 \rightarrow Cu_2O + SO_2$

$Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$

Also, $Cu_2S + 2O_2 \rightarrow Cu_2SO_4$

$Cu_2SO_4 + Cu_2S \rightarrow 4Cu + 2SO_2$

Molten Cu is put in large container and when it cools, SO_2 is escapes and forms blister Cu.

Refining: Cu containing 2-3% impurities As, Fe, S.

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Refining of Blister copper:

Blister copper contains 2-3% impuerities (as Fe, S, As).
It is seperated by the following process:

Blister Cu + Fe/S/As

↓ Poling,
removes $SO_2(g)$, As_2O_3 (volatile),
$FeSiO_3$ (slag)

Purer Cu (99.5% pure)

↓ Electrorefining
Electrolyte: 15% $CuSO_4$ + 5% H_2SO_4
Cathode: Pure Cu strip
Anode: Thick sheet of Cu (impure)

Pure Cu (99.9%)

In the poling step, little Cu_2O formed is reduced to metallic Cu by the reducing gases produced from charring of green wooden pole. The powdered anthracite (coke) spread on the top surface of the molten mass also helps produce a reducing environment.

In the electrorefining step, impurities like Fe, Ni, Zn get dissolved in the sol^n while Au, Ag, Pt are deposited as anode mud.

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~~Extraction of Fe~~ Extraction of Fe

Q. Iron pyrite is never used for extraction of Fe
Iron in this contains a lot of sulphur, making it brittle and of no use.

→ Roasted ore in smelting:
Roasted: 8 parts
Coke powder: 4 parts
Limestone: 1 part.

Molten metal is called Pig Iron.

Different forms of iron:

1) Cast or pig iron: Impure form, contains 2.5–4 % C along with S, Si, P & Mn. It is brittle, resistant to corrosion

2) Wrought or malleable iron: Purest form containing min amount of carbon (0.12–0.25 %), malleable, can be welded, structurally weak, can't be magnetized. Used to make wires, chains, electromagnets, etc

3) ~~Steel~~ Steel: 0.2–1.5% C, 0.2–0.5% C: Soft steel
0.5–1.5% C: Hard steel

Heat treatment of steel: To control hardness of steel

1) Quenching: Heat steel to redness & then cool it suddenly by plunging in water or oil. The obtained steel is hard & brittle
2) Annealing: Process of heating steel to redness & then cooling slowly. Soft steel obtained.

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3) Tempering : Heating quenched steel to temp much below redness (200-350°C) & then cooling slowly. Used to make razor blades, axes, knives, etc.

4) Case hardening : Heating wrough iron or mild steel in contact with charcoal and then quenching in oil.

5) Nitriding : Process of heating steels at about 700°C in an atmosphere of ammonia. It gives a hard coating of iron nitride on the surface of steel.

CHROMATOGRAPHIC REFINING

Principle : Different components of a mixture are differently adsorbed on an adsorbent.

1) Mix is put on a liquid / gaseous medium which is moved through adsorbent

→ Different components are adsorbed at different levels on the col

2) The adsorbed components are removed (eluted) by using suitable solvents (eluant)

Types of chromatography in class 11th NCERT (Chapter 12 Book 2)

Column chromatography : Col of Al_2O_3 / Silica gel / ion exchange resin (adsorbent), is used to form the stationary phase

The mixture is dissolved in a suitable solvent (mobile phase) and applied to the top of the column.

Colored solⁿ ↴

→ Let a mix contain A: strongly adsorbed
B: moderately adsorbed
C: weakly adsorbed.

Upon elution, the components seperate and form 3 different colored bands.

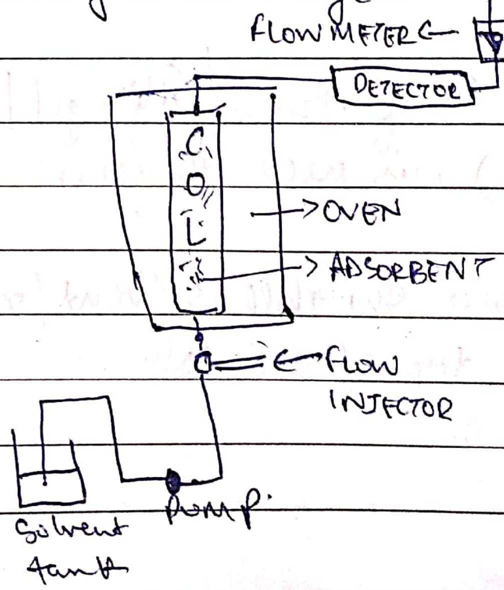
→ C, which is weakly adsorbed, travels down the col fastest and is near the bottom. Above it, B is eluted, then A

These are collected & the solvent is evaporated to give A, B, C.

Colorless solⁿ ↴

If colorless solⁿ, the col is ~~seperated~~ extracted with a suitable solvent or mix of solvents of several small fracts (20-25 ml vol) are collected in different flasks. With suitable physical or chem methods, flasks containing same components are identified & mixed. Solvent evaporated to get substances.

USES: For elements avlbl in very small qtys & their impurities are not very different in chem props from the element. Eg. Lanthanoids are seperated like this using using ion exchange as adsorbent.



: Industrial method

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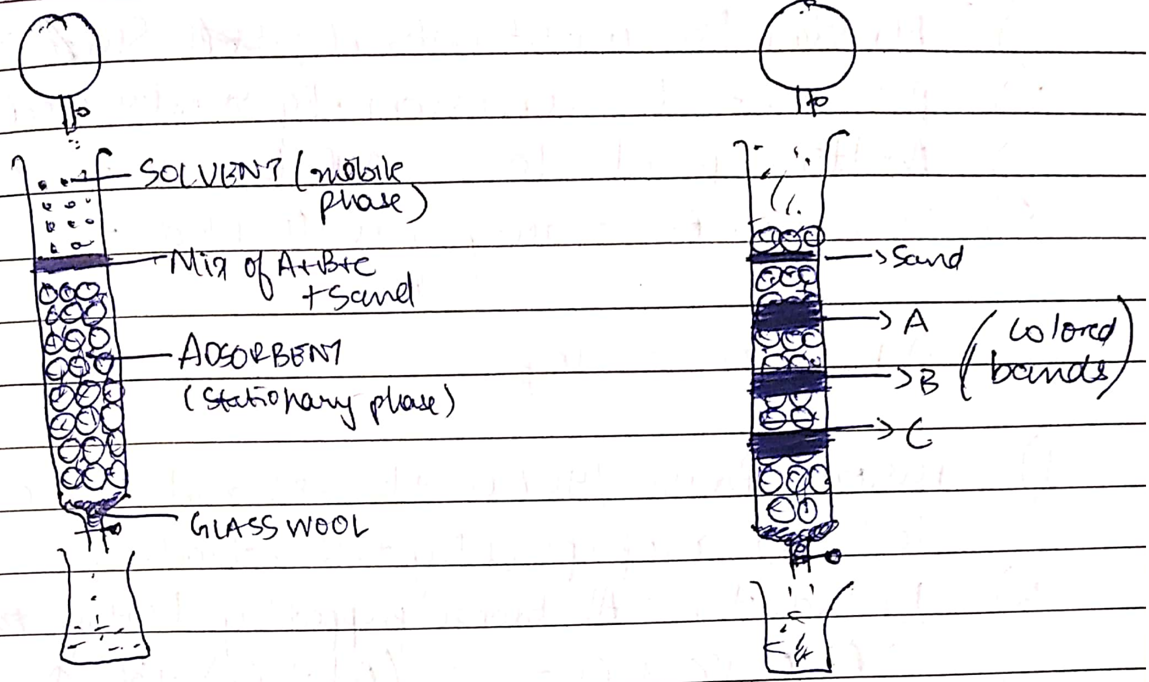

LAB METHOD ↗.

ALLOYS AND AMALGAMS

Alloy:
Homogenous metallic material containing 2 or more metals as a solid soln

Amalgam : One constituent is Hg.

→ Classification
1) Ferrous alloys : If one component is Fe
2) Non ferrous : Does not contain Fe

→ Chars of alloy :
They are prepared to develop some specific properties which are not found in the constituent elements. Props vary highly from const elements

1) Superior casting : Increases casting property. Eg Type metal (Pb – 80 %, Sb – 16 %, Sn – 4 %) increases casting prop of Pb allowing moulding.

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2) Harder than constituents, Eg ~~Stell~~ Steel > Cast iron
3) Resistant to corrosion. Eg stainless steel > Fe
4) Melting point: lower MP than constituents
5) Tenacity. Eg Tenacity of Cu doubled on adding 5% Si

Preparation of alloys:

1) Fusion: Brass: (90% Cu + 10% Zn) and Bronze (90% Cu + 10% Sn) are prepared by this method.
2) By reduction: Al bronze prepped by heating ~~Al~~
$$Al_2O_3 + 3C + Cu \longrightarrow (Al + Cu)_{(l)} + 3CO\uparrow$$
3) Compression: The req^d metals first converted into thin sheets and then are rolled together and hammered under high pressure to give the alloy. • Alloys like solder (50% Pb & 50% Sn) are prepped by this method.
4) Simultaneous electrodeposition: Aq. sol^n of salts of metals is taken in an electrolytic cell & current is passed. Desired metal alloys are obtained on cathode.
Eg Brass produced by electrolysis of a sol^n containing Cu & Zn cyanides in KCN sol^n.

Some important alloys:

Alloy	Composition	Use
(*) 1. Magnalium	Al: 98%, Mg: 2%	Chemical balances
(*) 2. Duralumin	Al: 95%, Cu: 4%, Mg: 0.5%, Mn 0.5%	Aircraft parts, boat machinery
(*) 3. Aluminium bronze	Al: 10%, Cu: 90%	Coins, photoframes, utensils, golden paints

Alloy	Composition	Use
*4 Alnico	Al: 20%, Ni: 20%, Co: 10%, Steel: 50%	Permanent magnets
5. Y-Alloy	Al: 92%, Cu 4%, Mg 1.5%, Ni 2.5%	Pistons & machinery parts
6. Nickeloy	Al: 95%, Cu: 2%, Ni: 1%	Aircraft parts
*7. Pewter	Pb: 20, Sn: 50	Utensiles
*8. Solder	Sn: 63, Pb: 37	Soldering
9. Type metal	Pb: 20, Sn: 5, Sb: 20	Printing type.
*10 Bell metal	Cu: 80, Sn: 20	Bell manuf
11. Babbit metal	Sn: 90, Sb: 7, Cu: 3	Machine bearings
12. Frary metal	Pb: 97%, Ba: 2, Ca: 1	" "
13. Lino type metal	Pb: 83, Sn: 3, Sb: 14	Printing type.
*14. Brass	Cu: 60, Zn: 40	Utensils
*15. Bronze	Cu: 88-96, Sn: 12-4	Utensils, coins, statues
16. Monel metal	Cu: 27, Ni: 68, Fe: 5	Pumps, ship turbines, boilers
*17. German silver	~~Cu: 50, Zn: 30, Ni: 20~~ Cu: 25-30, Zn: 25-30, Ni: 40-50	Flower vases, ornaments

• Cu + Ni = coinage metal

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	Alloy	Composition	Use
18	Electron	Mg:95, Zn:4.5, Cu:0.5	Parts of plane & cars
19	Dutch metal	Cu:80, Zn:20	Golden yellow color for decoration
(*) 20	Nichrome	Ni, Cr, Fe	Elements in heaters
21	Gun metal	Cu:87, Zn:3, Sn:10	
(*) 22	Constantan	Cu:60%, Ni:40%	Constant resistance.
23	Artificial gold	Cu:90, Al:10	
(*) 24.	14 Carat gold	Au:54, Ag:14-30, Cu:12-28	

(*) → Alloys of steel

	Alloy	Composition
1	Vanadium	V:0.2-1%
2	Chromium	Cr:2-4
3	Nickel	Ni- 3-5%
4	Manganese steel	Mn:10-18
5.	Stainless steel	Cr:12-14, Ni:2-4
6.	Tungsten	W:10-20
7.	Invar	Ni:36

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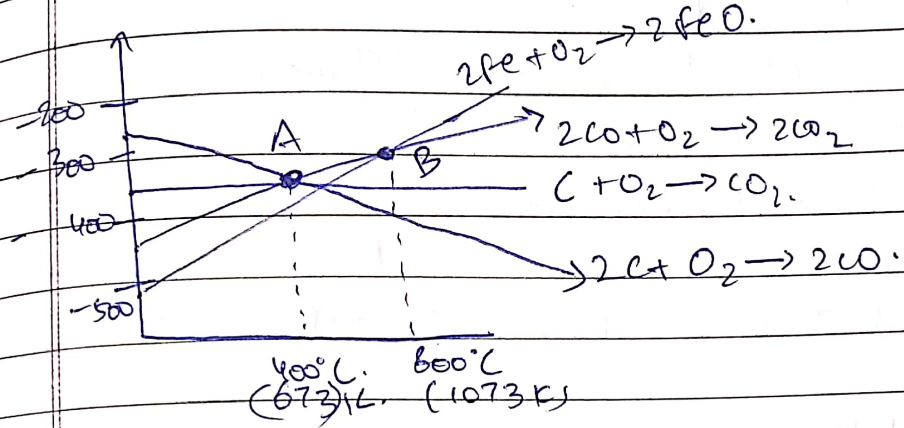
Using Ellingham diagram for reduction of FeO using C or CO.



At temp below 1073K

ΔG $CO \rightarrow CO_2$ is more negative than ΔG $C \rightarrow CO_2$.

So to reduce FeO, CO is used, as $\Delta G^0_{net} < 0$.

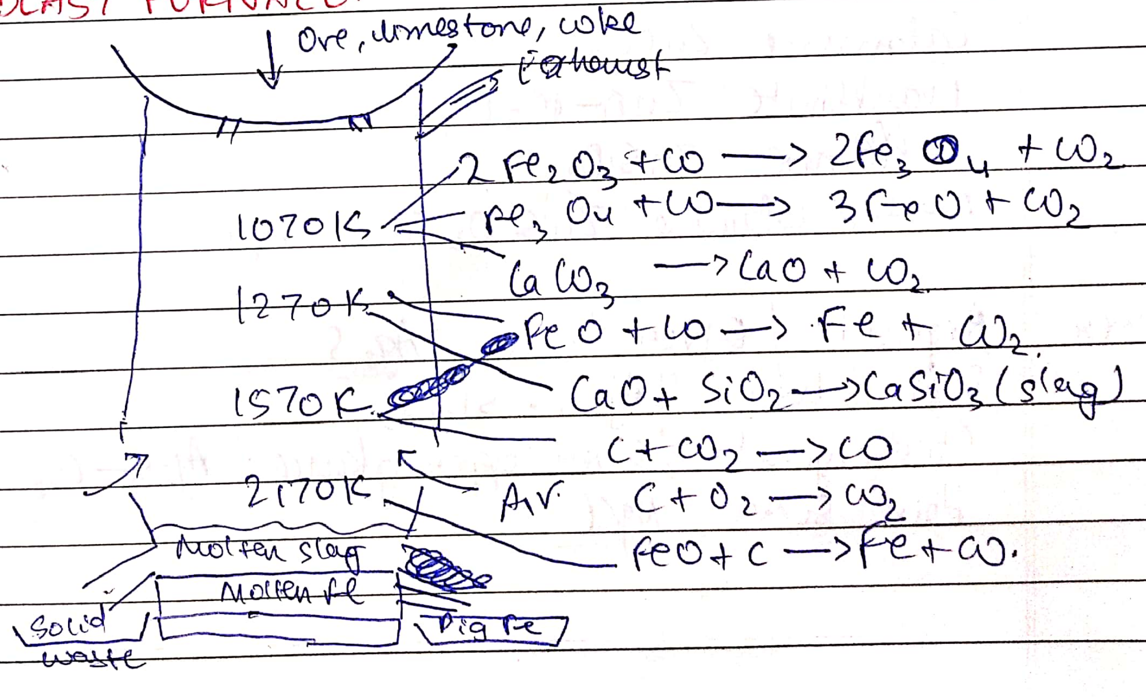
$$FeO(s) + CO \longrightarrow Fe(s/l) + CO_2.$$

At temp above 1073K

$C \rightarrow CO$ line goes to high −ve, so to reduce FeO, coke is used.

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

BLAST FURNACE



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IMPORTANT ORES:

Aluminium
Bauxite: $AlO_x(OH)_{3-2x}$, 0<x<1 or $Al_2O_3 \cdot xH_2O$
Cryolite: Na_3AlF_6
Kaolinite: $Al_2(OH)_4Si_2O_5$ / China clay
Feldspar: $K_2O \cdot Al_2O_3 \cdot 6SiO_2$
→ Red Bauxite: $Al_2O_3 \cdot 2H_2O + Fe_2O_3 + (SiO_2 + TiO_2)$ (maj impurity)
→ White bauxite: $Al_2O_3 \cdot 2H_2O + SiO_2 + (Fe_2O_3 + TiO_2)$ (maj)

Iron
Haematite: Fe_2O_3
Magnetite: Fe_3O_4
Siderite: $FeCO_3$
Iron pyrites: FeS_2 (not used as SO_2 makes useless

Copper:
Copper pyrites: $CuFeS_2$
Copper glance: Cu_2S
Malachite: $CuCO_3 \cdot Cu(OH)_2$
Cuprite: Cu_2O

Zinc:
Zinc blende (Sphalerite): ZnS
Zincite ZnO
Calamine: $ZnCO_3$
Franklinite: $ZnO-Fe_2O_3$
Willemite: $ZnSiO_3$
Electric calamine: $ZnSiO_3 \cdot ZnO-H_2O$

Silver:
Argentite / Silver glance: Ag_2S
Ruby Silver: $3Ag_2S \cdot Sb_2S_3$
Stromeyerite / Silver copper glance: Ag_2S-Cu_2S
Horn Silver: $AgCl$

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Lead: Galena : PbS
Cerussite : $PbCO_3$
Anglesite : $PbSO_4$
Crocoisite : $PbCrO_4$
Lanarkite : $PbO-PbSO_4$

Tin Cassiterite : SnO_2
Stannite : Cu_2FeSnS_4

Mg Dolomite : $CaMg(CO_3)_2$
Magnesite $MgCO_3$
Carnallite
Talc : Mg Silicate
Olivine
Brucite : $Mg(OH)_2$

Cinnabar : Hg
Wolframite : W
Rutile : Ti