Materials and Energy Balance

Charge calculations in pyrometallurgical processes
Charge calculations are carried out prior to operating a metallurgical process to determine the quantity of each type of raw material fed to the furnace in order to obtain the desired quantity of products.

It is similar to stoichiometric problems but the engineer has to have a detailed knowledge on the internal working of the process in order to write the relevant reactions.

Material balance by careful and detailed tracking of all elements in the input and output is the prerequisite of heat balance and complete definition of the system.

Multiple reactions in metallurgical process makes it hard to keep track of all the chemical species in the reactants and products.

Complex charge calculation problems can be solved easily by simplifying assumptions, e.g. It is safe to assume in iron blast furnace that all CaO, MgO and Al₂O₃ of the charge end up in the slag. Also molten pig iron can be considered to contain all Fe coming from the ore. All CO₂ in the flue gases can be thought to originate from the reactions and air is simply O₂ and N₂.
Charge calculation problems

Hints for effective material balance:
1 – Read the question to understand the process and materials
2 – Draw a diagram
3 – Define a base
4 – Write down the reactions
5 – Do stoichiometric and materials balance calculations
6 – Check your calculations

Example – Combustion of coal in furnace

<table>
<thead>
<tr>
<th>Ultimate Analysis wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>Coal</td>
</tr>
</tbody>
</table>

Base: 1000 kg coal
C = 0.85*1000 = 850 kg
H = 0.05*1000 = 5 kg
N = 0.01*1000 = 10 kg
S = 0.02*1000 = 20 kg
O = 0.07*1000 = 70 kg

Air = O₂, N₂

Flue gases
CO₂
SO₂
H₂O
N₂

Chemical reactions
C + O₂ = CO₂
H₂ + 1/2O₂ = H₂O
S + O₂ = SO₂
Calculate the volume of air necessary for complete combustion

Stoichiometry calculation

\[ n_C = \frac{850}{12} = 70.83 \text{ kg-atom} \quad \rightarrow \quad C + O_2 = CO_2 \]
\[ n_{H_2} = \frac{50}{2} = 25 \text{ kg-mole} \quad \rightarrow \quad H_2 + \frac{1}{2}O_2 = H_2O \]
\[ n_S = \frac{20}{32} = 0.625 \text{ kg-atom} \quad \rightarrow \quad S + O_2 = SO_2 \]
\[ n_O = \frac{70}{16} = 4.375 \text{ kg-atom} \]
\[ n_{O_2} = 2.1875 \text{ kg-mole} \]

Total \( O_2 \) required = 81.7675 kg-mole

Volume of air = \( \frac{81.7675 \times 22.4}{0.21} \) = 8721 \( m^3 \) per 1000 kg coal
Excess reactants

5000 m³ of regenerator gas of following composition is used to heat an open hearth furnace at 300 C per hour:

<table>
<thead>
<tr>
<th>Material</th>
<th>CO</th>
<th>CO₂</th>
<th>H₂</th>
<th>CH₄</th>
<th>H₂O</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaseous fuel</td>
<td>22</td>
<td>6</td>
<td>10</td>
<td>3</td>
<td>3</td>
<td>56</td>
</tr>
</tbody>
</table>

Air at 800 C is consumed 20% in excess of the theoretical requirement

Gaseous fuel 5000 m³/hr
56% N₂, 22% CO, 10% H₂,
6% CO₂, 3% CH₄, 3% H₂O

Air 800 C
79% N₂, 21% O₂

Combustion reactions
CO + 1/2 O₂ = CO₂
H₂ + ½ O₂ = H₂O
CH₄ + 2O₂ = CO₂ + 2H₂O
Air at 800 C is consumed 20% in excess of the theoretical requirement

Calculate the volume of air required to burn 1 m$^3$ of regenerator gas

Basis: 1 m$^3$ of regenerator gas

Gas composition @ 300 C
- 0.22 m$^3$ CO
- 0.10 m$^3$ H$_2$
- 0.03 m$^3$ CH$_4$
- 0.06 m$^3$ CO$_2$
- 0.03 m$^3$ H$_2$O
- 0.56 m$^3$ N$_2$

Gas composition @ 0 C
- CO = 0.22*(273/573) = 0.105 m$^3$
- H$_2$ = 0.10*(273/573) = 0.048 m$^3$
- CH$_4$ = 0.03*(273/573) = 0.014 m$^3$
- CO$_2$ = 0.06*(273/573) = 0.028 m$^3$
- H$_2$O = 0.03*(273/573) = 0.014 m$^3$
- N$_2$ = 0.56*(273/573) = 0.267 m$^3$

O$_2$ requirements from combustion reactions
- CO + 1/2 O$_2$ = CO$_2$ \[ O_2 = 0.0525 \text{ m}^3 \]
- H$_2$ + ½ O$_2$ = H$_2$O \[ O_2 = 0.024 \text{ m}^3 \]
- CH$_4$ + 2O$_2$ = CO$_2$ + 2H$_2$O \[ O_2 = 0.028 \text{ m}^3 \]

Total $O_2 = 0.1045 \text{ m}^3$

Volume of $O_2$ at STP = 0.1045 m$^3$
Volume of $O_2$ at 800 C = 0.412 m$^3$
Theoretical air volume = $0.421/0.21$ = 1.96 m$^3$
Real air volume = 1.96*1.2 = 2.35 m$^3$
Air at 800 C is consumed 20% in excess of the theoretical requirement

Calculate the composition of flue gases

Basis: 1 m$^3$ of regenerator gas

Gas composition @ STP

<table>
<thead>
<tr>
<th>Gas</th>
<th>STP Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>0.105 m$^3$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.048 m$^3$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.014 m$^3$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.028 m$^3$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.014 m$^3$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.267 m$^3$</td>
</tr>
</tbody>
</table>

Air composition @ STP

<table>
<thead>
<tr>
<th>Gas</th>
<th>STP Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>0.1255 m$^3$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.472 m$^3$</td>
</tr>
</tbody>
</table>

Flue gas composition

<table>
<thead>
<tr>
<th>Gas</th>
<th>STP Composition</th>
</tr>
</thead>
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<tr>
<td>CO$_2$</td>
<td>0.105 m$^3$</td>
</tr>
<tr>
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</tr>
<tr>
<td>N$_2$</td>
<td>0.267 m$^3$</td>
</tr>
</tbody>
</table>

Gaseous fuel 5000 m$^3$/hr

56% N$_2$, 22% CO, 10% H$_2$
6% CO$_2$, 3% CH$_4$, 3% H$_2$O
Nitriding Gas Treatment

Iron is nitrided by passing a mixture of gaseous ammonia and hydrogen through a furnace at 500 °C, 1 atm.

Reactions

\[ \text{NH}_3 = \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \]

\[ \frac{1}{2} \text{N}_2 = \text{N} \]

Calculate the amount of nitrogen, in gram/hr, that the iron picks up from the gas flowing in at a rate of 50 ml/min at 500 °C.

Basis: 3000 ml/hours of gas input

Input | Output
--- | ---
\( \text{NH}_3 = 300 \text{ ml} \) | \( \text{NH}_3 = (300-x) \text{ ml} \) where \( x \) is volume of decomposed \( \text{NH}_3 \)
\( \text{H}_2 = 2700 \text{ ml} \) | \( \text{H}_2 = (2700+3/2x) \text{ ml} \)
Total = 3000 ml | Total = 3000+1/2x

\[ \%\text{NH}_3 = \frac{7}{100} = \frac{(300-x)}{(3000+x/2)} \]

volume of decomposed \( \text{NH}_3 \), \( x = 86.96 \text{ ml} \)

\[ \text{NH}_3 = \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \longrightarrow \text{N}_2 \text{ generated per hour} = \frac{1}{2}x = \frac{1}{2}*86.96 = 43.48 \text{ ml} \]

\[ \frac{1}{2} \text{N}_2 = \text{N} \longrightarrow \text{N dissolved in steel} = 14 \text{ g/11200 ml} \text{ N}_2 = 0.5475 \text{ g N / 43.48 ml N}_2 \]

Rational Gas Analysis wt%

<table>
<thead>
<tr>
<th>Material</th>
<th>NH(_3)</th>
<th>H(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incoming gas</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>Outlet gas</td>
<td>7</td>
<td>93</td>
</tr>
</tbody>
</table>

Gas output 93% H\(_2\), 7% NH\(_3\)
Calcination
Calcination is a thermal treatment process applied to ores and other solid materials in order to induce removal of volatile components like CO$_2$ and H$_2$O by thermal decomposition.

Inputs – Solid ore, fuel gas, air
Outputs – Solid calcine, off-gas

Calcination temperature is below the melting point of the components of the raw material. Solid ores are treated in the solid state and the product is also solid except the volatile components.

Components of fuel gas are typically CO, hydrogen, oxygen and hydrocarbons which are the combustible components and CO$_2$, N$_2$ which are the diluents that do not take part in the combustion.
Calcination example
Limestone is not the preferred flux in various steel making processes since its decomposition is associated with a large amount of absorption of energy.
Charging of lime after calcination of limestone is more energy efficient.

Rotary kiln is very often used to produce lime by calcination of limestone.
Rotary kilns are very long kilns that rotate 2 to 3 degree from the horizontal axis.
The feed enters and from other side, the calcine material discharges and they are frequently heated by an externals source of energy.

Other commercial uses of rotary kiln is cement and the removal of water from alumina.
Calcination furnace analysis
Magnesium carbonate is decomposed to make MgO and CO₂ by heating in a rotary kiln, using as fuel a natural gas
CO₂ formed by decomposition of magnesium carbonate mixes with the products of combustion to form the flue gas product
Fuel consumption is 250 m³/ton MgO at STP

<table>
<thead>
<tr>
<th>Rational Gas Analysis wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>Natural gas</td>
</tr>
<tr>
<td>Flue gas</td>
</tr>
</tbody>
</table>

Basis 1000 kg of MgO
Ore
MgCO₃

Flue gases
73.45% N₂
4.55% O₂
22% CO₂

Rotary Kiln
Air
Fuel 250 m³/ton MgO
Calcine
MgO

Reactions
MgCO₃ = MgO + CO₂
CH₄ + 2O₂ = 2H₂O + CO₂
C₂H₆ + 7/2O₂ = 3H₂O + 2CO₂
C₃H₈ + 5O₂ = 4H₂O + 3CO₂
Calculate the air consumption in m³ per ton of MgO produced

Reactions

\[
\begin{align*}
\text{MgCO}_3 & = \text{MgO} + \text{CO}_2 \\
\text{CH}_4 + 2\text{O}_2 & = 2\text{H}_2\text{O} + \text{CO}_2 \\
\text{C}_2\text{H}_6 + 7/2\text{O}_2 & = 3\text{H}_2\text{O} + 2\text{CO}_2 \\
\text{C}_3\text{H}_8 + 5\text{O}_2 & = 4\text{H}_2\text{O} + 3\text{CO}_2
\end{align*}
\]

\[\text{CO}_2 \text{ balance}\]

\[
\begin{align*}
\text{kg-mole MgO} & = 1000/\text{MW}_{\text{MgO}} = 25 \text{ kg-mole} = \text{CO}_2 \text{ from MgCO}_3 \\
\text{kg-mole CH}_4 & = 250*(80/100) = 200 \text{ m}^3/\text{ton MgO} = 8.93 \text{ kg-mole CH}_4 \\
& = 8.93 \text{ kg-mole CO}_2 \\
\text{kg-mole C}_2\text{H}_6 & = 250*(15/100) = 37.5 \text{ m}^3/\text{ton MgO} = 1.67 \text{ kg-mole C}_2\text{H}_6 \\
& = 2*1.67 \text{ kg-mole C}_2\text{H}_6 = 3.34 \text{ kg-mole CO}_2 \\
\text{kg-mole C}_3\text{H}_8 & = 250*(5/100) = 12.5 \text{ m}^3/\text{ton MgO} = 0.56 \text{ kg-mole C}_3\text{H}_8 \\
& = 3*0.56 \text{ kg-mole C}_3\text{H}_8 = 1.68 \text{ kg-mole CO}_2
\end{align*}
\]

Total kg-mole CO₂ = 25 + 8.93 + 3.34 + 1.68 = 38.95 kg-mole

Total flue gas = 38.95*(100/22) = 177.05 kg-mole

Total N₂ = 177.05*(73.45/100) = 130.04 kg-mole N₂

Since N₂ in air = N₂ in flue gas, Air consumption = 130.04*(100/79) = 164.6 kg-mole air/ ton MgO

= 164.6*22.4 = 3687 m³ (STP) / ton MgO
Calculate the percent excess air

Excess $O_2 = 177.05 \times (4.55/100) = 8.055 \text{ kg-mole}$
Excess air $= 8.055 \times (100/21) = 38.36 \text{ kg-mole}$
% Excess air $= (38.36/(164.6-38.36))\times100 = 30.38$

Theoretical air $= 164.6-38.36 = 126.24 \text{ kg-mole}$
Roasting

Roasting is a preliminary step of metal extraction from sulphide ores. The process is partial or complete conversion of metal sulphide to oxide, sulphate or chlorides. Oxide can be easily reduced; sulphate and chloride can be easily dissolved.

Sulphide ores cannot be used to produce metal by pyrometallurgy. It is very difficult to reduce sulphide directly into the metal. Carbon and hydrogen are not effective reducing agent to produce metal from sulphide as seen in the Ellingham diagram.

Another issue with direct reduction of metal sulphides is that there exist a mutual solubility between metal and sulphides which makes it difficult to extract the metal by pyrometallurgy.

So the only route is to convert sulphide to oxide.

Inputs – Sulphide ore, air, fuel if necessary
Outputs – Calcine, off-gas
Roasting is carried out below the melting point of the components of the ore.
By virtue of this, the roast product is in solid state in addition to the solid ore concentrate.

Temperatures involved during roasting is of the order of 900 to 1100 degrees Celsius.

Byproducts of roasting are rich in SO$_2$ because sulphide ore has 20-30 % sulphur depending on the deposit.
So a large amount of a SO$_2$, SO$_3$ and nitrogen will be produced as the off-gas.
These sulphurous gases are used to produce H$_2$SO$_4$.

Oxidation of sulphides is exothermic and can supply all the energy needed for roasting to be self-sustaining.

Heats of formation of some sulphides:

- Cu$_2$S = -18950 kilocalories per kg mole
- ZnS = -44000 kilocalories per kg mole
- FeS$_2$ = -35500 kilocalories per kg mole
- CuO = -37100 kilocalories per kg mole
- SO$_2$ = -70940 kilocalories per kg mole
- SO$_3$ = -93900 kilocalories per kg mole
- CO$_2$ = -94450 kilocalories per kg mole
- CO = -26840 kilocalories per kg mole

\[
\text{Cu}_2\text{S} + \text{O}_2 = 2\text{CuO} + \text{SO}_2
\]

Heat generated by oxidation reaction:
-136900 kilocalories per kg mole

If fuel is also used, there is also carbon dioxide and carbon monoxide in the off-gas.
Types of roasting

Oxidizing roasting
Sulphide ore is oxidized by passing air and providing an oxidizing atmosphere. The amount of oxidation must be controlled so that the formation of metal sulphate is avoided if it is not desired. e.g. \( \text{PbS} + \text{O}_2 = \text{PbSO}_4 \) and \( \text{PbO} \)
High temperature is required to break up the metal sulphate

In dead roasting all sulphur is eliminated. However, if the extraction of metal is to be done through hydrometallurgical means, sulphate formation is preferred because sulphates dissolve easily in the solvent.

Sulphatising roasting
As the name suggests the objective is to convert all sulphide into sulphate in an oxidizing atmosphere.

Chloridizing roasting
The objective of chloridizing roasting is to convert a metal sulphide or oxide into chlorides. e.g. \( 2\text{NaCl} + \text{MS} + 2\text{O}_2 = \text{Na}_2\text{SO}_4 + \text{MCl}_2 \) direct chlorination
\( 4\text{NaCl} + 2\text{MO} + \text{S}_2 + 3\text{O}_2 = 2\text{Na}_2\text{SO}_4 + 2\text{MCl}_2 \) indirect chlorination
Roasting furnace analysis
Pyrometallurgical extraction of ores rich in CuS, FeS₂, ZnS is uneconomical due the difficulties involved in concentrating the ore
Roasting is needed to remove all of the sulfur and subsequently to leach the ore in dilute sulfuric acid for the recovery of copper and zinc by hydrometallurgical methods

Rational Analysis wt%

<table>
<thead>
<tr>
<th>Material</th>
<th>CuS</th>
<th>FeS₂</th>
<th>ZnS</th>
<th>SiO₂</th>
<th>S</th>
<th>CaO, Al₂O₃, etc</th>
<th>SO₂</th>
<th>SO₃</th>
<th>O₂, N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore</td>
<td>6</td>
<td>25</td>
<td>4</td>
<td>20</td>
<td>33.6</td>
<td>11.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Roast gases</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>Flue gases</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.5</td>
<td>0.4</td>
<td>97.1</td>
</tr>
</tbody>
</table>

Copper, iron and zinc of the ore oxidize to CuO, Fe₂O₃ and ZnO
Basis 1000 kg of copper ore

Ore
4% Zn as ZnS
6% Cu as CuS
25% Fe as FeS₂
20% SiO₂
11.4% CaO, Al₂O₃, etc
33.6% S

Reactions
CuS + 3/2O₂ = CuO + SO₂
2FeS₂ + 11/2O₂ = Fe₂O₃ + 4SO₂
ZnS + 3/2O₂ = ZnO + SO₂
SO₂ + 1/2O₂ = SO₃
Basis 1000 kg of copper ore
Ore
4% Zn as ZnS
6% Cu as CuS
25% Fe as FeS₂
20% SiO₂
11.4% CaO, Al₂O₃, etc
33.6% S
Air
Calcine
ZnO SiO₂
CuO CaO, Al₂O₃
Fe₂O₃
Leaching
Flue gases
2.5% SO₂
0.4% SO₃
O₂, N₂

Calculate the weight and approximate analysis of the calcine resulting from roasting 1 ton ore.
Base: 1000 kg ore
Input 1000 kg
Cu  60 kg
Fe  250 kg
Zn  40 kg
SiO₂ 200 kg
CaO, Al₂O₃, etc 114 kg
S  336 kg
Total 1000 kg

Output
CuO 60*(80/64) = 75 kg
Fe₂O₃ 250*(160/112) = 357 kg
ZnO 40*(81/65) = 50 kg
SiO₂ 200 kg
CaO, Al₂O₃, etc 114 kg
Total solids 796 kg

CuO = (75/796)*100 = 9.4%  Fe₂O₃ = (357/796)*100 = 44.9%
ZnO = (50/796)*100 = 6.3%  SiO₂ = (200/796)*100 = 25.1%
Others (CaO, Al₂O₃, etc) = (114/796)*100 = 14.3%
Calculate the volume of flue gases per ton of ore

Reactions

\[
\text{CuS} + \frac{3}{2}\text{O}_2 = \text{CuO} + \text{SO}_2
\]

\[
V_{\text{SO}_2} = 22.4 * 1 * \left( \frac{60 * 96}{64 * 96} \right) = 21 \text{ m}^3
\]

\[
2\text{FeS}_2 + \frac{11}{2}\text{O}_2 = \text{Fe}_2\text{O}_3 + 4\text{SO}_2
\]

\[
V_{\text{SO}_2} = 22.4 * 4 * \left( \frac{250 * 120}{120 * 112} \right) = 200 \text{ m}^3
\]

\[
\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3
\]

\[
V_{\text{SO}_2} = (235 - x) \text{ m}^3, \quad V_{\text{SO}_3} = x \text{ m}^3
\]

\[
\%\text{SO}_2 = \frac{2.5}{100} = \frac{(235-x)}{V_{\text{fluegas}}}
\]

\[
\%\text{SO}_3 = \frac{0.4}{100} = \frac{x}{V_{\text{fluegas}}}
\]

\[
V_{\text{fluegas}} = 8103.5 \text{ m}^3, \quad V_{\text{SO}_3} = x = 32.4 \text{ m}^3, \quad V_{\text{SO}_2} = 202.6 \text{ m}^3
\]
Calculate the volume roasting air, percent excess and the composition of the flue gases

Roasting reactions

\[
\begin{align*}
\text{CuS} + \frac{3}{2}O_2 &= \text{CuO} + \text{SO}_2 \\
2\text{FeS}_2 + \frac{11}{2}O_2 &= \text{Fe}_2\text{O}_3 + 4\text{SO}_2 \\
\text{ZnS} + \frac{3}{2}O_2 &= \text{ZnO} + \text{SO}_2 \\
\text{SO}_2 + \frac{1}{2}O_2 &= \text{SO}_3
\end{align*}
\]

Volume of \(O_2\) required

\[
\begin{align*}
V_{O_2} &= 22.4 \times \frac{3}{2} \times \left( \frac{60 \times 96}{96} \right) = 31.5 \text{ m}^3 \\
V_{O_2} &= 22.4 \times \frac{11}{2} \times \left( \frac{250 \times 120}{120} \right) = 275 \text{ m}^3 \\
V_{O_2} &= 22.4 \times \frac{3}{2} \times \left( \frac{40 \times 65}{97} \right) = 21 \text{ m}^3 \\
V_{O_2} &= 32.4 \times \frac{1}{2} = 16.2 \text{ m}^3
\end{align*}
\]

Theoretical air requirement \(V_{\text{air-th}} = (343.7/0.21) = 1636.67 \text{ m}^3\)

Percentage of excess air has to be calculated from \(O_2+N_2\) balance in order to obtain actual air

\[
\begin{align*}
V_{O_2+N2} &= V_{\text{air-th}} + V_{\text{excess}} - V_{O_2\text{consumed}} \\
7868.5 &= 1636.67 + 1636.67 \times y - 343.7 \\
y &= 4.02, V = 1636.67 + 1636.7 \times 4.02 = 8216.07 \text{ m}^3 \\
V_{O_2\text{excess}} &= 8216.07 \times 0.21 - 343.7 = 1381.67 \text{ m}^3, V_{N2} = 8216.07 \times 0.79 = 6490.69 \text{ m}^3
\end{align*}
\]
Smelting
It is a unit process similar to roasting, to heat a mixture of ore concentrate above the melting point
The objective is to separate the gangue mineral from liquid metal or matte
The state of the gangue mineral in case of smelting is liquid which is the main difference between roasting and smelting

Inputs – Ore, flux, fuel, air
Output – Metal or Matte, slag

When metal is separated as sulphide from smelting of ore, it is called Matte smelting
e.g. Cu$_2$S and FeS
When metal is separated as liquid, it is called reduction smelting
e.g. Ironmaking

Density of liquid metal or matte is around 5-5.5 g/cm$^3$
Density of slag is around 2.8-3 g/cm$^3$

The additives and fluxes serve to convert the waste or gangue materials in the charge into a low melting point slag which also dissolves the coke ash and removes sulphur
Ironmaking
About 1 billion tonnes of iron is produced in the world annually by blast furnaces. Blast furnace economics are such that larger units have lower unit production costs, hence modern blast furnaces are bigger and produce more than 10000 tonnes per day.

The blast furnace is a counter-current reactor in which the descending column of burden materials reacts with the ascending hot gases. The process is continuous with raw materials being regularly charged to the top of the furnace and molten iron and slag being tapped from the bottom of the furnace at regular intervals.

Free moisture is driven off from the burden materials and hydrates and carbonates are disassociated. The burden starts to soften and melt, direct reduction of the iron and other oxides and carbonization by the coke occurs at 1,000-1,600 C. Molten iron and slag start to drip through to the bottom of the furnace.

In the combustion zone at 1,850-2,200 C, coke reacts with the oxygen and steam in the blast to form carbon monoxide and hydrogen, as well as heat iron and slag melt completely.
The blast furnace itself is a steel shaft lined with fire resistant, refractory materials. The hottest part of furnace - where the walls reach a temperature >300 °C - are water cooled.

Coke is a principle source of thermal energy and as well as chemical energy in ironmaking. Carbon of the coke reduces iron oxide to iron. The combustion of carbon of coke also provides a thermal energy.

Hot blast air is introduced through the tuyere so a counter current against the descending burden is created by the gases travelling upward.

In any counter current heat and mass exchange reactor, which consists of gas and solid, the permeability of the bed and the distribution of the burden are very important issues.

For the smooth operation of the blast furnace, the upward rising gases should travel unhindered. They should also transfer their heat and mass to the descending burden. The burden distribution should be homogeneous so that it constitutes a uniform distribution of iron and facilitate smooth movement of burden gases.
Carbon of coke reacts with $O_2$ at the tuyere level because of availability of oxygen
\[
C + (O_2 + 3.76N_2) = CO_2 + 3.76N_2 \\
CO_2 + 3.76N_2 + C = 2CO + 3.76N_2
\]

Upward gas rising consists of CO, CO$_2$ and nitrogen

A temperature approximately around 1900-2100 C is created as a result of reaction of carbon of coke with oxygen at the tuyere level
The exit temperature of the gas is approximately somewhere between 200 to 250 C during the discharge from the top of the furnace

The following reactions do not require very high percentage of carbon monoxide
So they can occur towards the upper region
\[
3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \\
Fe_3O_4 + CO = 3FeO + CO_2
\]

whereas, the reaction $FeO + CO = Fe + CO_2$ requires high concentration of CO
So it occurs near the middle of the furnace where the concentration of CO is high
At around 900 C, the equilibrium concentration of CO in the CO-CO$_2$ mixture is around 65 to 70 percent for FeO to be able to reduce to iron

Some iron oxide is also reduced by directly carbon
This reduction is endothermic in nature, whereas all other reactions are exothermic reduction.
Iron blast furnace analysis

Consider an iron blast furnace charged with iron ore, limestone and coke of following analyses:

<table>
<thead>
<tr>
<th>Rational Analysis wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>Ore</td>
</tr>
<tr>
<td>Limestone</td>
</tr>
<tr>
<td>Coke</td>
</tr>
</tbody>
</table>

The ultimate analysis of the pig iron gives 93.8% Fe, 4% C, 1.2% Si, 1% Mn
For every ton of pig iron produced, 1750 kg of iron ore and 500 kg limestone are used and 4200 m³ of flue gas is produced
The rational analysis of flue gases gives 58% N₂, 26% CO, 12% CO₂, 4% H₂O

Basis 1000 kg of pig iron

Ore 1750 kg
Limestone 500 kg
Coke
Air

Blast furnace gas 4200 m³
Slag
Pig iron 1000 kg

Reactions
Fe₂O₃ + 3CO = 2Fe + 3CO₂
SiO₂ + 2C = Si + 2CO
CaCO₃ = CaO + CO₂
MnO + C = Mn + CO
C + 1/2O₂ = CO
CO₂ + C = 2CO
Basis 1000 kg of pig iron
Ore 1750 kg
80% Fe₂O₃, 12% SiO₂, 1% MnO, 3% Al₂O₃, 4% H₂O
Limestone 500 kg
95% CaCO₃, 1% H₂O, 4% SiO₂
Coke
10% SiO₂, 90% C
Air
Blast furnace gas 4200 m³
58% N₂, 26% CO, 12% CO₂, 4% H₂O
Slag
Pig iron 1000 kg
93.8% Fe, 4% C, 1.2% Si, 1% Mn

Reactions
Fe₂O₃ + 3CO = 2Fe + 3CO₂
CaCO₃ = CaO + CO₂
C + 1/2O₂ = CO
SiO₂ + 2C = Si + 2CO
MnO + C = Mn + CO
CO₂ + C = 2CO

Calculate the quantity of coke used per ton of pig iron
Carbon balance:
C_{coke} + C_{limestone} = C_{pig iron} + C_{flue gas}
let x be the weight of coke

\[
0.9x + \frac{0.95 \times 500 \times 12}{12} = \frac{0.04 \times 1000}{12} + \frac{4200 \times 0.26}{22.4} + \frac{4200 \times 0.12}{22.4}
\]

0.075x + 4.75 = 3.333 + 71.25,
\[
x = \frac{69.833}{0.075} = 931 \text{ kg coke per ton of pig iron}
\]

Calculate the air consumption per ton of pig iron
N₂ balance:
N₂(air) = N₂(flue gas) = 4200 \times 0.58 = 2436 m³,
Air consumption = 2436 \times \left(\frac{100}{79}\right) = 3083.5 m³
Calculate the composition of the slag

**Fe₂O₃ balance:**

\[ \text{Fe}_2\text{O}_3(\text{ore}) = \text{Fe}_2\text{O}_3(\text{pig iron}) + \text{Fe}_2\text{O}_3(\text{slag}) \]

\[ 1750 \times 0.8 = 0.938 \times 1000 \times \left(\frac{160}{112}\right) + \text{Fe}_2\text{O}_3(\text{slag}) \]

\[ \text{Fe}_2\text{O}_3(\text{slag}) = 1400 - 1340 = 60 \text{ kg} \]

**SiO₂ balance:**

\[ \text{SiO}_2(\text{ore}) + \text{SiO}_2(\text{limestone}) + \text{SiO}_2(\text{coke}) = \text{SiO}_2(\text{pig iron}) + \text{SiO}_2(\text{slag}) \]

\[ 1750 \times 0.12 + 500 \times 0.04 + 931 \times 0.1 = 0.012 \times 1000 \times \left(\frac{60}{28}\right) + \text{SiO}_2(\text{slag}) \]

\[ \text{SiO}_2(\text{slag}) = 210 + 20 + 93.1 - 25.7 = 297.4 \text{ kg} \]

**MnO balance:**

\[ \text{MnO}_{(\text{ore})} = \text{MnO}_{(\text{pig iron})} + \text{MnO}_{(\text{slag})} \]

\[ 1750 \times 0.01 + 0.01 \times 1000 \times \left(\frac{71}{55}\right) + \text{MnO}_{(\text{slag})} \]

\[ \text{MnO}_{(\text{slag})} = 17.5 - 12.9 = 4.6 \text{ kg} \]

**Al₂O₃ balance:**

\[ \text{Al}_2\text{O}_3(\text{ore}) = \text{Al}_2\text{O}_3(\text{slag}) = 1750 \times 0.03 = 52.5 \text{ kg} \]

**CaO balance:**

\[ \text{CaO}_{(\text{limestone})} = \text{CaO}_{(\text{slag})} = 500 \times \left(\frac{56}{100}\right) \times 0.95 = 266 \text{ kg} \]

**Total slag composition:**

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass (kg)</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>60</td>
<td>8.82%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>297.4</td>
<td>43.70%</td>
</tr>
<tr>
<td>MnO</td>
<td>4.6</td>
<td>0.67%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>52.5</td>
<td>7.71%</td>
</tr>
<tr>
<td>CaO</td>
<td>266</td>
<td>39.10%</td>
</tr>
<tr>
<td>Total</td>
<td>680.5</td>
<td></td>
</tr>
</tbody>
</table>