d-block

"Valence e⁻ is apart (n-1) d subshell."

Config :- $(n-1)d^{1-10}\ ns^{1-2}$

Transition elem : Element in which (n-1) d subshell in a partially filled.

→ Shows variable valency

Config : $(n-1)d^{1-9}\ ns^{0-2}$

Pseudo transition = $(n-1)d^{10}\ ns^{2}$

→ 40 elements in d-block.

4th Prd	Sc	Ti	V	(Cr)	Mn	Fe	Co	Ni	(Cu)	Zn
5th Prd	Y	[Zr]	(Nb)	(Mo)	Tc	(Ru)	(Rh)	*Pd	(Ag)	Cd
6th Prd	La ↔	[Hf]	Ta	W	Re	Os	Ir	(Pt)	(Au)	Hg
7th Prd	Ac ↔									

○ = $(n-1)d^{1-10}\ ns^{1}$

* = $(n-1)d^{10}\ ns^{0}$

Coinage metals - Cu / Ag / Au

Pseudo transition - Zn / Cd / Hg

Tc - synthetic

Zr & Hf - Twin elements

↔ Lanthanide series (58 to 71)

↔ Actinide series (90 to 103)

Properties:

1) Metallic solid
2) Metallic lustre
3) Shows magnetic prop
   - → Para (unpaired e⁻)
   - → Dia (paired e⁻)
   - → Ferro → Strong para (Fe / Co / Ni)

4) Shows catalytic prop.
5) Good conductor
6) Metallic strength ∝ unpaired e^-
7) Mag. moment ∝ unpaired e^-.
8) M.P. ∝ unpaired e^-. (sudden fall at Mn)
9) Tendency to form alloys.
* cond - Size of atom should be same or close same.

10) Tendency to form interstitial comp.
* cond - size gap should be high.
# C, H, B, N
ex Fe_3C
(cementite) → hardest comp. of iron

11) Atomic radii — S.E. → Responsible for increase in size.
E.N.C → " " decrease " "

Almost same (SE = ENC)

Sc Ti V Cr Mn Fe Co Ni Cu Zn

decreases
E.N.C > S.E.

Increases
S.E. > E.N.C.

12) Ionic radii — Decreases due to increases in E.N.C

Zinc- volatile nature
Cd
Hg

[Pseudo transition elements/Lassenite are volatile. Purified by distillation]

	unpaired e⁻
Sc - $3d^1 4s^2$	1
Ti - $3d^2 4s^2$	2
V - $3d^3 4s^2$	3
*Cr - $3d^5 4s^1$	6 ↕ Dip in M.P.
Mn - $3d^5 4s^2$	5 Sudden fall in M.P. due
Fe - $3d^6 4s^2$	4 to exactly half filled
Co - $3d^7 4s^2$	3 config.
Ni - $3d^8 4s^2$	2 * Least delocalised e⁻
*Cu - $3d^{10} 4s^1$	1 (Mn, Tc & Re)
Zn - $3d^{10} 4s^2$	0 + M.P 3d < 4d < 5d.

* Cr :

Chromite - $FeO.Cr_2O_3$

900-1200°C | $Na_2CO_3 + O_2$ (Roasting)

$Na_2CrO_4 + Fe_2O_3 + CO_2\uparrow$

↓ H_2O + Filter

Na_2CrO_4

↓ H_2SO_4 conc ← only medium

$Na_2Cr_2O_7 + Na_2SO_4 + H_2O$ ← separated by crystallization

$Na_2Cr_2O_7$: :

Δ ↓ : Δ ↓ NH_4Cl

$C + H_2O$: $N_2 + NaCl + Cr_2O_3 + H_2O$

↓

$NaOH + Cr_2O_3 +$

Co

Redⁿ of Cr_2O_3

Cr_2O_3 →
- $Si \rightarrow SiO_2 + Cr$
- $Al \rightarrow Al_2O_3 + Cr$
- $C \rightarrow CO$

* $K_2Cr_2O_7$:

$$K_2CrO_4 + H_2SO_4 \xrightarrow[conc]{} K_2Cr_2O_7 + K_2SO_4 + H_2O$$

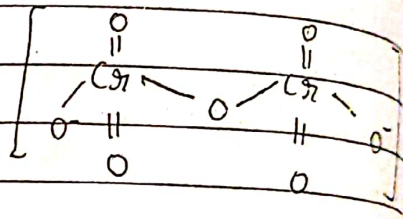
$$Na_2Cr_2O_7 + KCl \xrightarrow{\Delta} NaCl + K_2Cr_2O_7$$

→ orange solid, soluble, tetrahedral

→ Hygroscopic

→ $K_2Cr_2O_7 < Na_2Cr_2O_7$ (That's why not used in titrations)

$2K^+$



C.P:

* unique $K_2Cr_2O_7$ —
- $\Delta \rightarrow K_2CrO_4 + Cr_2O_3 + O_2$
- $HCl \rightarrow Cl_2 + KCl + CrCl_3 + H_2O$
- * HCl (hot conc.) $\rightarrow KCrO_3Cl + H_2O$ (Petigol's salt)
- $K_2CO_3 \rightarrow K_2CrO_4 + CO_2 + O_2$
- $KOH \rightarrow K_2CrO_4 + H_2O + O_2$
- H_2SO_4 (hot conc) $\rightarrow K_2SO_4 + CrO_3 + H_2O$

Red crystals

* $Cr_2O_7^{-2} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} CrO_4^{-2}$

Orange — Yellow — At pH = 11

Oxid. prop

$K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O + [O]$

$K_2Cr_2O_7$ —
- $KI \longrightarrow K_2 I_2 + K_2SO_4$
- $KNO_2 \longrightarrow KNO_3$
- $K_2SO_3 \longrightarrow K_2SO_4$
- $N_2H_4 \longrightarrow N_2$
- $H_2C_2O_4 \longrightarrow CO_2$
- $HX \longrightarrow X_2$
- $H_2S \longrightarrow S$

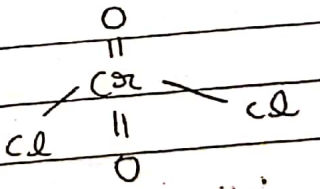
* Chromyl chloride

$CrO_3 + HCl \longrightarrow CrO_2Cl_2 + H_2O$

$H_2CrO_4 + HCl \longrightarrow CrO_2Cl_2 + H_2O$

P.P

Red orange, soluble, tetrahedral



C.P

CrO_2Cl_2 —
- $\xrightarrow{\Delta} Cr_2O_3 + O_2 + Cl_2$
- $\xrightarrow{H_2O} H_2CrO_4 + HCl$
- $\xrightarrow{F_2} CrO_2F_2 + Cl_2$
- $\xrightarrow{HF} CrO_2F_2 + Cl_2$
- $\xrightarrow{NaOH} Na_2CrO_4 + NaCl + H_2O$

Etard reaction

$\longrightarrow C_6H_5CHO + CrCl_2$

CrO_5

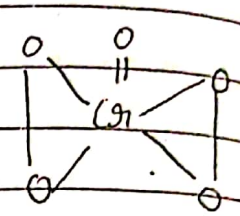
* only two reaction

$K_2Cr_2O_7$ / K_2CrO_4 $\xrightarrow{H_2SO_4 + H_2O_2}$ $CrO_5 + K_2SO_4 + H_2O + O_2$

→ Pale blue, peroxide, paramagnetic, unstable.

If H_2SO_4 not conc. then direct

$CrO_5 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + H_2O + O_2$



Mn

some compound: Pyrolusite / Hausmanite $\rightarrow MnO_2$

$MnO_2 \xrightarrow{Red^n}$ Explo

$MnO_2 \xrightarrow{\Delta} Mn_3O_4$ → Al → $Al_2O_3 + Mn$

→ C → Co + Mn

* $KMnO_4$:

alkaline medium with oxi agent.

MnO_2 + KOH + O_2 → $K_2MnO_4 + H_2O$

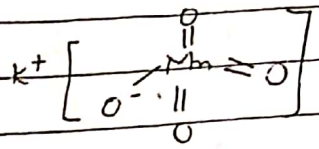
MnO_2 + $KClO_3 + O_2$ → $K_2MnO_4 + KCl$

Oxd^n of K_2MnO_4 → green

K_2MnO_4 →
- $\rightarrow Cl_2 \rightarrow KCl + KMnO_4$
- $\rightarrow O_3 + H_2 \rightarrow O_2 + KMnO_4 + KOH$
- $\rightarrow CO_2 \rightarrow K_2CO_3 + \overset{+4}{MnO_2} + KMnO_4$ (only medium (disp...))

P.P

→ Purple violet solid, soluble, tetrahedral



C.P

$KMnO_4$ →
- $\rightarrow \Delta \rightarrow K_2MnO_4 + MnO_2 + O_2$
- $\rightarrow KOH \rightarrow K_2MnO_4 + H_2O + O_2$
- $\rightarrow K_2CO_3 \rightarrow K_2MnO_4 + CO_2$
- $\rightarrow HCl \rightarrow KCl + MnCl_2 + H_2O + Cl_2$
- $\rightarrow H_2SO_4$ (Hot. conc) $\rightarrow K_2SO_4 + Mn_2O_7 + H_2O$

Oxid. prop:

$KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + H_2O + [O]$

$KMnO_4$ →
- $\rightarrow FeSO_4 \rightarrow Fe_2(SO_4)_3$
- $\rightarrow H_2S \rightarrow S$
- $\rightarrow K_2SO_3 \rightarrow K_2SO_4$
- $\rightarrow KNO_2 \rightarrow KNO_3$
- $\rightarrow KI \rightarrow I_2$

$\overset{+2}{KMnO_4} + KOH \rightarrow KOH + \overset{+4}{MnO_2} + [O]$ E.W = $\frac{KMnO_4}{5\ 1\ 3\ 2}$ (A B N)

$\overset{+2}{KMnO_4} + \underset{\text{strong}}{KOH} \rightarrow \overset{+6}{K_2MnO_4} + H_2O + [O]$

$\overset{+7}{KMnO_4} + H_2O \rightarrow KOH + \overset{+4}{MnO_2} + [O]$

* Sc - 2*, 3 → $Sc_2O_{3(b)}$

Ti - 2*, 3, 4 → $TiO_{(b)}$, $Ti_2O_{3(b)}$, $TiO_{2(c)}$

V - 2, 3, 4, 5 → $VO_{(b)}$, $V_2O_{3(b)}$, $VO_{2(c)}$, $V_2O_{5(a)}$

Cr - 1*, 2, 3, 4*, 5*, 6 → $CrO_{(b)}$, $Cr_2O_{3(c)}$, $CrO_{2(c)}$, $CrO_{3(a)}$, $Cr_2O_{3(a)}$

Mn - 2, 3, 4, 5*, 6, 7 → $MnO_{(b)}$, $Mn_2O_{3(b)}$, $MnO_{2(c)}$, $Mn_2O_{7(a)}$

Fe - 2, 3, 4* → $FeO_{(b)}$, $Fe_2O_{3(b)}$

Co - 2, 3, 4* → $CoO_{(b)}$

Ni - 2, 3, 4 → $NiO_{(b)}$

Cu - 1, 2 → $CuO_{(b)}$

Zn - 2 → $ZnO_{(c)}$

* → Rare

a → acidic
b → basic
c → ampho.

* Highest O.N → +8 → Os & Ru
Most number of O.N in 3d - Cr, Mn.

Colours of Vanadium.

O.N.	Ion	Colour
+5	VO_3^- or VO_2^+	Yellow
+4	VO^{+2}	Blue
+3	V^{3+}	Green
+2	V^{+2}	Blue

* All ores can be mineral but all minerals cannot be ore

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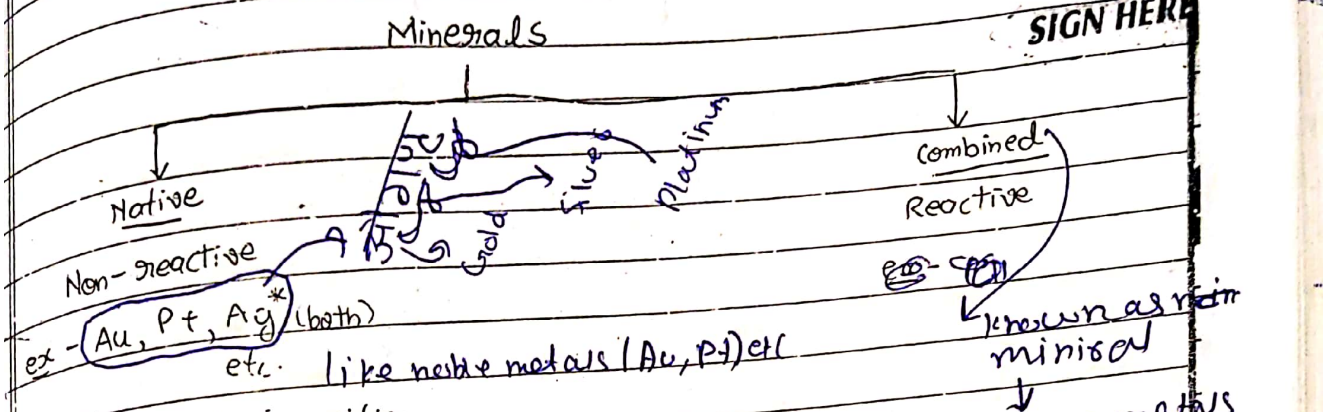
Metallurgy

Metallurgy is study of extraction of pure metals from their ores.

Mineral - Existence of metal in native or combined state in nature is called minerals.

Ores - Mineral from which metal is easily extracted.



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Steps involved :-
Selection of ore
Crushing or grinding
Conc. of ore
Heating of ore [Formation of metal oxide for reduction]
Red^{n} of metal oxides
Refining

Selection of ore-
Depends on 2 factors: Availability, purity

Crushing and grinding:
Lump of ore → crushing → small pieces
Pulverisation { → Ball stamp mill
powder form of ore [unwanted particles]

used for removal of non-metallic impurities

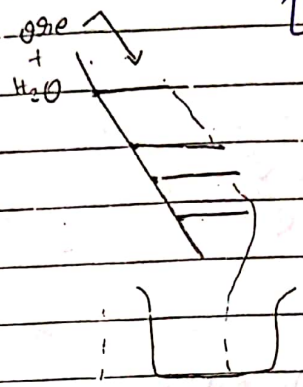
(3) Conc of ore / Dressing of ore / Beneficiation of ore / Purification of ore

Levigation / gravity separation process

→ Based on the difference in density / specific gravity of matrix & gangue ore.

ex: chromite, haematite, tin stone.

$[FeO \cdot Cr_2O_3]$

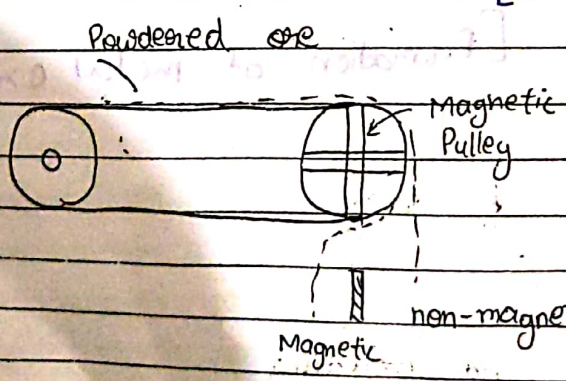


* Magnetic Separation Process

→ Based on the diff. in magnetic nature of matrix & ore.

ex: chromite, haematite, tin stone.

$[Fe_2O_3$

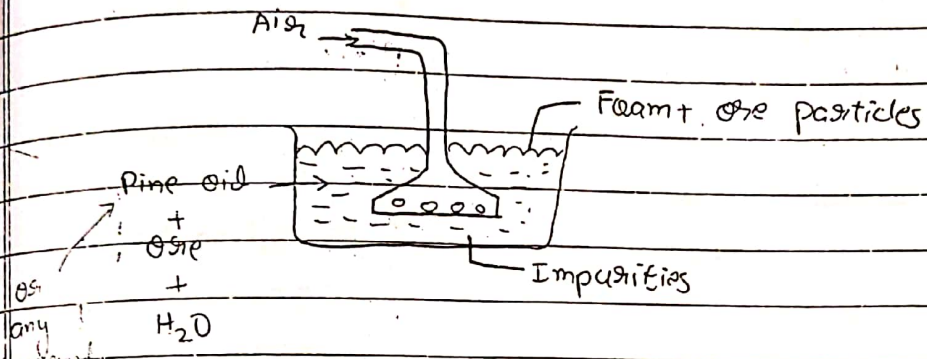


Foam - Sodium Lauryl sulphate
↓
ester

Froth flotation process

→ Based on the diff. in wetting nature of matrix and ore
ex: Mostly for sulphide ores.

Foam stabiliser - Aniline
Activator - $CuSO_4$
Depressant - NaCN
Collector - Ethyl xanthelate



Leaching - Based on the diff. in solubility of ore & matrix. Mostly of Al
ex. Bauxite (NaOH), Argentite (NaCN)

④ Heating of ore / Formation of oxide

Roasting	Calcination [In Reverberatory furnace]
→ In presence of air → Removal of moisture and water of crystallization → Removal of volatile impurities	(During this process ore become porous) × ✓ => hydrated to dehydrated ×
ex. Mostly for sulphide ores	ex. Mostly for carbonate ores & hydroxide ores.

⑤ Red^n of metal oxide

a) Pyro metallurgy / Thermal Red^n.

- Red^n by carbon – Fe, Sn, Zn, Pb etc.
- Red^n by CO – Fe, Cu etc.
- Red^n by Al – Cr, Mn, B etc.
- * Self/Auto Red^n – Pb, Cu, Hg.

b) Electro metallurgy – S-block, Al

c) Hydrometallurgy / Displacement process – Ag, Au etc.

cooling

* Flux: It is used for the removal of infeasible impurities.

→ Acidic flux – For the removal of basic impurities
ex SiO_2, B_2O_3, etc. P_2O_5

$$\underbrace{CaO}_{\text{Imp}} + \underbrace{SiO_2}_{\text{A.F}} \rightarrow CaSiO_3 \text{ (slag)}$$

→ Basic flux – For the removal of acidic impurities
ex. CaO, MgO etc

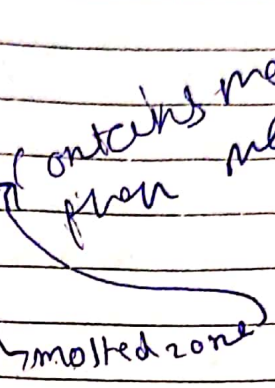
$$\underbrace{CaO}_{\text{B.F}} + \underbrace{SiO_2}_{\text{Imp}} \rightarrow CaSiO_3 \text{ (slag)}$$

Syllabus KCL

Refining

Liquation - Zn, Pb, Sn etc.
Poling Process - Cu, Sn etc.
Cupellation - Ag.
Zone Refining - Ge, Ga etc.
*Distillation - Zn, Cd, Hg
*Mond's process - Fe, Ni etc.

(contains more impurity than metal)



$$Fe + CO \xrightarrow{T_1} [Fe(CO)_5] \xrightarrow{T_2} Fe + CO\uparrow \quad (T_2 > T_1)$$

Non-Arkel's - Ti, Zr, Hf, B etc.

$$\text{Impure metal} + I_2 \xrightarrow{T_1} \text{Metal iodide} \xrightarrow[\Delta]{T_2} \text{Metal} + I_2\uparrow \quad (T_2 > T_1)$$

→ (converts metal into volatile stable compound)

Electro refining

Anode - Impure Metal
Cathode - Pure metal
Electrolyte - Metal salt + Acid (for conductivity)
* Anode mud - Impure metal
* 99.99% pure metal obtained at cathode.

COPPER :

Cuprite - Cu_2O (Ruby copper)
Malachite - $CuCO_3 . Cu(OH)_2$
Azurite - $CuCO_3 . Cu(OH)_2$ [1:2]
Chalcopyrite - $CuFeS_2$

Turaco - $(CuFe)_2(OH)_4 \cdot 4H_2O$

Selection of ore — Pearlock - FeS_4

Crushing

→ Conc of ore - Froth Floatation process

→ Heating of ore - Roasting
- Below 800°C.

As/Sb $\xrightarrow[\Delta]{O_2}$ Volatile oxides

Partially $CuFeS_2 + O_2 \rightarrow Cu_2O + FeO + SO_2\uparrow$

→ Smelting - (Roasted ore + SiO_2 (A.F.))

↓ Δ

Upper Part
Slag of Fe Ca Al
→ $FeSiO_3$, $CaSiO_3$,
$Al_2(SiO_3)_3$

Lower part
Copper Matte $Cu_2S + FeS$
↓ Δ | $O_2 + SiO_2$
$FeS + O_2 \xrightarrow{\Delta} FeO + SiO_2\uparrow$
↓ SiO_2
$FeSiO_3$
(Slag)

Bessemerisation

self red"
$Cu_2S + O_2 \rightarrow Cu_2O + SO_2$
$Cu_2O + Cu_2S \rightarrow Cu + SO_2$
↓
98% : blister copper (bubbles due to SO_2)

Cuprite
Copper Glance

impurity of Cu_2O

This impurity is removed by Poling Process.

→ Electrorefining

Anode - Impure Cu
Cathode - Pure Cu
Electrolyte - $CuSO_4 + H_2SO_4$
* Anode mud - Au, Ag, Pt etc. + Hg

99.9% Cu at cathode.

Lead:-

Anglesite - $PbSO_4$
cerussite - $PbCO_3$
* Galena - PbS

→ Selection of ore
→ Crushing and grinding
→ conc. of ore - Froth floatation
→ Heating of ore - Roasting
↳ Reverberatory Furnace

Partially $PbS + O_2 \xrightarrow{\Delta}$ $PbSO_4$ ~~Moderately high temp~~
$PbO + SO_2$ Very high temp

→ Smelting : Start along with roasting

Self: PbS — $PbSO_4$, PbO } $Pb + SO_2$

~~$PbS + PbO \rightarrow Pb + SO_2$~~
~~$PbSO_4 + PbO \rightarrow Pb + O_2$~~

→ Electrorefining
Anode - Impure Pb
Cathode - Pure Pb
Electrolyte - $PbSiF_6 + H_2SiF_6$
* Anode mud - Ag, Sn, Zn, Sb etc.

~~Impure~~ Reverberatory Furnace

Zinc

Zincite - ZnO

Calamine - $ZnCO_3$ → used in cosmetics

* Zinc Blande - ZnS

→ Selection of ore

→ Crushing and grinding

→ Concentration of ore .. Froth floatation

→ Heating of ore - Roasting

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

→ Smelting - Roasted ore + Coke

Belgian Process

$$ZnO + C \xrightarrow{\Delta} Zn + CO\uparrow$$

↓

Spelter Zinc (impure)

→ Electrorefining

Anode - Impure Zinc

Cathode - Pure Zn

Electrolyte - $ZnSO_4 + H_2SO_4$

* Anode mud - Cd, Bi, Pb, Sn etc.

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Tin

Cassiterite
Tin Stone
] SnO_2

Selection of ore
Crushing and grinding
Concentration of ore :

Gravity Separation

Magnetic Separation
(for the removal of
Wolframite ($FeWO_4 . MnWO_4$))

→ Heating of ore - Roasting
↓
for the removal of volatile impurities.

$S/As/P \xrightarrow{\Delta}$ volatile oxides

→ Smelting - Roasted ore + coke

$SnO_2 + C \rightarrow Sn + CO\uparrow$

→ Electro refining

Anode - Impure Sn
Cathode - Pure Sn
Electrolyte - $SnSO_4 + H_2SO_4$
* Anode mud - Pb, Si, Zn, Sb etc.

* Normally, nearby elements there in anode mud

Silver:

Horn Silver — AgCl — RUBY Silver

* Argentite — Ag_2S

→ Selection of ore

→ Crushing and grinding

→ Conc. of ore – Leaching → ∵ contains PbS

$$Ag_2S + NaCN + O_2 \xrightarrow{\text{air}} Na[Ag(CN)_2] + Na_2SO_4$$

→ If O_2 not used, Na_2S formed ∴ Reaction backward

→ Displacement – Hydrometallurgy → Filter of ppt

$$Na[Ag(CN)_2] + Zn \xrightarrow{\Delta} Na_2[Zn(CN)_4] + Ag$$

→ This process is called Mc. Arthur Forest cyanide process

→ Same for Au.

→ Electro refining:

Anode – Imp. Ag

Cathode – Pure Ag

Electrolyte – $AgNO_3 + HNO_3$

* Anode mud – Cu, Cd, Bi, Pb, Sn etc.

* Desilverisation from Argentiferrous (Alloy of Pb-Ag)

Pattinson's (≃ 2.6 % Ag)

M.P. → Ag 303°C
M.P. → Pb 372°C

Pb - Ag
↓ Δ
Slow cooling
→ crystals of Pb
↓
Ag

Repeat several times

Parke's

Pb - Ag
↓ Δ Zn
(Zn - Ag) + Pb
light weight
↓ Δ Distillation → cupletion
Ag + Zn ↑

Thermite mixture - ... ration mix of Fe_2O_3 & Al.

Iron

Natural ore

Haematite - Fe_2O_3 Limonite - $FeO(OH)$

Magnetite - Fe_3O_4

Siderite - $FeCO_3$ Fool's gold - FeS_2 (Iron pyrite)

Ilmenite - $Fe_2O_3 . x H_2O$

→ Selection of ore

→ Crushing and grinding

→ Conc. of ore → Gravity Separation
→ Magnetic Separation

→ Heating of ore -

Removal of volatile impurities.

S/As/P $\xrightarrow{\Delta}$ Volatile oxide

→ Smelting - Roasted ore + lime stone + coke

↓ Blast furnace

(a) Combustion zone

$C + O_2 \rightarrow CO$] Exothermic
$CO_2 + C \rightarrow CO$]

(b) Slag zone

$CaCO_3 \rightarrow CaO + CO_2$

$CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$ } slag (thermally stable)

$CaO + SiO_2 \rightarrow CaSiO_3$ }

Red^{n} Zone (250° - 600°c)

$Fe_2O_3 + CO \xrightarrow{\Delta} CO_2\uparrow + Fe$

95% (pig iron) + 4 carbon

↓ Cooling

Cast iron

Wrought iron (Purest) - Pudding process

Steel -- Bessemer process
- Siemen's Martin / Open heart process
- Basic Oxygen process

Wrought iron + Desired imp. → Steel

* Effect of impurities

C → Hardness ↑ & Tensile strength ↑ ← screws
Si → Fibrous nature ↑ ← metal pillars
Mn → Elasticity ↑ ← ball bearings
Cr → Chem. Resistivity ↑ ← utensils

* Heating effect

* Annealing

Red hot → Slow cooling
* softness ↑

2) Quenching

Red hot → Sudden cooling by H_2O/oil
* hardness & brittleness ↑

3) Tampering: Used to make sharp objects.

Below red hot → Slow cooling
* durability ↑

4) Nitriding

$$Fe + NH_3 \xrightarrow[5\text{-}6 \text{ days}]{500^\circ C - 700^\circ C} \text{Nitride coating}$$

* Types of furnaces:-

1. Blast furnace- Mainly smelting of ore is carried out in this furnace.
2. Reverberatory furnace - Mainly roasting and calcination is done in this kind of furnace.
3. Muffle furnace- Used in small scale metallurgical processes.
4. Electric furnace- Used when very high temp is necessary.