I. PRINCIPLES OF EXTRACTIVE METALLURGY

RAKESH KUMAR
Email : rakesh@nmlindia.org

Extractive metallurgy as a discipline deals with the extraction of metals from naturally occurring and man made resources. Separation is the essence of metal extraction. Development of efficient separation schemes calls for a through understanding of extractive metallurgy principles in terms of physical chemistry (thermodynamics & kinetics), materials and energy flow/balance, transport phenomena, reactor and reactor engineering, instrumentation and process control, and environment and waste management. **(Slide 1-4)**

In general, metallurgical separation processes involves chemical reactions, and classified as pyrometallurgical, hydrometallurgical, and electrometallurgical. The processes are also classified as ferrous [dealing with iron and steel] and nonferrous [dealing with all other metals, e.g. base metals (like Cu, Pb, Zn, Ni, …), light metals (Al, Mg, Ti), precious metals (Au, Ag, Pt, Pd, …), rare earth (Ce, Nd, Sm, …), nuclear metals (U, Th, …), rare metals (Os, Ru, …) etc]. **(Slide 6)**

Various pyrometallurgical unit processes are: calcination, roasting, smelting, converting, refining, distillation etc. Each of these processes serves a specific purpose from the point of view of separation. They require specialized reactor depending upon the phases (solid/liquid/gases) involved, mode of contact, temperature, environmental measures etc Calcination and roasting are used as pre-treatment prior to other pyro- and hydro- metallurgical operations. **(Slide 7, 8)** Smelting is the most common of pyrometallurgical operations. Reduction smelting is carried out for oxides. During the smelting, metal compound (e.g. oxide of metal) is reduced to metallic form, and the undesirable impurities (*gangue*) combine with flux to form *slag*. Immiscibility of metal and slag together with density difference forms the basis for separation. Ellingham Diagrams (ΔG vs. T plots), which are available for oxides, sulphides, chlorides etc serve as a fundamental guide in predicting the relative stability of compounds. Based on these diagrams, selection of reduction, reduction temperature, equilibrium partial pressures, can be indicated. Similarly, slag atlases are available for most common slag systems. Matte (liquid mixture of sulphides) smelting, which exploits the immiscibility between slag and matte, is used for metal extraction from sulphide ores. **(Slide 9-14)**

The word hydro- is derived from a Greek word which means water. Separation steps involved in hydrometallurgy are: leaching, purification and/or concentration, and precipitation/metal production. **(Slide 15)** *Leaching* involves preferential dissolution through water solvation, acid/alkali attack, base-exchange reaction, complex ion formation and oxidation/reduction reaction. The variables affecting leaching are pH, Eh, concentration, temperature, pressure, prcomplexing ion etc. Eh-pH diagrams are thermodynamic plots that give an idea of the stability of various solution and solid species in equilibrium under different acidity (pH) and reduction potential (Eh) conditions (ex. Cu-H2O-S system). Bacteria assisted leaching (bacteria leaching) is also used for the leaching/upgradation of ores (ex. U, Cu, bauxite etc). Depending upon nature of leaching system (means mode of contact of solid-liquid, pressure, temperature, stirring), wide variety of leaching systems are available to carry out leaching reaction, e.g. heap, column, stirred tank and autoclave. Leaching gives rise to a metal solution (*leach liquor*) and solid residue (*leach residue*). Leach liquor and residue are separated using filtration. A number of techniques are available for the purification of leach liquor. These include precipitation, liquid-liquid and solid-liquid ion-exchange (solvent extraction, ion exchange) and adsorption. Basic thermodynamic data are available in literature to predict the efficacy of various separation systems. Metal/metal compound can be precipitated from the purified solution through concentration, temperature adjustment, etc. Cementation exploits difference in standard reduction potential of metal ions. **(Slide 16-22)**

Electrometallurgy is the process of obtaining metals through electrolysis. Starting materials may be: (a) molten salt, and (b) aqueous solution. The separation is based on difference in Standard electrode potential and it is used for Electrowinning or Electrorefining purpose. Aluminium extraction is based on the fuse salt electrolysis. **(Slide 23-31)**

While 'separation is the essence of metal extraction'. The scope extends beyond separation. Number of issues that require attention includes:

- **Plant Size -** transportation, materials handling
- **Reactor -** Size, Mixing, Materials flow, Heat transfer (engineering skills), material selection, energy … …
- **Alloying -** Metals are generally used in the form of alloys
- **Waste disposal -** Huge quantity of waste is generated
- **Recycling -** Resource conservation, Energy saving, Waste mininimisation
- **Manufacturing -** large scale manufacturing, many techniques.

The overall design of a metallurgical plant may involve optimization from the point of view of process (energy, recovery, separation efficiency, productivity etc), cost of production and environmental factors. **(Slide 32-35)**

Principles of Extractive Metallurgy

Training Course on

Mineral Processing and Nonferrous Extractive Metallurgy

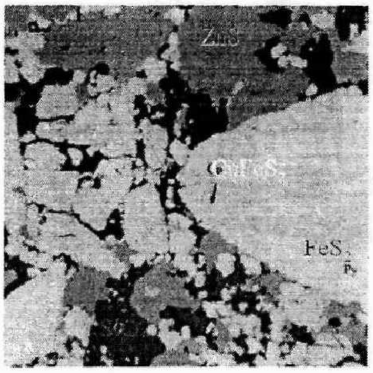
June 30 - July 5, 2008

Rakesh Kumar
National Metallurgical Laboratory
Jamshedpur – 831 007

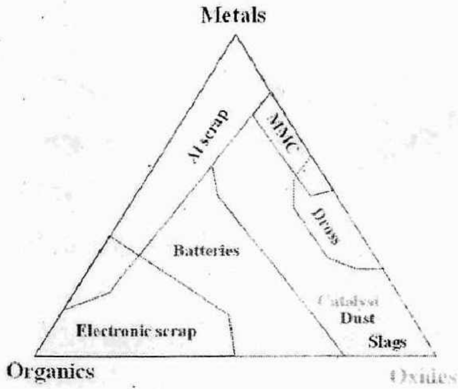
Resources for metals

- **Natural Resources**
  - **Gold is found in native state**
  - **Aggregates of minerals (or ores) – mostly oxides and sulphides, example Al, Fe (oxide ores), Cu, Pb, Zn, Ni etc (sulphide ores).**
    - (a) land-based (common)
    - (b) shallow sea (beach sand)
    - (c) deep-sea (Ferromanganese nodules)
  - **Seawater and natural brines, Ex. Mg and Li**
- **Man Made Resources**
  - **Metallic form - Consumer goods and process scrap**

Natural vs. Man Made Resources



Natural ore



Recyclables

Separation – Ore to Metal

What to separate?

Iron ore

Hematite (Fe_2O_3)

SiO_2, Al_2O_3, P, S bearing minerals

Aluminium ore (bauxite)

$Al_2O_3.xH_2O$ (x=1,3)

Fe_2O_3, FeOOH, SiO_2, TiO_2, $FeTiO_3$ (gangue).

Copper Ore

Chalcopyrite ($CuFeS_2$)

Sulphides of metal such Fe, Pb, Zn and silicates

Mineral Processing - Limits

Size Limit of Process (mm)

Wet treatment*
Sizing (0.06-2.0)
Gravity concentration (0.06-2.0)
Magnetic separation (0.015-1.8)
Flotation (0.007-0.3)

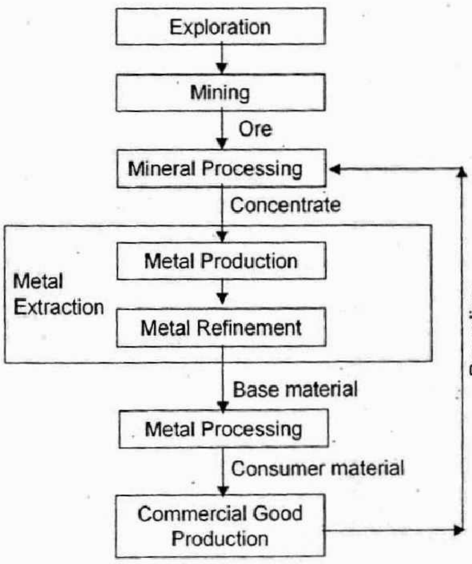
Dry treatment*
Sizing (0.06-2.0)
Gravity concentration (0.15-0.18)
Magnetic separation (0.1-2)
Electrical separation (0.1-1.2)

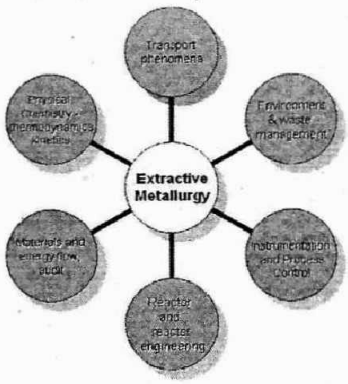
* values are only indicative

Energy

Focus of lecture

This lecture





Focus is generic - Separation

Metallurgical Separation Processes

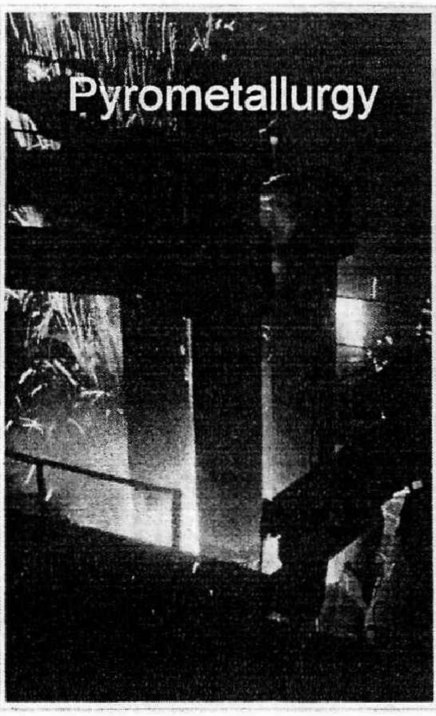
Most often involves chemical reactions

- **Pyro-metallurgical**
- **Hydro-metallurgical**
- **Electro-metallurgical**

Classification based on metals

Ferrous dealing with iron and steel

Non Ferrous includes all other metals
Base metals (Pb, Zn, Cu, and Ni), **Light metals (**Mg, Al, Sn, and Ti), **Precious metals (**Au and Ag and the Pt group metals), **Refractory metals** (W, Nb, Ta) etc.



- The word pyro- is derived from a greek word which means fire.
- A pyrometallurgical process may be defined as one involving the application of heat energy

Pyrometallurgy

Operation, purpose and basis of separation

Calcination	removal of H_2O/CO_2 decomposition
Roasting	conversion of form, chemical reaction
Smelting	
Reduction	metal oxide to metal, chemical reduction, slag/metal separation
Matte	Matte and slag, oxidation, matte/slag separation
Converting	metal sulphide to metal, selective conversion of matte into metal and slag
Fire refining	selective oxidation of impurities, slag-metal, gas-metal separation
Zone refining	purification, solubility
Distillation	purification/separation, difference in boiling point

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Pyrometallurgy

Iron ore

Hematite (Fe_2O_3)

SiO_2, Al_2O_3, P, S bearing minerals

Iron Making

Oxygen removal

$Fe_2O_3(s)+3\ C(s) = Fe(l)+3\ CO\ (g)$

$Fe_2O_3(s)+3\ CO(s) = Fe(l)+3\ CO_2\ (g)$

Carbon forms stronger bond with oxygen at the reaction temperature

Key Words

- Stability of Oxides
- Stability is temperature dependent

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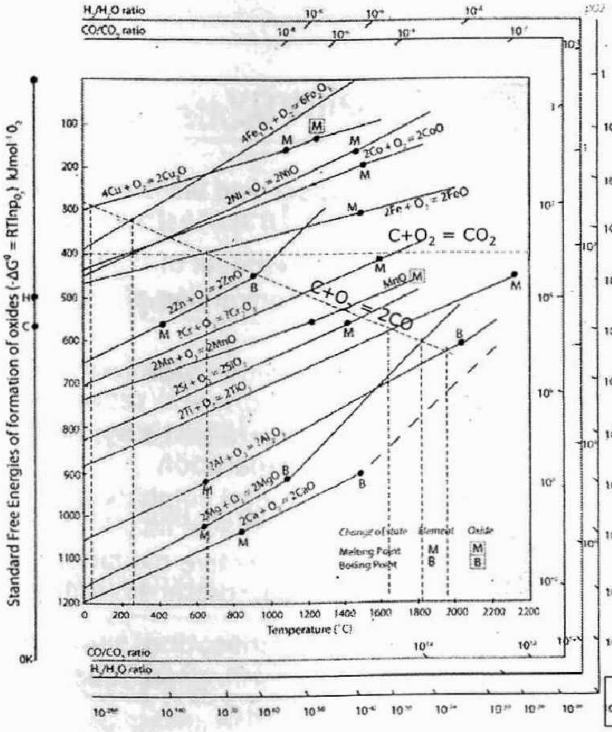
ΔG° vs. T

$\Delta G^o = \Delta H^o - T.\Delta S^o$

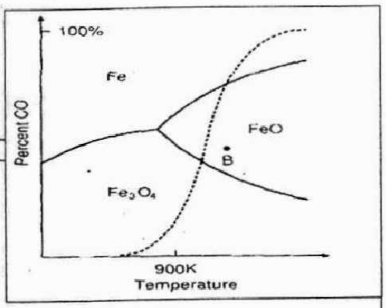
Ellingham Diagram **(for oxides)**

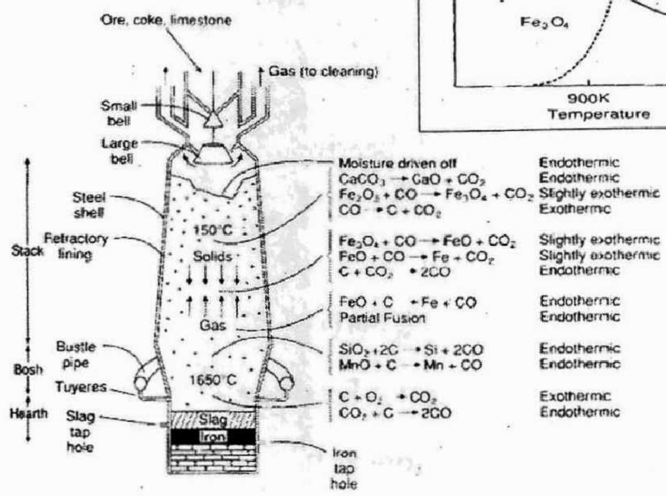


Similar diagrams for

- o sulphides
- o chlorides
- o carbides
- o nitrides

Reduction in BF





Pyrometallurgy

Iron ore

Hematite (Fe_2O_3)

SiO_2, Al_2O_3, P, S bearing minerals

Iron Making

Removal of impurities

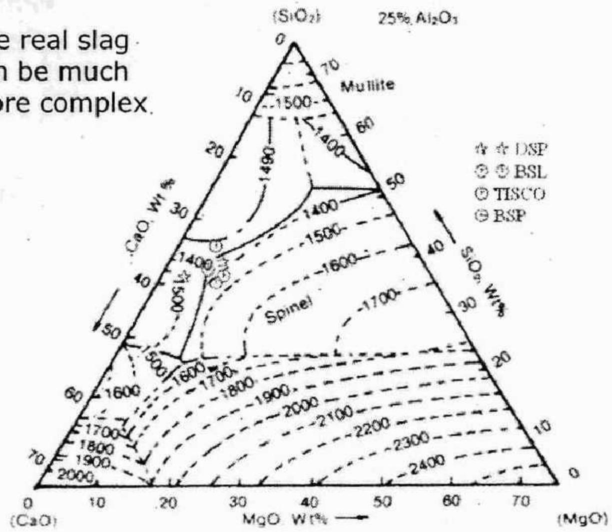
$CaO+SiO_2 = CaSiO_3$ (l) (1200°C)

$CaO+P_2O_5 = Ca_3(PO_4)_2$ (l) (1200°C)

Key Points
- Liquid-liquid separation
- Density of metal and slag
- Melting points of oxides
- Flux-low melting slag

Iron Making Slag

The real slag can be much more complex.



(Slag Atlas)

Matte Smelting of Cu

Copper Ore

Chalcopyrite ($CuFeS_2$)

Sulphides of metal such Fe, Pb, Zn and silicates

Matte smelting in a reverberatory furnace

Matte (Cu_2S+Fe_2S) & Slag (FeO-SiO_2)

Conversion of matte to metallic copper in a side blown converter

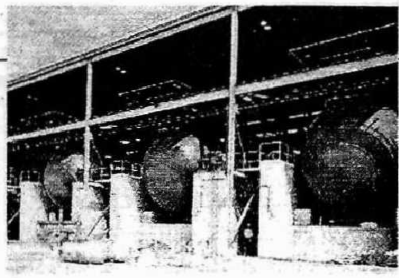
- **Oxidation of FeS to FeO to form slag**
- **Conversion of Cu_2S to Cu**

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

blister Cu

Components	Copper matte [wt-%]	Slag [wt-%]
S	20 - 25	-
Fe	6 - 40	-
Cu	29 - 70	0.3 - 0.8
SiO_2	-	29 - 40
FeO	-	32 - 50
Fe_3O_4	-	up to 10
CaO	-	up to 10
Al_2O_3	-	up to 10

Hydrometallurgy



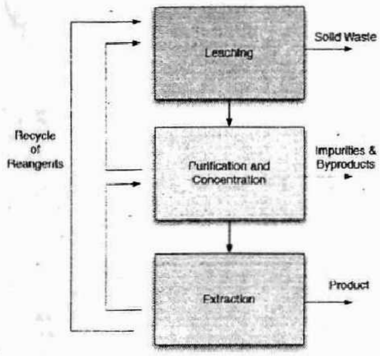
- The word hydro- is derived from a greek word which means water.
- A hydrometallurgical process may be defined as on involving water (organic solvents also)

Separation Steps

Leaching

Purification and/or Concentration

Precipitation/Metal Production



Hydrometallurgy

Leaching reactions

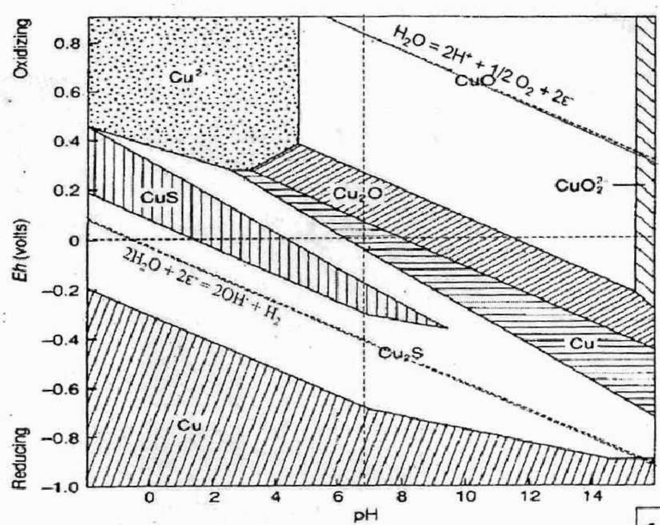
- Water solvation of metallic ions
  $MeX(s)=Me^{2+}(aq)+X^{2-}(aq)$, e.g. CuSO4, NaCl
- Acid (H^+) attack
  $ZnO(s)+2H^+(aq)=Zn^{2+}(aq)+H_2O$
- Alkali (OH^-) attack
  $Al_2O_3(s)+2OH^-(aq)=2AlO_2^-(aq)+H_2O$
- Base exchange
  $CaWO_4(s)+CO_3^{2-}(aq)=CaCO_3(s)+WO_4^{2-}$
- Complex ion formation
  $UO_3(s)+3CO_3^{2-}(aq)+H_2O=UO_2(CO_3)_4^{2+}(aq)+2OH^-(aq)$
- Oxidation of mineral
  $CuS(s)+2Fe^{3+}(aq)=Cu^{2+}(aq)+2Fe^{2+}(aq)+S^o(s)$
- Reduction of mineral
  $Mn(IV)O_2(s)+SO_2(g)=Mn^{2+}(aq)+SO4^{2-}(aq)$

Leaching variables

pH, Eh, concentration, temperature, pressure, complexing ion, etc.

Eh-pH Diagrams (Pourbaix Diagrams)

Cu-H_2O-S System



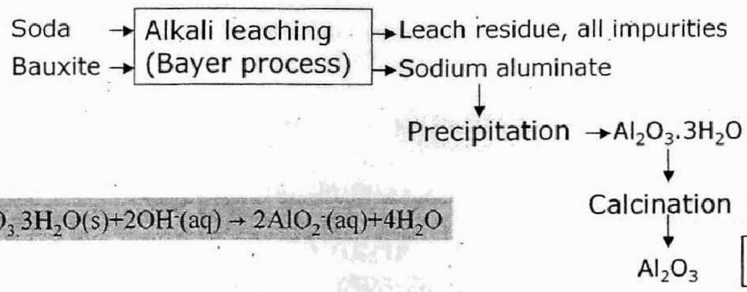
Leaching in Al extraction

Aluminium ore (buaxite)

$Al_2O_3.xH_2O$ (x=1,3)

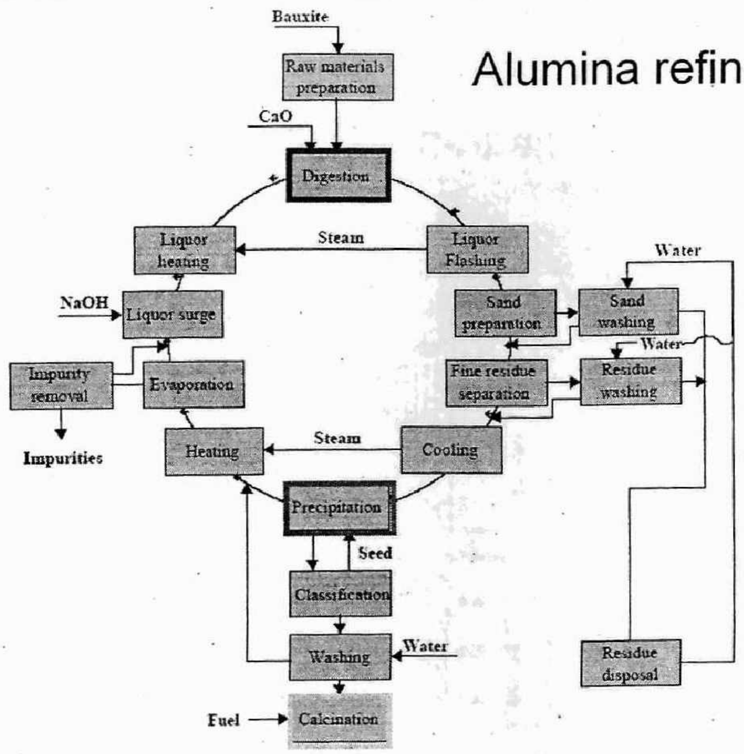
Fe_2O_3, FeOOH, SiO_2, TiO_2, $FeTiO_3$ (gangue).

Removal of gangue (selective alkali leaching)



$Al_2O_3.3H_2O(s)+2OH^-(aq) \rightarrow 2AlO_2^-(aq)+4H_2O$

Alumina refinery



Solution Purification

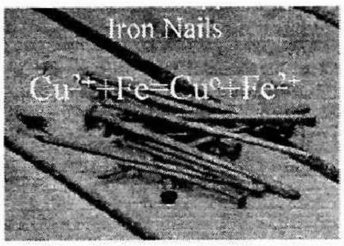
Separation of Impurities

- Precipitation
  - Thermal
  - Chemical/electrochemical
- Ion Exchange
  - Liquid-Solid Ion-Exchange
  - Liquid-Liquid Ion Exchange (Solvent Extraction)
- Adsorption on carbon
  - Carbon-in-pulp

Cementation

Standard Reduction Potential for some metals

Au^{3+}/Au	... +1.50
Ag^{+}/Ag	... +0.80
Hg^{+}/Hg	... +0.79
Cu^{2+}/Cu	... +0.34
H^{+}/H_2	... 0.00
Pb^{2+}/Pb	... - 0.13
Ni^{2+}/Ni	... - 0.25
Co^{2+}/Co	... - 0.28
Fe^{2+}/Fe	... - 0.44
Zn^{2+}/Zn	... - 0.76
Al^{3+}/Al	... - 1.66
Na+/Na	... - 2.71
Li^{+}/Li	... - 3.04
Mg^{2+}/Mg	... - 2.37

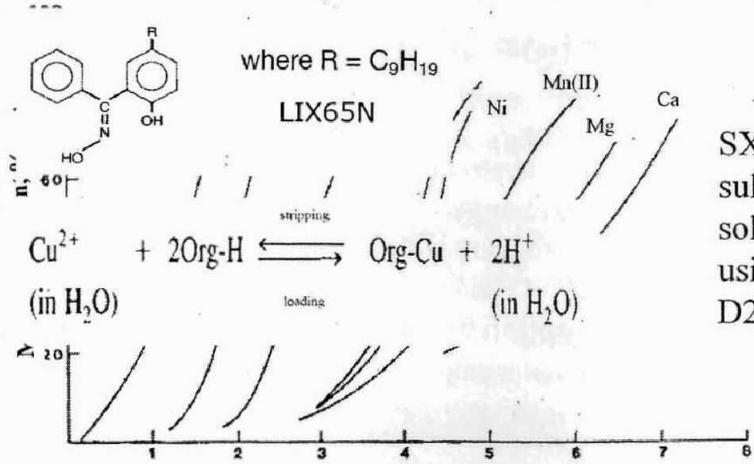


Separation of Impurities

Ion Exchange

Liquid-Liquid Ion Exchange

(Solvent Extraction)



$$Cu^{2+}\ (\text{in } H_2O) + 2Org\text{-}H \underset{\text{loading}}{\overset{\text{stripping}}{\rightleftharpoons}} Org\text{-}Cu + 2H^+\ (\text{in } H_2O)$$

o Equilibrium pH

SX from sulphate solutions using D2EHPA

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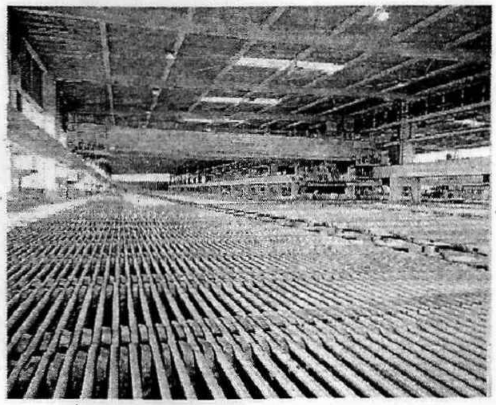
Electrometallurgy

- Electrometallurgy is the process of obtaining metals through electrolysis
- Starting materials:
  (a) molten salt
  (b) aqueous solution
- Purpose
  (a) Electrowinning
  (b) Electrorefining



- Basis
  Standard electrode potential

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Electrometallurgy

Standard electrode potential

Reaction	E_0 (v)
$Au^{3+} + 3\ e^- = Au$	1.5
$O_2 + 4H^+ + 4\ e^- = H_2O$	1.23
$Ag^{2+} + 2\ e^- = Ag$	0.80
$Cu^{2+} + 2\ e^- = Cu$	0.4
$2H^+ + 2\ e^- = H_2$	0.000
$Fe^{2+} + 2\ e^- = Fe$	-0.44
$Zn^{2+} + 2\ e^- = Zn$	-0.76
$Al^{3+} + 3\ e^- = Al$	-1.66
$Li^+ + e^- = Li$	-3.01

Cu Electrowinning

Reaction in Electrowinning

Anode (Pb) :

$2H_2O = O_2 + 4H^+ + 4e \quad E_o = -1.23\ V$

Cathode (Ti):

$Cu^{2+} + 2e^- \rightarrow Cu^o \quad E_o = -0.34\ V$

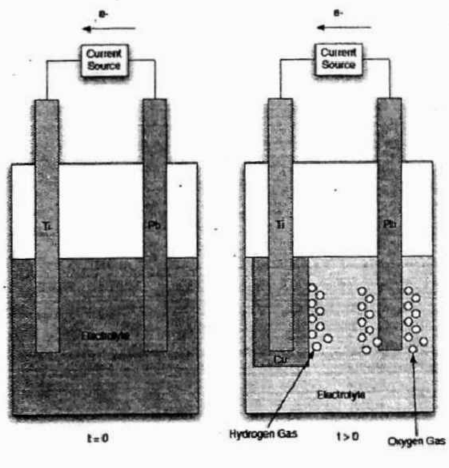
Reaction in Electrorefining

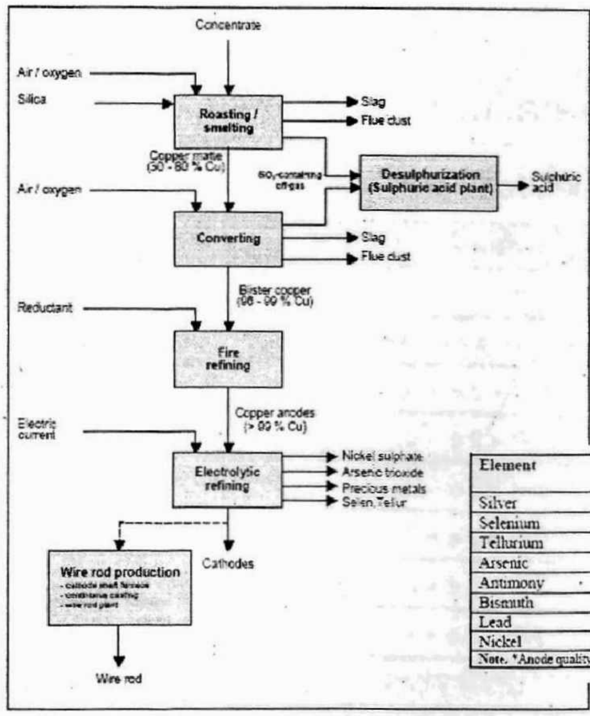
Anode (impure Cu):

$Cu^o \rightarrow Cu^2(aq) + 2e^- \quad E_o = +0.34\ V$

Cathode (Ti/SS):

$Cu^{2+} + 2e^- \rightarrow Cu^o \quad E_o = -0.34\ V$

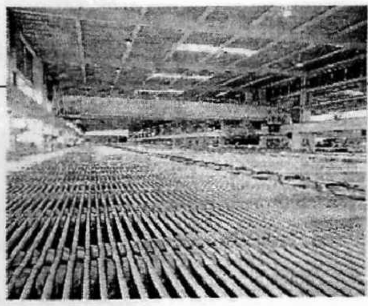


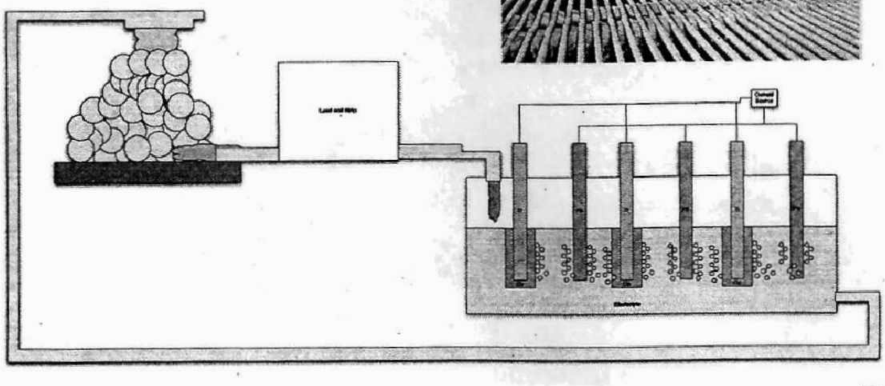


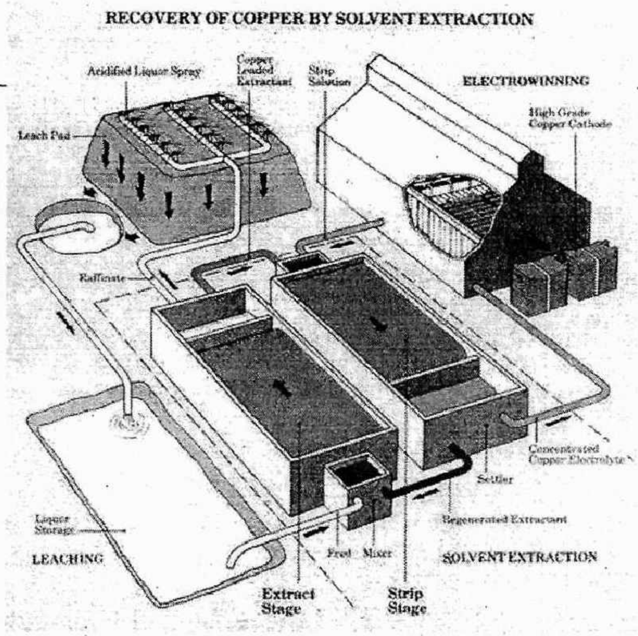
Element	Content in Anode* g/t	Content in Cathode g/t
Silver	600 - 720	9 - 10
Selenium	50 - 510	< 0.5
Tellurium	20 - 130	< 0.5
Arsenic	700 - 760	< 1
Antimony	330 - 700	< 1
Bismuth	60	< 0.5
Lead	990 - 500	< 1
Nickel	1000 - 5000	< 3
Note. *Anode quality depends on raw material contents		

Electrowinning

EW-SX







Electrometallurgy

Standard electrode potential

Reaction	E_0 (v)
$Au^{3+} + 3e^- = Au$	1.5
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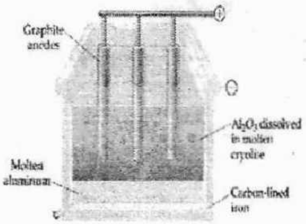
$Ag^{2+} + 2e^- = Ag$	0.80
$Cu^{2+} + 2e^- = Cu$	0.4
$2H^+ + 2e^- = H_2$	0.000
$Fe^{2+} + 2e^- = Fe$	-0.44
$Zn^{2+} + 2e^- = Zn$	-0.76
$Al^{3+} + 3e^- = Al$	-1.66
$Li^+ + e^- = Li$	-3.01

Electrometallurgy of Aluminium

Hall process electrolysis cell is used to produce aluminium.

Problem: Al_2O_3 melts at 2000°C and it is impractical to perform electrolysis on the molten salt.

Hall cell use purified Al_2O_3 in molten cryolite (Na_3AlF_6, melting point 1012°C).



Electrolysis

Anode:

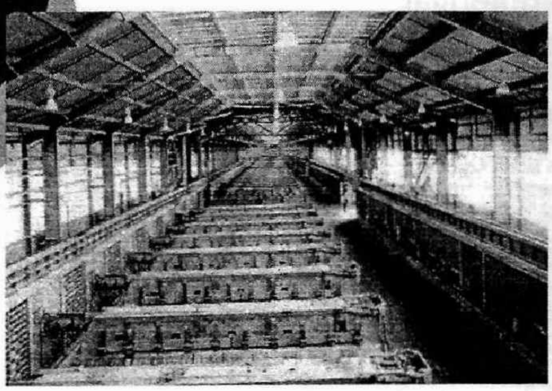
$C(s) + 2O^{2-}(l) \rightarrow CO_2(g) + 4e$

Cathode:

$3e + Al^{3+}(l) \rightarrow Al(l)$

The graphite rods are consumed in the reaction

Electrometallurgy of Aluminium



Each cell is 3 m by 10 m by 3 m

Each cell has 24 to 40 anode between which ~230 kA is distributed

Each cell runs at ~4.5 V

In each plant, there are typically 400 cells

Thus:

400 * 4.5 * 230 kA ~ 400 MW

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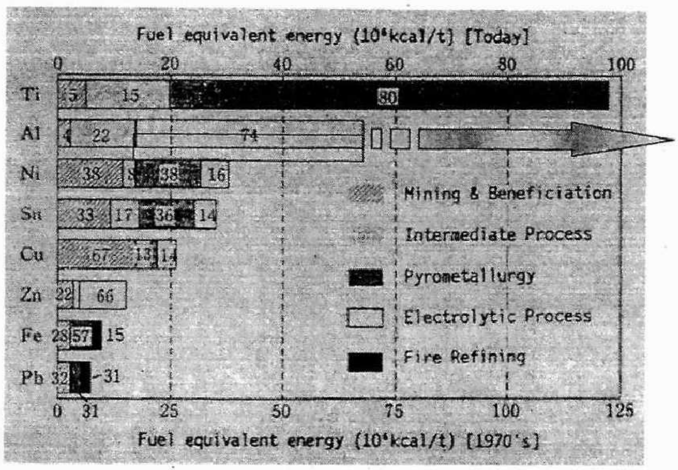
Highly Energy Intensive

Fuel equivalent energy required in the primary production of metals



Electrolytic process for Aluminium extraction is highly energy intensive

Source: Metallurgical Processes for the Early Twenty First Century, Vol II, TMS-AIME, 1994, p. 632)

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BEYOND SEPARATION...

- **Plant Size – transportation, materials handling**
- **Reactor – Size, Mixing, Materials flow, Heat transfer (engineering skills), material selection, energy … …**
- **Alloying – Metals are generally used in the form of alloys**
- **Waste disposal – Huge quantity of waste is generated**
- **Recycling – Resource conservation, Energy saving, Waste mininimisation**
- **Manufacturing – large scale manufacturing, many techniques**

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