

## Electrorefining of Copper

### 1. Electrorefining – General Introduction

In an electrorefining process, the anode is the impure metal and the impurities must be lost during the passage of the metal from the anode to the cathode during electrolysis, i.e. the electrode reactions are, at the anode:



and at the cathode:



Electrorefining is a much more common process than electrowinning and such plants occur throughout the world on scales between 1000-100,000 ton/year.

Usually they are part of a larger operation to separate and recover pure metals from both scrap and primary ores. Therefore, the process must be designed to handle a variable-quality metal feed and lead to a concentration of all the metals present in a form which can be treated further. Electrorefining often provides a particularly high purity of metal.

*Electrorefining processes using a molten salt* or non-aqueous electrolyte are used and, indeed, are the subject of further development. This is due to the possibilities they offer for increasing current densities and refining via lower oxidation states not stable in water (e.g. refining of copper via  $Cu^{+}$  would almost halve the energy requirement). However, *aqueous processes* presently predominate due to their ease of handling, more developed chemistry and familiarity with aqueous process liquors and electrolytes.

**Aqueous electrorefining** — The conditions used for the refining of five metals are summarized in Table 6.3.1. The electrolyte and other conditions must be selected so that both the anodic dissolution and the deposition of the metal occur with high efficiency while none of the impurity metals can transfer from the anode to the cathode. Certainly there must be no passivation of the anode (cf. chapter 3) and the objective is to obtain a good-quality, often highly crystalline, deposit at the cathode. Where necessary, additives are added to the electrolyte to enforce the correct behavior at both electrodes. Chloride ion is a common addition to enhance the dissolution process and, where essential, organic additives are used to modify the cathode deposit. Since, however, organic compounds can be occluded to some extent and reduce the purity of the metal, their use is avoided when possible.

• Table 6.3.1. Typical parameters for (aqueous) electrorefining processes.

Metal	Concentration of components in electrolyte/g dm <sup>-3</sup>	I/mA cm <sup>-2</sup>	Cell voltage/V	T/°C	Current efficiency/%	Impurity metals	
						Slime	Solution
Cu	CuSO <sub>4</sub> (100–140)	10–20	0.15–0.30	60	95	Ag, Au, Ni, Pb, Sb	Ni, As, Fe, Co
	H <sub>2</sub> SO <sub>4</sub> (180–250)						
Ni	NiSO <sub>4</sub> (140–160)	15–20	1.5–3.0	60	98	Ag, Au, Pt	Cu, Co
	NaCl (90)						
	H <sub>3</sub> BO <sub>3</sub> (10–20)						
Co	CoSO <sub>4</sub> (150–160)	15–20	1.5–3.0	60	75–85	—	Ni, Cu
	Na <sub>2</sub> SO <sub>4</sub> (120–140)						
	NaCl (15–20)						
	H <sub>3</sub> BO <sub>3</sub> (10–20)						
Pb	Pb <sup>2+</sup> (60–80)	15–25	0.3–0.6	30–50	95	Bi, Ag, Au, Sb	—
	H <sub>2</sub> SiF <sub>6</sub> (50–100)						
Sn	Na <sub>2</sub> SnO <sub>3</sub> (40–80)	5–15	0.3–0.6	20–60	65	Pb, Sb	—
	NaOH (8–20)						

## 2. Copper Refining

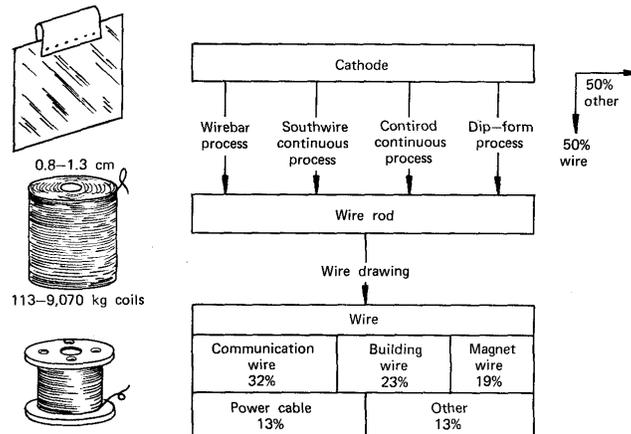
### Copper uses

The properties of copper and its alloys that make it a major metal of commerce may be summarized as follows: high electrical conductivity; high thermal conductivity; ease of casting, extrusion, rolling, and drawing to produce wire, tubing, and strip; low corrosion rate of copper when used for food preparation; excellent alloying characteristics; high esthetic appeal; and low toxicity to humans.

The occurrence of copper in nature in the metallic form led to its use since early times either as metallic copper, or alloyed with tin as bronze. It was used for tools, ornaments, pots for cooking, and coinage. Copper and brass, a copper-zinc alloy, continue to have appeal as ornaments.

The *major use* of copper in modern times has been as an *electrical conductor*, and about 50% of the current demand is for electrical uses. Copper has a very high electrical conductivity per unit volume. It can be drawn readily into wires, either single or multifilament, which can be bent readily and repeatedly without excessive work hardening. Copper wire is readily tinned, has excellent soldering characteristics, and resists corrosion at contact points.

Figure 6.3.1 shows the flow of copper from cathode through to copper wire and the relative demand for the various wire types.



• Figure 6.3.1. Wire production from copper cathodes.

The resistance to salt water corrosion of admiralty brass, an alloy with 71% copper, 28% zinc, and 0.75-1.0% impurities, led to extensive use of this alloy in ships. This alloy has been largely replaced, in water applications with copper-nickel alloys which consume thousands of metric tons of copper annually. The resistance to corrosion of copper by food and the nontoxicity of copper in dilute concentrations has encouraged its use for food preparation equipment. Low corrosion rates coupled with ease of forming, bending, and of soldering resulted in extensive use of copper tubing for domestic water pipe. Copper radiators for automobiles utilize the high thermal conductivity of copper, and the ease of mechanical working and brazing. Brass can be cast readily into intricate shapes and is used for many cast products having utilitarian or decorative applications. The ease of chrome plating brass has diversified the use of copper alloys where appearance and resistance to corrosion are major requirements.

## Electrorefined Copper

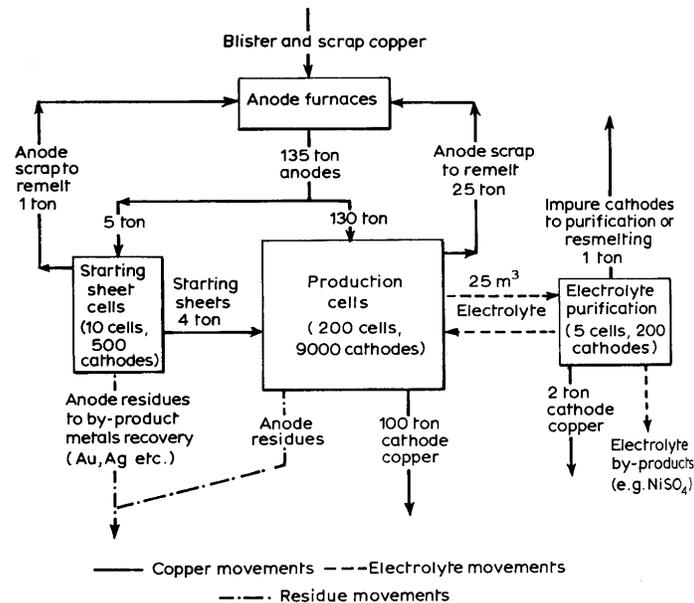
Fire-refined copper is adequate for noncritical applications such as water tubing, bar stock, or ingots for alloying. Copper intended for electrical uses, however, is produced by electrorefining or sometimes electrowinning techniques.

### Electrorefining process

Virtually all copper produced from ore receives an electrolytic treatment at some stage either via electrorefining from impure anodes or electrowinning from leach or solvent-extraction liquors. Electrorefining produces the majority of cathode copper ca. 95% as opposed to ca. 5% from electrowinning). 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) Separation of valuable impurities which can be recovered in other processes.

Figure 6.3.2 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.



• Figure 6.3.2. Typical flow sheet for a copper refinery.

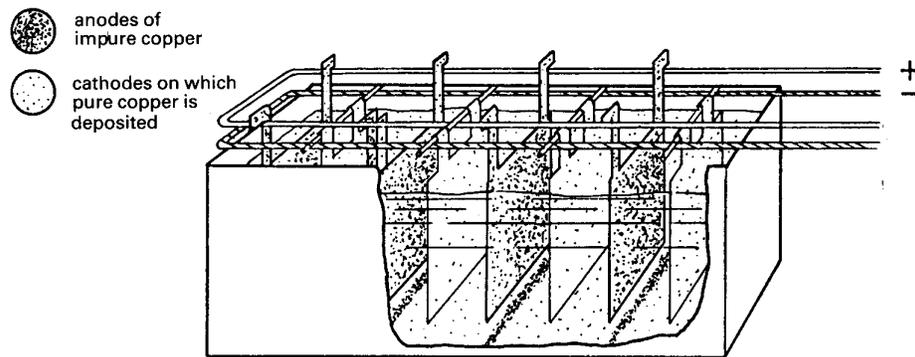
The process for electrorefining copper is typical of those carried out in aqueous solution. The electrolyte is copper sulfate (0.7 molar) and sulfuric acid (2 molar) and the way in which the purification of the copper occurs can be seen by considering the metals likely to be found as impurities :

- 3) Ag, Au and Pt are more noble than copper and therefore will not dissolve anodically. They will be found as metals in the anode slime;
- 4) Sn, Bi and Sb dissolve anodically but will precipitate in the electrolyte as oxide or hydroxide compounds which will be found in the anode slime;

- 5) Pb is oxidized anodically but will form insoluble lead sulfate in this electrolyte. Again, this will fall to the slime in the base of the cell;
- 6) Fe, Ni, Co and Zn all dissolve anodically and in the sulfate medium form species which are soluble in the electrolyte. The species formed, however, only reduce at potentials more negative than that at which the copper deposits and therefore remain in the electrolyte.

Hence, the impurities accumulate in either the electrolyte or the cell slime and these can be processed further to recover the significant metals (See Table 6.2.2 below).

The *electrolytic cells* are generally of a very simple open-tank and parallel-plate electrode design, similar to that described above for copper winning except that the anodes are now of the impure copper (Figure 6.3.3). The copper anodes must have the correct size and geometry (i.e. flat plates larger than the starter sheets of aluminum, titanium, steel, or thin Cu foil for the cathodes to avoid heavy edge deposits) and have a homogeneous composition. The flow rate of the electrolyte through the cells is low so that the slime drops to the base of the cell and does not come into contact with the cathode.



- Figure 6.3.3. Diagram showing the structure of the cells in which the electrolytic refining of copper is carried out. The anodes and cathodes are connected to the + and - current lines respectively. The elements which are more noble than Cu and the compounds are anodically insoluble and precipitate on the bottom of the cells beneath the anodes as 'anodic slimes' or 'anodic sludge'. In the figure, the 'anodic sludges' are shaded, and some idea of the greater purity of the copper cathode as compared with that of the anode is shown by the smaller density of spots on the cathodes. It should be added that, to reduce the effects of the ohmic drop, the anodes and cathodes are closer together than indicated in the figure.

The *electrolyte* additionally contains organic additives which serve to control copper electrocrystallization at the cathode (levellers and brighteners) and help prevent insoluble particulates from co-deposition (surfactants).

Temperature is usually maintained via steam-heating at 60-65°C (inlet to cell), falling to 55-60°C (cell outlet). Circulation rates are typically 0.01-0.03 m<sup>3</sup>/min, a cell achieving a nominal change of electrolyte every 4-6 h. This circulation helps to control temperature, gently increase the mass transport, prevent compositional gradients, replenish addition agents and serve as a convenient stream for bleeding-off impurities. The electrolyte composition is maintained by purification of the bleed stream in three sequential steps :

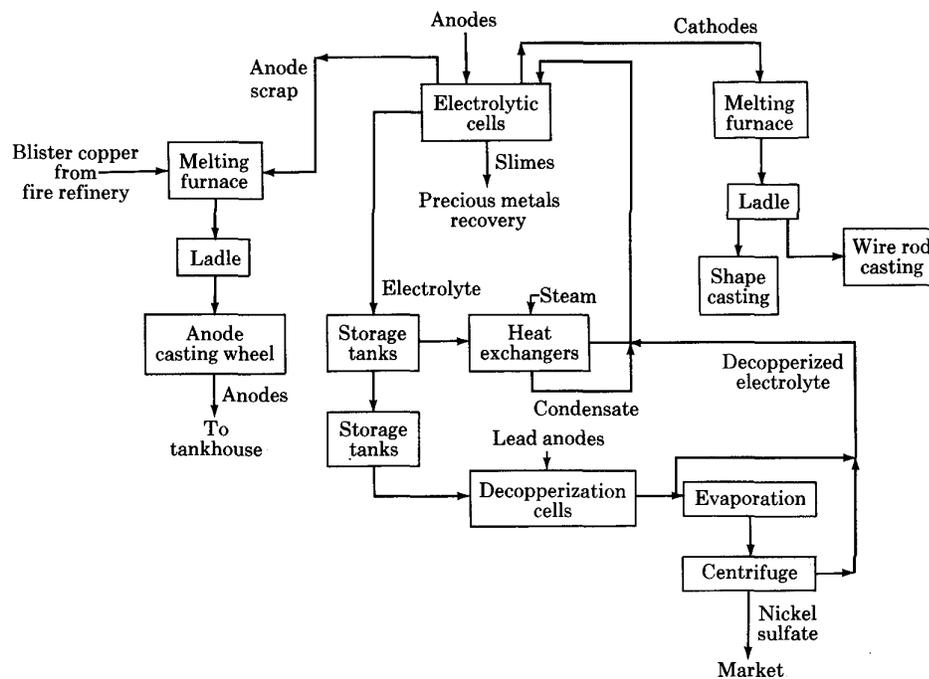
- 7) Removal and recovery of copper, usually by electrowinning in stage-1 "liberator" cells (Table 6.3.3).

- 8) Removal of As, Sb and Bi via electrowinning them onto an impure Cu deposit.
- 9) Evaporation of water and precipitation of Ni, Fe and Co as sulfides.

• Table 6.3.2. Typical electrolyte conditions for copper electrorefining

Component	Concentration/g dm <sup>-3</sup>
Cu	40–50
H <sub>2</sub> SO <sub>4</sub>	170–200
	Upper limits
Ni	20
As	10
Fe	2
Sb	0.5
Bi	0.2
Cl	0.03
Specific gravity	1.25 ± 0.03
Temperature	60–65° C

Figure 6.3.4 summarizes the total process. Normally, the sludge removal is by filtration of the electrolyte, although in some cases (e.g. Pb) the sludge collects on the anode which periodically must be removed from the cell and scraped. Before recycle, the electrolyte must be purified and the concentration of metal ion, electrolytes and addition agents adjusted to the correct values. The purification normally involves cementation or precipitation [by addition of hydroxide or sulfide ion or by change of oxidation state, e.g. Sn(II) → Sn(IV)]. The exact procedure will depend on the level and type of impurities in the electrolyte.



• Figure 6.3.4. Flow diagram of electrorefinery, including auxiliary product streams.

• Table 6.3.3. Liberator (decopperization) cell stages in the removal of copper from bleed streams.

Stage	Approximate change in copper concentration/g dm <sup>-3</sup>	Cathode product
1	45–15	Commercial purity cathodes
2	15–8	Cathodes may require remelting in the anode furnace and re-refining
3	8–0.2 (requires hooding as poisonous arsine (AsH <sub>3</sub> ) gas may be evolved)	Very impure, especially high in As and Bi. Cathodes require purification prior to remelting in the anode furnace

In order to achieve high production rates, high *current densities* are obviously desirable. However, an excessive current density causes at least two problems: (1) increased impurity levels in the cathode deposit; an increased roughness promotes occlusion of anode residues and electrolyte; and (2) anode passivity occurs at current densities above 25–28 mA/cm<sup>2</sup>.

Hence, it can be seen from the data in Table 6.3.1 that in order to obtain pure metals at the cathode, the current density is always low.

On the other hand, with the exception of tin, the *current efficiencies* are good and the *cell voltages* can be low. In modern refineries, cathode current efficiency is 90–97%, anode current efficiency being slightly higher. Inefficiency results from strong currents to ground (1–3%), anode-cathode short circuits (1–3%) and loss of copper deposit by air (or Fe<sup>3+</sup>) oxidation (ca. 1%). Ground leakage currents are minimized by the avoidance of electrolyte spillage. Short-circuiting is predominantly caused by nodular or dendritic growth which must be removed or restricted by suitable addition agents. A range of modern aids is available to monitor and identify shorts including computer monitoring of current distribution and infrared detection of “hot spots”.

In electrorefining the cathode reaction is the reverse of that at the anode and therefore, in the ideal case, the cell voltage is only required to drive the current through the electrolyte.

In practice, there may also be overpotentials associated with the anode and cathode reactions, and in the cases of nickel and cobalt these are considerable because the M/M<sup>2+</sup> couples are very irreversible. The typical voltage components are shown in Table 6.3.4.

• Table 6.3.4. Typical voltage components in a copper electrorefining cell.

	– Voltage/V
Voltage drop in the electrolyte	0.11–0.13
Cathode overpotential due to organics and polarization	0.04–0.08
Anode and cathode electrical connections	0.03–0.06
Busbar and lead losses	0.01–0.02
Anode polarization	0.0–0.01
Cell voltage	0.23–0.27

Specific electrolytic *energy consumption* is relatively low, around 0.22 kWh/kg cathode copper, which is increased to ca. 0.31 kWh/kg by additional power components.

To the present time this has led to the use of cells with relatively large interelectrode gaps (5-15 cm) which minimizes the labor costs for checking cells to prevent shorts and to handle electrode changes. The low current densities contribute to the low energy consumption (the  $iR$  term is small) but causes the cell houses to be large and, more importantly, the inventory of metal tied up in the cell house is large. The residence time of the metal in the cell is often 21-28 days and this is expensive, particularly in the case of silver, gold and the platinum group metals. Hence, increased current densities without loss in purity of the refined metal would be advantageous.

Perhaps the most significant **recent development** in copper refining has been periodic current reversal which permits an increase (of  $< 15\%$ ) in production rates via two effects: (1) the anodic current density at which passivations occur may be increased; and (2) selective removal of Cu high spots (e.g. nodules) during the reverse current gives smoother cathode deposits.

Optimum conditions of periodic current reversal permit cathode current densities of up to  $36 \text{ mA/cm}^2$ . The preferred ratio of forward-current time: reverse-current time is 20 or 30 to 1, with identical forward and reverse currents, for a cycle time of 0.5-3 min.