Materials and Energy Balance

Introduction

Materials and energy balance covers the basic chemical principles that relate thermodynamics to chemical metallurgy

The goal of a metallurgical engineer is to keep a metallurgical production process running as efficiently as possible

Charge calculations, fuel calculations and estimation of the product yield are primary responsibilities that are based on stoichiometry and theoretical thermodynamic relations

Basic principles of conservation of mass and energy are utilized in this course to estimate important thermodynamic properties of materials at equilibrium to a high degree of accuracy



Metallurgical processes consist of many chemical reactions

Stoichiometry calculations need to be done carefully for accurate estimation of what quantities of raw materials convert to the desired quantity of products

A metallurgical engineer has to know stoichiometry, mass balance, enthalpy calculations, heat balance, chemical reaction equilibria, and anticipate what components of the charge convert to which products in order to have full control on a process



General Overlook to Chemical Metallurgy

Metallurgy is the art of extracting metals from ores found concentrated in certain parts of the world, refining them and preparing for use

Earth's crust is 35 km thick above molten iron, filled with metallic ores and other minerals

On average the Earth's crust consists mostly of oxygen, silicon, aluminum, iron and calcium



Ore minerals of common and precious metals

Iron ores contain large amounts of the iron ore minerals and relatively small amounts of gangue

Although ores as low as 25-30% Fe are smelted after concentration, directly smelted ores mostly contain about 50% Fe

Hematite (Fe_2O_3) – Most important ore mineral of iron

Magnetite (Fe_3O_4) – Magnetic mineral

Limonite $(Fe_2O_3.xH_2O)$ – Not desirable due to low grade Siderite (FeCO3) – Not desirable due to low grade Pyrite (FeS_2) – Used after roasting as iron oxide ash



The only commercial **aluminum ore** is bauxite which is a rock consisting of hydrated oxides of aluminum with oxide ratio of 55-61% Al_2O_3 , 10-30% combined water, 1-25% Fe_2O_3 , 1-3% TiO_2 and 1-12% SiO_2 *Gibbsite* (Al_2O_3 .3H₂O) *Diaspore* (α -Al₂O₃.H₂O) *Boehmite* (γ -Al₂O₃.H₂O) *Corundum* (Al_2O_3) *Kaolinite* (Al_2O_3 .2SiO₂.2H₂O)

The primary copper ore mineral is chalcopyrite

Others are secondary minerals formed by the alteration of primary *chalcopyrite* and *chalcocite* CuS ores are usually associated with *pyrite* (FeS₂) and other base metal sulfides such as ZnS, Pt Copper minerals are usually associated with siliceous and other gangue minerals so that their

grades are as low as 1-2% Cu *Chalcopyrite* (CuFeS₂) *Bornite* (Cu₅FeS₄) *Chalcocite* (Cu₂S) *Covellite* (CuS) *Enargite* (CuAsS₄) *Malachite* (CuCO₃.Cu(OH)₂) *Cuprite* (Cu₂O) *Chrysocolla* (CuSiO₃.2H₂O)



Galena is the only important lead ore mineral

Most lead ores are found in veins and not suitable for bulk mining

The average grade of lead ore mined is higher than that of copper ore, around 3.0-8.0% Pb

Galena (PbS) Anglesite (PbSO₄) Cerussite (PbCO₃)



Sphalerite (ZnS) is the only important **zinc ore** mineral and is associated with PbS, $CuFeS_2$ or cadmium with an average grade around 2-12% Zn Smithsonite (ZnCO₃) and calamine (Zn₂(OH)₂.SiO₃ occur in the oxidized portions of ore bodies

Gold, **silver** and **platinum** most commonly occur in nature as native metals in metallic state but as alloys rather than pure metals Seldomly gold occurs as *calaverite* (AuTe₂) and silver occurs as *argentite* (Ag₂S), *pyrargyrite* (Ag₃SbS₃)

Gold, silver and platinum are usually associated with base-metal sulfides and pyrite

Chromite (FeO.Cr₂O₃) is the only economical **chromium ore** mineral Commercial chromium ores usually contain at least 40% Cr_2O_3

Journey of Metal Oxide from Ore to Ingot

Mineral Dressing

Minerals must be liberated from their intimately associated gangue minerals before they can be collected in separate products

The first part in mineral dressing is comminution which involves crushing and grinding of the ore to a point where each mineral grain is free

Crushing (3 stages)

- Coarse crushing Ore rocks are reduced to 10 cm in a jaw or gyratory crusher
- Intermediate crushing Jaw, cone or roll crushers break ores from 10 cm to 1-2 cm
- Fine crushing Short head cone, roll crushers, hammer mills break ores from 1-2 cm to 0.5 cm

Grinding (2 stages)

- Coarse grinding Ore feed as large as 50 mm are pulverized in rod mills to 300 microns
- Fine grinding Steel balls in ball mills reduce 0.5 mm particles to less than 100 microns in wet environment

The goals of comminution are

- 1- To obtain the correct degree of liberation of minerals
- 2- To increase the specific surface area of minerals for hydrometallurgical treatment

Ore particles are continuously screened after crushing in a closed loop process

Powder mineral mixtures are separated subsequently to two or more products according to their settling velocities in a suspending medium

Particles above a certain size and density settle down while lighter ones are carried away

Mineral Dressing

The second part in mineral dressing is separation of the liberated valuable minerals from gangue minerals or concentration

Physical concentration methods

- Separation dependent on optical or radioactive properties by hand picking, optical, radioactive sorting
- Separation dependent on density difference of minerals by sedimentation in heavy media
- Separation utilizing different surface properties of minerals by froth flotation
- Separation dependent on magnetic properties of minerals by dry and wet magnetic picking
- Separation dependent on electrical conductivity of minerals by electrostatic separation

Separation is mostly done by physical means because they do not change the characteristics of the raw materials

Three end products of concentration are Concentrate – Valuable minerals separated from ore Tailing – Fraction of ore discarded as a valueless part Middlings – Particles with valuable minerals and gangue locked together. Further liberation needed by comminution Drying

Minerals recovered from ores are not in the optimum physical and chemical state for conversion to metals

Drying is applied to moist concentrate powder to remove physically held water by evaporation

Therefore the heat of evaporation must be supplied to the minerals in addition to the heat needed to elevate its temperature – Energy intensive process

Drying is usually done in a fixed or fluidized furnace or a kiln by passing hot combustion gases through the concentrate

Calcination

The chemically bound water, CO₂ and other gases are removed from metal hydrate or carbonate particles by calcination

The temperature required for complete calcination of a mineral is much higher than drying T

Decomposition temperature (i.e. temperature required for decomposition gas product pressure to reach 1 atm) is different for each mineral

FeCO3T>200 CMnCO3T>400 CCaCO3T>900 CBaCO3T>1000 CAl(OH)3T>1000 C

Types of calcination furnaces Shaft furnace – Calcining coarse particles –

Rotary kiln – Particles of mixed coarse and fine size which disintegrate during the process Fluidized bed furnace – Particles of uniform and fine size

Roasting

Oxides are more conveniently reduced to metals than sulfides The metal might be more readily leached from the ore in sulfate, chloride or oxide form

Roasting is chemical conversion of sulfides to an oxide or sulfate in an oxidized atmosphere in

order to make them more soluble in acid

Typical ores or concentrates which are roasted – Cu, Fe, Zn, Pb $2ZnS + 3O_2 = 2ZnO + 2SO_2$ $2FeS_2 + 11/2 O_2 = Fe_2O_3 + 4SO_2$ $2PbS + 4O_2 = 2PbSO_4$ $2PbO + 2SO_2 + O_2 = 2PbSO_4$ $ZnO + Fe_2O_3 = ZnFe_2O_4$

Metal sulfides are partly or completely converted into metal oxides and SO₂ forms

Roasting temperatures should be higher than 500-600 C for the reductions to occur rapidly and less than 1000 C not to exceed the melting points and avoid ferrite formation

Types of roasting: Oxidizing, volatilizing, chloritizing, sulfating, magnetizing, carburizing and sinter roasting

Types of roasting furnaces: Multiple hearth furnaces, suspension roasting furnaces and <u>fluidized bed roasting furnaces</u>

Agglomeration

Particle size of concentrates may be too small for use in a later stage process like blast furnace where fine-grained material may plug up the gas passage and decrease gas permeability Fine particles are reformed into lumps of appropriate size and strength by agglomeration

Sintering

Relatively coarser particles are sintered into lumps of porous structure by partial melting and fusion at a $T > 2/3T_m$

• Pelletizing

Moist and fine particles are rolled to pellets in a drum or rotating inclined disc Green pellets are dried and fired at 1200 – 1375 C in order to impart strength

Typical fine ores or concentrates which are pelletized – Cu, Fe, Cr

Electrometallurgical Extraction

Chemical reduction processes that require electric current

Electrolytic refining to obtain Al, Cu, Fe, Co, Pb, Zn
 Electrolysis
 Fused salt electrolysis to obtain Na, Zr, Ti, K, Ca

• Electrowinning – Recovery of Cu, Au, Zn, Sb from pregnant leach solution

Hydrometallurgical Extraction Concentrates are dissolved (i.e. leached) and separated from insoluble gangue minerals in aqueous solutions

Steps of Hydrometallurgy

- 1- Leaching of valuable metal
- 2- Separation of pregnant solution from the leach residue
- 3- Recovery of metal from pregnant leach solution

Many advantages of Hydrometallurgy

High extraction yield

*Many minerals do not dissolve in aqueous solutions

One big disadvantage

- Little fuel required
- Simple and inexpensive equipment
- Recycling of some expensive solvents
- Suitable for treatment of low-grade ores as well as concentrates
- Less environmental problems

Solvents must preferentially dissolve the ore minerals and leave gangue minerals, must be cheap and must be recycled H_2O for $CuSO_4$, $ZnSO_4$ leaching H_2SO_4 for CuO_2 , ZnO sulfating NaOH for Al_2O_3 leaching NaCN or KCN salts for Au and Ag leaching Thio Bacillus Ferrooxidans for $Fe(SO_4)_3$ leaching

Recovery methods

Precipitation – Formation of a soluble compound and separation of metal as a precipitate

 $Zn_{dust} + 2NaAu(CN)_2 = Na_2Zn(CN)_4 + 2Au$

Electrowinning – Metal ions acquire electron to give metal and proton at elevated T and P

 $Ni^{++} + H_2 = Ni^0 + 2H^+$

<u>Solvent extraction</u> – Liquid ion exchange

Ion exchange – Used for low grade uranium ores, water leaching of rare-earth metals

 $UO_2(SO_4)_3^{4-} + 4RX = R_4(UO)_2(SO_4)_3 + 4X^{-}$

<u>Cementation</u>– A metal with more positive potential will pass into the solution and displace a metal with a less positive potential

 $Cu^{++} + Fe^{\circ} = Cu^{\circ} + Fe^{++}$ Fe potential= +0.440 volts, Cu potential= -0.337 volts $Cd^{++} + Zn^{\circ} = Cd^{\circ} + Zn^{++}$ Zn potential= +0.763 volts, Cd potential= +0.403 volts

Pyrometallurgical Extraction

Chemical reactions of metal ores up to 3000 C that involve a number of different solids, liquids, gases and take place in a variety of furnaces, converters, roasters

All iron and steel, lead, tin, most of copper and a small fraction of zinc produced in the world are won from their concentrates by pyrometallurgical methods

The most important pyrometallurgical extraction processes:

- Smelting
 - Matte smelting Cu, Ni
 - Smelting for metal Fe, Pb
- Converting Cu, Ni
- Reduction of oxides Direct reduction of iron ore, zinc ore
- Refining Cu, Pb
- Distillation Zn, Hg
- Halide metallurgy

Smelting

Simultaneous melting and separation of the charge into two immiscible liquid layers of slag and matte or slag and liquid metal

Smelting for matte – A pyrometallurgical concentration stage in the overall extraction of a metal from its sulphides

Matte – A molten mixture of metal sulphides

Slag – Siliceous or oxidized part of the concentrate

Metal sulphidesMatte smelting under neutral20-30% Cuor reducing conditions

Matte – Cu_2S , FeS (30-55% Cu) Slag – SiO₂, CaO, Al₂O₃

Matte smelting furnaces

- Reverberatory furnace for fine concentrates
- Flash furnace for fine concentrates
- Blast furnace for lumpy ore and agglomerated concentrates
- Electric furnace for fine concentrates

Inco Oxygen Flash Smelting Furnace

Smelting

Smelting for metal – Separation and reduction of metal oxides to metals and formation of slag containing gangue minerals, impurities and fluxes Liquid metal is an alloy containing various impurities Impure metal should subsequently be fire refined

Metal oxidesSmelting for metalLiquid metal – Pig iron (Fe+4%C+1%Si) $Fe_2O_{3,} Fe_3O_4$ with reducing agent (coal, coke)Liquid slag – SiO_{2,} CaO, Al_2O_3

Iron smelting furnaces

- Reverberatory furnace for fine concentrates
- Blast furnace for lumpy ore and agglomerated concentrates)
- Electric furnace for fine concentrates

Matte Converting Preferential oxidation of the more reactive impurity metal sulphides

Liquid matte containing metal sulphides Cu₂S, FeS air and oxygen blowing Liquid matte containing metal oxides Cu₂O, FeO

Air blowing is controlled to convert the remaining more noble metal sulphide to the required metal $Cu_2S + O_2 = 2Cu + SO_2$

Pierce-Smith converter for copper matte

Fire Refining

Preferential oxidation of impurity elements in liquid metal

Impure metal from		 Fire refined metal
matte smelting	Fire refining in presence of oxygen	Pure copper
Blister copper	and hydrocarbon fuels	99.5% Cu, 0.003% S,
98.5% Cu, 0.1% S, 0.8% O		0.2% O
		Slag, SO ₂
Steelmaking is also a refir	ning process since impurities in pig iron a	are lowered to acceptable →
Impure metal from		Fire refined metal
metal oxide smelting	Fire refining in presence of oxygen	Steel
Pig iron	and fluxes	Fe, 0.3% C, 0.001% Si,
Fe, 4%C, 1%Si, 1%Mn		0.3% Mn
		Slag

Distillation

Metals with low boiling point are separated from higher boiling point impurities by evaporation and subsequent condensation to the pure metal

Liquid mixture Distillation with or without vacuum

Recovery of vapor Residue

The metals that may be refined by distillation are limited to those with boiling temperatures less than 1000 C Vacuum distillation extends the range of materials that can be distilled

Zinc and mercury are separated by distillation of mercury around 357 C Lead and zinc are separated by vacuum distillation of zinc around 900 C

Halide metallurgy

Metal halides produced by roasting with halogens Cl, Br, F, I are subsequently reduced to metal

ZrO	Chloridizing	ZrCl ₂	Reduction with Mg	Zirconium
metal	roasting	~	by Kroll process at 900 C	

Some volatile halides $SnCl_{4}$, $TiCl_{4}$, $AlCl_{3}$ can be separated and purified by distillation

Pyrometallurgical Extraction and Refining Processes

Fuels

Cost of energy is a high proportion of the total cost of pyrometallurgy A fuel is any substance that may be burned rapidly enough for its heat of oxidation to be utilized in industrial operations

Most important heat producing elements

C – used in elemental form (charcoal, coke), combined form (hydrocarbons), partly combined form (lignite coal)

H – used in elemental form in gaseous fuels, or combined form in hydrocarbons

S – used as fuel in roasting and matte converting but is undesirable as an impurity in metals Si, Mn, Al and P compounds are also used as fuels

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Sulphide concentrateExothermic RoastingSteam productionFeS2Fe_2O_3 + SO_2Solid fuelsSolid fuelsSolid fuelsNatural – Wood, peat, lignite coal, bituminous coal, anthracite coal<br/>Artificial – Pulverized coal, briquetted fuels, carbonized fuels (charcoal, coke)Liquid fuelsNatural – Petroleum<br/>Artificial – Distilled oils, coal tar, residual oils (fuel oil)Gaseous fuelsNatural – Natural gas (CH4, C2H6, C3H8)<br/>Artificial – Coal gas, oils gas, blast furnace gas (N2, CO, H2, CO2)
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Material balance is the basic procedure that enables engineers specify all the amount of species without a knowledge of the complete system

Charge calculations enable engineers estimate the amount and ratio of the initial reactant charge of a furnace required to obtain the desired yield

The equilibrium concentration of both products and reactants in a chemical reaction can be determined when the temperature, pressure, and equilibrium constant at that T and P is provided

Knowledge on the initial or equilibrium state of a system is important since thermodynamic state properties do not depend on the path taken

Material balance should be supplemented with accurate material analysis results

Various types of photometers, spectrophotometers and other advanced instruments like ICP, XRF, XRD enable a rapid quantitative measurement of sample composition with high accuracies

Analyses of metallurgical interest

%

1. Ultimate analysis: Percentages of elements are reported. Instruments used: XRF, ICP

Element	Weight
0	46.60
Al	35.85
Са	3.63
	•••

2. Rational analysis: Percentages of compounds forming the sample are reported by gas analysis

Ultimate analysis can be combined with the information from XRD analysis to obtain rational Phases present in the sample: Al_2O_3 , CaO,...

Weight %	
80.45	
5.72	

3. Mineralogical analysis: Rational analysis given in terms of percent minerals making up sample
 Mineral Weight %
 Corundum 80.45

Limestone 5.72

4. Proximate analysis: Commercial specification of the results of standardized test Quantities reported in coal analysis: Fixed carbon, volatile matter, moisture, ash

ICP-AE spectrometry

Atomic emission spectroscopy uses quantitative measurement of the optical emission from excited atoms to determine the concentration of a solution

Atoms in solution are energized into the excitation region where they are de-solvated, vaporized, and atomized by a flame, discharge, or plasma (Inductively **C**oupled **P**lasma)

High-temperature atomization source provides sufficient energy to promote the atoms into high energy levels

The atoms decay back to lower levels by emitting light

Light emitted due to transitions between distinct atomic energy levels are recorded as spectra The spectra of samples containing many elements can be very crowded, and spectral separation of nearby atomic transitions requires a high-resolution spectrometer

XRF spectrometry When a material is hit with X-rays, fluorescent X-Rays are analyzed in order to gain information on the elemental composition

An energy dispersive detection system directly measures the different energies of the emitted X-Rays from the sample

An XRF spectrum is generated by counting and plotting the relative numbers of X-Rays at each energy

X-ray Diffraction

Analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions

Crystalline substances and spacing of planes in a crystal lattice act as three-dimensional diffraction gratings for X-ray wavelengths

X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, and directed toward the sample

The interaction of the incident rays with the sample produces constructive interference and a diffracted ray when conditions satisfy Bragg's Law

Gas analysis

Orsat apparatus is used to analyse gases in terms of volume percentages of molecular species present on a dry and dust-free basis

Mole percentages which are equivalent to the ratios of partial pressures of gaseous components to total pressure are also used interchangably

Orsat apparatus consists of a measuring burette to take about 100 cm³ of gas and a number of bulbs attached

Pyrogallol solution is used to determine the oxygen content, KOH solution for CO_2 content, CuCl, HCl solution for CO content. Other bulbs can be added for hydrocarbon contents

This apparatus, being movable, can be transported to a boiler house or similar place and the analysis of waste gas made there without the delay

Orsat apparatus gives the percentages on a dry basis since it is saturated with water

A similar apparatus exists for the determination of sulfur gases in roasting