Chapter (5)

Industrial Applications of Metal Electrodeposition

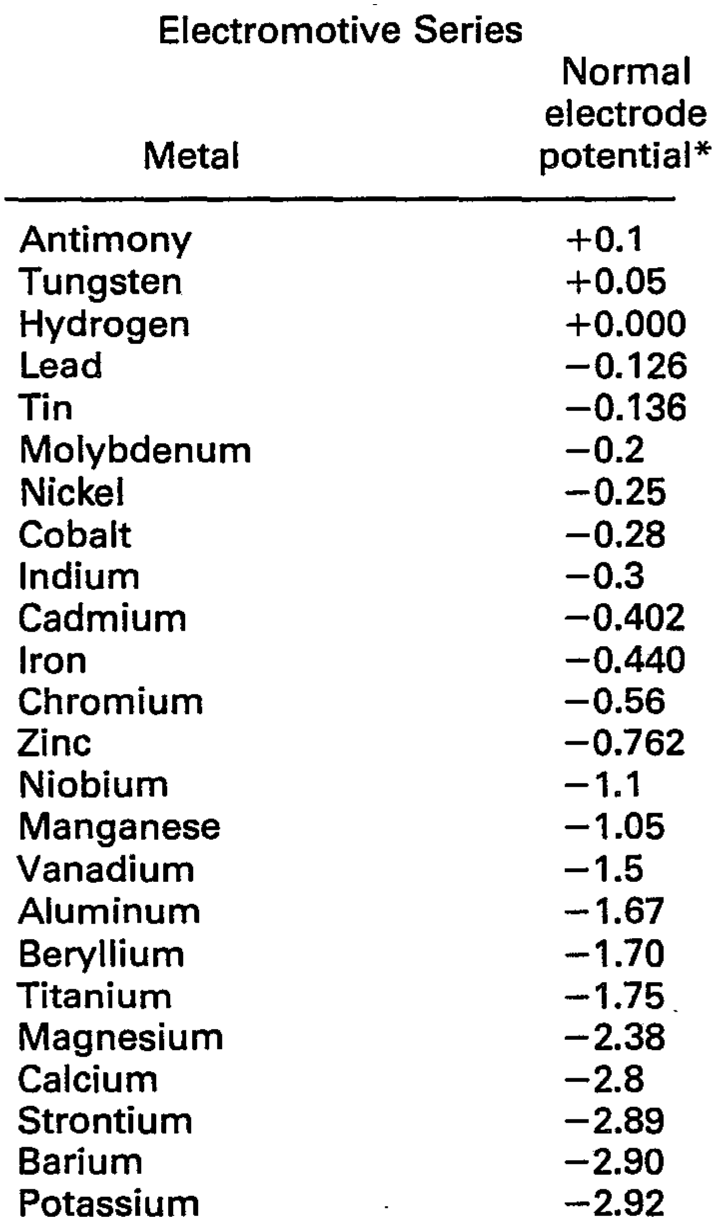
Electrowinning of Metals

Electrowinning of Metals

- Electrowinning of metals is the recovery of metals from their compounds or natural ores by electrolysis and it is the oldest industrial electrolytic process.
- Sodium metal was first prepared in 1807 by the Humphrey Davy, who obtained it using electrolysis of molten sodium hydroxide.
- Several industrially important metals (the active metals which react with water) are produced commercially today by electrolysis of molten salts.
- Exampled on metals that are electrowon include zinc, aluminum and magnesium.

Electrowinning of Metals

- Metals which are more noble than H_2 in the electromotive series such as Cu, Ag and Au deposit with a current efficiency of 100% while metals which are less noble than H_2 deposit with a current efficiency less than 100 % owing to the simultaneous evolution of H_2 with the metal.
- Metals with very high oxidation potential such as Mg and Al cannot be deposited from aqueous solutions because H2 is discharged from these solutions instead of the metals. Such metals are electrowon from molten baths.



Electromotive Series

Metal	Normal electrode potential*
Antimony	+0.1
Tungsten	+0.05
Hydrogen	+0.000
Lead	−0.126
Tin	−0.136
Molybdenum	−0.2
Nickel	−0.25
Cobalt	−0.28
Indium	−0.3
Cadmium	−0.402
Iron	−0.440
Chromium	−0.56
Zinc	−0.762
Niobium	−1.1
Manganese	−1.05
Vanadium	−1.5
Aluminum	−1.67
Beryllium	−1.70
Titanium	−1.75
Magnesium	−2.38
Calcium	−2.8
Strontium	−2.89
Barium	−2.90
Potassium	−2.92

Electrowinning of Metals: Zn

- The process of zinc electrowinning (Zn production from ZnS) ore) consists of three steps:

A) Leaching by dissolving the ore in a suitable acid (see Figure 5.1 & 5.2:

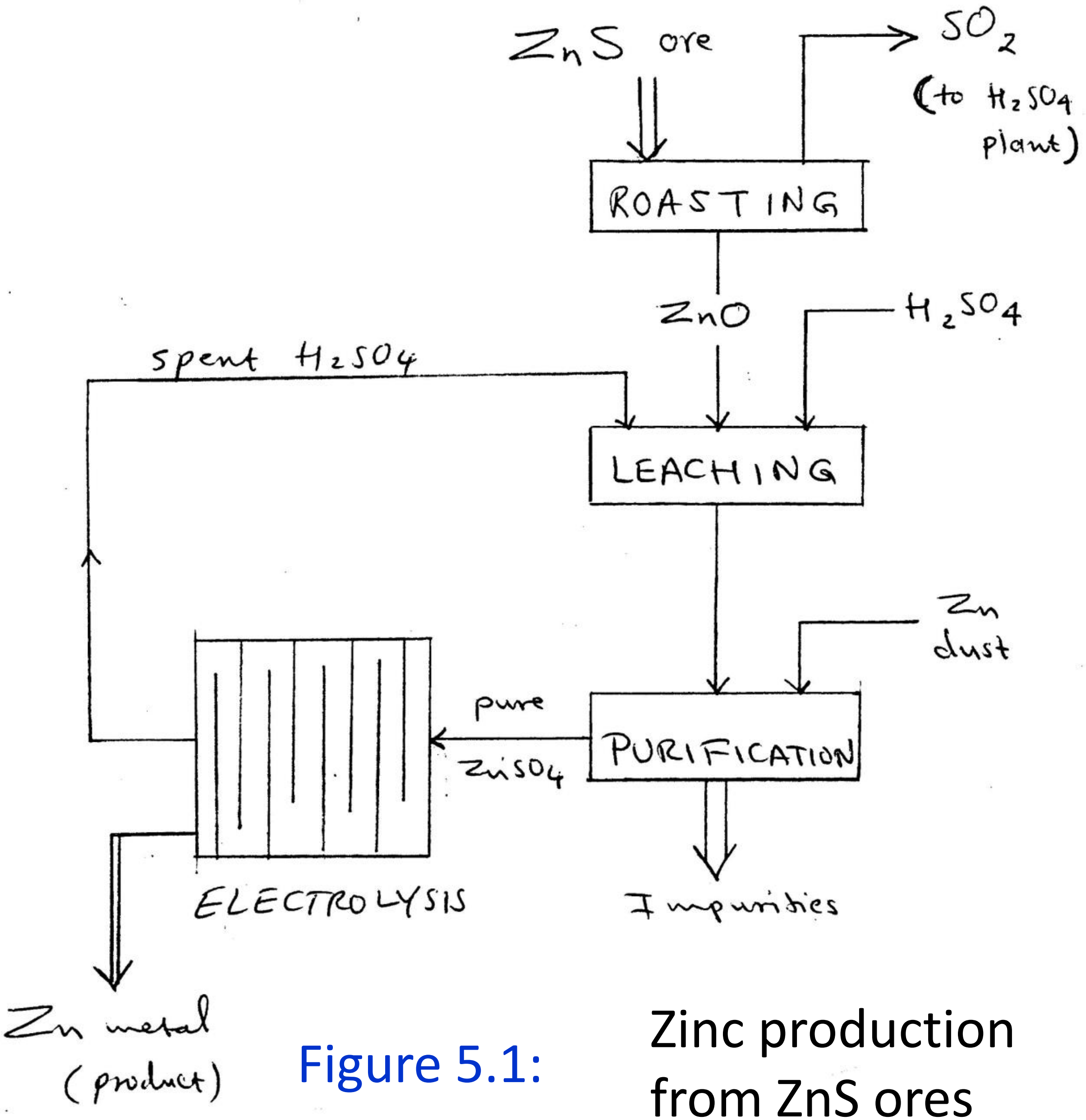


Figure 5.1: Zinc production from ZnS ores

Electrowinning of Metals: Zn

B) Purification of the leach liquor by one of the following methods:

a) fractional crystallization b) fractional precipitation
c) solvent extraction d) cementation; which is the addition of pure zinc dust to precipitate the impurities and to free zinc ions:

Zn (powder) + $CuSO_4$ (aq) → Cu (solid deposit) + $ZnSO_4$ (aq)

C) Pure electrolyte is **electrolyzed** in a cell under the suitable conditions to obtain the required metal and a spent acid which is circulated to the leaching tank. In electrowinning, usually an insoluble anode is used (e.g. Pb, carbon and Pt).

- At the cathode, the following reactions take place:

$$Zn^{2+} + 2e^- \rightarrow M \quad \text{and} \quad 2H^+ + 2e^- \rightarrow H_2$$

- At the anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

Electrowinning of Metals: Zn

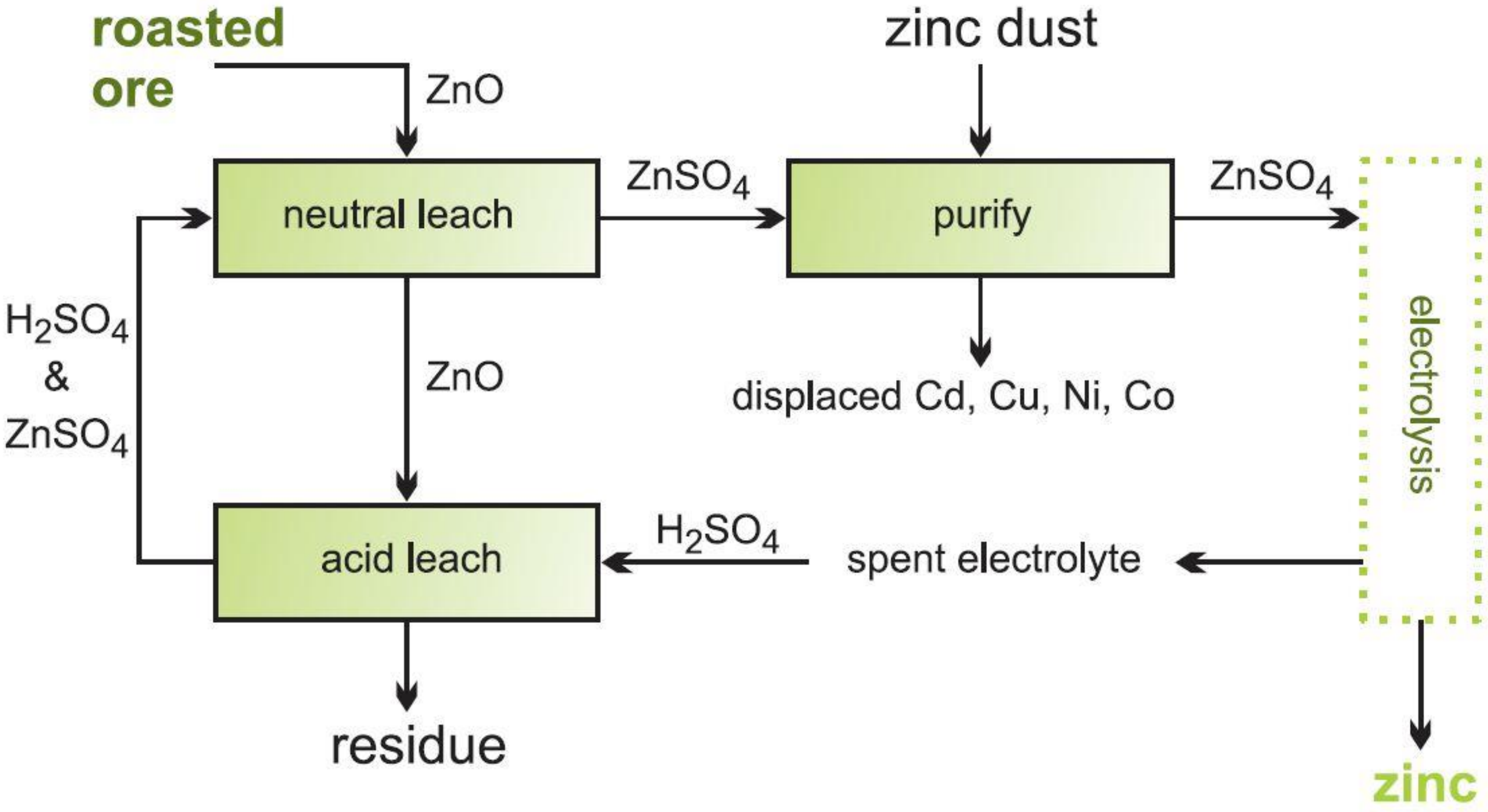


Figure 5.2

Flow diagram showing the stages in recovering zinc oxide from zinc ore

Electrowinning of Metals: Al

- Aluminum compounds, primarily the oxide in forms of various purity and hydration, are fairly widely distributed in nature. The major ore of aluminum is bauxite, a hydrated aluminum (III) oxide (Al2O3.xH2O).
- In the industrial Bayer process, bauxite is concentrated to produce aluminum hydroxide. When this concentrate is calcined at temperatures in excess of 1000oC, anhydrous aluminum oxide, Al2O3, is formed.
- In the well-known Hall process (Figure 5.3), purified Al2O3 is dissolved in molten cryolite, Na3AlF6, which has a melting point of 1012oC and is an effective conductor of electric current.
- Graphite rods are employed as anodes and are consumed in the electrolysis process.
  - The carbon anodes slowly disappear because each molecule of carbon dioxide which is given off takes a little piece of carbon away with it.
  - The carbon anodes need to be replaced when they become too small.

Electrowinning of Metals: Al

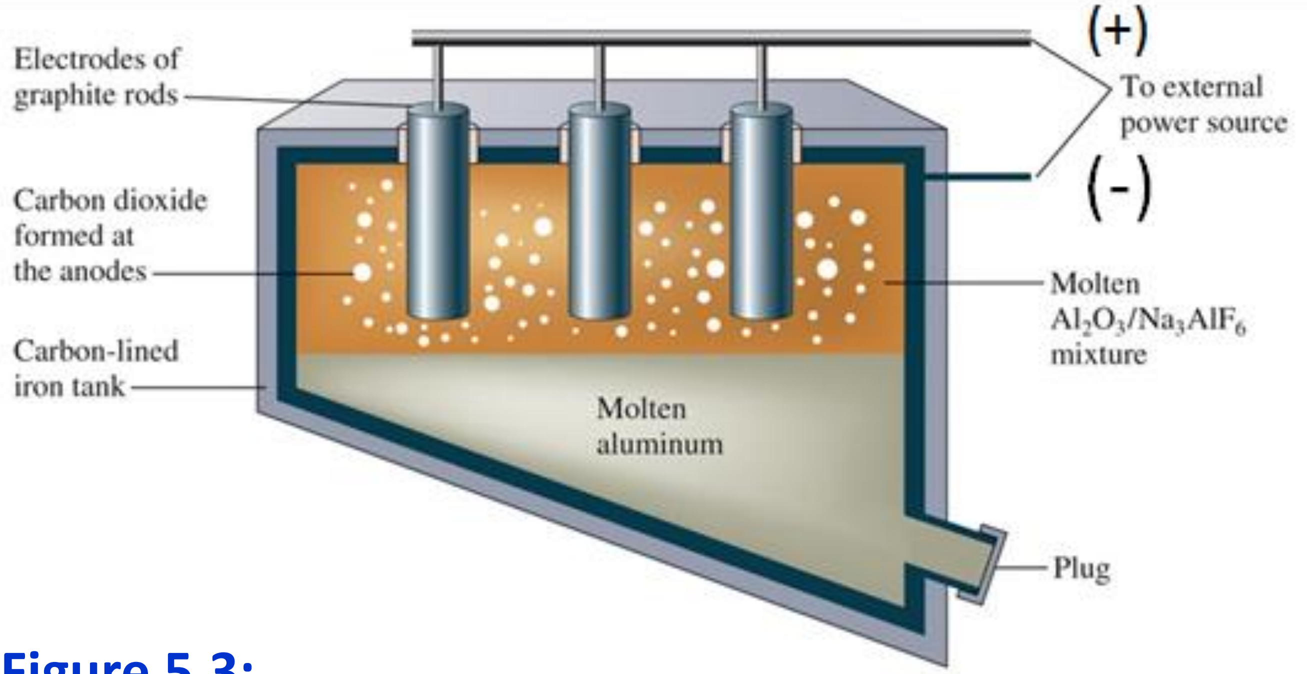
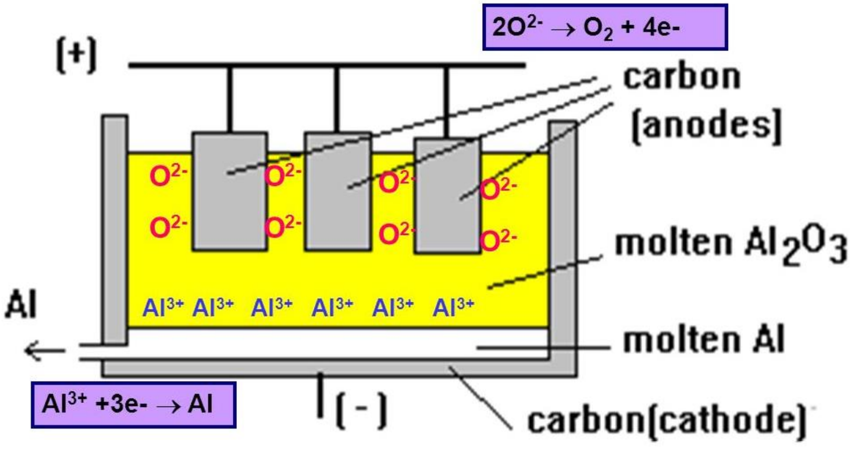


Figure 5.3:
Electrochemical reactor configuration for aluminum electrowinning.



- Multi-carbon (graphite) rod anode (+)
- Carbon tank-lining cathode(-)

Electrowinning of Metals: Al

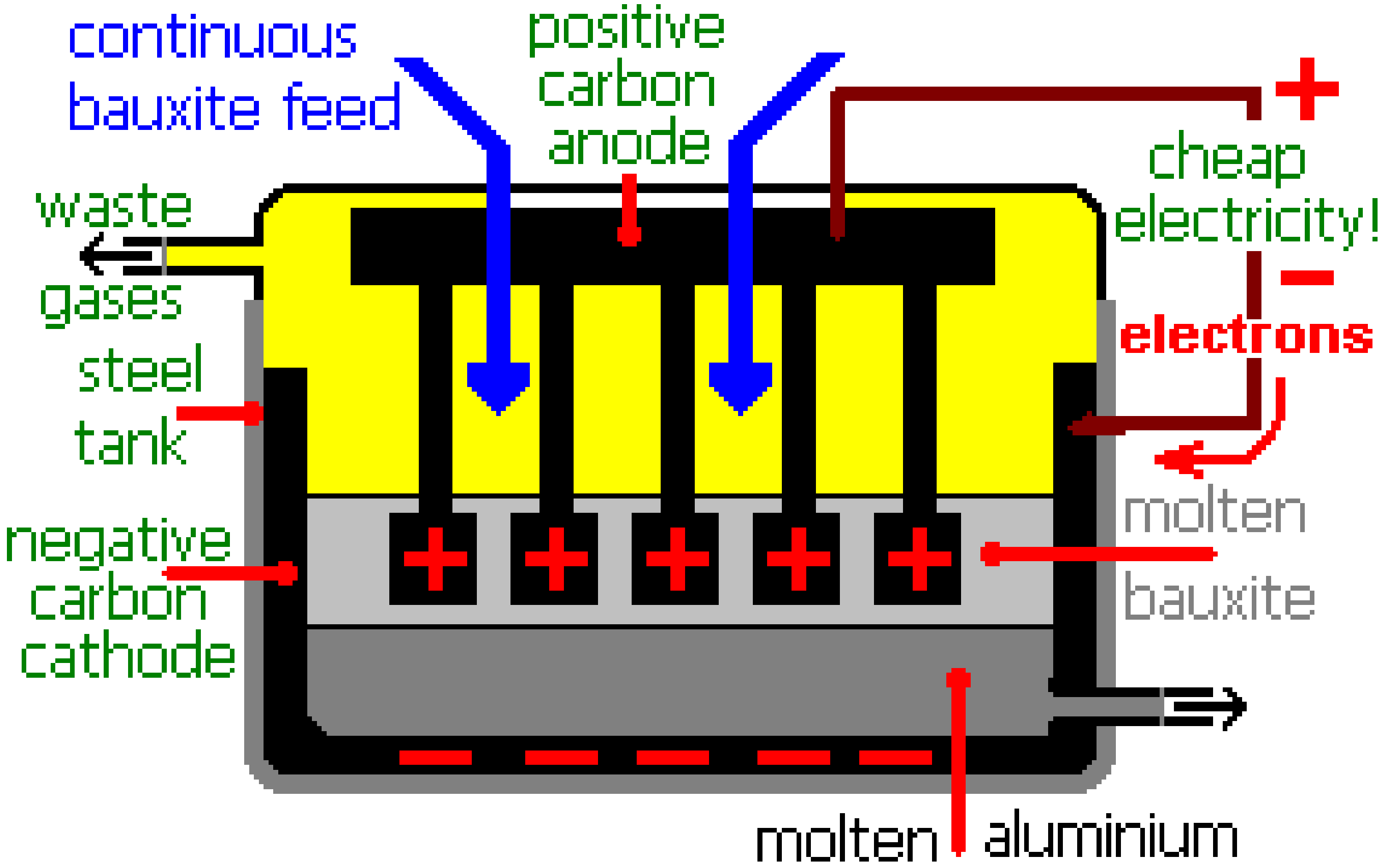


Figure 5.3:

Electrochemical reactor configuration for aluminum electrowinning.

Electrowinning of Metals: Al

- The cell electrolytic reactions are:

Cathode:

$Al^{+3} + 3\ e^{-} \rightarrow Al$

Anode:

$O^{-2} + C \rightarrow CO + 2\ e^{-}$

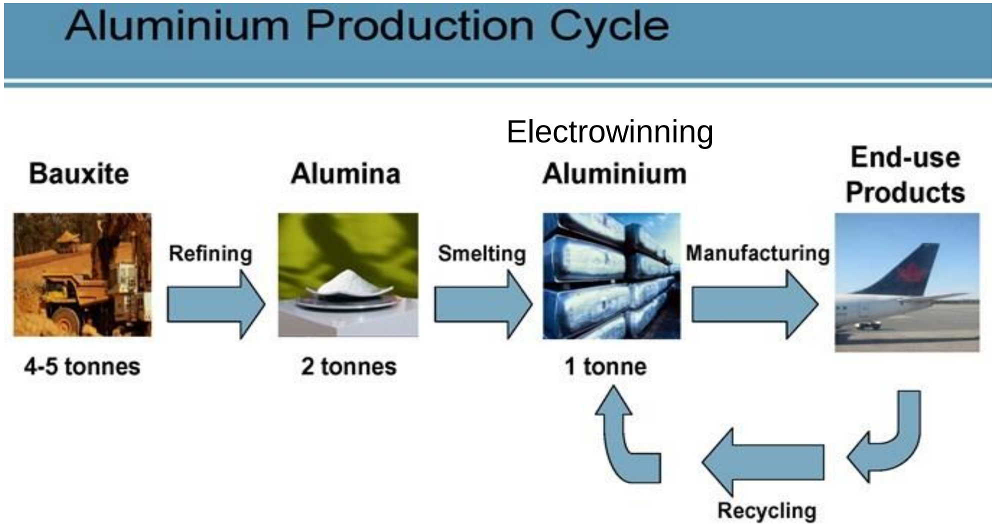
Overall:

$Al_2O_3 + 3\ C \rightarrow 2\ Al + 3\ CO$

In reality much more CO_2 is formed at the anode than CO:

$$Al_2O_3 + 3/2\ C \rightarrow 2\ Al\ (l) + 3/2\ CO_2\ (g)$$

- Electrolysis can happen at temperatures between 940 and 980°C.
- Current density is ~ 5 Volts
- Cell voltage is ~ 1 A/cm2



Electrowinning of Metals: Al

- Because molten aluminum is more dense than the molten mixture of Na3AlF6 and Al2O3, the metal collects at the bottom of the cell.
- The cells are designed to use 8000 A/m2 and upwards, and a given cell requires about 5 V although only 2.1 V are theoretically required to decompose aluminum oxide.
- The excess 2.9 V, plus the heat of combustion of carbon, is used as heat to keep the cell warm.
- The production of one ton of aluminum requires about 65-70 GJ (18-20 MWh) and about half a ton of carbon.
- The process is generally non-polluting but is a heavy consumer of electricity:
  - Approximately 36% of the electricity is used in the Faradaic process,
  - The rest being lost as heat.

Electrowinning of Metals: Mg

- The most commonly used industrial process for magnesium production.
- Raw material for magnesium production is well brines or seawater, which is about 0.13% magnesium by mass.
    - The Mg2+ ion is precipitated from seawater by addition of CaO (lime): **Ca (OH)2 + Mg2+ → Mg(OH)2 + Ca2+**
    - The insoluble Mg (OH)2 is removed by filtration.
    - Acidification of a slurry of this solid and an aqueous MgCl2 solution with HCl converts the Mg (OH)2 to soluble MgCl2, which is recovered as solid MgCl2 by evaporation.
    - This is dried to the **hydrate MgCl2.1.5H2O**, which is used as the feedstock to an electrolytic cell.

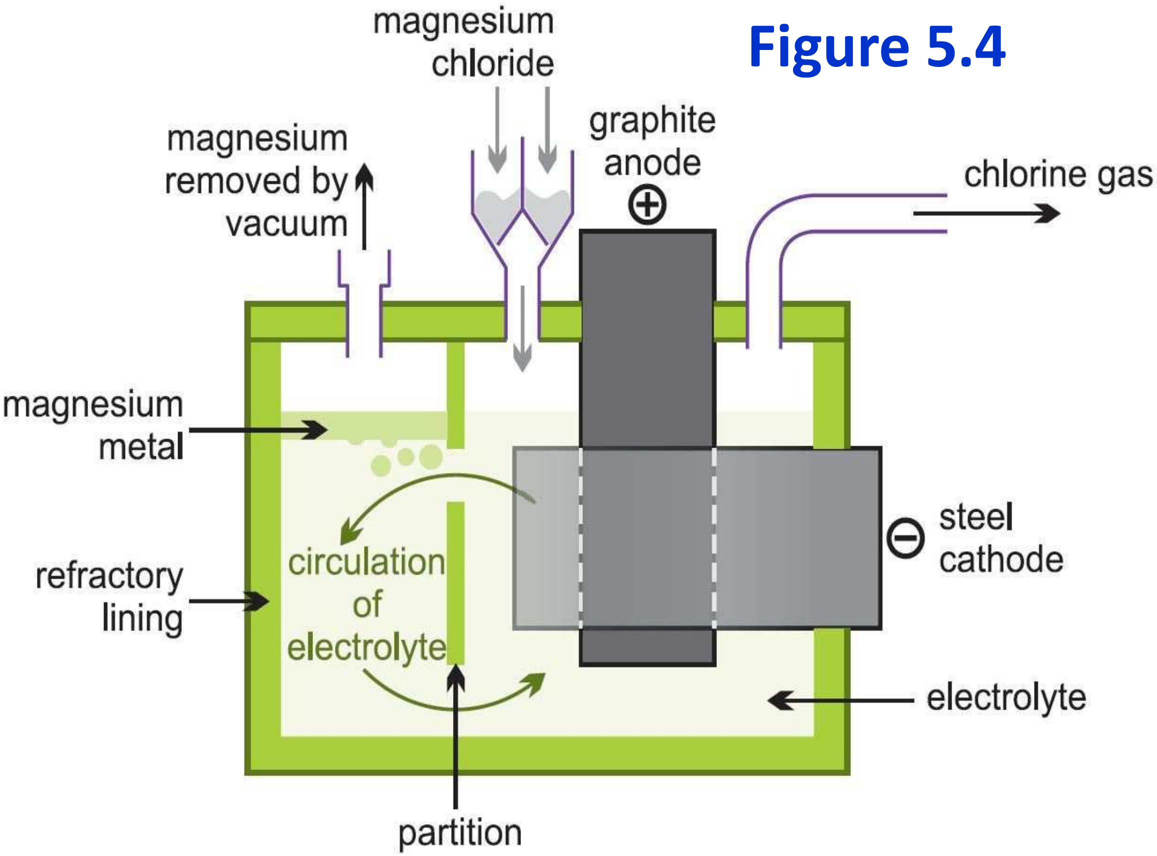
Electrowinning of Metals: Mg

- The cell electrolyte is a molten mixture containing about 25% $MgCl_2$ - 15% $CaCl_2$ - 60% NaCl, and the cell is operated between 700oC and 750oC. The cell electrolytic reaction is:

$$MgCl_2 \rightarrow Mg\ (l) + Cl_2\ (g)$$

- The magnesium produced is about 99.9% pure as it comes from the cell, since neither sodium nor calcium is reducible more easily than is magnesium.
- The chlorine produced in the cell is converted to HCl for use in the acidification process.

Figure 5.4



Example

- How long (in hours) would it take to produce 25 g of Cr from a solution of Cr^{3+} by a current of 2.75 A?

$$\mathbf{Cr^{3+}_{(aq)} + 3\,e^{-} \dashrightarrow Cr_{(s)}}$$

1 mole Cr = 3 moles e^{-} = 3 F = 3 x 96500 Coulombs

- **Solution:**

$$25\ \text{g Cr} \times \frac{1\ \text{mole Cr}}{52\ \text{g Cr}} \times \frac{3\ \text{F}}{1\ \text{mole Cr}} = 1.44\ \text{F}$$

$$1.44\ \text{F} \times \frac{96500\ \text{coulombs}}{\text{F}} = 139000\ \text{coulombs}$$

$$\frac{139{,}000\ \text{A.s}}{} \times \frac{1\ \text{hr}}{} = \underline{14\ \text{hr}}$$

Electroplating of Metals

Electroplating of Metals

- **Definition**: Process of electro deposition of an adherent metallic film of uniform thickness on the surface of the substrate for the purpose of modifying its surface properties.
- Electroplating is a type of surface finishing. Examples of electroplated objects are countless. They include household faucets, jewelry and the trim on automobiles
- One of the most significant metal electroplated today is tin.
- A tin can used to contain food or other preserved items is actually made of thin steel plate which has been electroplated with a very thin layer of tin to protect the steel from corrosion reactions between the steel and the can contents or environment.
- Cadmium, chromium, copper, lead, nickel, silver, and zinc are also metals for which large-scale electroplating processes are used.

Electroplating of Metals

- Non-metal surfaces such as those of plastics can be electroplated with metals after a conductive surface is placed on them.
  - This can be done by evaporation or chemical reaction of a metal, usually copper or silver, or by adhesion of a conductive powdered material such as graphite.

Electroplating of Metals

A. Objectives of Electroplating:

- The main reasons for carrying out an electroplating process are:
  1) To give a good appearance to the metal (ornamental or decorative purposes).
  2) To protect the metal against corrosion by covering it with a metal which resists corrosion.
  3) To confer an engineering property to the metal, e.g. copper is electroplated with Cr to confer hardness.
  4) To produce a material with special surface properties, e.g. conductivity of plastic.
- The object to be plated is made the cathode of the plating cell.
- The cell anode is often a bar or other shape of the metal to be plated from solution, so that the anode reaction of metal dissolution replaces the metal ion consumed from solution by cathodic deposition (**see Figure 5.5**).

Common Example of Electroplating

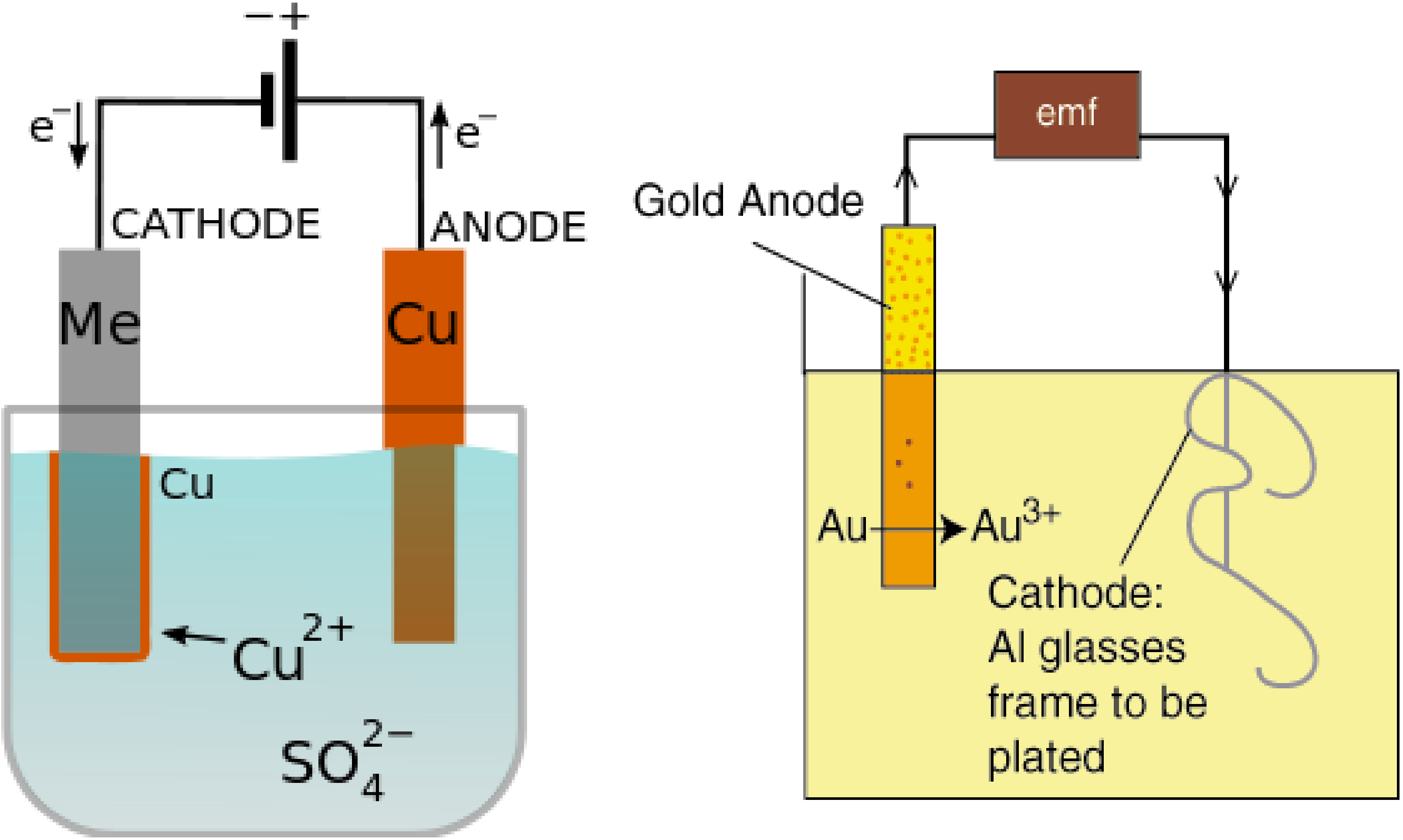


Figure 5.5: Simple electroplating cells

Electroplating of Metals

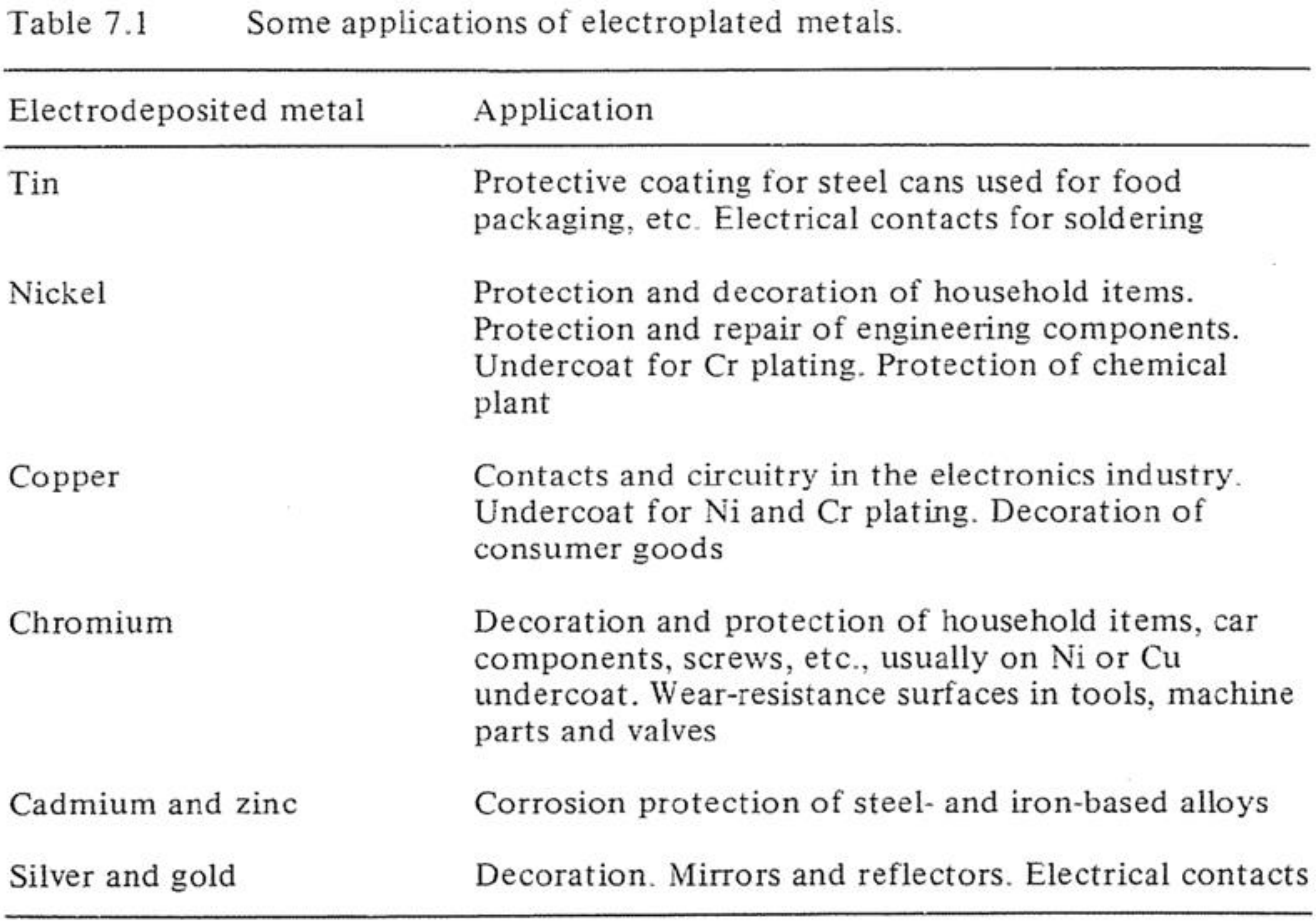


Table 7.1 Some applications of electroplated metals.

Electrodeposited metal	Application
Tin	Protective coating for steel cans used for food packaging, etc. Electrical contacts for soldering
Nickel	Protection and decoration of household items. Protection and repair of engineering components. Undercoat for Cr plating. Protection of chemical plant
Copper	Contacts and circuitry in the electronics industry. Undercoat for Ni and Cr plating. Decoration of consumer goods
Chromium	Decoration and protection of household items, car components, screws, etc., usually on Ni or Cu undercoat. Wear-resistance surfaces in tools, machine parts and valves
Cadmium and zinc	Corrosion protection of steel- and iron-based alloys
Silver and gold	Decoration. Mirrors and reflectors. Electrical contacts

Electroplating of Metals

Common Coating Metals:

1) Tin - widely used for corrosion protection in "tin cans" and other food containers.
2) Nickel - for corrosion resistance and decorative purposes on steel, brass, zinc die castings, etc. Also used as base coat for chrome plate
3) Copper - decorative coating on steel and zinc, either alone or alloyed as brass. Also important in printed circuit boards
4) Chromium - decorative coating widely used in automotive, office furniture, and kitchen appliances. Also one of the hardest electroplated coatings for wear resistance
5) Zinc - plated on steel products such as fasteners, wire goods, electric switch boxes, and sheet metal parts as a sacrificial barrier to corrosion
6) Precious metals (gold, silver) - plated on jewelry. Gold is also used for electrical contacts

Electroplating of Metals

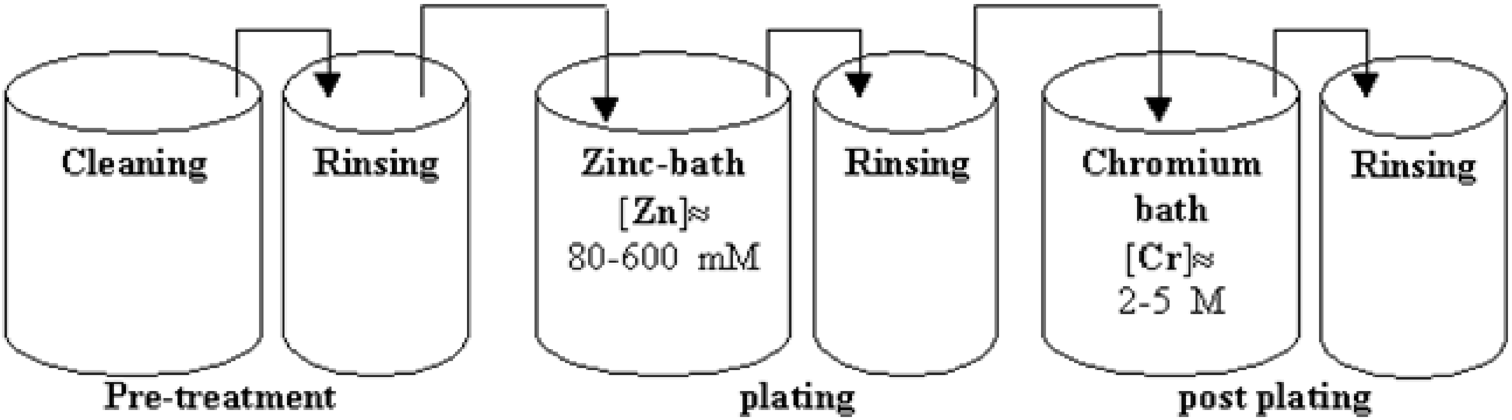
B. Pretreatment of the Article before Plating:

- Electroplating of metals requires careful preparation of the conductive surface of the cathode, which must be as clean and uniform as possible. The article to be plated should be cleaned from (i) greases and (ii) metal oxides.
- De-greasing is carried out by:
  - Treating the article with hot NaOH to remove the saponifiable greases (e.g. lead stearate).
  - Non- saponifiable greases (e.g. petroleum lubricating oils) are removed by organic solvents such as CCl_4 or chloroform.
- Scales and oxides are removed either mechanically by treating the article with emery paper, or chemically by acid pickling.
  - Acid pickling is carried out by placing the article in dilute acid (e.g. 5 % HC1 or H_2SO_4) for few minutes. Degreasing should be carried out before acid pickling.

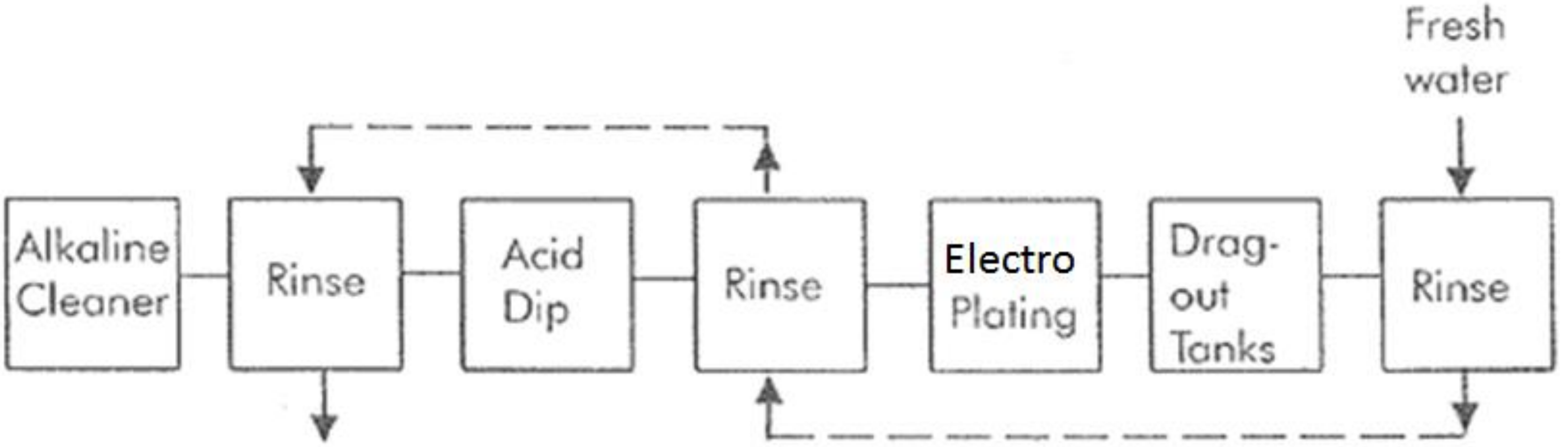
Electroplating of Metals

- Illustrative flowcharts of a general electroplating process are shown in **Figures 5.6-5.10**.
- Many rinsing steps are involved which indicates a necessity to manage the environmentally hazardous process effluent.

Figures 5.6



Figures 5.7



Electroplating of Metals

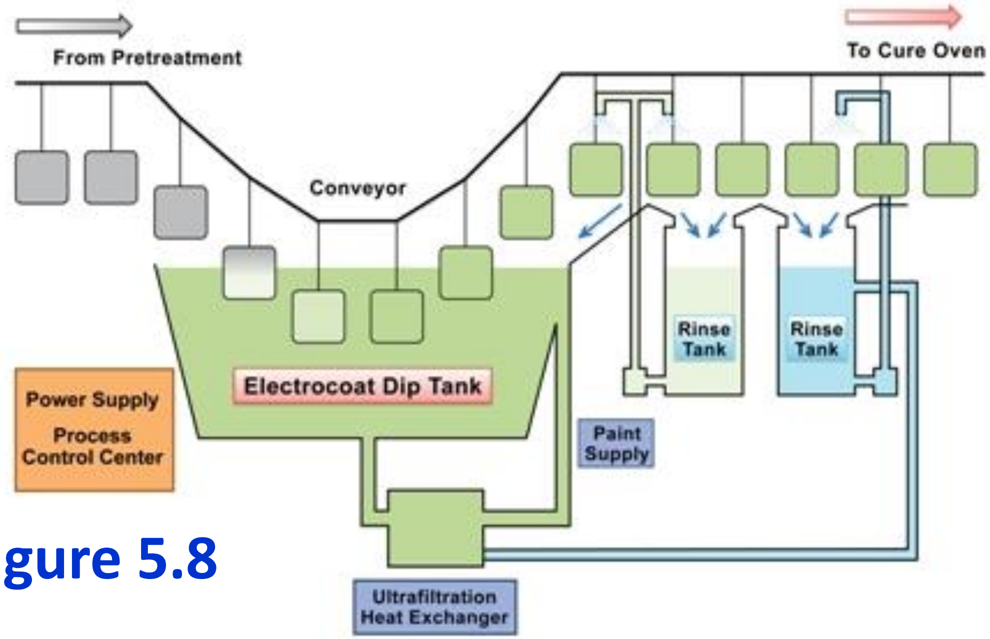


Figure 5.8

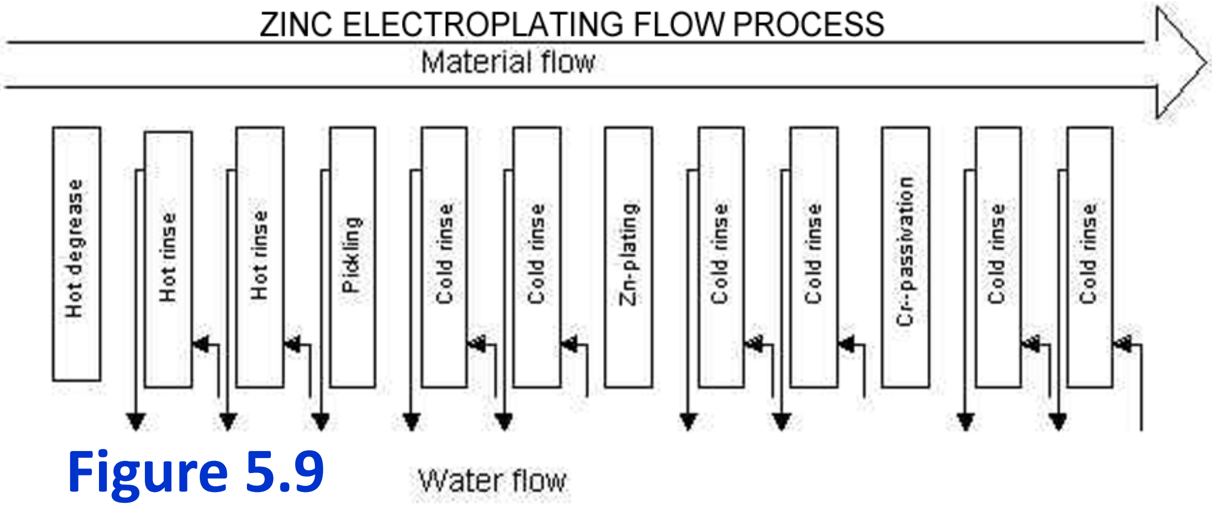


Figure 5.9

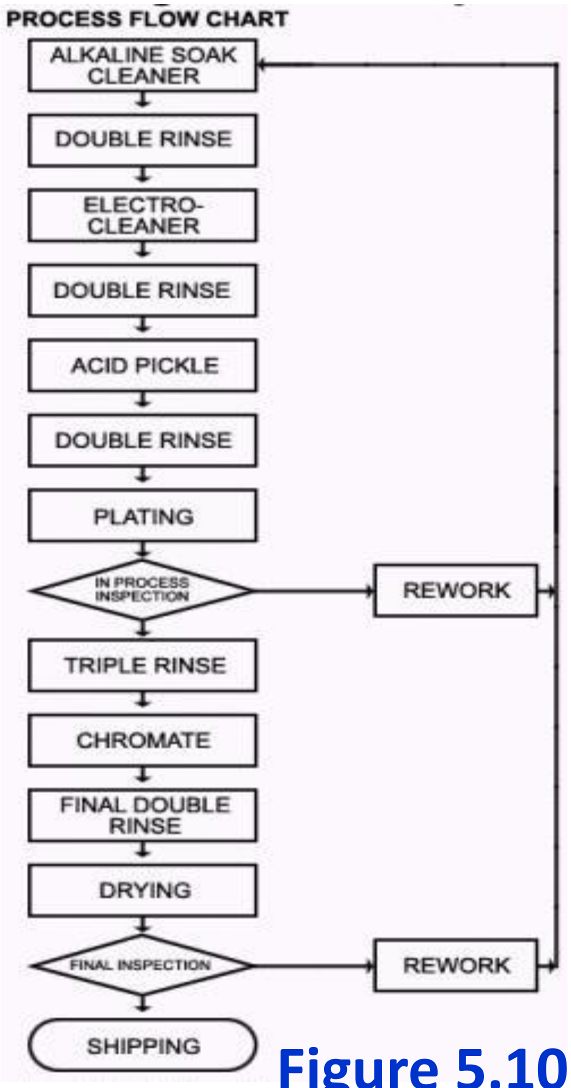


Figure 5.10

Electroplating of Metals

C. Constituents of a Plating Bath:

A typical electroplating bath would contain the following:

1) A salt containing the ion to be deposited (e.g. NiSO4 for plating with nickel).
2) A conducting salt (e.g. Na2SO4 to improve the conductivity of solution containing NiSO4).
3) A buffer solution to adjust the pH of the plating bath, otherwise the alkalinity which is produced in the bath as a result of H2 evolution at the cathode may deposit the metal ions as hydroxides
4) Colloidal matter (e.g. glue) to give a smooth and bright deposit.
5) Chloride ions to prevent the formation of an oxide film on the anode arising from oxygen evolution reaction.

Electroplating of Metals

D. Properties of an Ideal electrodeposit

- An ideal electrodeposit should be coherent, adherent, continuous (free of pores) and uniform.
- Uniformity (or good ***throwing power, TP%*** **)** describes the ability of the electroplating bath to give a deposit of uniform thickness on a cathode of irregular shape.
  - If the bath is able to give a uniform deposit on the irregular cathode, the bath is said to have a ‘good throwing power’.
  - If the bath is unable to give a continuous uniform deposit on the irregular cathode, the bath is said to have a ‘bad throwing power’ as shown in **Figure 5.11**.
- A good throwing power (uniform deposit) is obtained by designing the electroplating cell in such away that the anode geometry is similar to the cathode geometry, as illustrated in **Figure 5.12.**

Electroplating of Metals

Figure 5.11

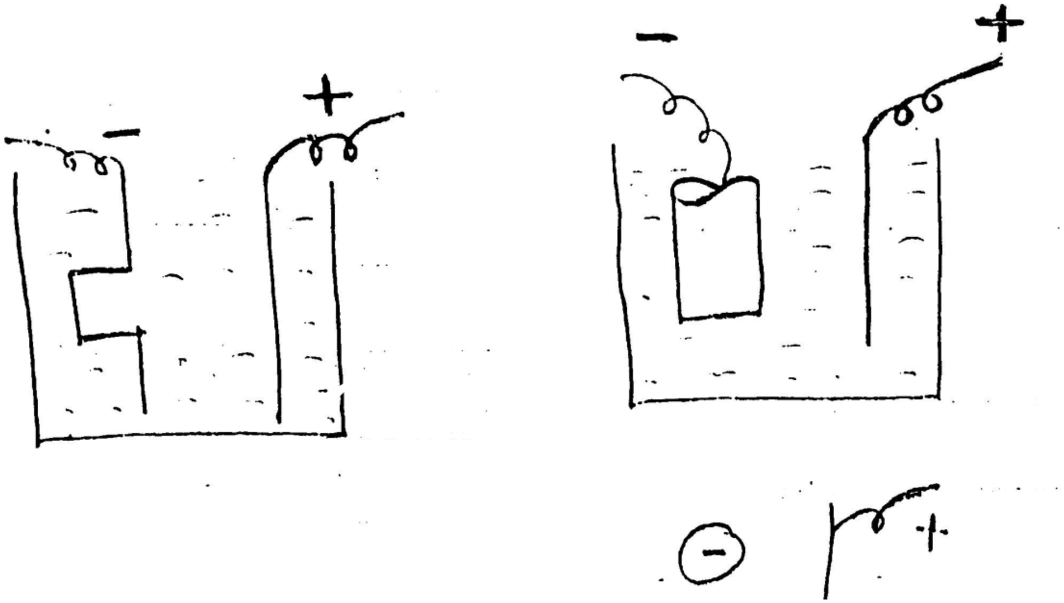
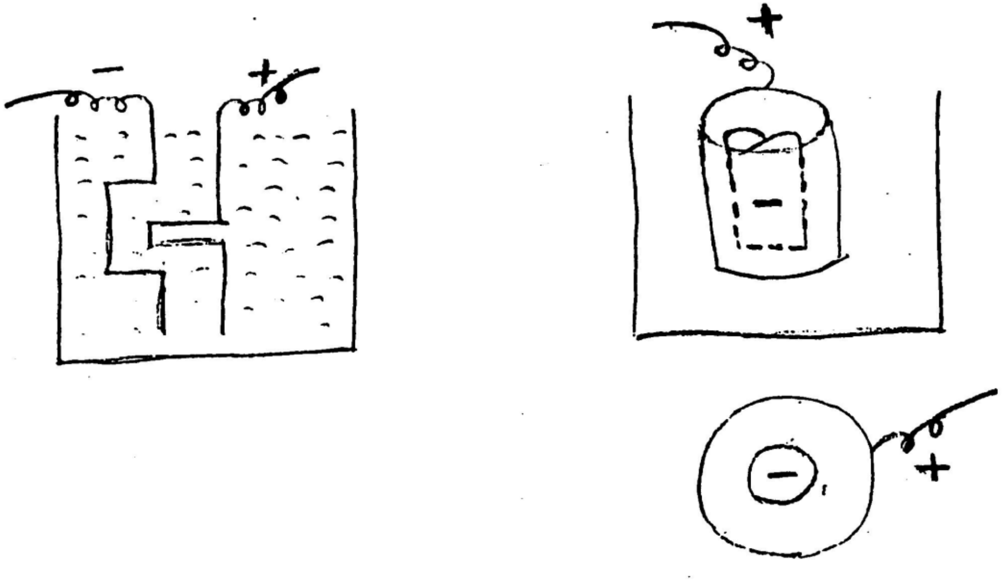


Figure 5.12



Electroplating of Metals

Throwing power of a solution is a measure of its ability to deposit metal uniformly on a cathode of irregular shape.

Current density would be more at the part of cathode nearest to the anode -receive a very heavy deposit

The part farthest away from the anode would receive a very thin deposit.

If the part is deeply recessed, no deposit would be formed on it.

FACTORS INFLUENCING THROWING POWER

Physical:

geometry of the electrodes and their position relative to each other and the tank walls; type of cathode, whether it is flat, projected, or recessed; agitation; and temp.

Chemical:

Bath composition; pH; nature and extent of impurities; and addition agents

Electrical:

Current density, current efficiency, and conductivity

$$\text{Throwing Power} = \frac{L - M}{L + M - 2} \times 100$$

L is the linear ratio i.e., the ratio of the distances from the anode to the remote and the near cathodes

M is the metal ratio ie., the ratio of the weights of the metal deposited on the near and the remote cathodes

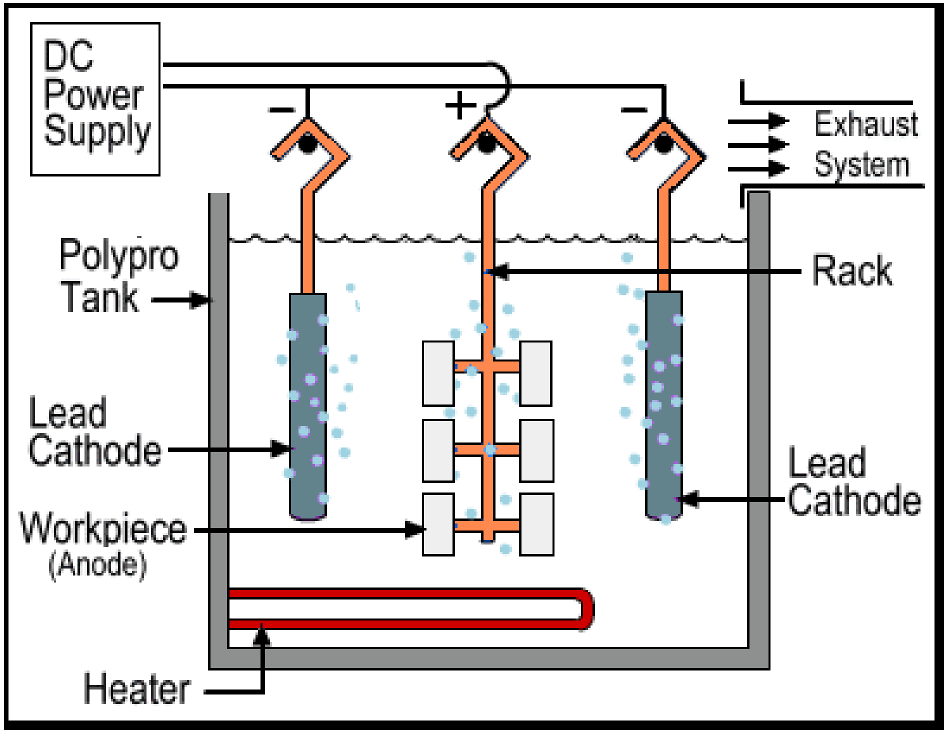
E. Controlling the Properties of Electrodeposit:

- The quality of the electro-pate and its properties can be controlled by adjusting:
  - The current density,
  - The contact time, and
  - the plating bath properties, and
  - The pre-treatment and surface preparation.

- The plating bath properties include:
  - the metal ion concentration,
  - the solution pH and
  - the temperature, and
  - the bath composition of salts, ions and added colloidal matter,

Example: Copper Plating

- This process involves coating an object with a thin layer of metal by electro-deposition.
- Metals that are most commonly deposited by electroplating are copper, nickel, chromium, tin , zinc, brass, gold and silver.
- Taking copper plating as an example, refer to **Figure 5.13** (below).



Example: Copper Plating

- A direct current (DC) is passed from a pure copper plate (the anode) to the workpiece (the cathode) through a copper sulfate solution (the electrolyte).
- A rather complicated electro-chemical process results in copper going into solution from the anode and being deposited from the solution at the cathode.
- The *thickness of the resulting plated finish* on the cathode depends on the plating time and the current strength.
- The anode surface area should be at least 1.5 times the cathode area.
- The current density should be about 50 A/m^2.
- The direct current (DC) voltage varies in the range 0.5 to 2.0 V.

Electroplating of Metals

General Features:

- Direct current from an external power supply is passed between anode and cathode

Theoretical Electroplating Equation:

- Faraday's laws can be summarized: **$V = C. I. t$**
- Where:

V = volume of metal plated, mm3 (in3);

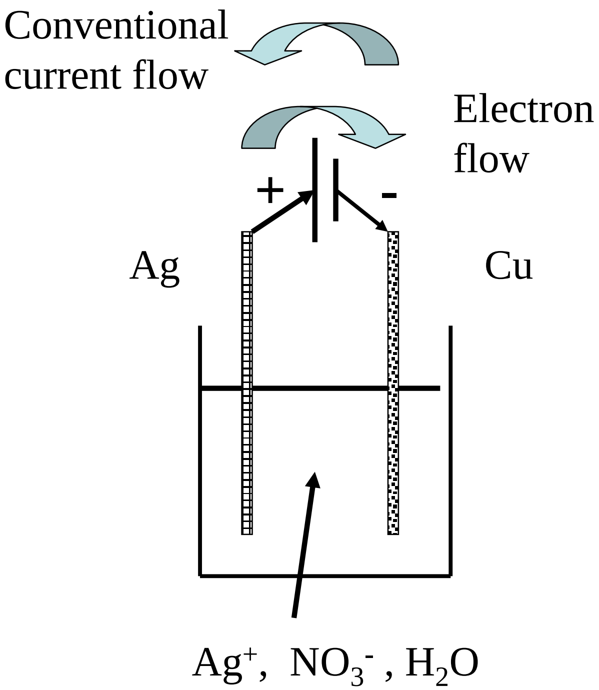
C = plating constant which depends on electrochemical equivalent and density, mm3/A. s;

I.t (current . time) = electrical charge, A.s

- C indicates the amount of plating material deposited onto the cathodic workpart per electrical charge.

Example:

- An electroplater wants to coat a 10.0 cm by 10.0 cm copper plate with 12.5 micrometers of silver.
  - How many electrons must pass in the external circuit?
  - How many coulombs are passed?
  - If the plating takes 1200 s; what's the electrical current in amperes (A) in the external circuit?



Solution:

Atomic mass of Ag is 108 kg/kmol. Its density is 10,500 kg/m3. Avogadro's number (N_A) is 6.02×10^{26} atoms/kmol. What we call current is nothing but the rate of flow of electrons, so 1.0 A = 1.00 coulomb/s and one electron carries -1.60×10^{-19} coulombs.

Solution:

- Atomic mass of Ag is 108 kg/kmol.
- Its density is 10500 kg/m3.
- Avogadro's number (N_A) is 6.02×10^{26} atoms/kmol.
- What we call current is nothing but the rate of flow of electrons, so
- 1.0 A = 1.00 coulomb/s and
- one electron carries -1.60×10^{-19} coulombs.
- The reaction at the anode is **Ag(s) → Ag+ + e-** and the reaction at the cathode is **Ag+ + e- → Ag(s)** ; hence one atom of silver dissolves at the anode and one atom of silver is deposited at the cathode.
- For each atom of silver dissolving at the anode and depositing at the cathode, one electron must circulate in the external circuit.

Solution:

$$\text{Mass} = \frac{12.5\times10^{-6}\times100.\times10{,}500}{1.00\times10^{4}}[\mu\text{m}]\left[{}^{\text{m}}\!/_{\mu\text{m}}\right]\left[\text{cm}^{2}\right]\left[\text{kg/m}^{3}\right]/\left[{}^{\text{cm}^{2}}\!/_{\text{m}^{2}}\right]$$

$$=1.31\times10^{-3}\,\text{kg}$$

- Next convert to kmols:

$$\text{kmols} = \frac{1.31\times10^{-3}}{108}[\text{kg}]\left[\frac{\text{kmols}}{\text{kg}}\right]=1.22\times10^{-5}\,\text{kmols}$$

- Next convert to atoms of Ag(s):

$$\text{Ag atoms deposited} =$$

$$1.22\times10^{-5}\times6.02\times10^{26}$$

$$=7.32\times10^{21}[kg][atoms/kg]$$

$$=7.32\times10^{21}\,\text{atoms}$$

- Next convert to mass of Ag(s):

$$7.32\times10^{21}\times1.6010^{-19}[e^{-}][\text{coulombs/e}^{-}]$$

$$=1.17\times10^{3}\,\text{coulombs}$$

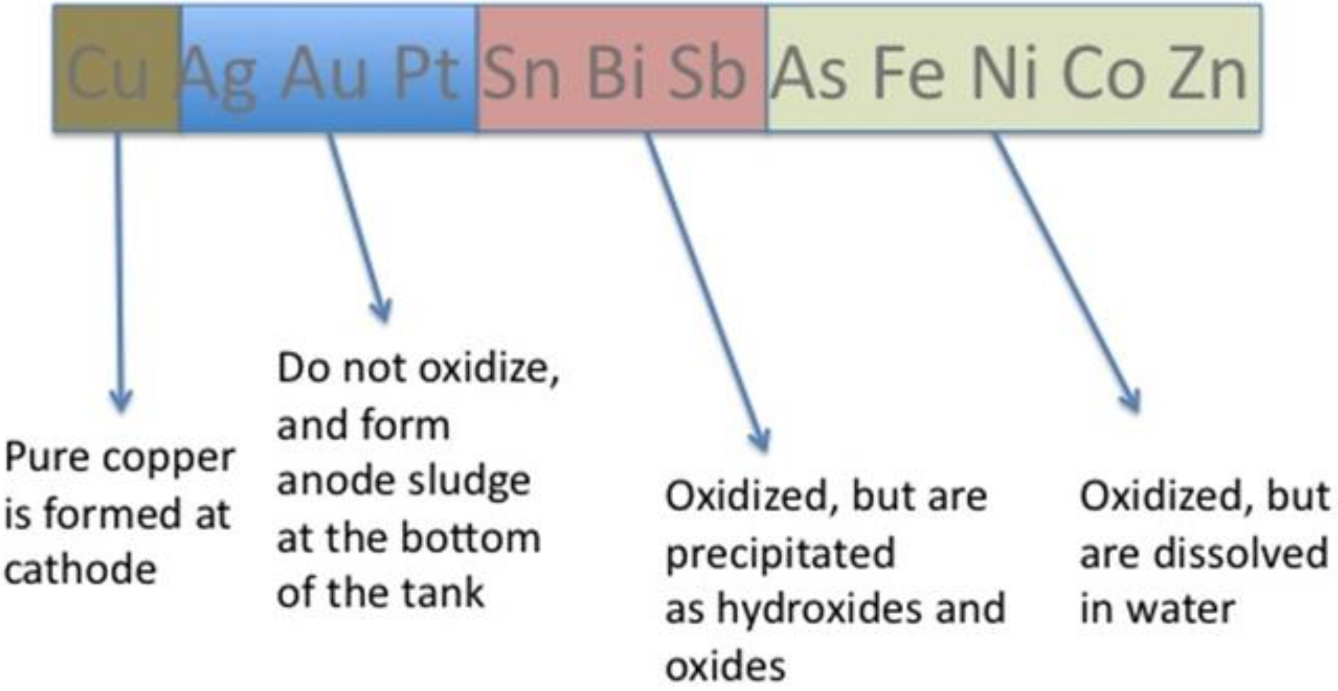
$$\text{Hence current} = \frac{1.17\times10^{3}}{1200.}[\text{C/s}] = 0.975\text{A}$$

Electrorefining of Metals

Electrorefining of Metals

- In electrorefining (electrolytic purification) processes the crude metal (impure metal) is made as the anode in an electrolytic cell, while a cathode of the same metal is used.
  - Conditions are adjusted in order to deposit that metal alone at the cathode surface.
- Crude copper, which is obtained by thermal reduction, consists of two types of impurities (See **Figure 5.14)** :
  a) Impurities which are more noble than copper (e.g. Ag, Au, Se and Te).
  b) Impurities which are less noble than copper (e.g. Zn, Pb, Fe and Ni).
- To illustrate the process of electro refining, the example of copper refining is considered (**Figure 5.15).**
- If the anode potential is adjusted on the value required to dissolve (oxidize) Cu, only the less noble impurities will dissolve with copper, while the more noble metals will not dissolve and will precipitate at the cell bottom as slimes.

Electrorefining of Metals



Cu | Ag Au Pt | Sn Bi Sb | As Fe Ni Co Zn

Pure copper is formed at cathode

Do not oxidize, and form anode sludge at the bottom of the tank

Oxidized, but are precipitated as hydroxides and oxides

Oxidized, but are dissolved in water

- **EMF series**

metal	V^{o}_{metal}
Au	+1.420 V
Cu	+0.340
Pb	- 0.126
Sn	- 0.136
Ni	- 0.250
Co	- 0.277
Cd	- 0.403
Fe	- 0.440
Cr	- 0.744
Zn	- 0.763
Al	- 1.662
Mg	- 2.262
Na	- 2.714
K	- 2.924

↑ more cathodic

↓ more anodic

Figure 5.14: metallic impurities with copper

Electrorefining of Metals

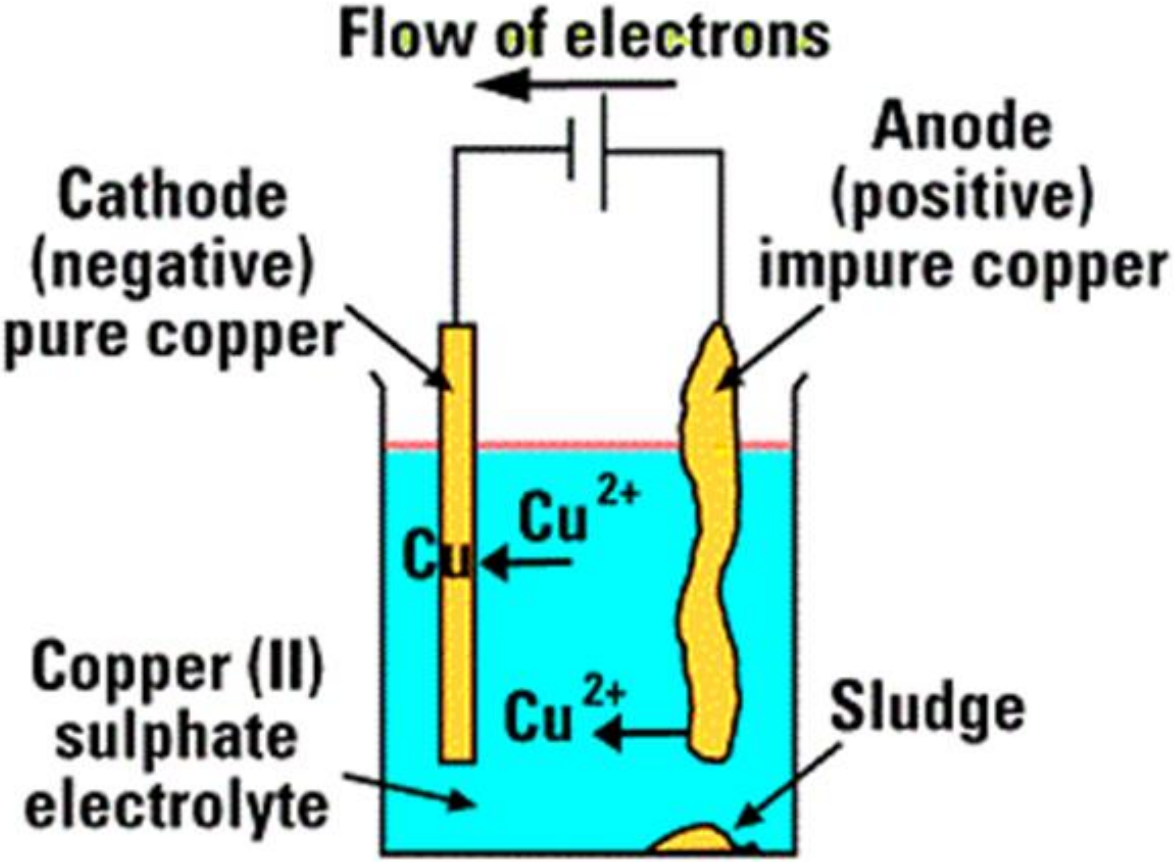


Figure 5.15: Electrorefining cell for copper

Electrorefining of Metals

- The electrorefining process refines metals or compounds at a high purity for a low cost.
- The pure metal can coat an otherwise worthless object.
- Let's consider the electrorefining process of copper:
  - At the anode, there is an impure piece of copper that has other metals such as Ag, Au, Pt, Sn, Bi, Sb, As, Fe, Ni, Co and Zn.
  - The copper in this impure ore is oxidized to form Cu2+ at the anode, and moves through an aqueous sulfuric acid-Copper (II) sulfate solution into the cathode.
  - When it reaches the cathode, the Cu2+ is reduced to Cu.

Electrorefining of Metals

- This whole process takes place at a fairly low voltage (about .15 to .30 V), so Ag, Au, and Pt are not oxidized at the anode, as their standard oxidation electrode potentials are -.800, -1.36 and -1.20 respectively.
  - These un-oxidized impurities turn into a mixture called anode mud, a sludge at the bottom of the tank. This sludge can be recovered and used in different processes.
- Unlike Ag, Au and Pt, the impurities of Sb, Bi and Sn in the ore are indeed oxidized at the anode, but they are precipitated as they form hydroxides and oxides.
- Finally, Fe, Ni, Co and Zn are oxidized as well, but they are dissolved in water.
- Therefore, the only solid we are left with is the pure solid copper plate at the cathode, which has a purity level of about 99.999%.

Electrorefining of Metals

- At the anode, the potential is adjusted at the value required to dissolve (oxidize) Cu:

$$Cu \rightarrow Cu^{2+} + 2\,e^{-}$$

$$E_{anode} = E^{\circ}_{anode} - (RT/zF)\ \ln\ [Cu^{2+}]$$

- At the cathode, the potential is adjusted at the value required to deposit (reduce) Cu^{2+} .
- The less noble impurities which exist in the solution will not deposit because their deposition potential is not yet reached:

$$Cu^{2+} + 2\,e^{-} \rightarrow Cu$$

$$E_{cathode} = E^{\circ}_{cathode} + (RT/zF)\ \ln\ [Cu^{2+}]$$

- The theoretical cell voltage is the sum of the two electrode voltages above.

Electrorefining of Metals

- To determine the actual cell voltage, concentration and activation overpotentials as well as voltage drop across various cell resistances should be added:

$$E_{actu} = E_{theo} + \acute{\eta}_c + \acute{\eta}_a + IR$$

- The overpotentials and voltage drop are usually small compared to the theoretical voltage required.
- Since the theoretical cell voltage is equal to zero, it is concluded that the voltage required to operate electrorefining cells is small.
- In other words: Electrorefining is a low operating cost process.

Electroforming of Metals

Electroforming of Metals

- Electrochemical technology, particularly metal electrodeposition has been employed for fabrication of many shapes of articles and products using specific shapes of molds or models known in industry as mandrels.

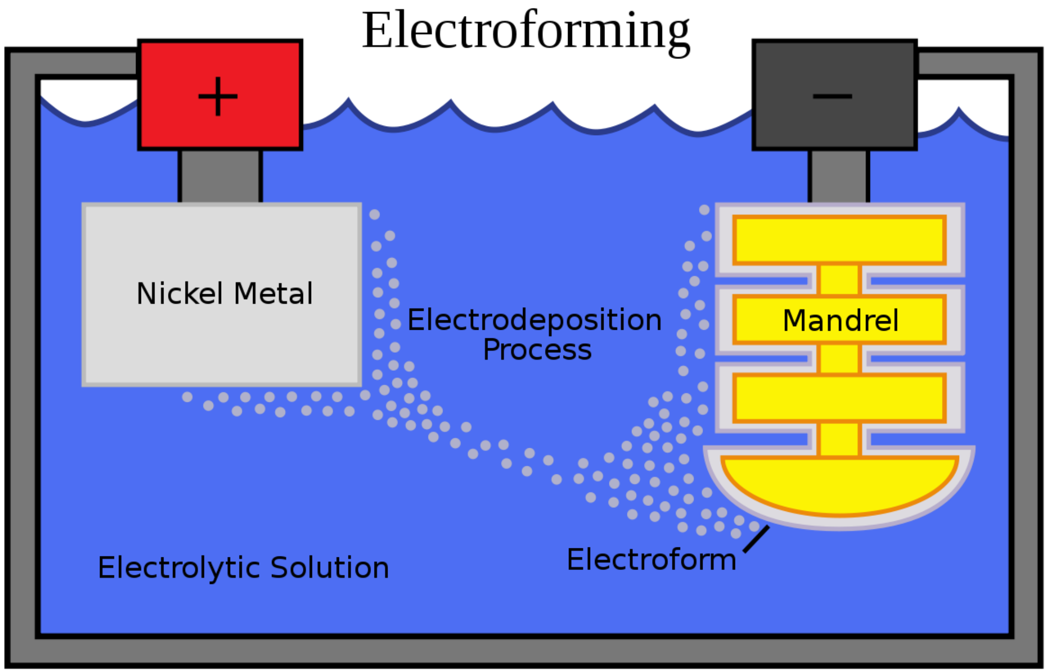


Figure 5.16: Electroforming mandrels

Electroforming of Metals

- Articles such as seamless tubes are fabricated by electrodepositing of metal on a wax mold; which is subsequently easily removed.
  - The surface of the wax mold is first rendered electrically conducting by spraying powder graphite or depositing a layer of silver mirror on it from ammoniacal solution of AgNO3 and a reducing agent such as formaldehyde.
  - The metalized mold is placed in an electrolytic cell to deposit the required metal.
  - Finally, the mold is taken out of the cell, heated to melt the wax and obtain the metallic seamless tube (**Figure 5.17**).

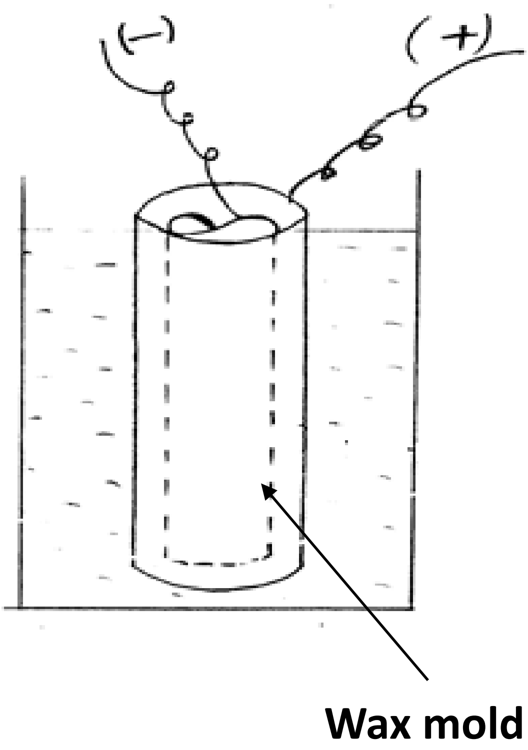
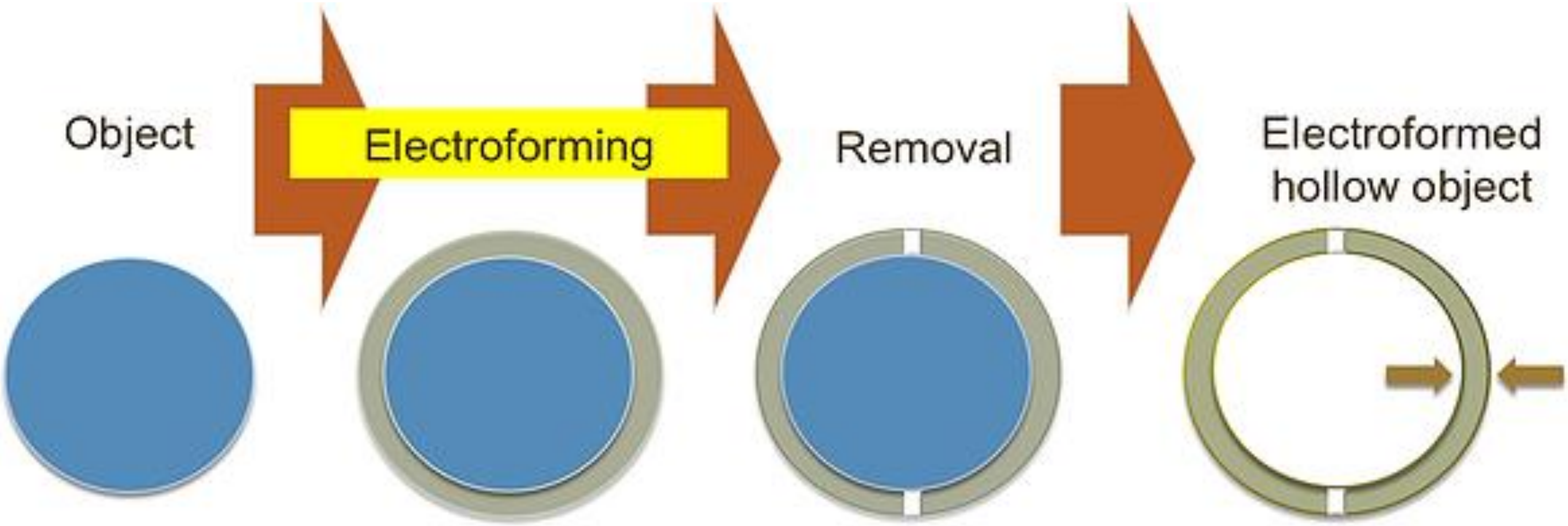


Figure 5.17

Electroforming of Metals



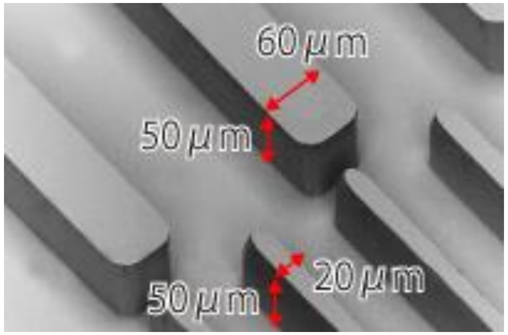
Object

Electroforming

Removal

Electroformed hollow object

Thickness upto 500 microns



Electroforming of Metals

- Electroforming is to used to build out worn parts of machines by depositing metal on the worn part, while other parts are insulated (**Figure 5.18**).

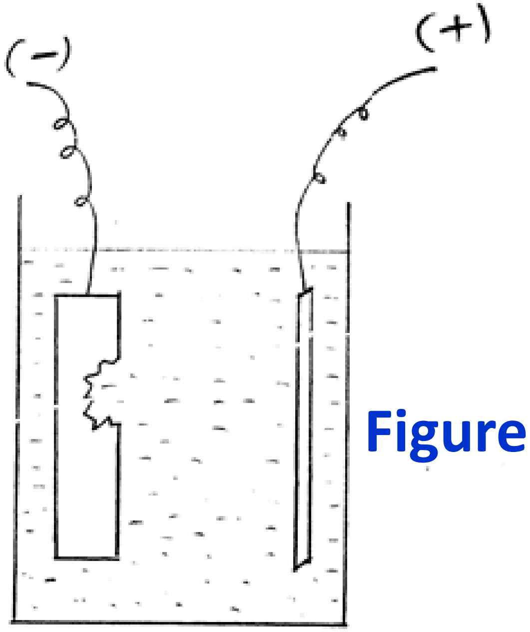


Figure 5.18

- Metal sheets or foils with the desired dimensions can also be made by electroforming

(See **Figure 5.19**).

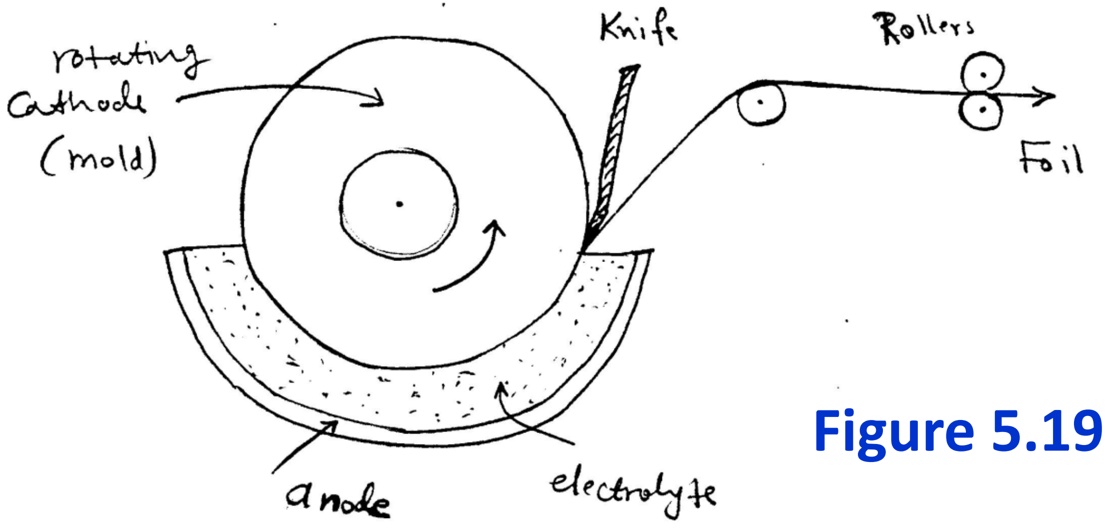


Figure 5.19