7.1 HEAVY METALS- COPPER

🎯 Learning outcomes

After completion of the chapter, Students should be able to:

- ✓ Describe the occurrence and important ores of copper
- ✓ Explain the main steps in the extraction of copper from copper pyrites
- ✓ Describe properties (reaction with air, acids, aqueous ammonia, and metal ions) of copper
- ✓ List the important uses of copper.
- ✓ Explain the chemistry (preparation, properties, and uses) of blue vitriol.
- ✓ State the formula and uses of red and black oxide of copper.

Heavy metals are elements with high densities ($\geq 5\ g/cm^3$) and relatively high atomic masses. Many of them are important in industry and biology.

Copper (तामा)

Symbol: Cu Atomic number: 29 Appearance: reddish-brown metal

Important property: excellent electrical conductivity Main ore: chalcopyrite

Occurrence

Copper occurs both in **native (free)** and **combined forms**.

- Found naturally in countries like **Chile, USA, Russia, China, and Zambia**
- Present in **trace amounts in plants and animals**
- In Nepal, copper deposits are found in many regions and have been used since ancient times

It has been found in deposits in about 107 localities.

Copper mainly occurs in the ores listed below.

Ores	Formula
Copper pyrites or chalcopyrites	$CuFeS_2$
Cuprite or ruby ore	Cu_2O
Copper glance or chalcocite	Cu_2S
Malachite(green)	$Cu(OH)_2.CuCO_3$
Azurite (blue)	$2CuCO_3.Cu(OH)_2$
Tenorite	CuO
Bornite	$2Cu_2S.CuS.FeS$

Extraction of copper from copper pyrites

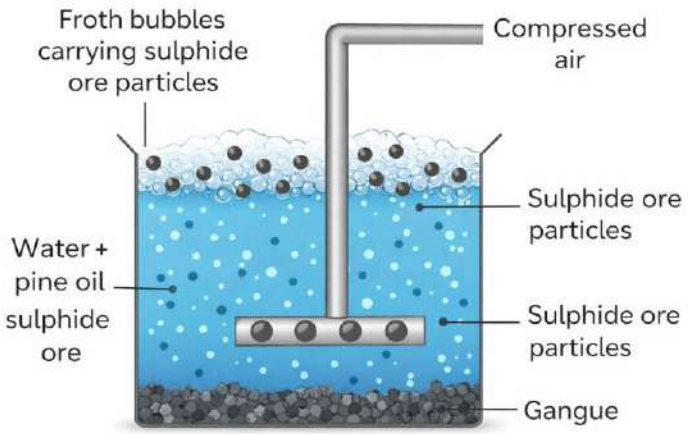
The extraction of Cu metal from copper pyrites, $CuFeS_2$, involves several steps.

A) Crushing and Pulverisation

The ore is first crushed in large jaw crushers and finely ground in ball mills.

B) Concentration (by Froth Flotation)

- Removes impurities (gangue) from ore.
- Gangue - unwanted material, such as sand or rock, that surrounds and mixes with the valuable mineral in an ore deposit
- The Froth Flotation Process concentrates the sulfide ores.
  - A suspension is created in water with the powdered ore, and pine or eucalyptus oil is added.
  - The suspension is stirred by a constant blast of compressed air.
  - The oil (froth) wets the metal sulfide, and the water wets the gangue.
  - This frothy metal sulfide ore is skimmed off from the top.
  - The gangue particles remain at the bottom and are removed.
- Thus, the copper content of the ore is increased to 25-30%.



Froth flotation process

C) Roasting

- The concentrated ore is heated strongly in a current of air on the hearth of a reverberatory furnace.

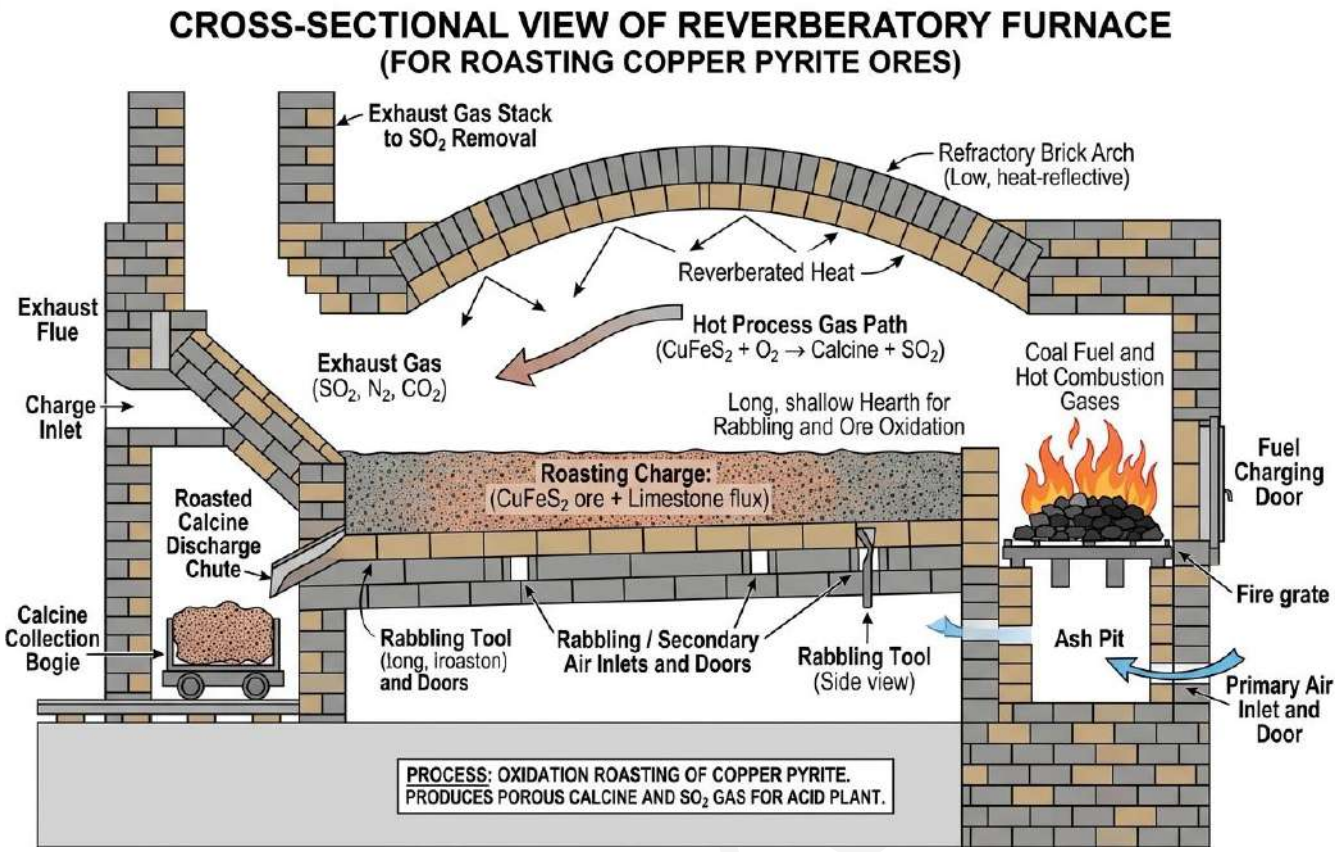


Figure: Roasting of Copper pyrites

- The process removes arsenic and antimony impurities as their volatile oxides.
- The pyrite ore is converted into a mixture of cuprous sulfide, ironsulfide and ferrous oxide.

$$2CuFeS_2 + O_2 \xrightarrow{\Delta} Cu_2S + 2FeS + SO_2$$

$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$$

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

D) Smelting (Formation of Matte)

- The roasted ore is mixed with sand and coke in a water-jacketed blast furnace. It is made of sheet steel and lined inside with firebricks. A blast of air enters from the lower part of the furnace to combust coke.

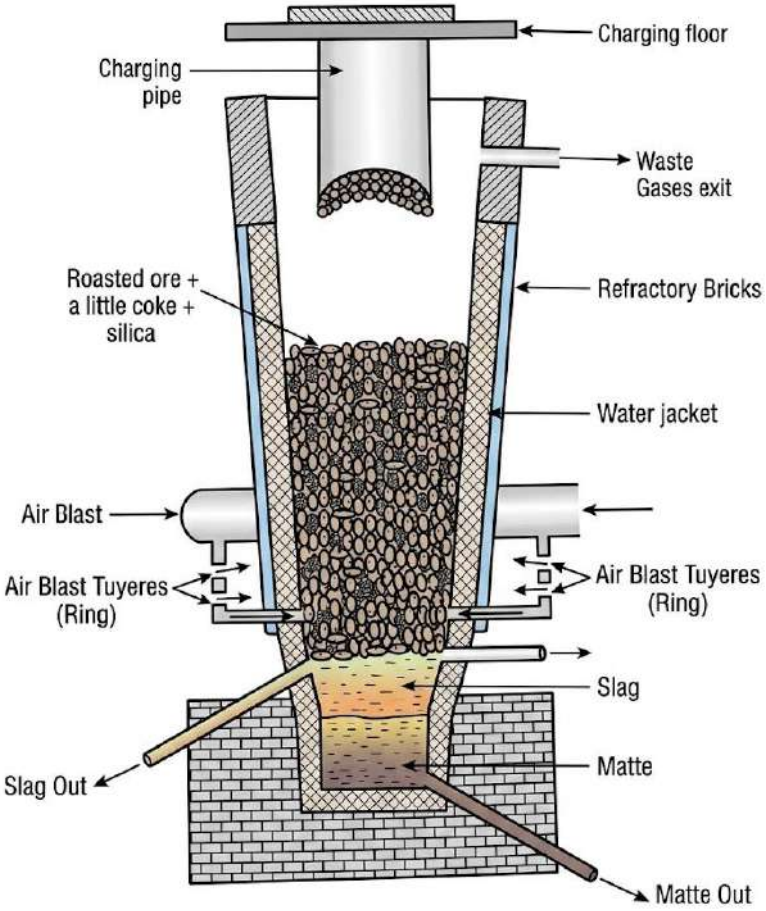


Figure: Smelting in a blast furnace

- The oxidation of FeS, which already started in the roasting step, goes on further. The ferrous oxide formed combines with sand (SiO_2) to give easily fusible silicate slag.

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

$$\underset{\text{(Flux)}}{FeO + SiO_2} \xrightarrow{\Delta} \underset{\text{(Fusible slag)}}{FeSiO_3}$$

$$\underset{\text{(Flux)}}{Al_2O_3 + 3SiO_2} \xrightarrow{\Delta} \underset{\text{(Fusible slag)}}{Al_2(SiO_3)_3}$$

- The copper oxide is also converted into sulfide.

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

- The molten mass below the slag consists of a mixture of sulfides of copper and iron, along with SiO_2, which is known as **Matte** or **Coarse Metal**. The slag is removed/runoff, and matte is poured into water, where it is obtained as granules. It consists of about 50% Cu.

E) Bessemerisation

- The molten matte with little silica is run into a Bessemer converter, and a blast of air is passed in. Iron present in the matte is first oxidised into ferrous oxide, which combines with silica to give slag.

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

$$\underset{\text{(Flux)}}{FeO + SiO_2} \xrightarrow{\Delta} \underset{\text{(Fusible slag)}}{FeSiO_3}$$

- The slag is removed, and the blast is continued; self-reduction of oxide and sulfide occurs. Cu_2S is then oxidised to Cu_2O, and when two-thirds of it is oxidised, the oxide of copper reacts with the remaining Cu_2S togive elemental copper and Sulphur dioxide. The slag is removed, the blast of air is stopped, the converter is tilted, and blister copper is taken out.

$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$$

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

- The molten mass is allowed to cool, and it slowly releases the dissolved SO_2 gas as bubbles. This gives the shapes of blisters to the surface of the solidified Cu, hence called blister Copper.
- Blister copper is ~ 98%-99% pure.

Think!
Why is silica added during copper extraction?

F) Refining of Blister Copper (Purification)

Blister copper is refined mainly by the following two methods;

Furnace/ Thermal Refining

The blister copper, containing impurities such as Fe, S, As, and Pb, is melted in a reverberatory furnace provided with a silica lining, and air is blown in.

Oxides of Pb, S, Zn, As, Sb, etc., formed, being volatile, escape.

The non-volatile oxides of Mn, Fe, Co, Ni, Bi, etc., form slag with silica.

The slag is removed. The remaining molten mass consists mainly of copper with some copper oxide.

It is stirred with a pole of green wood (**Poling**) to reduce the copper oxide to copper (nearly **99.5% pure**).

Electro-refining of Copper

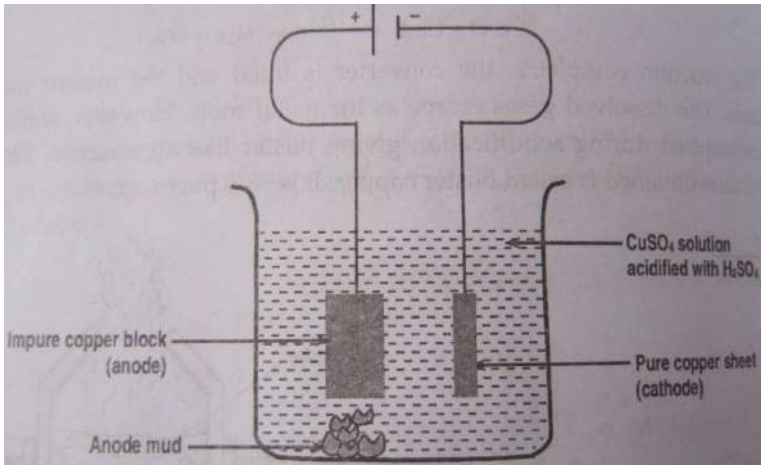
An impure copper block is made the anode, and a thin sheet of pure copper is made the cathode in an acidified $CuSO_4$ solution.

When an electric current is passed, the Cu^{2+} ions get reduced and deposit on the cathode as copper.

The Copper anode is oxidised to Cu^{2+} ions and dissolves in solution.

The impurities present in the impure copper anode settle at the bottom as anode mud.

Nearly 99.9% pure copper metal is obtained.



Properties of Copper

1. Action of Air

Copper is not affected by dry air at ordinary temperature, but it slowly converts into green basic carbonate in moist air and in the presence of CO_2.

$$2Cu + H_2O + CO_2 + O_2 \longrightarrow \underset{\text{(basic carbonate of copper)}}{CuCO_3.Cu(OH)_2}$$

When copper is heated in air below 1100°C, black oxide of copper is formed.

$$2Cu + O_2 \xrightarrow[\Delta]{< 1100\ ^oC} \underset{\text{(Black oxide)}}{2CuO}$$

But above 1100°C, red oxide of copper is formed.

$$4Cu + O_2 \xrightarrow[\Delta]{> 1100\ ^oC} \underset{\text{(Red oxide)}}{2Cu_2O}$$

2. Action with acid:

With HCl: Copper does not react with dilute HCl under ordinary conditions. In the presence of oxygen, copper can slowly dissolve in warm hydrochloric acid.

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

With H_2SO_4: Copper does not react with cold dil. H_2SO_4 under ordinary conditions. It reacts with warm dil. H_2SO_4 in the presence of air.

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

On heating with conc. H_2SO_4, SO_2 gas is produced.

$$\underset{\text{(conc.)}}{Cu + 2H_2SO_4} \longrightarrow CuSO_4 + 2H_2O + SO_2$$

With HNO_3: Copper reacts with different concentrations of HNO_3, evolving different gases like N_2, NO_2, NO, and N_2O.

$$Cu + 4HNO_3(conc.) \longrightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$$

$$\underset{\text{(dil)}}{3Cu + 8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 4H_2O + {}_2NO$$

3. Action of Ammonia

Copper dissolves in ammonia solution in the presence of oxygen.

$$Cu + NH_4OH \longrightarrow [Cu(NH_3)_2]OH \xrightarrow{NH_4OH} \underset{\substack{\text{Tetrammine copper (II) hydroxide}\\\text{(Deep blue colour)}}}{[Cu(NH_3)_4](OH)_2}$$

4. Action with Metal Ions (Copper as reductant)

Copper acts as a reducing agent and displaces less electropositive metals Ag, Pt, and Au from their water-soluble salts.

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

Uses of Copper

1. As conducting wires and cables.
2. **Electronics industry**
   Used in printed circuit boards(PCBs), microchips, motors, transformers, and electronic components.
3. To form Alloys like brass, bronze, etc., used in machinery parts, tools, and utensils.
4. Containers and utensils.
5. Coins of currency(historical use)
6. Electroplating.
7. Salts of Cu are used in agriculture as insecticides and pesticides.
8. To prepare copper sulfate.

Some alloys of copper:

Alloys	Composition
Brass	Cu 60-80% + Zn 20-40%
Bronze	Cu 88% + Sn 12%
Bell metal	Cu 80% + Sn 20%
Gun metal	Cu 88% + Sn 10% + Zn 1% + Pb 1%
German Silver	Cu 56% + Zn 24% + Ni 20%

Blue vitriol ($CuSO_4.5H_2O$)

It is commonly known as "नीलो तुथो" in Nepali.

Preparation

1) **In the laboratory**, copper sulfate is prepared by the action of dilute sulphuric acid on cupric oxide CuO, cupric hydroxide $Cu(OH)_2$, or basic carbonate $CuCO_3.Cu(OH)_2$,

$$CuO + \text{dil. } H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$Cu(OH)_2 + \text{dil. } H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$CuCO_3 + \text{dil. } H_2SO_4 \longrightarrow CuSO_4 + CO_2 + H_2O$$

On the commercial scale, it is produced by the action of dil. H_2SO_4 on copper in the presence of air.

$$2\,Cu + 2\,H_2SO_4 + O_2 \rightarrow 2\,CuSO_4 + 2\,H_2O$$

$$CuSO_4\,(aq.) \xrightarrow[\Delta]{\text{Crystallization point}} CuSO_4.5H_2O$$

Properties of Blue Vitriol

- A blue crystalline solid.
- Readily soluble in water, insoluble in alcohol.

- **Action of heat:**

When blue vitriol is heated, it loses its water of crystallisation, turning from blue to whitish blue to white anhydrous copper sulfate. On further heating, the anhydrous copper sulfate decomposes to

produce CuO and SO_3.

$$CuSO_4.5H_2O \xrightarrow{100^oC} CuSO_4.H_2O + 2\,H_2O$$

$$CuSO_4\,.H_2O \xrightarrow{250^oC} CuSO_4 + H_2O$$

When this anhydrous salt comes in contact with water, it turns blue.

$$CuSO_4 + 5\,H_2O \longrightarrow CuSO_4\,.5H_2O$$

Further heating decomposes the anhydrous salt(white) into black oxide of copper and sulphur trioxide.

$$CuSO_4 \xrightarrow{750^oC} CuO + SO_3$$

- **Action with Ammonia:**

When copper sulfate is treated with ammonia, a bluish-white precipitate of $Cu(OH)_2$ is seen. On adding excess ammonia, a deep blue colouration of the tetramine cupric sulphate complex is formed.

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

(Bluish white ppt.)

$$Cu(OH)_2 + (NH_4)SO_4 + 2NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$$

Tetra ammine copper(II) sulphate
(Deep blue coloration)

Did you know?

This deep blue solution is known as ***Schweitzer's reagent***. It can dissolve cellulose and is used in the manufacture of artificial silk.

You must have seen such a colour change during the confirmatory test of Cu^{2+} basic radical.

- **Action with potassium iodide:**

When copper sulfate is treated with potassium iodide, dark brown iodine is precipitated.

$$CuSO_4 + KI \longrightarrow CuI_2 + K_2SO_4 \quad] \times 2$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

$$2CuSO_4 + 4\,KI \longrightarrow Cu_2I_2 + I_2 + 2K_2SO_4$$

(Dark brown ppt.)

- **Action with potassium ferrocyanide solution:**

When a copper sulfate solution is treated with potassium ferrocyanide, a chocolate-brown precipitate of cupric ferrocyanide forms.

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow Cu_2[Fe(CN)_6] + K_2SO_4$$

(Chocolate brown ppt.)

Uses of Blue Vitriol

- Insecticides and fungicides in agriculture.
- Electrolyte solution in electroplating.
- Mordant in dyeing and calico printing.
- Preservative for timber.

Black oxide of copper (CuO, cupric oxide)

Uses

Glass and ceramics industry – used as a black/blue-green pigment in glass, enamel, and ceramic glazes.

Manufacture of copper salts – used as a raw material to produce compounds like copper sulfate ($CuSO_4$).

Catalyst in industries – used in oxidation reactions and some gas purification processes.

Battery and electronics industry – used in dry cells and certain electronic materials.

Red oxide of copper (Cu_2O, cuprous oxide)

Uses

Antifouling paints (marine industry)

Used in paints for ship bottoms to prevent the growth of algae, barnacles, and other marine organisms.

Glass and ceramic industry

Used as a **red pigment** to produce red, ruby, or reddish-brown colours.

Manufacture of copper salts and chemicals

Agriculture (fungicide)

Used to control fungal diseases in crops (especially in seed treatment and crop protection).

Chapter Summary

- Copper is an important **transition metal** widely used in industry
- Extracted mainly from **chalcopyrite** through roasting, smelting, and refining
- Forms important compounds like **$CuSO_4$ $5H_2O$**
- Shows characteristic **blue complex formation with ammonia**
- Used extensively due to its **conductivity, durability, and alloy-forming ability**

⚠ **Don't confuse** **CuO → black oxide** **Cu_2O → red oxide**
$CuSO_4$ $5H_2O$ → blue **$CuSO_4$ → white**

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