Principles of Extractive Metallurgy

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Learning objectives of the course

- Knowledge of various techniques, unit process and operations used in metal extraction and refining.

- To apply the fundamental knowledge for design of a reactor and process flow sheets.

- To develop computational and mathematical abilities to be applied for process design and control. It may be C++, MATLAB, Excel-Solver, FlowBal, FactSage or any other language of interest.

- To be able to select the correct process routes, reactors and be able to optimize and control them.

- To develop the leaders for coming future who are able to bring new and economic technologies for metal extraction.
Text books:
3. Extractive Metallurgy of Copper, W.G. Davenport, A.K. Biswas, PERGAMON publishing company

Marks distribution (All exam problems will be computational in nature)
1. Quiz 1: 10%
2. Quiz 2: 10%
3. Assignments: 20%
4. Term project: 10%
5. Final Exam: 50%

Assignments
One every week. Students may use computer coding/techniques to solve them. It is advised to solve the assignment problems by their own if want to perform well in exams.

Attendance
There is no weightage for the attendance.

Since the course involves a lot of computational work and fundamental understanding about various principles which would be difficult to understand for those who miss the classes. It would be in the interest of the all the students to attend all the classes if they want to score enough to pass the course.
What is Extractive Metallurgy?

- Deals with extraction of metals from its naturally existing ore/minerals and refining them.

- Minerals: Inorganic compounds with more than one metal in association with non-metals like S, O, N etc.

- Naturally existing minerals are sulphides, oxides, halides like: Hematite (Fe2O3), Magnetite (Fe3O4), Chalcopryite (CuFeS2), Dolomite (CaCO3.MgCO3) ..list is endless.

- What are the sources of metals?
  - Earth Crust (Aluminum: 8.1%, Iron 5.1%, Calcium: 3.6%, Sodium: 2.8%, Potassium: 2.6%, Magnesium: 2.1%, Titanium: 2.1%, Manganese: 0.10%)

- Ocean water: (Na: 10500 g/ton, Mg: 1270 g/ton, Ca: 400 g/ton, K: 380 g/ton) ; Ocean nodules (Mn: 23.86%, Mg 1.66%, Al 2.86%, Fe 13.80%..)

- Recycled scrap (at the end of metals’ life)
Resources of metal containing minerals in India

- **Abundant**: Al, Be, Cr, Fe, Mn, Mg, Ti, Zr, Th, Pb and Zn, raw earth metals
- **Very small**: Co, Ni, Cu, Sn, Au, V, Ni, Cd and U.
- **Poor or not found**: Sb, Bi, Co, Hg, Mo, Nb, Ta, Sr, Se, Ag, W, Pt
Types of ores

- **Oxide ores**: Examples: Fe$_2$O$_3$, Fe$_3$O$_4$
  Apart from Fe, other heavy metals which are produced from oxide ores are:
  Manganese, Chromium, Titanium, Tungsten, uranium and Tin.

- **Sulphide ores**: Copper ore (CuFeS$_2$, Chalcopryite), sphalerite (Zn,Fe)S, Galena PbS, Pyrite FeS$_2$.
  Others: Nickel, Zinc, Mercury and Molybdenum

- **Halide ores**: Rock salts of Sodium, Magnesium chloride in sea water
Commercial production of metals

- Availability of ore deposits
- Concentration of metal in the ore
- Availability of technology of extraction and refining of that metal
- Physical and chemical properties of the metal
- Market demand of that metal

- Economy of the process: Readily available, Easily produced and available at low processing cost with desired properties
Some interesting facts...

• The first metal produced was copper and bronze, produced by smelting copper and tin ores in charcoal fire.
• World production (yearly) Steel: 1400 MT, Aluminum: 40 MT, Copper: 17 MT, Lead: 8 MT, Ni: 2 MT, Magnesium: 1 MT, Ti: 0.15 MT
• Steel is the highly consumed material and its per capita consumption is the index of economic prosperity of any nation.
• Growth rate of metal production was highest during 1950-1970.
• China exhibited very high growth rate in last ten years (182 MT in 2002 to 700 MT in 2011)
Unit processes and Unit operations

- Any metal extraction process is the combination of similar and unique kind of steps known as Unit processes/unit operations.
- Unit operations: Physical operations like crushing, grinding, sizing, mixing through agitation, filtration, distillation, comminution
- Unit processes: Chemical processes like leaching, smelting, roasting, Electrolysis, decarburization, Dephosphorization, Degassing, Deoxidation etc.

Combination of all unit steps/processes are resulting in Flow-Sheets
Flow sheet for copper extraction process

- Crushing, Grinding, Floatation are unit processes
- Roasting, smelting, Blowing, Refining, Electrolysis are Unit processes
Flow sheet for iron and steel extraction process
Flow sheet for Zinc extraction process
Various reactors: a) Fixed bed reactor b) Shaft furnace c) Fluidized bed d) Retort e) Rotary kiln f) Reverberatory furnace g) Electric arc furnace h) Pneumatic/top blown converter
Classification of unit processes/operation by different criteria

- According to phases involved:
  - Gas-Solid: Roasting, Gas reduction
  - Gas-liquid: steelmaking blowing/refining, Distillation
  - Liquid-Liquid: Slag metal reactions
  - Solid-solid: Leaching, precipitation etc.

- According to equipments involved:
  - Fixed bed: Sintering, percolation leaching
  - Fluidized bed: Fluidized roasting and reduction
  - Shaft furnace: Iron blast furnace, lime calcination kiln
  - Rotary kiln: Drying and calcination
  - Ritort: Coke open, carbothermic zinc production, Mg production by pidgeon
  - Reverberatory furnace: Matte smelting (Cu etc.), open hearth steelmaking
  - Electric arc furnace: Steelmaking, matte smelting, ferro alloy production
  - Cell for salt fuse electrolysis: Production and refining of aluminium
  - Cell for aqueous electrolysis: Electrolytic reduction and refining
Classification according to chemical reactions:

- Oxidation: Roasting, sintering, LD steelmaking
- Reduction: Blast furnace ironmaking
- Slag metal reactions: Steelmaking, matte smelting
- Chlorination: Titanium (converting to tetrachloride)
- Electrolytic reduction: Zinc and Aluminum production
- Electrolyte refining: Refining of Copper and Nickel
Classification based upon methods of metal extraction

- **Physical separation/Mineral processing**
  The objective is to concentrate the metallic content in the ore, achieved by a series of comminution (crushing and grinding), screening and separation process.

- **Pyrometallurgy**
  It involves the smelting, converting and refining of metal concentrate.

- **Hydrometallurgy**
  It involves the precipitation of metal in an aqueous solution.

- **Electrometallurgy**
  Electrolysis process to extract metal. Electrowinning: Extraction of the metal from electrolyte; Electrorefining: Refining of impure metals in the form of an anode.

**Majority of metals are extracted by pyrometallurgical route because it is fast, easily adaptable and cheaper.**
Principles you must know?

- **Heat and mass balance**: to know the material requirement
- **Thermodynamics**: Feasibility criteria
- **Kinetics and rate of process**: How long it take to complete the process
- **Heat transfer**: For improving the thermal efficiency of the process
- **Fluid dynamics**: To know the mixing of the reactor
- **High temperature properties of metals/slag**: To know the physical properties of various phases, their mobility and role in metal refining processes.
- **Electrochemistry**: To estimate, overpotential, current efficiency
- **Hydrometallurgy**: Eh-pH diagram, rate estimation of leaching process
Physical separation/mineral processing

Comminution process:
Size reduction of mineral
By crushing/grinding

a) Jaw crusher
b) Roll crusher
c) Gyratory crusher
d) Cone crusher
e) Hammer mill
f) Ball mill
Screening: Sieve analysis

Finer particles are collected in lower boxes
• Classification process: Due to different size, shape and densities, materials are classified in fluids/water. It depends upon following factors:

1. Smaller particles fall more slowly in fluids than do larger ones (Stokes' law)

2. In cyclonic movement (hydrocyclone), centrifugal force have larger influence on larger size particles than smaller ones.

3. Small particles having low inertia behaves like suspended medium.

4. Larger particles require higher velocity for separation.

Classifiers: 1. simple Box Classifier
2. Bowl/rake classifier
3. Hydro cyclones
a) Simple sluice box classifier
b) Bowl/rake classifier
• **Separation process (Froth Floatation)**
  
  Due to different surface free energies of the different minerals, there is selective adsorption on to the air bubbles

• **Frothers:** To stabilize the air bubbles

• **Collectors:** Selective adsorption by lowering interfacial energies.

• **Modifying agents:** Intensify the collector performance

![Diagram of froth floatation process](image)
• **Agglomeration process:** Example: Sintering of iron ores)
  Moving bed of fine iron ore (<6 mm), mixed with coal fines (5-6%, as a fuel and water (10-12%, for permeability) is ignited for agglomeration of oxide and sulphide fines.
Pyrometallurgy: High temperature processes

• **Calcination:** Thermal treatment of an ore to decompose and eliminate the volatile products (like CO2, water)

Example: $\text{CaCO}_3(s) = \text{CaO} (s) + \text{CO}_2 (g)$

Feasible temperature for above reaction is 910°C (at partial pressure of 1 atm.)

Calcination temperatures for others:

- MgCO3: 417°C
- MnCO3: 377°C
- FeCO3: 400°C
• Roasting: Involves heating of ores below fusion point to in excess of air

• It is of three types:
  • Oxidizing roast: to oxidise sulphur in sulphide ores:
    \[ \text{PbS} + 1.5 \text{O}_2 = \text{PbO} + \text{SO}_2 \]
  • Volatilizing roast: To remove volatile oxides like ZnO, As2O3, Sb2O3 etc.
  • Chloridizing roast: To convert metal compounds to chlorides to be reduced later:
    \[ 2\text{NaCl} (s) + \text{PbS} (s) + 2\text{O}_2(g) = \text{Na}_2\text{SO}_4(s) + \text{PbCl}_2 \]
• Smelting: It is a process for the production of metal/metal rich phase known as ‘matte’ along with gangue known as ‘slag’

• Reduction of metal oxide ore is done by smelting process:

\[ \text{MO (s,l)} + \text{C (s)} = \text{M (s,l)} + \text{CO (g)} \]

\[ \text{MO (s,l)} + \text{CO (g)} = \text{M (s,l)} + \text{CO}_2 (g) \]

Example: Blast furnace for ironmaking
Carbothermic reduction: Examples: Fe, Sn, Pb, Zn, Ferroalloys

- Carbothermic reduction of iron ore (Hametite) in blast furnace is a well known process. Overall process is written as:
  - Iron ore oxide mineral + gangue + Reducer (C) + flux + hot blast oxygen enriched air = Pig iron (liquid) + Slag (liquid) + waste gas (CO, CO2, N2)
  - Iron ore contains Fe2O3, along with gangue materials such as SiO2, Al2O3.
  - Charge materials are: Iron ore + limestone (flux) + Coke
  - Output is
    - Pig iron (1300°C), 4.5% C, 0.4-0.6% Si, 0.1-0.2% P, 0.040-0.050% S, 0.1-0.5% Mn
    - Slag: CaO/SiO2 = 1.1; CaO = 30-40%; Al2O3 = 10-23%; FeO <1%; MgO <8%
    - Waste Gas: CO = 20-25%, CO2 = 20-25%, rest N2
Blast furnace layout with auxiliary equipments
Reaction zones in a blast furnace
a) Gas temperature along stack
b) Reduction zones along stack
c) Carbon reduction degree (O/Fe) with stack height
Chemical reactions in a blast furnace

- **Zone 1** (<950 C), upper zone of stack, reduction of Fe2O3, Fe3O3 takes place:
  
  \[3\text{Fe}_2\text{O}_3(s) + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4(s) + \text{CO}_2\]
  
  \[\text{Fe}_3\text{O}_4(s) + \text{CO} \rightarrow 3\text{FeO}(s) + \text{CO}_2\]

- **Zone 2** (950-1000 C), chemical reserve zone, FeO is in equilibrium with gaseous phase:
  
  \[\text{FeO}(s) + \text{CO} = \text{Fe}(s) + \text{CO}_2\]

- **Zone 3**: (950<T<1050 C), the reduction of FeO by rising CO gas takes place:
  
  \[\text{FeO}(s) + \text{CO} \rightarrow \text{Fe} + \text{CO}_2\]

- **Zone 4**: (>1000-1050C), direct reduction of FeO to carbon takes place.
  
  Reaction in raceway zone: \(\text{C} + \text{O}_2 \rightarrow \text{CO}_2\)
  
  followed by \(\text{CO}_2 + \text{C} \rightarrow 2\text{CO}\) (Boudward reaction)
  
  Overall \(\text{C} + \text{O}_2 = 2\text{CO}\)

  Boudward reaction is thermodynamically feasible at \(T > 1050\) (below zone 4). It supports the conversion of \(\text{CO}_2\) to CO in raceway and bosh region where \(T>1050\) C.
Metallothermic reduction

• Thermite welding:
  \[ \text{Fe}_2\text{O}_3(s) + 2\text{Al} = \text{Al}_2\text{O}_3(l) + 2\text{Fe}(l) \]

• Ferroalloy production:
  \[ \text{Cr}_2\text{O}_3 + 2\text{Al} = 2\text{Cr}(l) + \text{Al}_2\text{O}_3(l) \]

• Titanium production by Kroll’s process:
  \[ \text{TiCl}_4(l) + 2\text{Mg} = 2\text{MgCl}_2(l) + \text{Ti}(s) \]

Solid state reduction of oxides:

Tungsten: \[ \text{WO}_3(s) + 3\text{H}_2 = \text{W}(s) + 3\text{H}_2\text{O} \]

Iron: \[ \text{Fe}_2\text{O}_3 + 3\text{H}_2 = 2\text{Fe} + 3\text{H}_2\text{O} \]
Low pressure/high pressure pyrometallurgical processes

- **Low pressure process**
  - Magnesium extraction process:
  - \(2\text{MgO.CaO(s)} + \text{Si (as Fe-Si)(s)} = 2\text{Mg(g)} + 2\text{CaO.SiO2 +Fe}\)
    - This reaction moves in right direction at low pressures.
  - Vacuum degassing of steels:
    - \([C] + [O] = \{CO\}\)

- **High pressure process**
  - \(\text{ZrO2(s)} + 2\text{Ca(g)} = \text{Zr(s)} + 2\text{CaO (s)}\)
Extraction of metals from sulphide ores (Examples: Cu, Ni, Zn, Pb)

- **Extraction of lead**
  - Lead ore consists of PbS (galena) along with Sphalerite (ZnS), Pyrite (FeS2), Cu2S and some precious metals like gold and silver as gangue.
  - First of all lead ore (3-10% lead) is concentrated to 60-70% by froth flotation, then roasted to remove sulphur and form oxides, followed by reduction in blast furnace using coke.

- **Extraction of Zinc**
  - Zinc ore consists of Sphalerite (ZnS) along with sulphides of copper, lead and cadmium with some precious metals as gangue.
  - First of all sulphide is converted to oxide by roasting process, followe by carbothermic reduction:
    \[
    \text{ZnO(s)} + \text{C (s)} = \text{Zn(g)} + \text{CO(g)} \text{.. vacuum needed to push reaction if forward direction.}
    \]
Extraction of copper

• The copper ore is known as Chalcopyrite (CuFeS2). Copper is less than 2%, which is concentrated by froth floatation.

• Roasting of chalcopyrite is done to remove iron sulphide in the form of FeO.
  \[2\text{CuFeS}_2(s) + \text{O}_2(g) = \text{Cu}_2\text{S} + 2\text{FeS} + \text{SO}_2(g)\]
  \[\text{FeS} + 1.5\text{O}_2(g) = \text{FeO}(s) + \text{SO}_2(g)\]

• Roasted ore is charged into a reverberatory furnace/flash smelting unit along with Silica (SiO2) as a flux.

• Output of the furnace is matte (Cu rich liquid melt) along with FeO.SiO2 slag. Matte and slag are easily seperable.
Reverberatory Furnace for Producing Molten Cu-Fe-S Matte

(a) Outokumpu O₂-enriched air flash furnace

(b) Inco oxygen flash furnace
Converting of Cu-matte in Pierce-Smith converter

- It involves air oxidation of molten matte received from smelting. It involves two step process:
  (a) FeS removal and slag formation:
  \[ 2\text{FeS (l)} + 3\text{O}_2 + \text{SiO}_2 \rightarrow 2\text{FeO.SiO}_2(\text{l}) + 2\text{SiO}_2(\text{g}) \]
  Process temperature: 1200 C
  (b) Blister copper (>99% Cu) formation stage:
  \[ \text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2\text{Cu} + \text{SO}_2 (\text{g}) \]

Point to be noted: Cu loss in slag starts after sulphur in matte falls below 0.02%
Copper conversion does not start till Fe in matte is below 1%. 
Extraction of reactive metal by halide route

- Extraction of Titanium
  - Titanium ore exists in the form of oxide (Rutile, TiO2) or Ilmenite (FeO.TiO2).
  - As a first step TiO2 is chlorinated at 900 C:
    \[ \text{TiO}_2 (s) + \text{C}(s) + 2\text{Cl}_2(g) = \text{TiCl}_4 (g) + \text{CO}_2 (g) \]
  - TiCl4 is removed by selective distillation, followed by reduction of TiCl4 by Magnesium, known as Kroll’s process.
    \[ \text{TiCl}_4(l) + 2\text{Mg}(l) = 2\text{MgCl}_2(l) + \text{Ti} (s) \]
Refining process

• Oxidation to remove C,Si,P,Mn etc (steelmaking)
• Sulphidation to remove :Cu,Ni,Co from lead; Cu from tin etc.
• Chlorination to remove Zn from lead; Zn,Cu and Pb from bismuth
• Electrochemical method by cathodic deposition; examples: Cu,Ag,Au,Ni,Co,Pb,Sb,Bi etc.
Oxygen Steelmaking process for refining of pig iron

Selective oxidation of C, Si, Mn, P, Fe with the help of high speed oxygen blow. Process done in a basic lined vessel and Lime added as slag former to combine SiO2. Oxidizing and enough volume of slag is formed to promote phosphorous removal. Process generates a lot of heat of oxidation which is compensated by iron ore/scrap additions as a coolant.
Next Class task:

• Material and heat balance of processes.

• Come prepared with Solver model applying MS-Excel

• Flow-Bal software will be introduced and student groups will be formed.