Extraction Metallurgy Of Copper

Pyrometallurgy of copper

Reminder: Pyrometallurgy is the use of heat to reduce the mineral to the free metal, and usually involves 4 main steps:

1. Calcination: thermal decomposition of the ore with associated elimination of a volatile product.

2. Roasting: a metallurgical treatment involving gas-solids reactions at elevated temperatures.

3. Smelting: a melting process which separates the chemical reaction products into 2 or more layers.

4. Refining: treatment of a crude metal product to improve its purity.

Pyrometallurgy of copper

Cu ore usually associated with sulphide minerals.

Most common source of Cu ore is the mineral chalcopyrite ($CuFeS_2$), which accounts for ± 50% of Cu production.

Other important ores include:

chalcocite [Cu_2S],
malachite [$CuCO_3 \cdot Cu(OH)_2$],
azurite [$2CuCO_3 \cdot Cu(OH)_2$],
bornite ($3Cu_2S \cdot Fe_2S_3$),
covellite (CuS).

Pyrometallurgy of copper

The following steps are involved in Cu extraction:

1. Concentration
2. Roasting
3. Smelting
4. Conversion
5. Refining

Pyrometallurgy of copper

1. Concentration

Finely crushed ore concentrated by the froth-flotation process:

- Ground ore mixed with xanthates (salts & esters of xanthic acid), dithiophosphates, or thionocarbamates. These make the ore surface hydrophobic.
- Ore then introduced into a water bath where air is bubbled through the suspension.
- Finely divided hydrophobic ore particles latch on to the air bubbles and travel to the surface where a froth is formed.

Pyrometallurgy of copper

1. Concentration (*cont.*)

- The froth containing the Cu ore is skimmed off and reprocessed.
- The remaining material (sand particles & other impurities) sink to the bottom & is discarded or reprocessed to extract other elements.

Pyrometallurgy of copper

2. Roasting

- Involves partial oxidation of the sulphide mineral with air at between 500°C and 700°C.
- For chalcopyrite, the main reactions are:

$$CuFeS_2(s) + 4O_2(g) \longrightarrow CuSO_4(s) + FeSO_4(s)$$

$$4CuFeS_2(s) + 13O_2(g) \longrightarrow 4CuO(s) + 2Fe_2O_3(s) + 8SO_2(g)$$

- Reactions are exothermic, $\therefore$ roasting is an autogenous process requiring little or no additional fuel.
- NB, not all the sulphides are oxidised, only around 1/3. Rest remain as sulphide minerals.
- The gases produced contain around 5 – 15% SO_2, which is used for sulphuric acid production.

Pyrometallurgy of copper

2. Roasting (*cont.*)

Objectives of roasting:

1) Remove part of the sulphur.

2) Convert iron sulphides into iron oxide and iron sulphate to facilitate removal during smelting.

3) To pre-heat the concentrate to reduce amount of energy needed by the smelter.

Pyrometallurgy of copper

3. Smelting

- Smelting consists of melting the roasted concentrate to form 2 molten phases:
    1) a sulphide “matte”, which contains the iron-copper sulphide mixture.
    2) an oxide slag, which is insoluble in the matte, and contains iron oxides, silicates, and other impurities
- Smelting is carried out at around 1200°C, usually with a silica flux to make the slag more fluid.
- The matte layer sinks to the bottom, and the slag layer floats on top of the matte & is tapped off & disposed of.

Pyrometallurgy of copper

3. Smelting (*cont.*)

- The main reaction is the reduction of copper oxides (formed during roasting) back into copper sulphide to ensure that they migrate into the matte phase:

$$FeS(l) + 6CuO(l) \longrightarrow 3Cu_2O(l) + FeO(l) + SO_2(g)$$
$$FeS(l) + Cu_2O(l) \longrightarrow FeO(l) + Cu_2S(l)$$
$$Cu_2S(l) + FeS(l) \longrightarrow Cu_2S{\bullet}FeS(l) \text{ (matte)}$$

Pyrometallurgy of copper

4. Conversion

- After smelting, matte contains from between 30 to 80% Cu in the form of copper sulphide.
- The sulphur is removed by selective oxidation of the matte with O_2 to produce SO_2 from S, but leave Cu metal.
- Converting is carried out in two stages: 1) an iron removal stage, and 2) a copper-making stage.

Pyrometallurgy of copper

4. Conversion (*cont.*)

Iron removal

- A silica flux is added to keep the slag (see below) molten.
- Air is blown into the converter to oxidize the iron sulphide according to the following reaction:

$$2Cu_2S{\bullet}FeS(l) + 3O_2(g) + SiO_2(l) \rightarrow 2FeO{\bullet}SiO_2(l) + 2SO_2(g) + Cu_2S(l)$$

- The oxidized Fe and Si form a slag (insoluble in matte) that is skimmed off & disposed off.

Pyrometallurgy of copper

4. Conversion (*cont.*)

Copper making

- The sulphur in the Cu_2S can now be oxidized to leave behind metallic copper according to the following reaction:

$$Cu_2S(l) + O_2(g) \rightarrow 2Cu(l) + SO_2(g)$$

- The end product is around 98.5% pure & is known as blister copper because of the broken surface created by the escape of SO_2 gas.

Pyrometallurgy of copper

5. Refining

- The copper is refined by electrolysis.
- The anodes (cast from blister copper) are placed into an aqueous $CuSO_4/H_2SO_4$ solution.
- Thin sheets of highly pure Cu serve as the cathodes.
- Application of a suitable voltage causes oxidation of Cu metal at the anode.
- Cu^{2+} ions migrate through the electrolyte to the cathode, where Cu metal plates out.

Pyrometallurgy of copper

5. Refining (*cont.*)

- Metallic impurities more active then Cu are oxidized at the anode, but don't plate out at the cathode.
- Less active metals are not oxidized at the anode, but collect at the bottom of the cell as a sludge.
- The redox reactions are:

$$Cu(s) \rightarrow Cu^{2+}(aq)\ 2e^{-}$$
$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s) \quad E^{\circ}_{red} = -0.83V$$

Hydrometallurgy of copper

Advantages

- Much more environmentally friendly than pyrometallurgy.
- Compared to pyrometallurgy, only a fraction of the gases liberated into the atmosphere.
- Emissions of solid particles comparatively non-existent.

Disadvantages

- Large amount of water used, $\therefore$ greater potential for contamination.
- Waste waters contain soluble metal compounds, chelating compounds & organic solvents.

Hydrometallurgy of copper

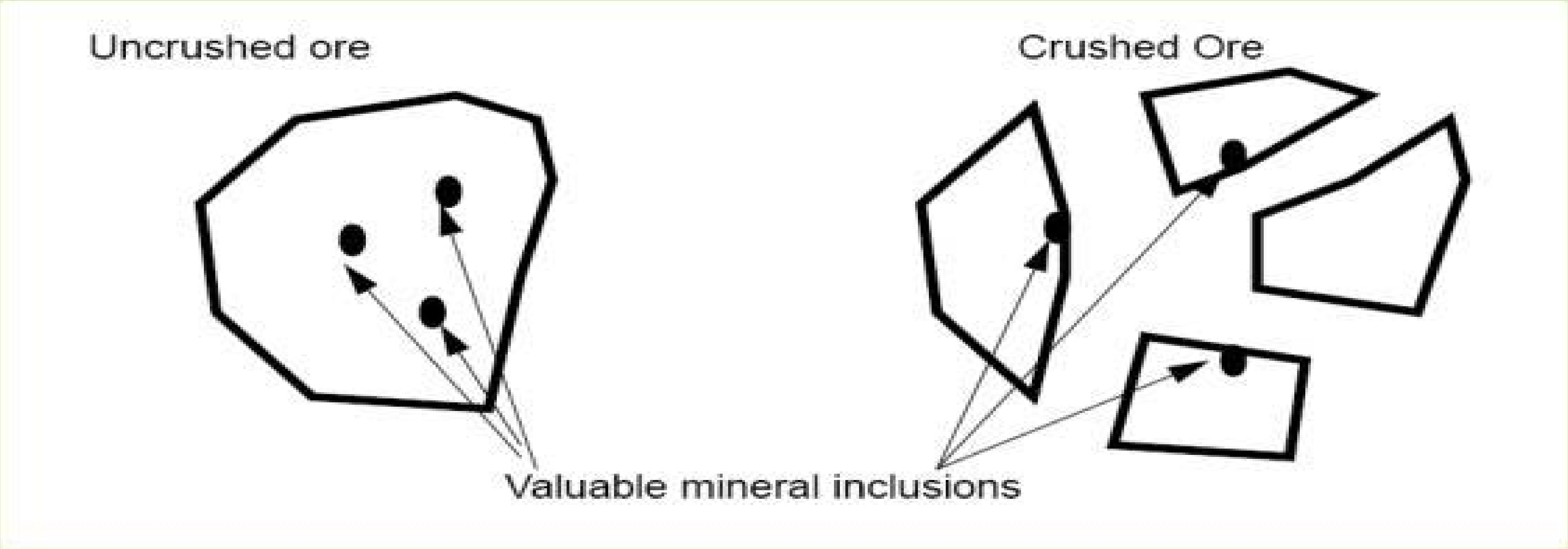
The following steps are involved:

1. Ore preparation
2. Leaching
3. Solution purification
4. Metal recovery

Hydrometallurgy of copper

1. Ore preparation

- Ore undergoes some degree of comminution (crushing & pulverisation) to expose the Cu oxides & sulphides to leaching solution.



Hydrometallurgy of copper

2. Leaching

Definition : The dissolution of a mineral in a solvent, while leaving the gangue (rock or mineral matter of no value) behind as undissolved solids.

- Cu is normally leached by one of three methods:

  (a) Dump leaching

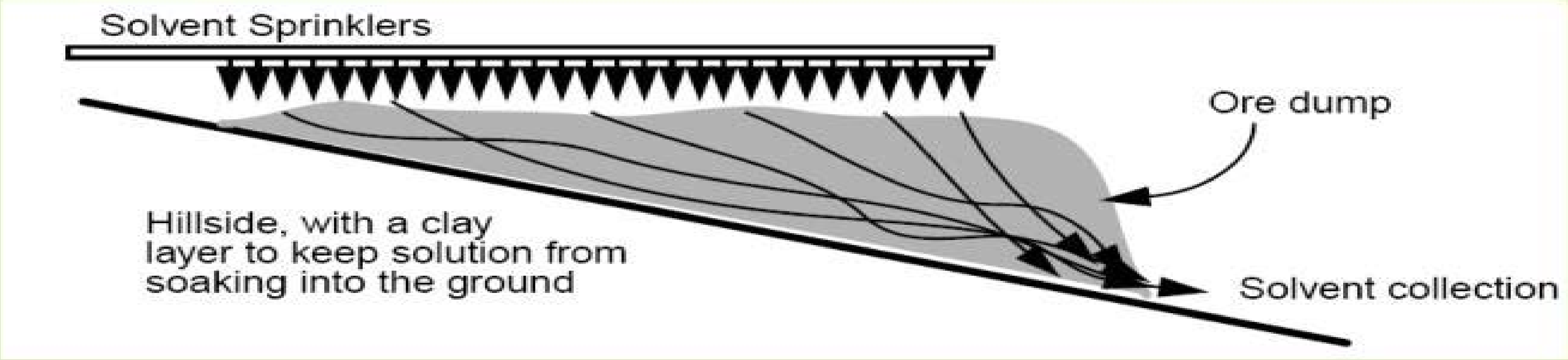
  (b) Heap leaching

  (c) Bacterial leaching

Hydrometallurgy of copper

2. Leaching (*cont.*) (a) Dump leaching

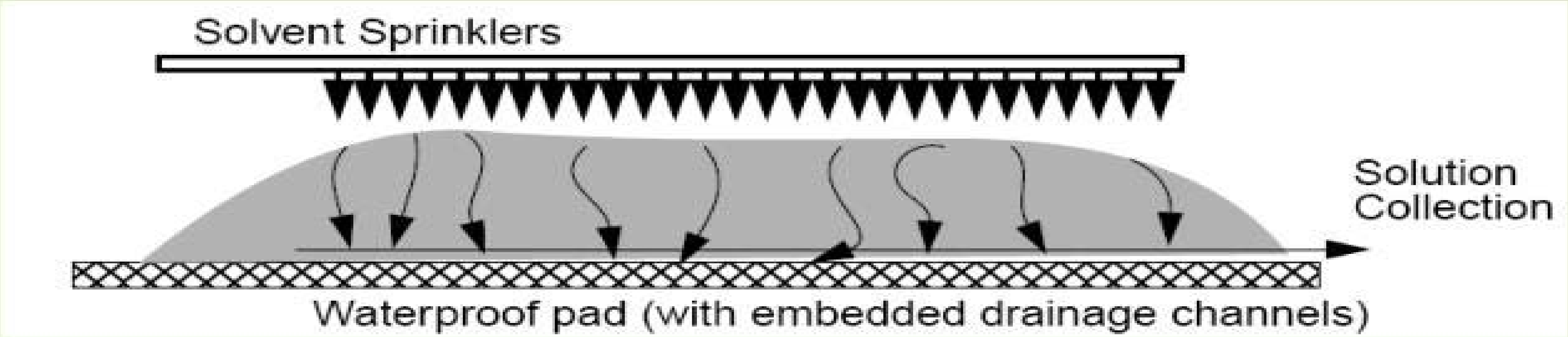
- Leaching solution trickled over a dump.
- Runoff solution collected & the Cu recovered from it.
- A slow process that takes months or years to complete.
- Typically only around 60% of the Cu in the dump is recovered.



Hydrometallurgy of copper

2. Leaching (*cont.*) (b) Heap leaching

- Similar to dump leaching except ore not simply dumped on a hillside, but is crushed to gravel size & piled onto an artificial pad.
- After leaching (6 months to 1 year) gangue is removed from pad, disposed of & replaced with fresh ore.



Hydrometallurgy of copper

3. Solution Purification

- Leaching reactions not perfectly selective ∴ other elements in solution as well, not just Cu. These need to be removed.

- After leaching, Cu in solution can be very dilute. ∴ need a way to concentrate it.

- Both of these are generally done using ion exchange processes, the two most common being ion exchange chromatography, and solvent extraction.

Hydrometallurgy of copper

3. Solution Purification

Ion exchange chromatography

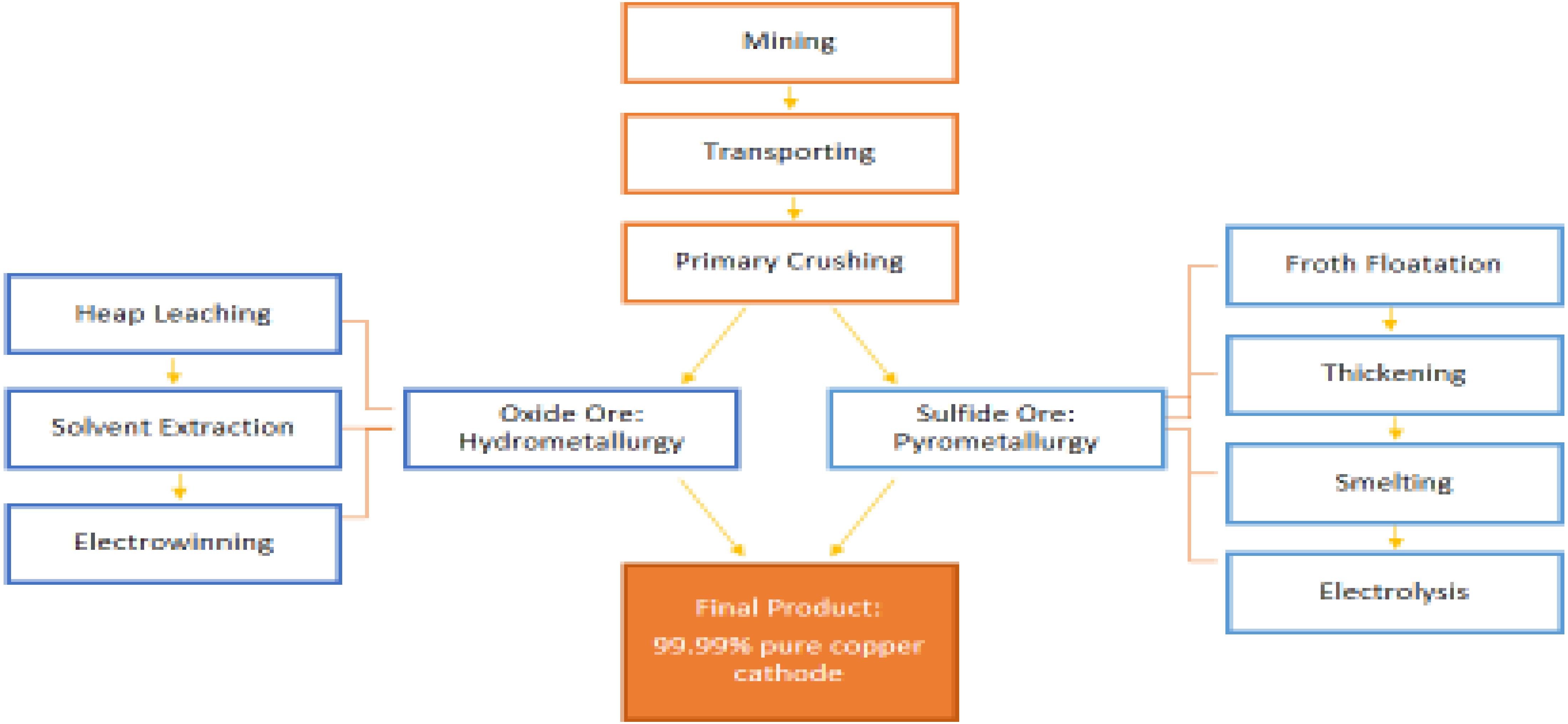
- DEFINITION: a solution containing a mixture of metal ions is contacted with a resin that is insoluble in the metal-ion solution.
- Ion-exchange resin consists of an inert solid phase to which labile functional groups are chemically bonded.
- Functional groups can either be acidic (H^+) or basic (OH^-) groups that exchange with cations (M^+) or anions (M^-), respectively.
- The ion-exchange process is reversible.

Hydrometallurgy of copper

3. Solution Purification: **Solvent extraction**

- DEFINITION: a method to separate compounds based on their relative solubilities in 2 different immiscible liquids.
- In industry, this is usually set up as a continuous process

The copper ores undergo different processing depending on their chemistries



Processing of Copper Ores