I. PRINCIPLES OF EXTRACTIVE METALLURGY

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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 thorough 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, precomplexing 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
- **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)
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

Separation – Ore to Metal

**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

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

Focus of lecture

This lecture
- Exploration
- Mining
- Ore
- Mineral Processing
- Concentrate
- Metal Extraction
- Metal Production
- Metal Refinement
- Base material
- Metal Processing
- Consumer material
- Commercial Good
- Production

Focus is generic - Separation

Energy 4
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

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination</td>
<td>removal of H₂O/CO₂ decomposition</td>
</tr>
<tr>
<td>Roasting</td>
<td>conversion of form, chemical reaction</td>
</tr>
<tr>
<td>Smelting</td>
<td></td>
</tr>
<tr>
<td>Reduction</td>
<td>metal oxide to metal, chemical reduction, slag/metal separation</td>
</tr>
<tr>
<td>Matte</td>
<td>Matte and slag, oxidation, matte/slag separation</td>
</tr>
<tr>
<td>Converting</td>
<td>metal sulphide to metal, selective conversion of matte into metal and slag</td>
</tr>
<tr>
<td>Fire refining</td>
<td>selective oxidation of impurities, slag-metal, gas-metal separation</td>
</tr>
<tr>
<td>Zone refining</td>
<td>purification, solubility</td>
</tr>
<tr>
<td>Distillation</td>
<td>purification/separation, difference in boiling point</td>
</tr>
</tbody>
</table>

Pyrometallurgy

Iron ore

Hematite (Fe₂O₃)

SiO₂, Al₂O₃, P, S bearing minerals

Oxygen removal

Fe₂O₃(s) + 3 C(s) = Fe(l) + 3 CO (g)

Fe₂O₃(s) + 3 CO₂(g) = Fe(l) + 3 CO₂ (g)

Carbon forms stronger bond with oxygen at the reaction temperature

Iron Making

Key Words

• Stability of Oxides

• Stability is temperature dependent
\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]

Ellingham Diagram (for oxides)

Similar diagrams for:
- sulphides
- chlorides
- carbidites
- nitrides

Reduction in BF
Pyrometallurgy

Iron ore

Hematite \((\text{Fe}_2\text{O}_3)\)

\[\text{SiO}_2, \text{Al}_2\text{O}_3, \text{P}, \text{S bearing minerals}\]

Iron Making

Key Points

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

Removal of impurities

\[
\text{CaO} + \text{SiO}_2 = \text{CaSiO}_3 (l) \quad (1200°C)
\]

\[
\text{CaO} + \text{P}_2\text{O}_5 = \text{Ca}_3\text{(PO}_4\text{)}_2 (l) \quad (1200°C)
\]

Iron Making Slag

The real slag can be much more complex.

(Slag Atlas)
**Matte Smelting of Cu**

**Copper Ore**

Chalcocylrite (CuFeS₂)

Sulphides of metal such Fe, Pb, Zn and silicates

Matte smelting in a reverberatory furnace

Matte (Cu₂S+Fe₂S) & Slag (FeO-SiO₂)

Conversion of matte to metallic copper in a side blown converter

- Oxidation of FeS to FeO to form slag
- Conversion of Cu₂S to Cu

Cu₂S (l) + O₂(g) → 2Cu(l) + SO₂(g)

blistet Cu

<table>
<thead>
<tr>
<th>Component</th>
<th>Copper matte wt-%</th>
<th>Slag wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>20 - 25</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>6 - 40</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>29 - 70</td>
<td>0.3 - 0.8</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-</td>
<td>29 - 40</td>
</tr>
<tr>
<td>FeO</td>
<td>-</td>
<td>32 - 50</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>-</td>
<td>up to 10</td>
</tr>
<tr>
<td>CaO</td>
<td>-</td>
<td>up to 10</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>up to 10</td>
</tr>
</tbody>
</table>

**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
\[ \text{MeX(s)} = \text{Me}^{2+}(\text{aq}) + \text{X}^{2-}(\text{aq}), \text{ e.g. CuSO}_4, \text{ NaCl} \]

Acid (H⁺) attack
\[ \text{ZnO(s)} + 2\text{H}^+(\text{aq}) = \text{Zn}^{2+}(\text{aq}) + \text{H}_2\text{O} \]

Alkali (OH⁻) attack
\[ \text{Al}_2\text{O}_3(s) + 2\text{OH}^-(\text{aq}) = 2\text{AlO}_2^-(\text{aq}) + \text{H}_2\text{O} \]

Base exchange
\[ \text{CaWO}_4(s) + \text{CO}_3^{2-}(\text{aq}) = \text{CaCO}_3(s) + \text{WO}_4^{2-} \]

Complex ion formation
\[ \text{UO}_2(s) + 3\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O} = \text{UO}_2(\text{CO}_3)_2^{2-}(\text{aq}) + 2\text{OH}^-(\text{aq}) \]

Oxidation of mineral
\[ \text{CuS(s)} + 2\text{Fe}^{3+}(\text{aq}) = \text{Cu}^{2+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) + \text{S}^2(s) \]

Reduction of mineral
\[ \text{Mn(IV)}\text{O}_2(s) + \text{S}_2\text{O}_3^2(g) = \text{Mn}^{2+}(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq}) \]

Leaching variables

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

Eh-pH Diagrams (Pourbaix Diagrams)
Leaching in Al extraction

**Aluminium ore (bauxite)**

Al₂O₃·xH₂O (x=1,3)

Fe₂O₃, FeOOH, SiO₂, TiO₂, FeTiO₃ (gangue).

Removal of gangue (selective alkali leaching)

\[
\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} (s) + 2\text{OH}^{-}(aq) \rightarrow 2\text{AlO}_2^{-}(aq) + 4\text{H}_2\text{O}
\]

**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

<table>
<thead>
<tr>
<th>Metal</th>
<th>Standard Reduction Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au⁺⁺/Au</td>
<td>+1.50</td>
</tr>
<tr>
<td>Ag⁺/Ag</td>
<td>+0.80</td>
</tr>
<tr>
<td>Hg²⁺/Hg</td>
<td>+0.79</td>
</tr>
<tr>
<td>Cu²⁺/Cu</td>
<td>+0.34</td>
</tr>
<tr>
<td>H⁺/H₂</td>
<td>0.00</td>
</tr>
<tr>
<td>Pb²⁺/Pb</td>
<td>-0.13</td>
</tr>
<tr>
<td>Ni²⁺/Ni</td>
<td>-0.25</td>
</tr>
<tr>
<td>Co²⁺/Co</td>
<td>-0.28</td>
</tr>
<tr>
<td>Fe²⁺/Fe</td>
<td>-0.44</td>
</tr>
<tr>
<td>Zn²⁺/Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>Al³⁺/Al</td>
<td>-1.66</td>
</tr>
<tr>
<td>Na⁺/Na</td>
<td>-2.71</td>
</tr>
<tr>
<td>Li⁺/Li</td>
<td>-3.04</td>
</tr>
<tr>
<td>Mg²⁺/Mg</td>
<td>-2.37</td>
</tr>
</tbody>
</table>
Separation of Impurities
Ion Exchange
Liquid-Liquid Ion Exchange
(Solvent Extraction)

where \( R = C_9H_{19} \)

\[
\text{LIX65N}
\]

\[
\begin{align*}
\text{Cu}^{2+} & + 2\text{Org-H} \rightleftharpoons \text{Org-Cu} + 2\text{H}^+ \\
(\text{in } H_2O) & \rightleftharpoons (\text{in } H_2O)
\end{align*}
\]

SX from sulphate solutions using D2EHPA

Electrometallurgy

* Electrometallurgy is the process of obtaining metals through electrolysis

* Starting materials:
  (a) molten salt
  (b) aqueous solution

* Purpose
  (a) Electrowinning
  (b) Electrefining

* Basis
  Standard electrode potential
Electrometallurgy

Standard electrode potential

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E_0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Au}^{3+} + 3; \text{e}^- \rightarrow \text{Au}$</td>
<td>1.5</td>
</tr>
<tr>
<td>$\text{O}_2 + 4\text{H}^+ + 4; \text{e}^- \rightarrow 2\text{H}_2\text{O}$</td>
<td>1.23</td>
</tr>
<tr>
<td>$\text{Ag}^{2+} + 2; \text{e}^- \rightarrow \text{Ag}$</td>
<td>0.80</td>
</tr>
<tr>
<td>$\text{Cu}^{2+} + 2; \text{e}^- \rightarrow \text{Cu}$</td>
<td>0.4</td>
</tr>
<tr>
<td>$2\text{H}^+ + 2; \text{e}^- \rightarrow \text{H}_2$</td>
<td>0.000</td>
</tr>
<tr>
<td>$\text{Fe}^{2+} + 2; \text{e}^- \rightarrow \text{Fe}$</td>
<td>-0.44</td>
</tr>
<tr>
<td>$\text{Zn}^{2+} + 2; \text{e}^- \rightarrow \text{Zn}$</td>
<td>-0.76</td>
</tr>
<tr>
<td>$\text{Al}^{3+} + 3; \text{e}^- \rightarrow \text{Al}$</td>
<td>-1.66</td>
</tr>
<tr>
<td>$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$</td>
<td>-3.01</td>
</tr>
</tbody>
</table>

Cu Electrowinning

Reaction in Electrowinning
Anode (Pb):
$2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\; \text{e}^- \quad E_0 = -1.23\; \text{V}$
Cathode (Ti):$\text{Cu}^{2+} + 2\; \text{e}^- \rightarrow \text{Cu}^0 \quad E_0 = -0.34\; \text{V}$

Reaction in Electrorefining
Anode (impure Cu):
$\text{Cu}^0 \rightarrow \text{Cu}^2(\text{aq}) + 2\; \text{e}^- \quad E_0 = +0.34\; \text{V}$
Cathode (Ti/SS):
$\text{Cu}^{2+} + 2\; \text{e}^- \rightarrow \text{Cu}^0 \quad E_0 = -0.34\; \text{V}$
**Element Content in Anode Content in Cathode**

<table>
<thead>
<tr>
<th>Element</th>
<th>Anode g/</th>
<th>Cathode g/</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>800-120</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Selenium</td>
<td>32-250</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Tellurium</td>
<td>25-130</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Antimony</td>
<td>700-750</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Bismuth</td>
<td>60</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Lead</td>
<td>990-500</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Nickel</td>
<td>1000-5000</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

*Note: The table depicts the anode cathode contents.*

**Electrowinning**

**EW-SX**
Electrometallurgy

Standard electrode potential

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Au^{3+} + 3 e^- = Au$</td>
<td>1.5</td>
</tr>
<tr>
<td>$O_2 + 4H^+ + 4 e^- = H_2O$</td>
<td>1.23</td>
</tr>
<tr>
<td>$Ag^{2+} + 2 e^- = Ag$</td>
<td>0.80</td>
</tr>
<tr>
<td>$Cu^{2+} + 2 e^- = Cu$</td>
<td>0.4</td>
</tr>
<tr>
<td>$2H^+ + 2 e^- = H_2$</td>
<td>0.000</td>
</tr>
<tr>
<td>$Fe^{2+} + 2 e^- = Fe$</td>
<td>-0.44</td>
</tr>
<tr>
<td>$Zn^{2+} + 2 e^- = Zn$</td>
<td>-0.76</td>
</tr>
<tr>
<td>$Al^{3+} + 3 e^- = Al$</td>
<td>-1.66</td>
</tr>
<tr>
<td>$Li^+ + e^- = Li$</td>
<td>-3.01</td>
</tr>
</tbody>
</table>
Electrometallurgy of Aluminium

Hall process electrolysis cell is used to produce aluminium.

Problem: \( \text{Al}_2\text{O}_3 \) melts at 2000°C and it is impractical to perform electrolysis on the molten salt.

Hall cell use purified \( \text{Al}_2\text{O}_3 \) in molten cryolite (\( \text{Na}_3\text{AlF}_6 \), melting point 1012°C).

Electrolysis

Anode:

\[
\text{C(s)} + 2\text{O}^2- (l) \rightarrow \text{CO}_2 (g) + 4e
\]

Cathode:

\[
3e + \text{Al}^3+(l) \rightarrow \text{Al}(l)
\]

The graphite rods are consumed in the reaction.

Each cell is 3 m by 10 m by 3 m
Each cell has 24 to 40 anode between which \(~ 230\ \text{kA}~\) is distributed
Each cell runs at \(~ 4.5\ \text{V}~\)
In each plant, there are typically 400 cells.
Thus:

\[
400 \times 4.5 \times 230\ \text{kA} = 400\ \text{MW}
\]

Highly Energy Intensive
Fuel equivalent energy required in the primary production of metals

Electrolytic process for Aluminium extraction is highly energy intensive

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
- **Manufacturing** – large scale manufacturing, many techniques