Heavy metals. 12 A

→ Heavy metals defined as metals with relatively high densities i.e. $> 5 g cc^{-1}$ and high atomic weight (or atomic number)

eg. Iron (Fe), Cu, Ag, gold, mercury (Hg), lead (Pb), iridium (Ir) etc.

Iridium is heavest metal known.

Occurance :-

→ Heavy metals are naturally occurring elements that are found throughout the earth's crust.

~~They are extracted from ore~~

② # Propertis of heavy metals.

① → Hard, high sp. gravity, high M.P. & B.P.

② Good conductor of heat and electricity because of free mobile electrons.

③ Generally give coloured compounds because of excitation of d-electron

Ferrous salt → light green.

Ferric salt → brownish.

Copper salt → blue.

④ Variable oxidation states (variable valency) because of availability of both $(n-1)d$ and ns electron for bonding.

Coinage metals. (IB) Group of

Cu, Silver, gold. ⇒ coinage metal.

⇒ used for making coin or currency.

~~Copper~~

General properties of coinage metal

① → occur in native or combined state.

② High. MP, BP, hard, malleable ductile.

③ electronic configuration $(n-1)d^{10}ns^1$
→ quite inert than alkali metals.

④ Variable oxidation state
Cu (+1 & +2)
Au (+1 & +3.

⑤ lower oxidation state salts of coinage metals are water-insoluble
eg. - AgCl
- Cu_2Cl_2 } colourless
- AuCl

$CuCl_2$ → blue
$AuCl_3$ → yellow.
(Colour)

Copper: (Cu) (cuprum)

- Atomic mass 63.57 amu.
  valency 1 & 2.
  Electronic configuration $[Ar]\ 3d^{10}\ 4s^1$

occurrence

→ Native as well as combined state

→ Native state, - Canada
- china
- USA
- Mexico
- Russia

Nepal → Chalcopyrite in
- Makawanpur
- chitwan,
- Udaypur
- Darchula. etc.

Ores of cupper

(1) Chalcopyrites or cupper pyrites.
$CuFeS_2$ or $Cu_2S.Fe_2S_3$.

(2) Chalcocite or copper glance (Cu_2S.)

(3) Ruby copper or copper glance (Cu_2O)

(4) Malachite (green) $CuCO_3.Cu(OH)_2$

(5) Azurite (blue) $2CuCO_3.Cu(OH)_2$.

Extraction of copper (Cu I).

Chief ore
→ copper pyrites. $CuFeS_2$.
→ Extracted from copper pyrites.
~~Steps~~

Steps.

(2) crushing, grinding (pulverization) and concentration.

(i) crushing :-
The process of breaking of the lumps of the ore into smaller gravels is called crushing.
The big lumps of ore are crushed into smaller pices by Jaw crusher.

(ii) Pulverization (grinding)
process of grinding crushed ore into fine powder is called pulverization.
→ Ball mill. or stamp mills.

(iii) concentration :-
The process of removing gangue particles like mudy rock matter sand. etc from ore is called concentration.
It is carried out in fourth flotation process.

Froth = small bubbles in liquid caused by agitation.

~~Forth~~ Froth floatation process.

In this process (~~Concentrated~~ Pulverized) Powdered ore is mixed with water and pine oil. The mixture is vigorously stirred by passing compressed air. Forth is produced which rises (lighter particles) ~~water~~ from where it is skimmed off. The gangue settles at the bottom.

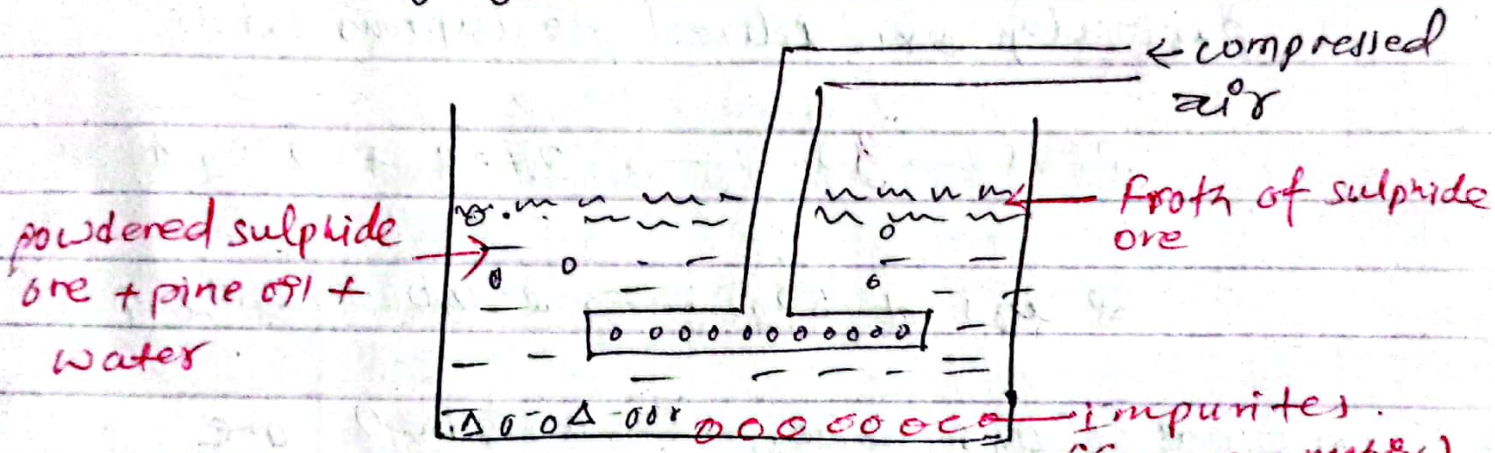


Fig: Froth floatation process.

2* Roasting.

The concentrated ore is heated strongly in excess of air in reverberatory furnace.

Impurities, of S, P, As, & Antimony are removed as their volatile oxides.

$$S + O_2 \xrightarrow{\Delta} SO_2 \uparrow$$

$$4P + 5O_2 \longrightarrow 2P_2O_5 \uparrow$$

$$4As + 3O_2 \longrightarrow 2As_2O_3 \uparrow$$

During this process, copper pyrite is converted into a mixture of ferrous sulphide and cuprus sulphide.

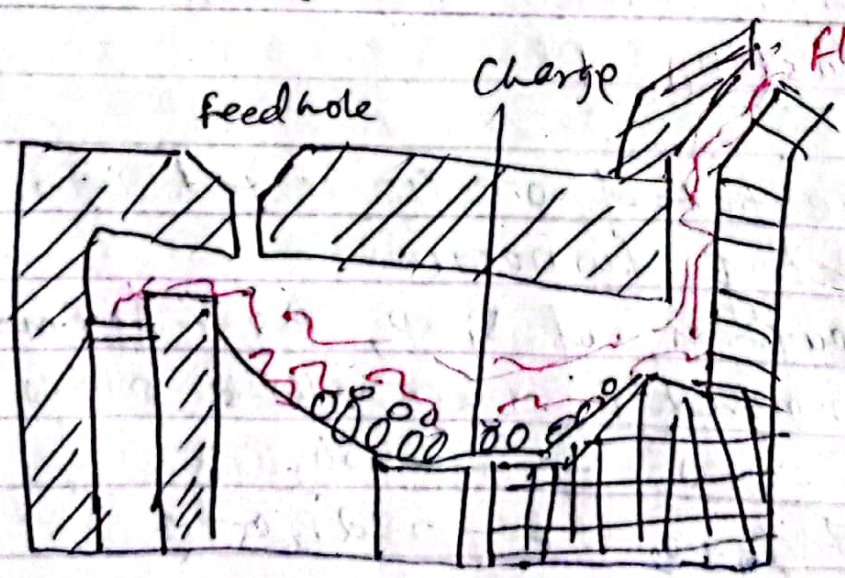
$$2CuFeS_2 + O_2 \longrightarrow Cu_2S + 2FeS + SO_2\uparrow$$

Ferrous sulphide get converted into ferrous oxide and cuprous sulphide is partraly oxidedized to cuprous oxide

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2\uparrow$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

Mixture of Cu_2S, $2FeS$, Cu_2O & FeO are obtained.



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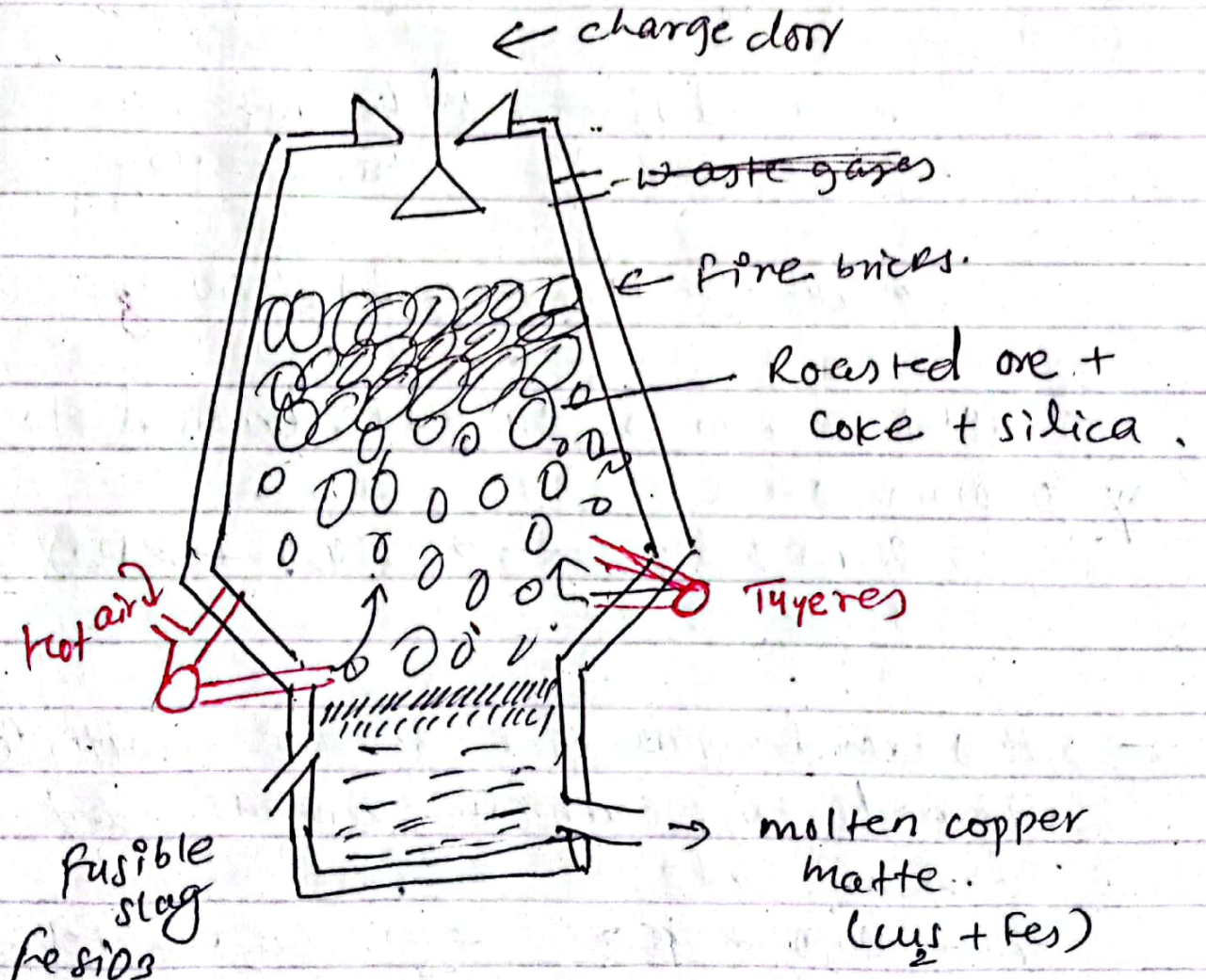
3Q. Smelting

The roasted ore is mixed with coke and sand, then it is charged into blast furnance. (fed)

A blast of hot air at 800°C is introduced at the lower part of furnance through tuyeres (nozzle). Coke burns and temp rises to 1000°C.



FeS, Cu_2S.

1). Ferrous sulphide gets converted into ferrous oxide.

$$2FeS + 3O_2 \xrightarrow{\Delta} 2FeO + 2SO_2.$$

Alumina and little iron oxide combine with silica to form fusible slag.

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

$$Al_2O_3 + 3SiO_2 \rightarrow Al_2(SiO_3)_3$$

little cuprous sulphide oxidised to cuprous oxide.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2.$$

* Thus formed cuprous oxide combine with FeS Formed Cu_2S Cuprous sulphide and ferrous oxide

$$FeS + Cu_2O + SiO_2 \xrightarrow{\Delta} Cu_2S + FeO.$$

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

$$Cu_2O + C \xrightarrow{\Delta} 2Cu + CO\uparrow.$$

Two molten layers are formed at the bottom of furnance. i.e slag which is removed as waste and another is ~~matte of~~ copper matte. used for next process.

matte → mixture of (50% Cu_2S) + Cu_2S & small amount of FeS.

4. Bessemerization.

The molten matte is mixed with a little silica and transferred in a Bessemer converter. [a pear-shaped steel furnance lined inside with lime or mgo (magnesium oxide)]. A blast of air is blown through the side tuyers. FeS present in matte convert into slag.

$$2FeS + 3O_2 \xrightarrow{\Delta} 2FeO + 2SO_2.$$

$$FeO + SiO_2 \xrightarrow{\Delta} FeSiO_3 \text{ (slag)}.$$

The slag is removed and air blast is continued. Cu_2S oxidized to Cu_2O. this Cu_2O react with remaining Cu_2S and gives Cu.

$$2Cu_2S + 3O_2 \longrightarrow Cu_2O + SO_2 \uparrow$$

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

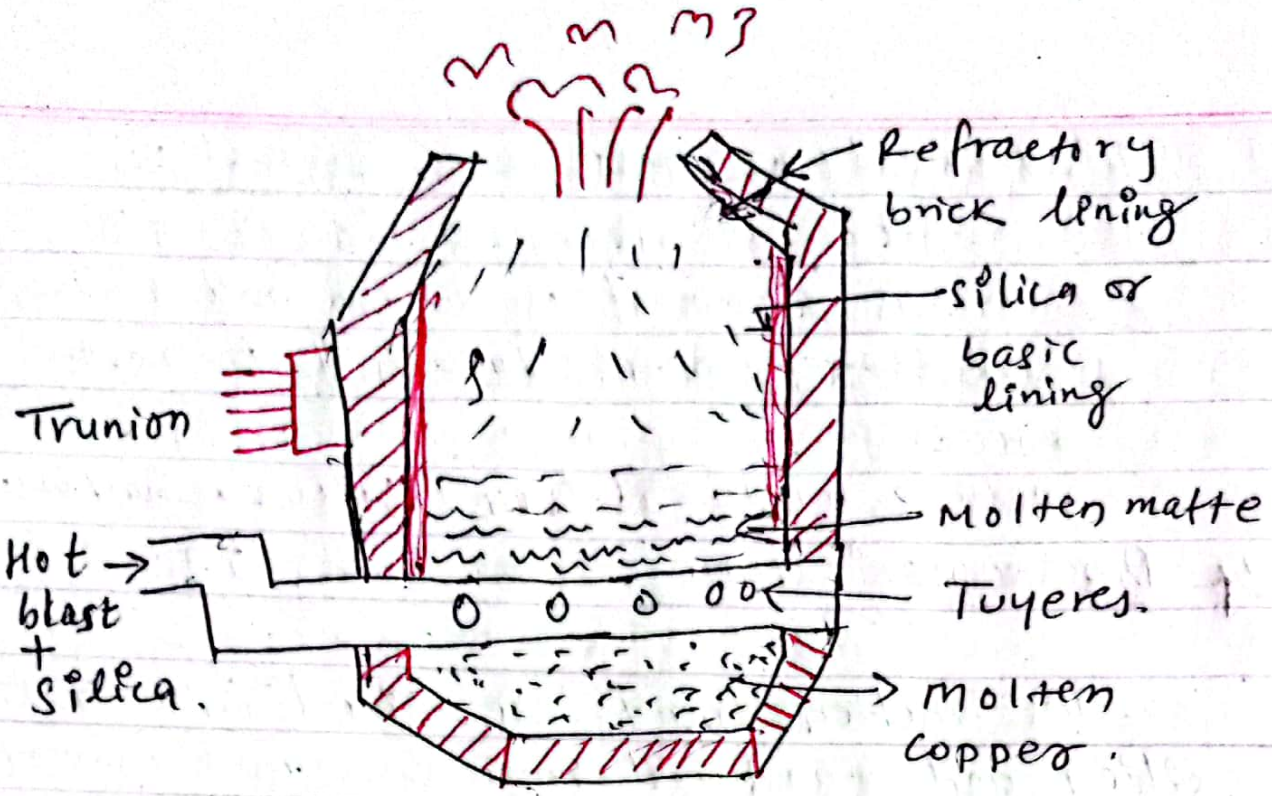


Fig:- Bessemer converter

The molten copper is allowed to cool. it slowly gives off the SO_2 in the form of bubbles. Hence there is appearance of blisters at the surface of solid copper, known as blister copper. it is 98 % pure & 2 % impurities (Ag, Au, Ni, Zn etc.) are present.

5 (b). Purification:- of copper blisters:-

→ Blister copper is not 100 % pure so to obtain high purity following methods are applied.

(a) # (a) Poling (Thermal refining):-

→ The blister copper melted again and stirred with poles of green wood.

Hydrocarbon (organic matter) in the poles act as reducing agent and reduces the oxide impurities. copper in this state is called tough-cake which is 99.5% pure.

$$3Cu_2O + CH_4 \xrightarrow{\Delta} 6Cu + 2H_2O + CO.$$

(b) This process is known as poling.

(b) Electrolytic refining :-

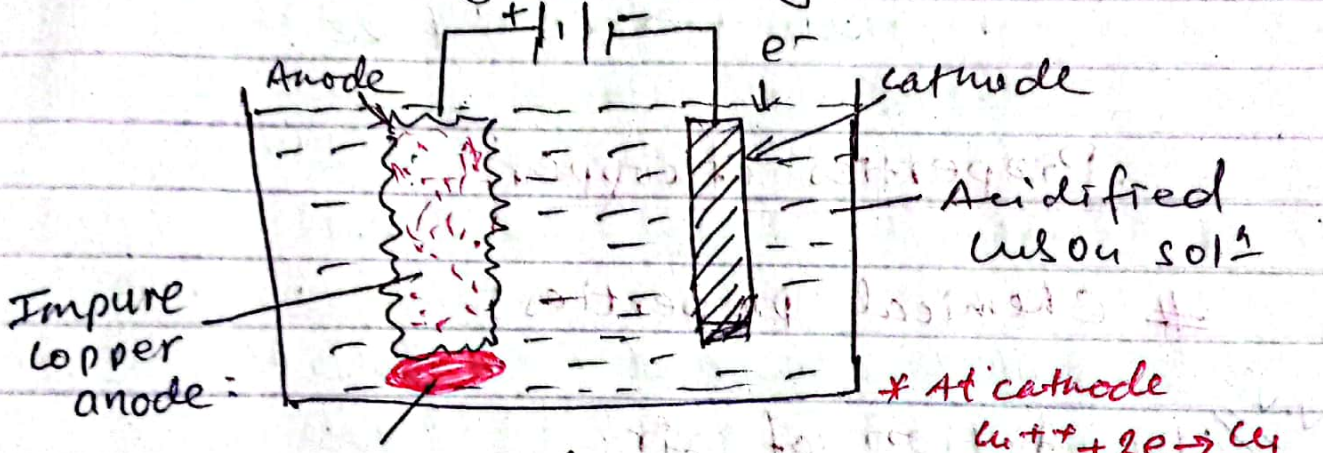


Fig :- Electrolytic refining.

In this process impure copper metal is made anode an then sheet of pure copper metal is made cathode. These electrode are suspended in electrolyte (5% H_2SO_4 + 15% $CuSO_4$) and electricity is passed at 40-45°C temperature, impure copper dissolve and pure copper deposited

at the cathode. Impurities like Fe, Au, Ag which are collected below the anode is called anode mud.

Copper obtained by this process is 99.99% pure.

At cathode :

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

At anode

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

Properties of copper.

Chemical properties :-

V.V.I

1. Action of air.

On heating with dry air, copper is first converted to red cuprous oxide and finally to black cupric oxide at high temperature.

$$2Cu + O_2 \xrightarrow{300-1100^\circ C} 2CuO$$

Black oxide

$$4Cu + O_2 \xrightarrow{\text{above } 1100^\circ C} 2Cu_2O$$

Red oxide.

only dry air has no action on copper.

⇒ on exposure to moist air, it gets slowly covered by green layer of basic copper carbonate.

$$2Cu + H_2O + CO_2 + O_2 \longrightarrow CuCO_3 \cdot Cu(OH)_2$$

green.

basic copper carbonate

When Cu is exposed to H_2S it gives copper sulphide.

$$Cu + H_2S \longrightarrow CuS + H_2$$

in air. black

2. Action of acids:-

(a) with cold HCl.

It does not react with dil HCl & dil H_2SO_4.

But in presence of air it gives salts.

$$2Cu + 4HCl + O_2 \longrightarrow 2CuCl_2 + 2H_2O$$

dil.

$$2Cu + H_2SO_4 + O_2 \longrightarrow 2CuSO_4 + 2H_2O.$$

(b) Cu with hot and conc HCl

$$2Cu + 4HCl + O_2 \longrightarrow 2CuCl_2 + 2H_2O.$$

With Hot and conc H_2SO_4 gives SO_2 gas.

$$Cu + 2H_2SO_4 \xrightarrow{\Delta} CuSO_4 + SO_2 + 2H_2O$$

conc.

(iv) Reducing properties:- copper reduces ferric salt to ferrous salt.

$$Cu + 2FeCl_3 \longrightarrow 2FeCl_2 + CuCl_2$$

v-vs

(v) Displacement reaction.

copper displaces less electropositive metal from their salt solutions.

$$Cu + 2AgNO_3 \longrightarrow Cu(NO_3)_2 + 2Ag\downarrow$$

$$3Cu + 2AuCl_3 \longrightarrow 3CuCl_2 + 2Au\downarrow$$

But zinc and iron displaces copper from its salt. solution.

$$Fe + CuSO_4 \longrightarrow FeSO_4 + Cu\downarrow$$

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu\downarrow$$

(vi) Action with non metals.

$$Cu + Cl_2 \xrightarrow{\Delta} CuCl_2$$ (cupric chloride.)

~~cupric chloride~~

$$Cu + S \xrightarrow{\Delta} CuS$$

V.V.I.

Blue vitrol ($CuSO_4 \cdot 5H_2O$)

Compounds of copper

Copper sulphate penta-hydrate is called blue vitrol. It is commonly called "Nilo Tootho" in Nepali. It's molecular formula is $CuSO_4 \cdot 5H_2O$.

Preparation:

It is prepared by the reaction of cupric oxide or cupric hydroxide or cupric carbonate with dilute sulphuric acid.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O.$$

or

$$Cu(OH)_2 + H_2SO_4 \longrightarrow CuSO_4 + 2H_2O.$$

or

$$CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + H_2O + CO_2\uparrow$$

then,
The $CuSO_4$ solution is evaporated up to crystallization point and on cooling yields crystal of blue vitrol.

$$\text{aqueous } CuSO_4 \xrightarrow[\Delta]{\text{crystallization}} CuSO_4 \cdot 5H_2O.$$

$\Rightarrow$ On commercial scale $CuSO_4$ is produced by the

action of dil H_2SO_4 on copper scrap in the presence of air

$$2Cu + H_2SO_4 + O_2 \longrightarrow 2CuSO_4 + H_2O$$

Properties:

- Physical properties.

i) Anhydrous $CuSO_4$ is white but pentahydrated $CuSO_4$ is blue

ii) It is soluble in water but insoluble in alcohol.

Chemical properties:-

1) Action of heat.

The following changes occurs when blue vitrol is heated.

$$CuSO_4 \cdot 5H_2O \xrightarrow{\text{Expose to air}} CuSO_4 \cdot 3H_2O \xrightarrow{100^\circ C}$$

blue — pale blue

$CuSO_4 \cdot H_2O$ (blue / white)

$$\xleftarrow{300^\circ C} CuSO_4 \xleftarrow{>510^\circ C} \uparrow SO_3 + CuO$$

$CuSO_4$: black

CuO: cupric oxide

anhydrous salt $CuSO_4$ turns blue on contact with water.

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② Action with alkali

With NaOH solution it gives bluish-white precipitate of cupric hydroxide.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2\downarrow + Na_2SO_4$$

blue ppt

③ Action with H_2S

It gives black ppt of CuS.

$$CuSO_4 + H_2S \longrightarrow CuS\downarrow + H_2SO_4$$

black ppt

④ Action with ammonia.

It gives deep blue solution of tetraamine copper(II) sulphate when treated with ammonia solution.

$$CuSO_4 + 2NH_4OH \longrightarrow Cu(OH)_2\downarrow + (NH_4)_2SO_4$$

bluish white ppt

$$Cu(OH)_2 + 2NH_4OH + (NH_4)_2SO_4 \longrightarrow$$

excess

$$\longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$$

Tetraamine copper(II) Sulphate

deep blue solution

KI = potassium iodide.

v.v.i/ Action with KI → cuprous iodide is formed. which is dark brown ppt.

$CuSO_4 + KI \longrightarrow Cu_2I_2 + K_2SO_4$

$2Cu_2I_2 \longrightarrow Cu_2I_2 \downarrow + I_2$

dark brown ppt.

due to oxidation of KI by $CuSO_4$.

Uses of Blue vitrol.

① → Used in electroplating and electrorefining

② → Used as a preservative for wood.

③ Used as fungicide and germicide in Agriculture.

Molecular formula of of black oxide of copper

→ It is cupric oxide and has molecular formula CuO. (copper(II) oxide)

Uses →

→ Used in green or blue coloured glass.

→ used to remove sulphur from petroleum.

Molecular formula and uses of red oxide of copper

cuprous oxide [copper(I) oxide] is called red oxide of copper and has molecular

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formula Cu_2O.

Uses:-

→ Used for making ruby red glass.

→ Used as red antirust paint.

Zinc (Zn)

Groups IIB elements, placed ~~with~~ along with the d-block elements.

electronic configuration ~~$[Ar]3d^{10}4s^1$~~

$(Ar)3d^{10}, 4s^2$

Atomic number: 30

Oxidation state: +2

Occurrence:-

zinc does not occur in free state. The important ore are

1) zinc blende : ZnS
2) zinc spar or calamite $ZnCO_3$.
3) zincite or red zinc ore; ZnO
4) willemite ~~Zn_2SiO_4~~ Zn_2SiO_4

The chief (main) one of zinc is zinc blende (ZnS)