Non-Ferrous Metals:
Copper and Its Alloys

Principal copper-containing minerals are chalcopryite (CuFeS₂), chalcocite (Cu₂S), and bornite (Cu₃FeS₄). However, most ores typically contain only a small percentage (sometimes < 1%) of copper compounds and must be concentrated.

Concentration of ores is accomplished using froth flotation technique:

1.) Crushed low-grade ore is mixed with water, oil, and a detergent.

2.) Stream of compressed air produces a foamy mixture, in which oil-wetted particles of ore are buoyed up by clinging to air bubbles, while water-wetted earth and rock sink to bottom.

3.) Copper-rich froth is skimmed off, oil is separated for re-use, and (after drying) a solid mass enriched in CuFeS₂ (if a chalcopryite-containing ore is used). Copper content of concentrated ore is 25 - 30%.

Dried concentrated ore is then roasted in air at high temperatures to convert the iron to its oxide, while leaving the copper as a sulfide:

\[ 6 \text{CuFeS}_2(s) + 13 \text{O}_2(g) \rightarrow 3 \text{Cu}_2\text{S}(s) + 2 \text{Fe}_3\text{O}_4(s) + 9 \text{SO}_2(g) \]
The Cu₂S / Fe₂O₄ mixture is then heated to ~1100°C, and limestone (CaCO₃) and silica (SiO₂) are added as a flux to remove the iron:

\[
\text{Fe}_3\text{O}_4 (s) + \text{CaCO}_3 (s) + \text{SiO}_2 (s) \rightarrow \text{CO}_2 (g) + \text{CaO} \cdot \text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot (\text{SiO}_2)_2 (l) \]

(slag, composition variable)

Because Cu₂S (l) is insoluble in the Ca/Fe slag and is more dense, it settles to the bottom, allowing the molten slag to be drawn off.

The liquid Cu₂S is then run into another furnace, through which an air stream is blown to produce metallic copper:

\[
\text{Cu}_2\text{S} (l) + \text{O}_2 (g) \rightarrow 2 \text{Cu} (l) + \text{SO}_2 (g)
\]

The liquid copper is then cooled and cast into large slabs of “blister copper” for further purification, usually by electro-refining.
FIGURE 19.9  Froth flotation for the enrichment of ore. Frothing agents are added to a water suspension of the pulverized ore. As compressed air is bubbled in, the desired mineral (CuFeS₂, in the case of copper production) is concentrated at the surface of a foam and borne upward while the unwanted rocky material settles to the bottom. (Sunshine Mining Company)
Copper Electro-Refining Cell

The anodes cast from processed blister copper are placed into an aqueous solution of 3-4% copper sulfate and 10-16% sulfuric acid. Cathodes are thin rolled sheets of highly pure copper. A potential of only 0.2 - 0.4 volts is required for the process to commence.

At the anode, copper and less noble metals dissolve. More noble metals, such as silver and gold, which do not oxidize at the anode (\(E^\circ = +0.80\) V and \(+1.40\) V, respectively), as well as selenium and tellurium, settle to the bottom of the cell as anode slime, which forms a saleable by-product.

Copper(II) ions migrate through the electrolyte to the cathode. At the cathode, copper metal plates out, but less noble constituents such as arsenic and zinc remain in solution.

The reactions are:

At the anode: \(\text{Cu} (s) \rightarrow \text{Cu}^{2+} (aq) + 2 \text{e}^-\) \(E^\circ = -0.34\) V

At the cathode: \(\text{Cu}^{2+} (aq) + 2 \text{e}^- \rightarrow \text{Cu} (s)\) \(E^\circ = +0.34\) V
Problems in Copper Smelting:

1.) Pollution caused by $\text{SO}_2$ by-product.

Emission control regulations have required the development of modified processes, in which nearly all of the $\text{SO}_2$ is captured and converted into commercially important $\text{H}_2\text{SO}_4$.

2.) Disposal of calcium-iron-silicate slag.

The by-product slag can contain toxic heavy-metal impurities, such as cadmium. Modern smelters allow the water that is used to be re-cycled, thus greatly decreasing the amount of heavy metals that are leached out of the slag.

3.) Energy costs of high-temperature furnaces.

New hydrometallurgical methods provide an alternative, low-temperature, method for separating the copper and iron in the ore. An aqueous mixture of $\text{CuCl}_2$ and $\text{FeCl}_3$ is added to the concentrated ore, which results in reduction of Cu (II) and oxidation of the sulfur:

\[
\text{CuFeS}_2 (s) + 3 \text{CuCl}_2 (aq) \rightarrow 4 \text{CuCl} (s) + \text{FeCl}_2 (aq) + 2 \text{S} (s)
\]

\[
\text{CuFeS}_2 (s) + 3 \text{FeCl}_3 (aq) \rightarrow \text{CuCl} (s) + 4 \text{FeCl}_2 (aq) + 2 \text{S} (s)
\]

Excess NaCl is added to the solids that form to convert the solid CuCl to the soluble complex ion $[\text{CuCl}_2]^{aq}$, which is separated from the sulfur and converted into metallic copper in a disproportionation reaction, regenerating the original CuCl$_2$:

\[
2 \text{CuCl}_2^{aq} \rightarrow \text{Cu} (s) + \text{CuCl}_2 (aq) + 2 \text{Cl}^{aq}
\]

This method has the multiple advantages of decreasing energy costs by eliminating the need for high-temperature furnaces, as well as avoiding the formation of both $\text{SO}_2$ and the Ca-Fe-silicate slag.
Other Copper Smelting Processes:

- Cu₂O
- CuSO₄·3Cu(OH)₂ etc.

Leaching with H₂SO₄ → CuSO₄ → Cementation → Copper cement → Casting to form ingots → Commercial copper

- Cu₂O + CaMg(CO₃)₂

Leaching with (NH₄)₂CO₃ → Cu(NH₃)₂CO₃ → Boiling → Oxidation and the removal of iron in a slag in Bessemer converters → OXIDATION

- Calcopryltes (Cu₂Fe₂S₄)

Partial roasting and slag formation → Matte

- Cu₂S

Impurities → Cu & impurities → Electrolysis → Cu 99.99%

Fig. 13.29—Block diagram of the 'wet', 'wet and dry', and 'completely dry' metallurgical processes which are carried out, according to their nature, on copper minerals.
Metallic copper is used for the following applications:

1.) Building construction (46%).

2.) Electrical and electronic products (23%).

3.) Transportation equipment (10%).

4.) Consumer and general products (11%).

5.) Industrial machinery and equipment (10%).

Pure copper is too soft to be used for cutting tools and precision parts, but certain copper alloys are important for these purposes:

**Bronze** - Copper alloy containing ~10% tin. Hard, without being brittle, can be cast in a mold, and melts at a temperature (950°C) that is well below that (1084°C) of pure copper.

**Brass** - Copper alloy containing up to ~40% zinc. Useful for making precision parts and instruments because it is hard, easy to machine, and corrosion-resistant.
Aluminum Production

Most common ore of Al is **bauxite**, which consists primarily of Al₂O₃, but also contains varying amounts of FeOₓ, SiO₂, TiO₂, and various silicate materials, which must all be removed prior to processing.

Pure hydrated alumina (Al₂O₃ • nH₂O) is obtained by treating crude bauxite with aqueous NaOH, which dissolves the amphoteric Al₂O₃ but not the basic oxide impurities:

\[
\text{Al}_2\text{O}_3 (s) + 2 \text{OH}^- (aq) \rightarrow 2 \text{AlO}_2^- (aq) + \text{H}_2\text{O} (l)
\]

Resulting solution containing aluminate ion (AlO₂⁻) is separated from the sludge of undissolved impurity oxides and is then acidified with CO₂, causing the hydrated alumina to re-precipitate:

\[
2 \text{CO}_2 (g) + 2 \text{AlO}_2^- (aq) + (n+1) \text{H}_2\text{O} (l) \rightarrow 2 \text{HCO}_3^- (aq) + \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O} (s)
\]

Because of the large negative reduction potential of the Al³⁺/Al⁰ couple (E° = -1.66 V), metallic Al cannot easily be generated by chemical reduction of Al₂O₃ and must be produced from the oxide by electrolysis. Although pure Al₂O₃ has an impractically high M.P. (>2000°C), it dissolves readily in molten cryolite (Na₃AlF₆), which melts at "only" 1000°C and serves as the electrolyte in the so-called **Hall-Heroult Process**:

\[
\text{Al}_2\text{O}_3 + 4 \text{AlF}_6^{3-} \rightarrow 3 \text{Al}_2\text{OF}_6^{2-} + 6 \text{F}^-
\]
Because the electrolyte solution contains a large number of Al-containing ions, its chemistry is not completely understood. However, the electrode reactions are believed to be the following:

**Cathode Reaction:** \[ \text{AlF}_6^{3-} + 3 \text{e}^- \rightarrow \text{Al} + 6 \text{F}^- \]

**Anode Reaction:** \[ 2 \text{Al}_2\text{OF}_6^{2-} + 12 \text{F}^- + \text{C} \rightarrow 4 \text{AlF}_6^{3-} + \text{CO}_2 + 4 \text{e}^- \]

**Overall Reaction:** \[ 2 \text{Al}_2\text{O}_3 + 3 \text{C} \rightarrow 4 \text{Al} + 3 \text{CO}_2 \]

The carbon that is oxidized at the anode is the graphite of the electrode itself, which must be periodically replaced.

Aluminum produced by the Hall-Heroult process is 99.5% pure. To be used as a structural material, it is alloyed with metals such as Zn and/or Mg (for trailer and aircraft construction) or with Mn (for cooking utensils, storage tanks, and highway signs).

Production of Al consumes almost 5% of all electricity that is generated in the U.S.
FIGURE II.22

A schematic diagram of an electrolytic cell for producing aluminum by the Hall-Heroult process. Because molten aluminum is more dense than the mixture of molten cryolite and alumina, it settles to the bottom of the cell and is drawn off periodically. The graphite electrodes are gradually eaten away and must be replaced from time to time. The cell operates at a current flow of up to 250,000 A.