Hydrometallurgy

Hydro- Versus Pyrometallurgy:

- **Pyrometallurgy:**
  - Very ancient technology
  - was most successful with high-grade, simple ores, large scale
  - High temperature, fast reaction
  - Problems can include pollution of the environment, high energy consumption, and excessive dust formation

- **Hydrometallurgy:**
  - works better with low grade, complex ores, smaller scale
  - Lower temperature, slower reaction
  - First hydrometallurgical process: alumina from bauxite, at start of 20th century

◆Purposes of **Hydrometallurgy**:

1. **Recovery of salts** – directly from their deposits.

2. **Production of pure solutions** - high purity metals can then be produced by electrolysis.

3. **Production of pure compounds** - can be subsequently used for producing the pure metals by other methods.

4. **Chemical beneficiation** - undesirable components of the raw material are leached away and the remaining solids are the valuable product that has to be processed further.

5. **Direct production of pure metals** - suitable for the market after a subsequent minor treatment.

Leaching

◆ The choice of a leaching agent depends on the following factors:

1. *Solubility*
2. *Cost*
3. *Materials of construction*. If the leaching agent is corrosive and has to be handled in tanks made of stainless steel
4. *Selectivity*. An ideal reagent will extract only the desired component.
5. *Regeneration*. Ability of regenerating the reagent for recycle is also an important criteria.

Leaching Techniques

A range of techniques and a variety of equipment are employed for leaching, namely: in-situ leaching, dump and heap leaching, percolation leaching, pulp (slurry) leaching.

- ***In-situ leaching*** refers to either the leaching of ore left in a mine after it has been worked out or to the direct leaching of an ore body in the ground, usually after it has been shattered by explosives. The leach solution is introduced above the ore body and allowed to percolate by gravity before being collected at lower levels by a network of sumps. It is then pumped to the surface and processed for metal recovery. The method has been applied to low grade copper and uranium ores, and although the cost of mining is cheap, these savings may be offset by low extraction rates and efficiencies and the loss of leach liquor into the ground water.

Heap Leaching of Low Grade Ores

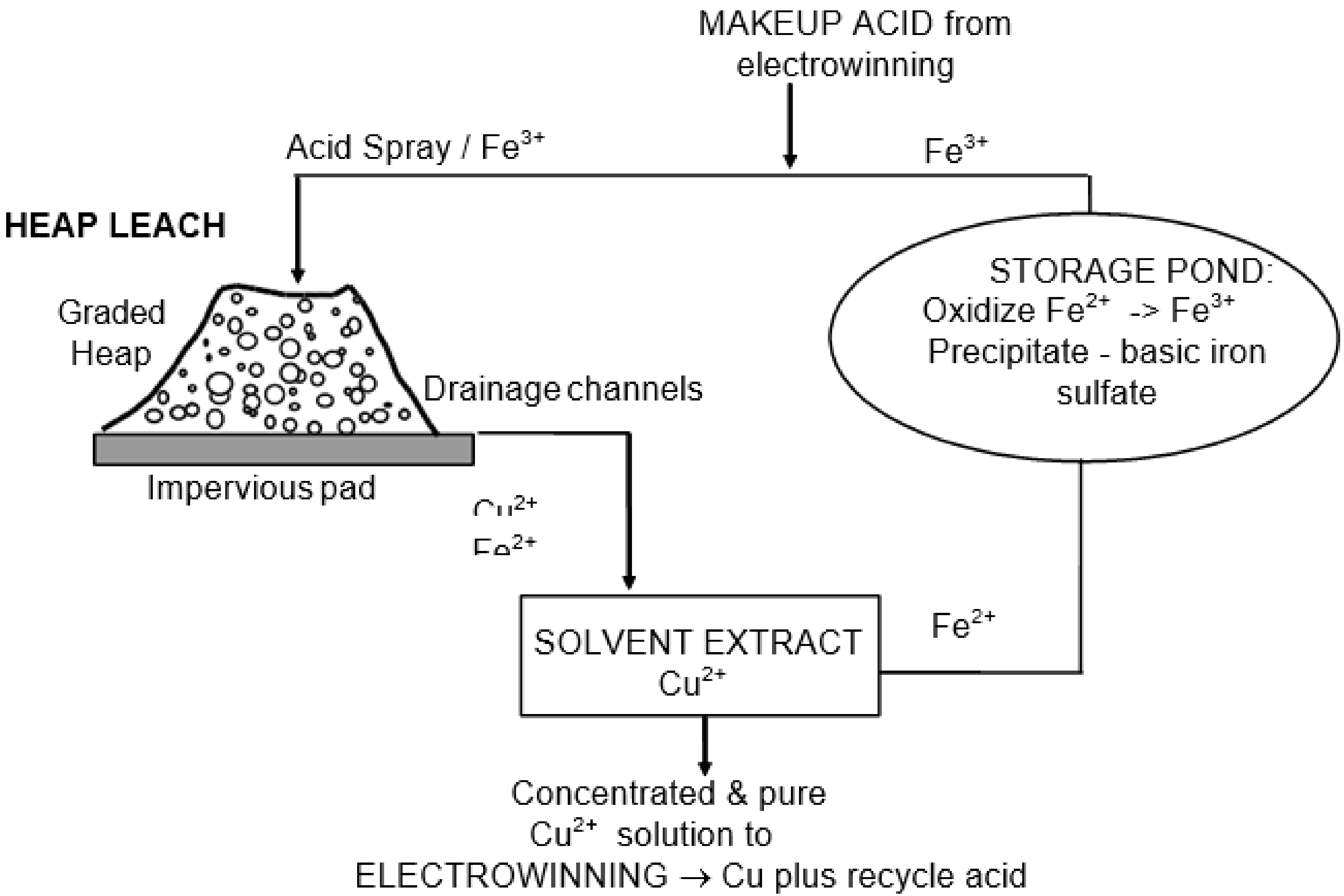
Heap leaching is an important method for treating low grade ores and can be used for, *copper sulfides* (especially chalcopyrite) using Fe^{3+} as oxidant in the presence of bacteria, *copper and uranium oxides* using dilute H_2SO_4 (and Fe^{3+}/air in the case of uranium) and *gold ores* using NaCN and air as source of oxidant.

A significant proportion of the world's copper is produced by heap leaching of low grade oxide and sulfide ores, with the latter being bacterially assisted. Copper is selectively extracted from the low grade solution by solvent extraction, and is then electrowon from the concentrated strip solution, where acid is regenerated. This can be recycled to the leaching step if electrowinning is carried out on-site. Figure 2 shows a typical flowsheet for heap leaching of a low grade copper ore.

The leaching of copper oxide and chalcopyrite may be represented by the following equations:

$$CuO + H_2SO_4 \rightarrow Cu^{2+} + H_2O + SO_4^{2-}$$

$$CuFeS_2 + 4Fe^{3+} \xrightarrow{\text{bacteria}} Cu2+ + 6Fe^{2+} + 2S^0$$



MAKEUP ACID from electrowinning

Acid Spray / Fe^{3+}

Fe^{3+}

HEAP LEACH

Graded Heap

Drainage channels

Impervious pad

STORAGE POND:
Oxidize Fe^{2+} -> Fe^{3+}
Precipitate - basic iron sulfate

Cu^{2+}
Fe^{2+}

SOLVENT EXTRACT
Cu^{2+}

Fe^{2+}

Concentrated & pure Cu^{2+} solution to ELECTROWINNING → Cu plus recycle acid

Heap Leaching of Low Grade Ores

In *percolation leaching*, ore is coarsely crushed (to 5-20 mm) and charged into large vats having false bottoms. Countercurrent leaching is usually employed to ensure extraction efficiencies of around 80%. Once the ore is spent, the vats are emptied mechanically and the process repeated. Applications are for copper, gold and uranium.

Pulp or slurry leaching involves the leaching of finely milled ores (200 mm) in agitated and usually aerated vessels, at either atmospheric pressure in open vats or at higher pressures in sealed autoclaves. The additional costs of these techniques limit their application to high value metals (e.g. gold cyanidation in open vats) or to concentrated minerals (e.g. NiS and ZnS oxidation in autoclaves). Open vats may be agitated by injection of compressed air at the bottom (pachuca tanks) or mechanically using paddles or rakes (low turbulence) or propellors and turbines (high turbulence). Autoclaves may also be agitated by compressed air or mechanically

Solution Purification and Concentration

Leach solutions may be treated directly to recover their metal values. Or they may first have to be purified and concentrated before the metal values can be recovered efficiently. Many impurities are themselves valuable and are often recovered in separate by-product stream(s).

1. Impurity removal

Two important methods are used, namely

(i) cementation, which is based on metal displacement using the electrochemical series

(ii) precipitation of insoluble salts such as sulfides, hydroxides, sulfates and carbonates, which is based on the classical table of group separation of metal ions (recall solubility products of metals) developed by inorganic and analytical chemists.

The processes of solvent extraction and ion exchange can also be used and continue to offer new purification possibilities, but these are still mainly used for concentration and will be discussed below.

2. Concentration

This is achieved by selective extraction of the valuable metal ion from low grade leach solutions by "loading" into an ion specific organic solvent (solvent extraction) or onto an ion specific resin (ion exchange). Once the exchange media is fully loaded, it is separated from the leach solution and the valuable ion chemically stripped from it in a process called "elution". The exchange media is regenerated for use in another process cycle and the valuable ion collected in a more concentrated solution, ready for subsequent recovery

a. Ion Exchange (IX)

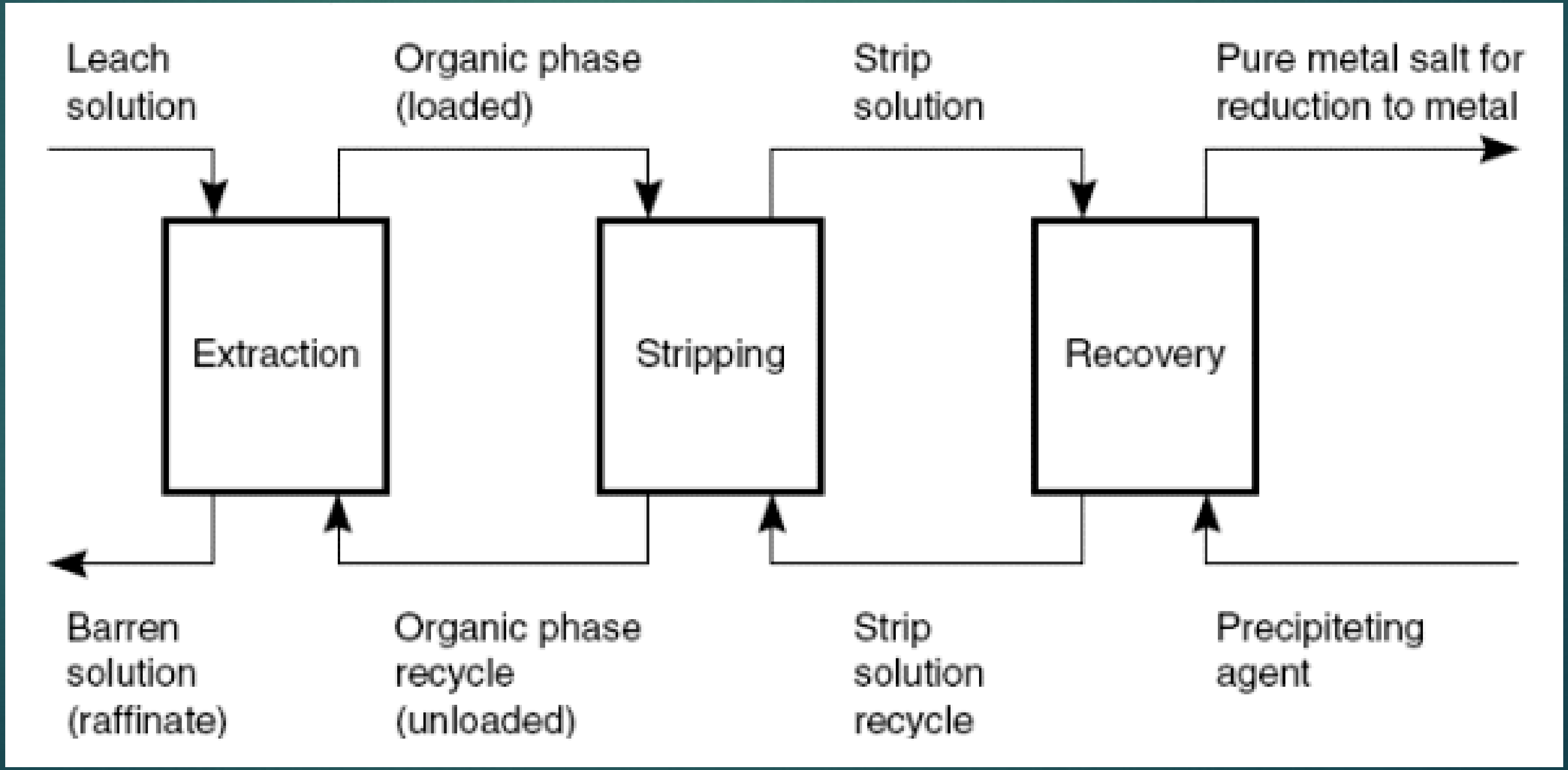
For example, concentration of uranium from low grade leach solutions. Uranium is present in acid leach solutions mainly as UO2(SO4)22 . If an aqueous solution containing this anion is brought into contact with an anion exchange resin (i.e. a resin on which the anion is loosely bound), the following anion exchange equilibrium will be established:

$$2R^{+}X^{-} + UO_2(SO_4)_2^{2-} \Leftrightarrow [R^{+}]_2\, UO_2(SO_4)_2^{2-} + 2X^{-}$$

- Here R^+ stands for the resin cation and X for anions like Cl . Since uranium is one of the few metals which can form anions in sulfuric acid solutions the exchange is very selective, other metals such as Ca, Fe, etc., being retained in the aqueous phase as cations.

b. Solvent Extraction

1. **leach solution is mixed with an immiscible organic solvent so the desired metal ion in aqueous phase is transferred to organic phase**
2. **The two phases are then allowed to separate.**
3. **The process is then reversed by contacting the loaded organic phase with an aqueous (strip) solution that transfers the desired metal ion back out of the organic.**
4. **The aqueous phase obtained is a pure and concentrated solution suitable for metal recovery while the stripped organic phase is suitable for recycle**



Electrometallurgy

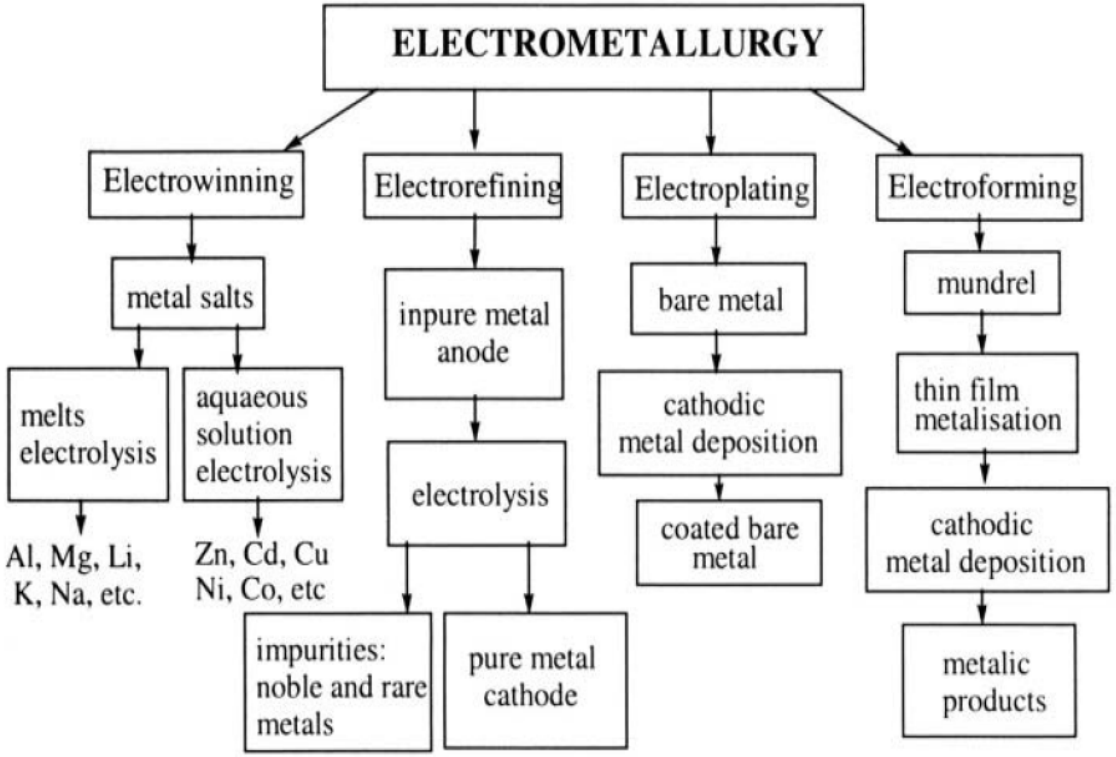
Dr. Wafaa K. Mahmood

What Is Electrometallurgy?

Electrometallurgy deals with technical aspect of metal electrodeposition. The electrometallurgical processes can be categorized into four main groups:

1. Electrowinning,
2. Electrorefining,
3. Electroplating,
4. Electroforming.

The schematic representation of electrometallurgical processes is shown in Fig. 1.



- **Electrowinning** is the extraction of metals by **electrodeposition** from aqueous solution or melts of their salts. On a large scale electrodeposition from molten salts is used for extraction of **electronegative elements**, such as aluminum and magnesium, as well as very pure copper, zinc and cadmium by electrodeposition from an aqueous solutions of the metal salts.

- **Electrorefining** is the purification of metals by electrolysis. The impure metals is dissolved anodically and pure metal is deposited catodically, while the impurities being left as anode sludge or as ions in the solution. Many metals are electrorefined such as copper because of conducting application and precious metals because of theirs cost. Electrorefining is also a part of processes in recycling of metals.

- **Electroplating** can be defined as a treatment that modifies the surface of a metal or occasionally a nonmetal, without changing its bulk properties, in order to improve the appearance of a surface, to increase the corrosion and abrasion resistivity, etc. The improving the appearance was the aim of electroplating earlier, now it is mainly the change of surface properties from those of substrate material to those of electroplated metal.

- **Electroforming** is the manufacture of articles by electrodeposition. If deposit is good from electroplating point of view except adhesion, and can be removed from the cathode as an entity in itself, it has been electroformed. Electroforming is a branch of electroplating technology, but involve some additional steps, as for example the production, preparation and extraction of the master

Theoretical Aspects Of Electrowinning

Electrowinning of a metal is based on the electrolysis of aqueous solutions or melts of metal salts with insoluble anode. The basic reactions during electrowinning from aqueous solutions are:

1. cathodic deposition of the desired metal:

■ $$Me^{n+} + ne^{-} \rightarrow Me \qquad \text{(cathode)}$$

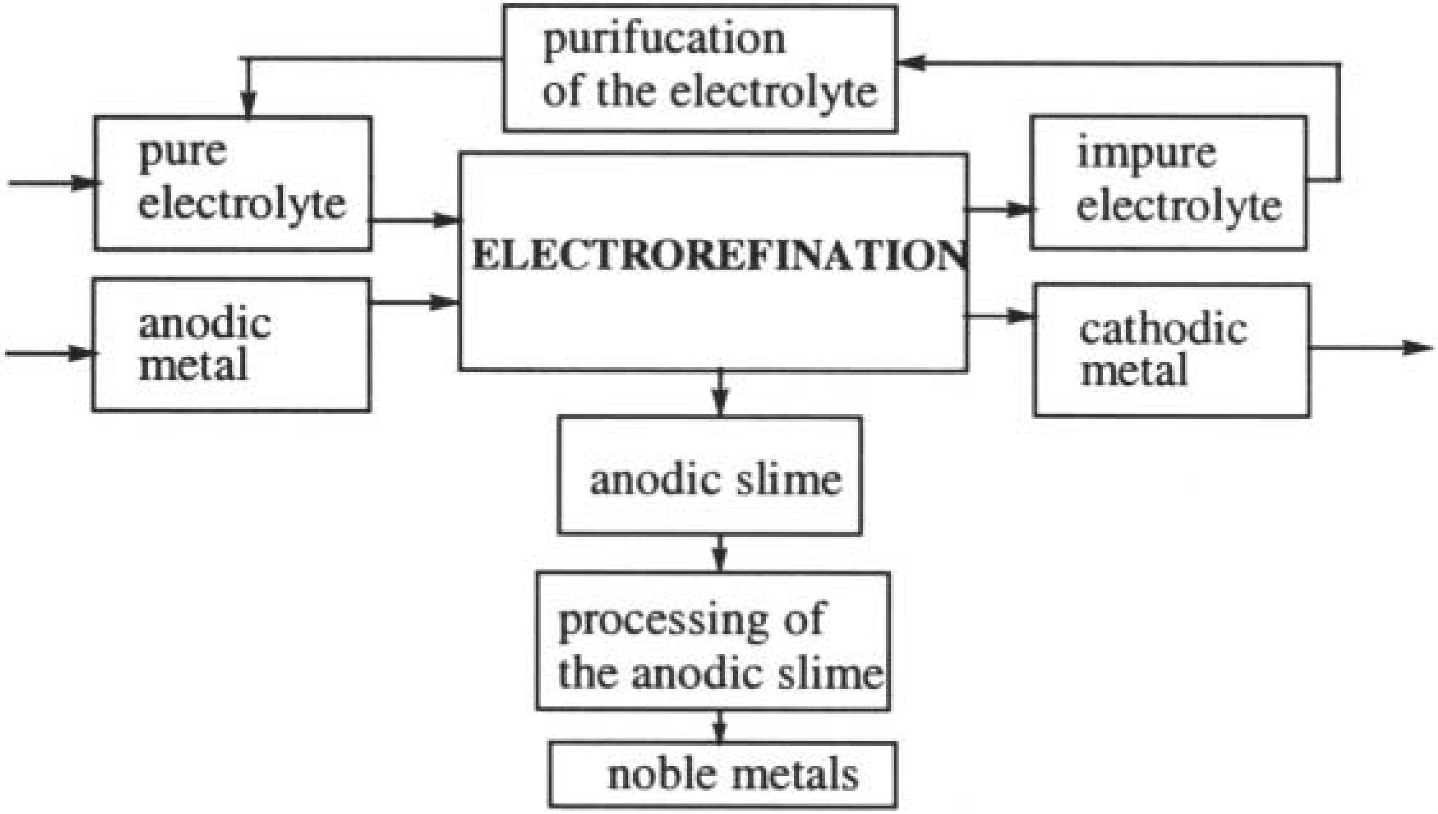
2. oxygen evolution on the anode:

$$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-} \quad \text{(anode)}$$

Electrowinning of a metal by the electrolysis is usually performed in an aqueous solution of the sulfates of a metal in dilute sulfuric acid, with the aim to avoid problems related with the deposition of the hydroxide of the metal. Sulfuric acid is chosen because of its relatively low price

Theoretical Aspects Of Electrorefining

Electrorefining of a metal by electrolysis is a way of purification of a metal previously extracted by classical metallurgical or electrochemical processes, with the aim of removing impurities, which could exhibit in negative effects on the physico–chemical and mechanical properties of the metal. In principle, almost all metals can be electrorefined, but judging by the amount of 8 million tones per year, copper electrorefining outweighs all others



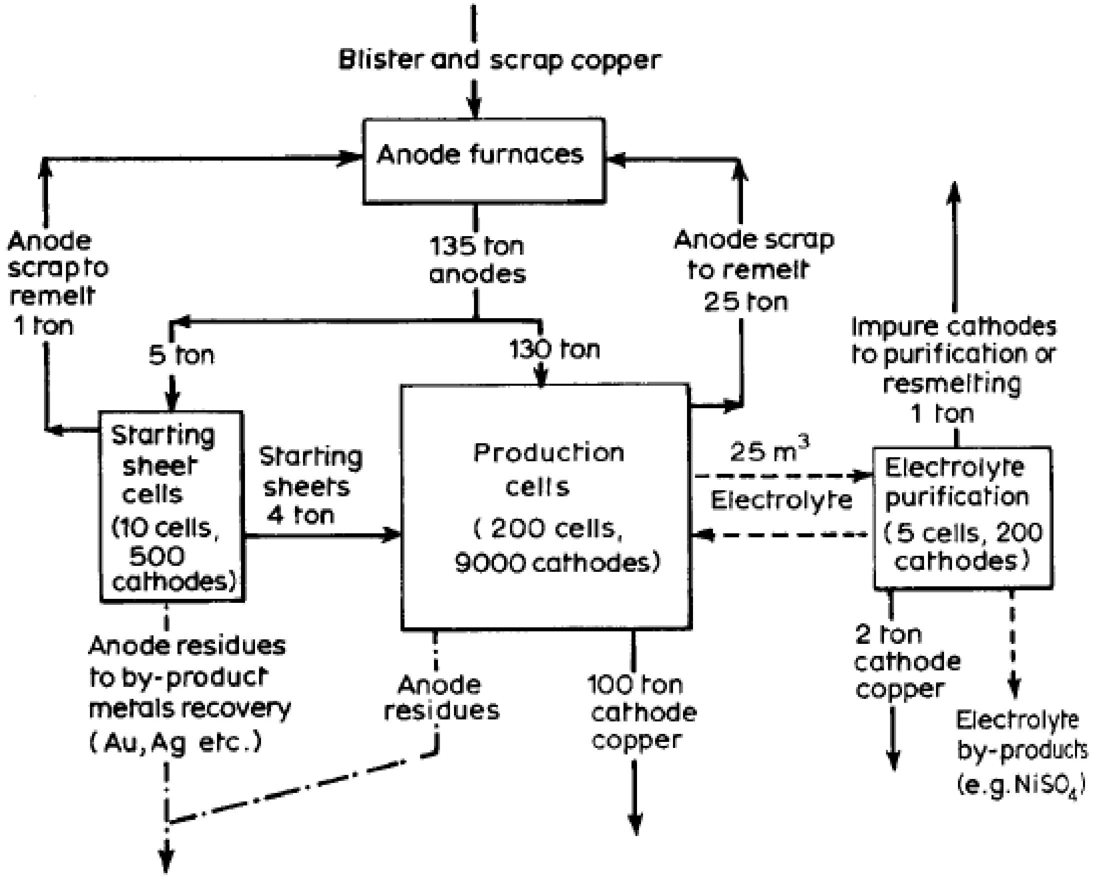
Electrorefining Process

Virtually all copper produced (for example) from ore receives an electrolytic treatment at some stage either via electrorefining from impure anodes or electrowinning from leach or solventextraction liquors.

The electrorefining step serves two purposes:

1) Elimination of unwanted impurities; cathode copper typically has a purity > 99.9 % wt Cu, with < 0.005 % total metallic impurities
2) 2) Separation of valuable impurities which can be recovered in other processes.

The Figure shows a general flowsheet of the copper refining operation. The major technical factors in electrorefining are the cathode purity, the production rate and the specific energy consumption. These factors are influenced primarily by anode quality, electrolyte conditions and cathode current density.



Electroplating is both an art and a science. Although based on several technologies and sciences, including chemistry, physics, chemical and electrical engineering, metallurgy, and perhaps others, it retains in some ways the aspects of an art, in which experience is the only teacher.

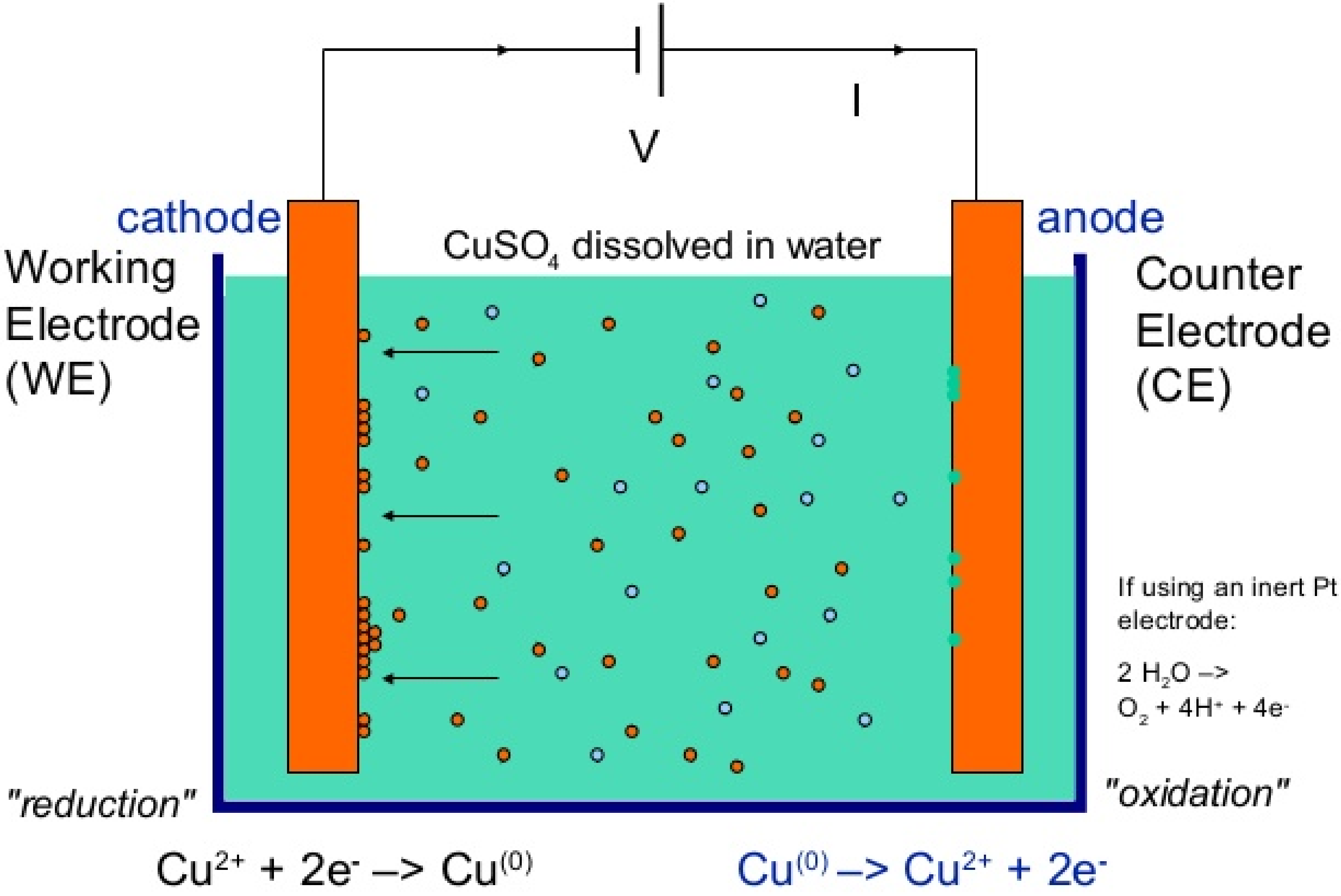
THE PURPOSES OF ELECTOPLATING

Some of the purposes for which articles are electroplated are:
(1) Appearance
(2) Protection
(3) Special surface properties
(4) Engineering or mechanical properties.

There are many applications of electroplating, some of them of increasing importance at present, in which neither corrosion prevention or decorative appeal is the reason for using a finish.

Copper is an excellent conductor of electricity and is therefore basic to such items as printed circuits and communications equipment. It does, however, quickly form tarnish films that interfere with joining operations such as soldering and that also render contact resistances unacceptably high in relays and switches.

Electroplating Cell



V

I

cathode

Working Electrode (WE)

CuSO$_4$ dissolved in water

anode

Counter Electrode (CE)

If using an inert Pt electrode:

$2\,H_2O \rightarrow O_2 + 4H^+ + 4e^-$

"reduction"

$Cu^{2+} + 2e^- \rightarrow Cu^{(0)}$

"oxidation"

$Cu^{(0)} \rightarrow Cu^{2+} + 2e^-$