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 and iron.

### Composition of Earth's Crust

<table>
<thead>
<tr>
<th>Element</th>
<th>Common charged Form</th>
<th>Wt% in Earth's crust</th>
<th>Resulting mineral groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>O (Oxygen)</td>
<td>O²⁻</td>
<td>46.4</td>
<td>Oxides</td>
</tr>
<tr>
<td>Si (Silicon)</td>
<td>Si⁴⁺</td>
<td>28.2</td>
<td>Silicates</td>
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<tr>
<td>Al (Aluminum)</td>
<td>Al³⁺</td>
<td>8.1</td>
<td></td>
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<tr>
<td>Fe (Iron)</td>
<td>Fe³⁺</td>
<td>5.4</td>
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<tr>
<td>Ca (Calcium)</td>
<td>Ca²⁺</td>
<td>4.1</td>
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<tr>
<td>Na (Sodium)</td>
<td>Na²⁺</td>
<td>2.4</td>
<td></td>
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<tr>
<td>Mg (Magnesium)</td>
<td>Mg²⁺</td>
<td>2.3</td>
<td></td>
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<tr>
<td>K (Potassium)</td>
<td>K⁺</td>
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<tr>
<td>Ti (Titanium)</td>
<td>Ti⁴⁺</td>
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<tr>
<td>H (Hydrogen)</td>
<td>H⁺</td>
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<td></td>
</tr>
<tr>
<td>P (Phosphorus)</td>
<td>P⁵⁺</td>
<td>0.11</td>
<td>Phosphates</td>
</tr>
<tr>
<td>Mn (Manganese)</td>
<td>Mn⁴⁺</td>
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<td></td>
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<tr>
<td>F (Fluorine)</td>
<td>F⁻</td>
<td>0.065</td>
<td>Halides</td>
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<tr>
<td>Ba (Barium)</td>
<td>Ba²⁺</td>
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<tr>
<td>Sr (Strontium)</td>
<td>Sr²⁺</td>
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<tr>
<td>S (Sulfur)</td>
<td>S²⁻ &amp; S⁶⁺</td>
<td>0.030</td>
<td>Sulfates &amp; Sulfides</td>
</tr>
<tr>
<td>C (Carbon)</td>
<td>C⁴⁺ &amp; C⁴⁻</td>
<td>0.022</td>
<td>Carbonates</td>
</tr>
<tr>
<td>Zr (Zirconium)</td>
<td>Zr⁴⁺</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td>Cl (Chlorine)</td>
<td>Cl⁻</td>
<td>0.013</td>
<td>Halides</td>
</tr>
</tbody>
</table>
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, most directly smelted ores contain about 50% Fe.

*Hematite* (Fe$_2$O$_3$) – Most important ore mineral of iron.

*Magnetite* (Fe$_3$O$_4$) – Magnetic mineral.

*Limonite* (Fe$_2$O$_3$·xH$_2$O) – Not desirable due to low grade.

*Siderite* (FeCO$_3$) – 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$_2$O$_3$, 10-30% combined water, 1-25% Fe$_2$O$_3$, 1-3% TiO$_2$, and 1-12% SiO$_2$.

*Gibbsite* (Al$_2$O$_3$·3H$_2$O)

*Diaspore* (α-Al$_2$O$_3$·H$_2$O)

*Boehmite* (γ-Al$_2$O$_3$·H$_2$O)

*Corundum* (Al$_2$O$_3$)

*Kaolinite* (Al$_2$O$_3$·2SiO$_2$·2H$_2$O)
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* (FeS$_2$) and other base metal sulfides such as ZnS, PbS. Copper minerals are usually associated with siliceous and other gangue minerals so that their grades are as low as 1-2% Cu.

- *Chalcopyrite* (CuFeS$_2$)
- *Bornite* (Cu$_5$FeS$_4$)
- *Chalcocite* (Cu$_2$S)
- *Covellite* (CuS)
- *Enargite* (CuAsS$_4$)
- *Malachite* (CuCO$_3$.Cu(OH)$_2$)
- *Cuprite* (Cu$_2$O)
- *Chrysocolla* (CuSiO$_3$.2H$_2$O)

*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* (PbSO$_4$)
- *Cerussite* (PbCO$_3$)

*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* (ZnCO$_3$) and *calamine* (Zn$_2$(OH)$_2$.SiO$_3$) 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 (AuTe$_2$) and silver occurs as argentite (Ag$_2$S), pyrargyrite (Ag$_3$SbS$_3$). Gold, silver and platinum are usually associated with base-metal sulfides and pyrite.

Chromite (FeO.Cr$_2$O$_3$) is the only economical chromium ore mineral. Commercial chromium ores usually contain at least 40% Cr$_2$O$_3$. 
Journey of Metal Oxide from Ore to Ingot

Metal ore

Mineral dressing
Mechanical separation of
the ore mineral grains from
the gangue minerals to
produce a concentrate

Drying
Removal of mechanically
held water from
concentrate in a high T or
low P furnace

Calcination
Removal of chemically
bound H₂O or CO₂ in a
furnace at a higher T

Roasting
Converting metal sulfides partly
or completely, into oxides that
are more conveniently reduced
to metals in a high temperature
furnace

Agglomeration
Concentrates are reformed into
agglomerates of appropriate size
and strength to be used in a later
treatment requiring coarse
particles

Pyrometallurgical, Hydrometallurgical, Electrometallurgical Extraction
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 a 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 mechanically 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 – an 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, CO$_2$ 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 temperature.

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

- FeCO$_3$ T>200 C
- MnCO$_3$ T>400 C
- CaCO$_3$ T>900 C
- BaCO$_3$ T>1000 C
- Al(OH)$_3$ T>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 or 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:

\[
2\text{ZnS} + 3\text{O}_2 = 2\text{ZnO} + 2\text{SO}_2 \\
2\text{FeS}_2 + 11/2\text{O}_2 = \text{Fe}_2\text{O}_3 + 4\text{SO}_2 \\
2\text{PbS} + 4\text{O}_2 = 2\text{PbSO}_4 \\
2\text{PbO} + 2\text{SO}_2 + \text{O}_2 = 2\text{PbSO}_4 \\
\text{ZnO} + \text{Fe}_2\text{O}_3 = \text{ZnFe}_2\text{O}_4
\]

Metal sulfides are partly or completely converted into metal oxides and \(\text{SO}_2\) 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, chloridizing, sulfating, magnetizing, carburizing and sinter roasting.

Types of roasting furnaces: Multiple hearth furnaces, suspension roasting furnaces and fluidized bed roasting furnaces.
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 $T > \frac{2}{3}T_m$.

- 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

Typical fine ores or concentrates which are pelletized – Cu, Fe, Cr
Electrometallurgical Extraction
Chemical reduction processes that require electric current

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

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

Hall-heroult cell
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
• 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

One big disadvantage
*Many minerals do not dissolve in aqueous solutions

Solvents must preferentially dissolve the ore minerals and leave gangue minerals, must be cheap and must be recycled
H₂O for CuSO₄, ZnSO₄ leaching
H₂SO₄ for CuO₂, ZnO sulfating
NaOH for Al₂O₃ leaching
NaCN or KCN salts for Au and Ag leaching
Thio Bacillus Ferrooxidans for Fe(SO₄)₃ leaching
Leaching methods

In situ leaching – Mine water for leaching CuSO₄

Heap leaching – Ore rocks in dumps

Sand – Percolation – leaching - Sand-sized ores in large tanks

Agitative leaching – Fine concentrates in agitated steel tanks

Pressure leaching – Hard to dissolve concentrates in autoclaves
Recovery methods

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

\[ \text{Zn}_{\text{dust}} + 2\text{NaAu(CN)}_2 = \text{Na}_2\text{Zn(CN)}_4 + 2\text{Au} \]

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

\[ \text{Ni}^{++} + \text{H}_2 = \text{Ni}^0 + 2\text{H}^+ \]

Solvent extraction – Liquid ion exchange

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

\[ \text{UO}_2(\text{SO}_4)_3^{4-} + 4\text{RX} = \text{R}_4(\text{UO})_2(\text{SO}_4)_3 + 4\text{X}^- \]

Cementation— A metal with more positive potential will pass into the solution and displace a metal with a less positive potential

\[ \text{Cu}^{++} + \text{Fe}^o = \text{Cu}^o + \text{Fe}^{++} \quad \text{Fe potential}= +0.440 \text{ volts}, \quad \text{Cu potential}= -0.337 \text{ volts} \]

\[ \text{Cd}^{++} + \text{Zn}^o = \text{Cd}^o + \text{Zn}^{++} \quad \text{Zn potential}= +0.763 \text{ volts}, \quad \text{Cd potential}= +0.403 \text{ volts} \]
Pyrometallurgical Extraction

Chemical reactions of metal ores at up to 3000°C that involve a number of different solids, liquids, and 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 liquid metal

Smelting for matte – A pyrometallurgical concentrating 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 sulphides \[\text{Matte smelting under neutral or reducing conditions}\] Matte – \(\text{Cu}_2\text{S}, \text{FeS (30-55\% Cu)}\) Slag – \(\text{SiO}_2, \text{CaO, Al}_2\text{O}_3\)

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
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 oxides
Fe₂O₃, Fe₃O₄

Smelting for metal
with reducing agent (coal, coke)

Liquid metal – Pig iron (Fe+4%C+1%
Liquid slag – SiO₂, CaO, Al₂O₃

Matte 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 $\text{Cu}_2\text{S}, \text{FeS}$

Air blowing

Liquid matte containing metal oxides $\text{Cu}_2\text{O}, \text{FeO}$

Air blowing is controlled to convert the remaining more noble metal sulphide to the required metal

$$\text{Cu}_2\text{S} + \text{O}_2 = 2\text{Cu} + \text{SO}_2$$

Pierce-Smith converter for copper matte
Reduction of metal oxides
Metals form from metal oxides with reducer agents
C, CO, H₂ reducing agents
Main metal oxides reduced with carbon are Fe, Mn, Cr, Sn, Pb, Zn
2MO + C = 2M + CO₂ below 650°C
MO + C = M + CO above 650°C

Metallothermic reduction by metals having lower standard free energy change of oxidation
3MO + 2Al = 3M + Al₂O₃
2MO + Si = 2M + SiO₂

Ellingham diagrams are useful to assess various reducing agents
Fire Refining
Preferential oxidation of impurity elements in liquid metal

Impure metal from matte smelting \[\rightarrow\] Fire refining in presence of oxygen and hydrocarbon fuels \[\rightarrow\] Fire refined metal Pure copper
Blister copper 99.5\% Cu, 0.003\% S, 0.2\% O
98.5\% Cu, 0.1\% S, 0.8\% O
Slag, SO₂

Steelmaking is also a refining process since impurities in pig iron are lowered to acceptable levels.

Impure metal from metal oxide smelting \[\rightarrow\] Fire refining in presence of oxygen and fluxes \[\rightarrow\] Fire refined metal Steel
Pig iron Fe, 4\% C, 1\% Si, 1\% Mn
Fe, 0.3\% C, 0.001\% Si, 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 \[\xrightarrow{\text{Distillation with or without vacuum}}\] 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.

\[
\text{ZrO} \xrightarrow{\text{Chloridizing}} \text{ZrCl}_2 \xrightarrow{\text{Reduction with Mg}} \text{Zirconium metal}
\]

Some volatile halides SnCl\(_4\), TiCl\(_4\), AlCl\(_3\) can be separated and purified by distillation.
Pyrometallurgical Extraction Processes

Ore concentrate (28% Cu) → Oxygen flash furnace → Sulfuric acid

O₂ → Flux → SO₂ → Slag

Copper matte (Cu (50%) + Fe + S) → Converter furnace → SO₂ → Fe in process gas

Air → Blister copper (98% Cu + O) → Converter furnace → CO₂

Natural gas → Anode furnace → Anode copper (98-99% Cu)

Oxygen Flash Furnace

CuFeS₂ + O₂ → CuS + FeO + SO₂

Chalcopyrite CuFeS₂

Sand, SiO₂
Limestone, CaCO₃

CaCO₃ + SiO₂ → CaSiO₃
FeO + SiO₂ → FeSiO₃

Converter: Cu₂S + O₂ → Cu (matte copper) + SO₂

C. Ophardt et al, 1997
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

Sulphide concentrate \[ \text{FeS}_2 \] \[ \text{Exothermic Roasting} \] \[ \text{Steam production} \]
\[ \text{Fe}_2\text{O}_3 + \text{SO}_2 \]

Solid fuels
Natural – Wood, peat, lignite coal, bituminous coal, anthracite coal
Artificial – Pulverized coal, briquetted fuels, carbonized fuels (charcoal, coke)

Liquid fuels
Natural – Petroleum
Artificial – Distilled oils, coal tar, residual oils (fuel oil)

Gaseous fuels
Natural – Natural gas (\( \text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8 \))
Artificial – Coal gas, oils gas, blast furnace gas (\( \text{N}_2, \text{CO}, \text{H}_2, \text{CO}_2 \))
For effective control on a metallurgical process consisting of multiple reactions, engineers have to carefully keep detailed account of each element in each species taking place in all reactions.

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 estimation of sample composition with high accuracies.
Analyses of metallurgical interest

1. Ultimate analysis: Percentages of elements are reported

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>46.60</td>
</tr>
<tr>
<td>Al</td>
<td>35.85</td>
</tr>
<tr>
<td>Ca</td>
<td>3.63</td>
</tr>
</tbody>
</table>

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

Ultimate analysis can be combined with the information from XRD analysis to obtain rational Phases present in the sample: $\text{Al}_2\text{O}_3$, $\text{CaO}$,...

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>80.45</td>
</tr>
<tr>
<td>CaO</td>
<td>5.72</td>
</tr>
</tbody>
</table>

3. Mineralogical analysis: Rational analysis given in terms of percent minerals making up sample

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corundum</td>
<td>80.45</td>
</tr>
<tr>
<td>Limestone</td>
<td>5.72</td>
</tr>
</tbody>
</table>

3. 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 desolvated, vaporized, and atomized by a flame, discharge, or plasma (Inductively Coupled Plasma).

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 interchangeably

Orsat apparatus consists of a measuring burette to take about 100 cm$^3$ 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

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