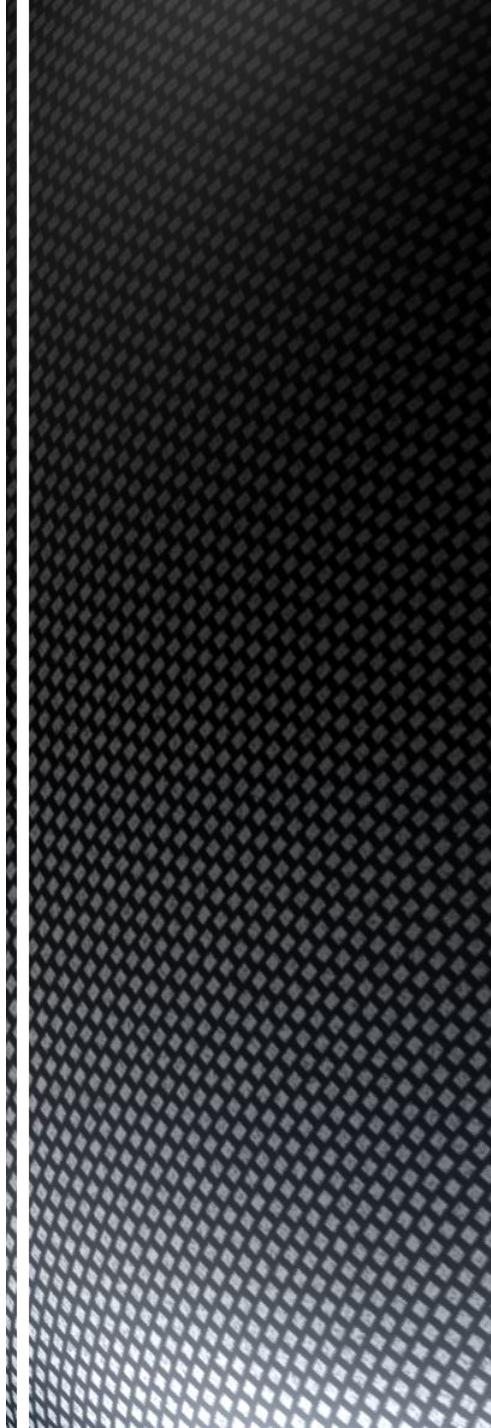


# Materials and Energy Balance

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  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  of the charge end up in the slag

Also molten pig iron can be considered to contain all Fe coming from the ore

All  $\text{CO}_2$  in the flue gases can be thought to originate from the reactions and air is simply  $\text{O}_2$  and  $\text{N}_2$

## 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

Ultimate Analysis wt%					
Material	C	H	N	S	O
Coal	85	5	1	2	7

Base: 1000 kg coal

$$C = 0.85 \cdot 1000 = 850 \text{ kg}$$

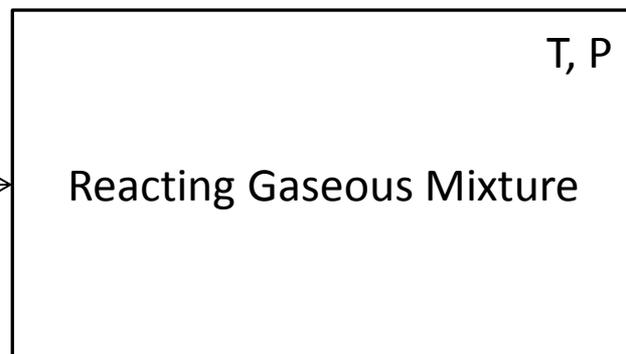
$$H = 0.05 \cdot 1000 = 5 \text{ kg}$$

$$N = 0.01 \cdot 1000 = 10 \text{ kg}$$

$$S = 0.02 \cdot 1000 = 20 \text{ kg}$$

$$O = 0.07 \cdot 1000 = 70 \text{ kg}$$

Air = O<sub>2</sub>, N<sub>2</sub>



Chemical reactions

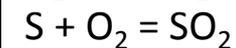
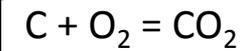
Flue gases

CO<sub>2</sub>

SO<sub>2</sub>

H<sub>2</sub>O

N<sub>2</sub>



Base: 1000 kg coal

$$C = 0.85 \cdot 1000 = 850 \text{ kg}$$

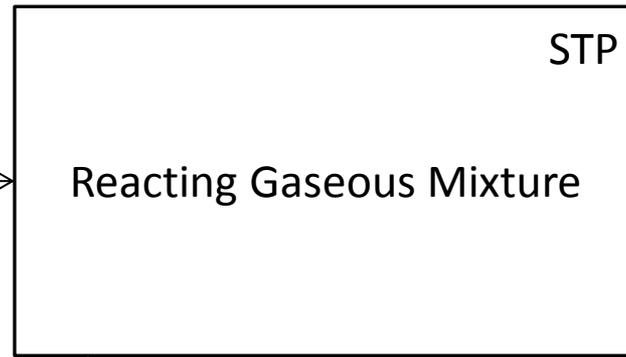
$$H = 0.05 \cdot 1000 = 5 \text{ kg}$$

$$N = 0.01 \cdot 1000 = 10 \text{ kg}$$

$$S = 0.02 \cdot 1000 = 20 \text{ kg}$$

$$O = 0.07 \cdot 1000 = 70 \text{ kg}$$

Air = O<sub>2</sub>, N<sub>2</sub>



STP

Flue gases

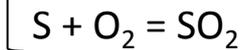
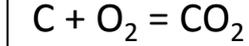
CO<sub>2</sub>

SO<sub>2</sub>

H<sub>2</sub>O

N<sub>2</sub>

Chemical reactions



Calculate the volume of air necessary for complete combustion

Stoichiometry calculation

$$n_C = 850/12 = 70.83 \text{ kg-atom} \longrightarrow C + O_2 = CO_2$$

$$n_{H_2} = 50/2 = 25 \text{ kg-mole} \longrightarrow H_2 + 1/2O_2 = H_2O$$

$$n_S = 20/32 = 0.625 \text{ kg-atom} \longrightarrow S + O_2 = SO_2$$

$$n_O = 70/16 = 4.375 \text{ kg-atom} \quad n_{O_2} = 2.1875 \text{ kg-mole}$$

$$O_2 \text{ required} = 70.83 \text{ kg-mole}$$

$$O_2 \text{ required} = 12.5 \text{ kg-mole}$$

$$O_2 \text{ required} = 0.625 \text{ kg-mole}$$

$$O_2 \text{ from coal} = 2.1875 \text{ kg-mole}$$

$$\underline{\text{Total } O_2 \text{ required} = 81.7675 \text{ kg-mole}}$$

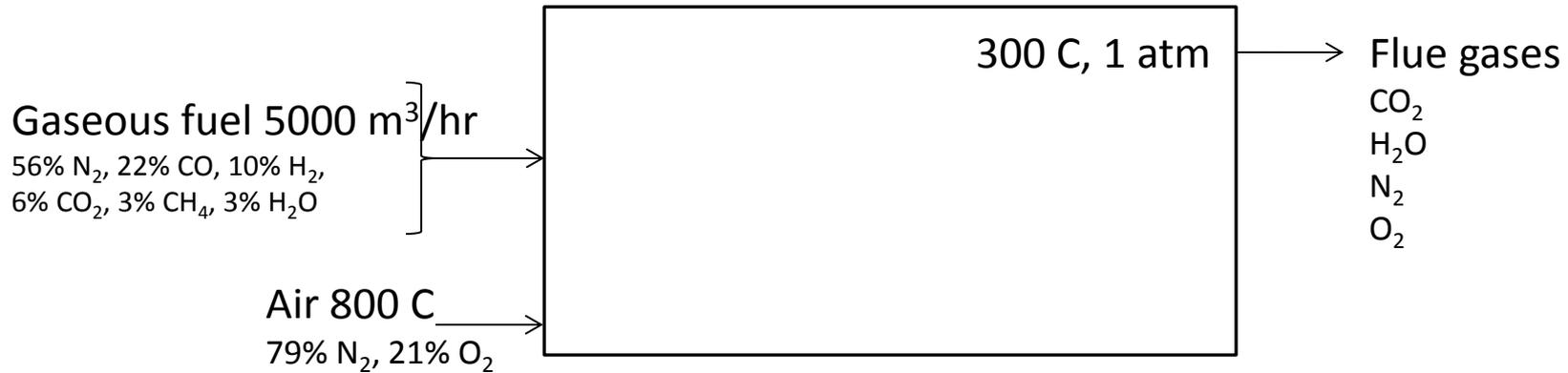
$$\text{Volume of air} = \frac{81.7675 \cdot 22.4}{0.21} = 8721 \text{ m}^3 \text{ per 1000 kg coal}$$

## Excess reactants

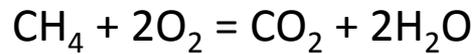
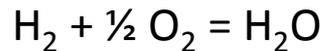
5000 m<sup>3</sup> of regenerator gas of following composition is used to heat an open hearth furnace at 300 C per hour:

Rational Analysis wt%						
Material	CO	CO <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> O	N <sub>2</sub>
Gaseous fuel	22	6	10	3	3	56

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



### Combustion reactions



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



Calculate the volume of air required to burn 1 m<sup>3</sup> of regenerator gas

Basis: 1 m<sup>3</sup> of regenerator gas

Gas composition @ 300 C

0.22 m<sup>3</sup> CO

0.10 m<sup>3</sup> H<sub>2</sub>

0.03 m<sup>3</sup> CH<sub>4</sub>

0.06 m<sup>3</sup> CO<sub>2</sub>

0.03 m<sup>3</sup> H<sub>2</sub>O

0.56 m<sup>3</sup> N<sub>2</sub>

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_1 = P_2 = 1 \text{ atm}$$

$$V_1 = V_2 \frac{T_1}{T_2}$$

Gas composition @ 0 C

CO = 0.22\*(273/573) = 0.105 m<sup>3</sup>

H<sub>2</sub> = 0.10\*(273/573) = 0.048 m<sup>3</sup>

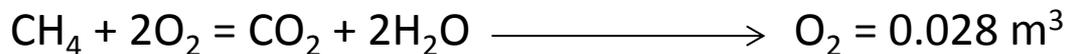
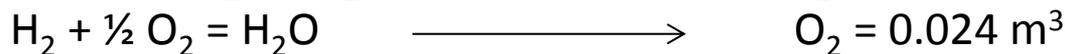
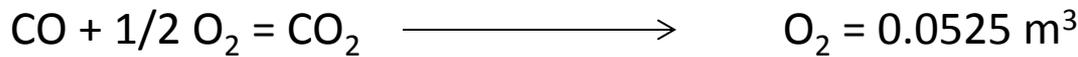
CH<sub>4</sub> = 0.03\*(273/573) = 0.014 m<sup>3</sup>

CO<sub>2</sub> = 0.06\*(273/573) = 0.028 m<sup>3</sup>

H<sub>2</sub>O = 0.03\*(273/573) = 0.014 m<sup>3</sup>

N<sub>2</sub> = 0.56\*(273/573) = 0.267 m<sup>3</sup>

O<sub>2</sub> requirements from combustion reactions



$$\text{Total O}_2 = 0.1045 \text{ m}^3$$

Volume of O<sub>2</sub> at STP = 0.1045 m<sup>3</sup>

Volume of O<sub>2</sub> at 800 C = 0.412 m<sup>3</sup>

Theoretical air volume = 0.421/0.21  
= 1.96 m<sup>3</sup>

Real air volume = 1.96\*1.2 = 2.35 m<sup>3</sup>

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



Calculate the composition of flue gases

Basis: 1 m<sup>3</sup> of regenerator gas

Gas composition @ STP

$$\text{CO} = 0.22 \cdot (273/573) = 0.105 \text{ m}^3$$

$$\text{H}_2 = 0.10 \cdot (273/573) = 0.048 \text{ m}^3$$

$$\text{CH}_4 = 0.03 \cdot (273/573) = 0.014 \text{ m}^3$$

$$\text{CO}_2 = 0.06 \cdot (273/573) = 0.028 \text{ m}^3$$

$$\text{H}_2\text{O} = 0.03 \cdot (273/573) = 0.014 \text{ m}^3$$

$$\text{N}_2 = 0.56 \cdot (273/573) = 0.267 \text{ m}^3$$

Air composition @ STP

$$\text{O}_2 = 0.1045 \cdot 1.2 = 0.1255 \text{ m}^3$$

$$\text{N}_2 = 0.1255 \cdot (79/21) = 0.472 \text{ m}^3$$

Flue gas composition

$$\text{CO}_2 = \text{CO}_{2(\text{combustion1})} + \text{CO}_{2(\text{combustion3})} + \text{CO}_{2(\text{gas})} = 0.105 + 0.014 + 0.028 = 0.147 \text{ m}^3 / 14.8\%$$

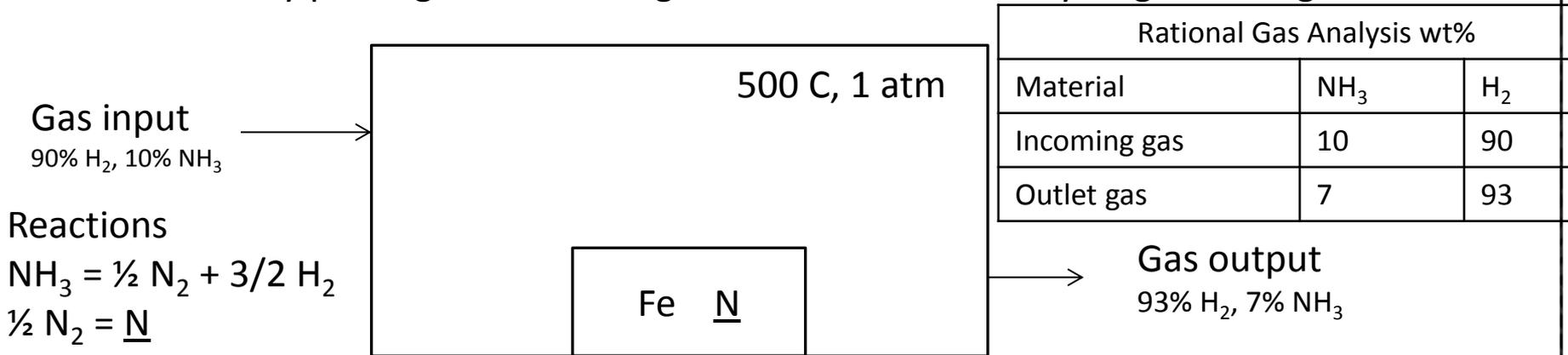
$$\text{H}_2\text{O} = \text{H}_2\text{O}_{(\text{combustion2})} + \text{H}_2\text{O}_{(\text{combustion3})} + \text{H}_2\text{O}_{(\text{gas})} = 0.048 + 0.028 + 0.014 = 0.090 \text{ m}^3 / 9.1\%$$

$$\text{N}_2 = \text{N}_{2(\text{gas})} + \text{N}_{2(\text{air})} = 0.267 + 0.472 = 0.739 \text{ m}^3 / 74.0\%$$

$$\text{O}_2 = \text{O}_{2(\text{air})} - \text{O}_{2(\text{combustion1,2,3})} = 0.1255 - 0.1045 = 0.021 \text{ m}^3 / 2.1\%$$

## Nitriding Gas Treatment

Iron is nitrided by passing a mixture of gaseous ammonia and hydrogen through a furnace



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	
NH <sub>3</sub> = 300 ml	NH <sub>3</sub> = (300-x) ml	where x is volume of decomposed NH <sub>3</sub>
H <sub>2</sub> = 2700 ml	H <sub>2</sub> = (2700+3/2x) ml	
Total = 3000 ml	Total = 3000+1/2x	
%NH <sub>3</sub> = 7/100 = (300-x)/(3000+x/2)		volume of decomposed NH <sub>3</sub> , x = 86.96 ml

NH<sub>3</sub> = ½ N<sub>2</sub> + 3/2 H<sub>2</sub> —————> N<sub>2</sub> generated per hour = 1/2x = ½\*86.96 = 43.48 ml

½ N<sub>2</sub> = N —————> N dissolved in steel = 14 g/11200 ml N<sub>2</sub> = 0.5475 g N / 43.48 ml N<sub>2</sub>

## Calcination

Calcination is a thermal treatment process applied to ores and other solid materials in order to induce removal of volatile components like  $\text{CO}_2$  and  $\text{H}_2\text{O}$  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  $\text{CO}$ , hydrogen, oxygen and hydrocarbons which are the combustible components and  $\text{CO}_2$ ,  $\text{N}_2$  which are the diluents that do not take part in the combustion

## Calcination example

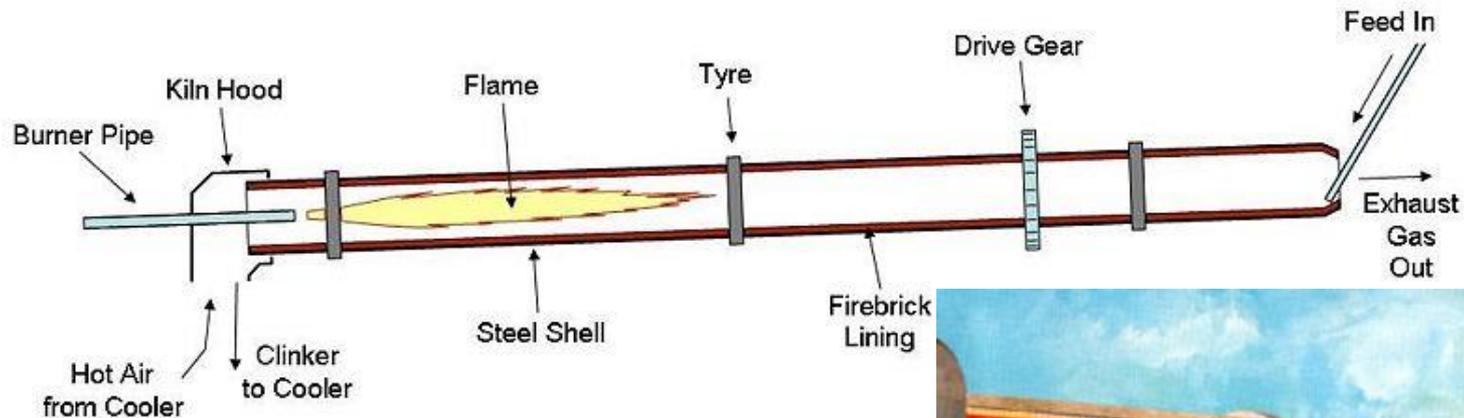
Limestone is not the preferred flux in various steel making processes since its decomposition is associated with a large amount of absorption of energy

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 external 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 CO<sub>2</sub> by heating in a rotary kiln, using as fuel a natural gas

CO<sub>2</sub> formed by decomposition of magnesium carbonate mixes with the products of combustion to form the flue gas product

Fuel consumption is 250 m<sup>3</sup>/ton MgO at STP

Rational Gas Analysis wt%						
Material	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	CO <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>
Natural gas	80	15	5			
Flue gas				22	73.45	4.55

Basis 1000 kg of MgO

Ore  
MgCO<sub>3</sub> →

Flue gases ←

73.45% N<sub>2</sub>  
4.55% O<sub>2</sub>  
22% CO<sub>2</sub>

Rotary Kiln

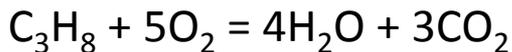
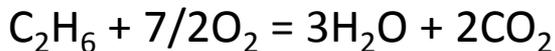
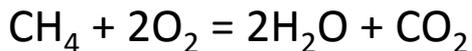
← Air

← Fuel 250 m<sup>3</sup>/ton MgO

→ Calcine  
MgO

80% CH<sub>4</sub>  
15% C<sub>2</sub>H<sub>6</sub>  
5% C<sub>3</sub>H<sub>8</sub>

### Reactions



Basis 1000 kg of MgO

Ore  
MgCO<sub>3</sub>

Flue gases  
73.45% N<sub>2</sub>  
4.55% O<sub>2</sub>  
22% CO<sub>2</sub>

Rotary Kiln

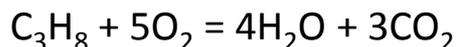
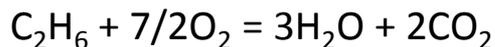
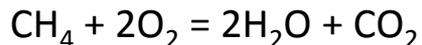
Air

Fuel 250 m<sup>3</sup>/ton MgO

Calcine  
1000 kg MgO  
80% CH<sub>4</sub>  
15% C<sub>2</sub>H<sub>6</sub>  
5% C<sub>3</sub>H<sub>8</sub>

Calculate the air consumption in m<sup>3</sup> per ton of MgO produced

Reactions



CO<sub>2</sub> balance

kg-mole MgO = 1000/MW<sub>MgO</sub> = 25 kg-mole = CO<sub>2</sub> from MgCO<sub>3</sub>

kg-mole CH<sub>4</sub> = 250\*(80/100) = 200 m<sup>3</sup>/ton MgO = 8.93 kg-mole CH<sub>4</sub>  
= 8.93 kg-mole CO<sub>2</sub>

kg-mole C<sub>2</sub>H<sub>6</sub> = 250\*(15/100) = 37.5 m<sup>3</sup>/ton MgO = 1.67 kg-mole C<sub>2</sub>H<sub>6</sub>  
= 2\*1.67 kg-mole C<sub>2</sub>H<sub>6</sub> = 3.34 kg-mole CO<sub>2</sub>

kg-mole C<sub>3</sub>H<sub>8</sub> = 250\*(5/100) = 12.5 m<sup>3</sup>/ton MgO = 0.56 kg-mole C<sub>3</sub>H<sub>8</sub>  
= 3\*0.56 kg-mole C<sub>3</sub>H<sub>8</sub> = 1.68 kg-mole CO<sub>2</sub>

Total kg-mole CO<sub>2</sub> = 25 + 8.93 + 3.34 + 1.68 = 38.95 kg-mole

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

Total N<sub>2</sub> = 177.05\*(73.45/100) = 130.04 kg-mole N<sub>2</sub>

Since N<sub>2</sub> in air = N<sub>2</sub> in flue gas, Air consumption = 130.04\*(100/79) = 164.6 kg-mole air/ ton MgO  
= 164.6\*22.4 = 3687 m<sup>3</sup> (STP) / ton MgO

Basis 1000 kg of MgO

Ore  $\text{MgCO}_3$   $\longrightarrow$

Flue gases  $\longleftarrow$   
177.05 kg-mole  
73.45%  $\text{N}_2$   
4.55%  $\text{O}_2$   
22%  $\text{CO}_2$

Rotary Kiln

$\longleftarrow$  Air 3687  $\text{m}^3$

$\longleftarrow$  Fuel 250  $\text{m}^3/\text{ton MgO}$

$\longrightarrow$  Calcine  
1000 kg MgO  
80%  $\text{CH}_4$   
15%  $\text{C}_2\text{H}_6$   
5%  $\text{C}_3\text{H}_8$

Calculate the percent excess air

$$\text{Excess O}_2 = 177.05 \cdot (4.55/100) = 8.055 \text{ kg-mole}$$

$$\text{Excess air} = 8.055 \cdot (100/21) = 38.36 \text{ kg-mole}$$

$$\% \text{ Excess air} = (38.36 / (164.6 - 38.36)) \cdot 100 = 30.38$$

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

# 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

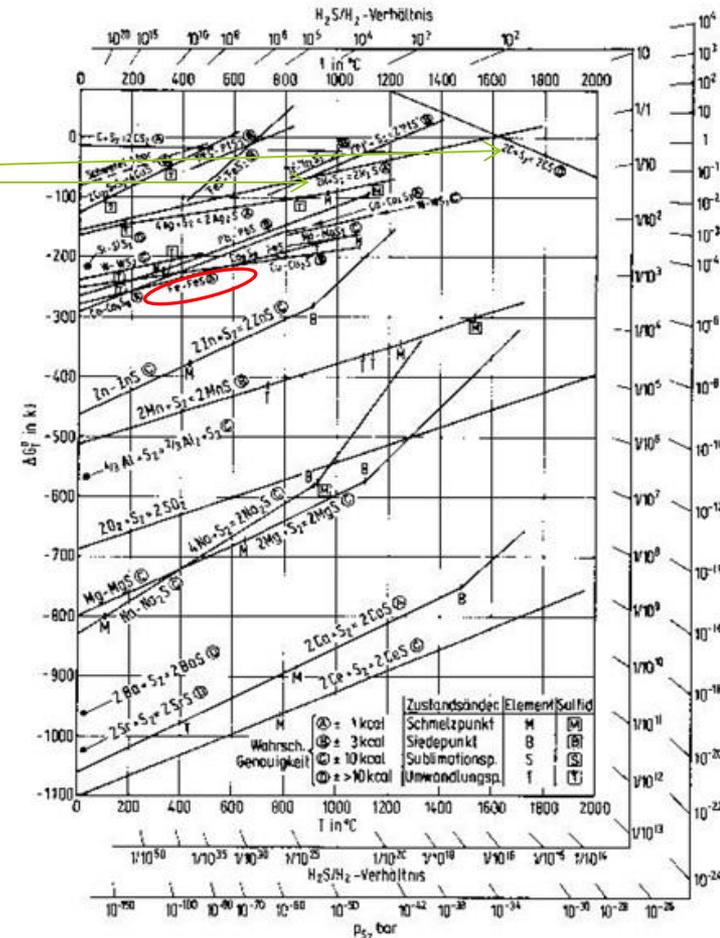
It is very difficult to reduce sulphide directly into the metal  
Carbon and hydrogen are not effective reducing agent to produce metal from sulphide as seen in the Ellingham

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  $\text{SO}_2$  because sulphide ore has 20-30 % sulphur depending on the deposit

So a large amount of a  $\text{SO}_2$ ,  $\text{SO}_3$  and nitrogen will be produced as the off-gas

These sulphurous gases are used to produce  $\text{H}_2\text{SO}_4$

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

Heats of formation of some sulphides:

$\text{Cu}_2\text{S}$  = -18950 kilocalories per kg mole

$\text{ZnS}$  = -44000 kilocalories per kg mole

$\text{FeS}_2$  = -35500 kilocalories per kg mole

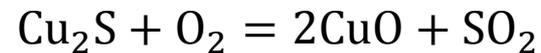
$\text{CuO}$  = -37100 kilocalories per kg mole

$\text{SO}_2$  = -70940 kilocalories per kg mole

$\text{SO}_3$  = -93900 kilocalories per kg mole

$\text{CO}_2$  = -94450 kilocalories per kg mole

$\text{CO}$  = -26840 kilocalories per kg mole



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, FeS<sub>2</sub>, 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%									
Material	CuS	FeS <sub>2</sub>	ZnS	SiO <sub>2</sub>	S	CaO, Al <sub>2</sub> O <sub>3</sub> , etc	SO <sub>2</sub>	SO <sub>3</sub>	O <sub>2</sub> , N <sub>2</sub>
Ore	6	25	4	20	33.6	11.4			
Roast gases							2.5	0.4	97.1

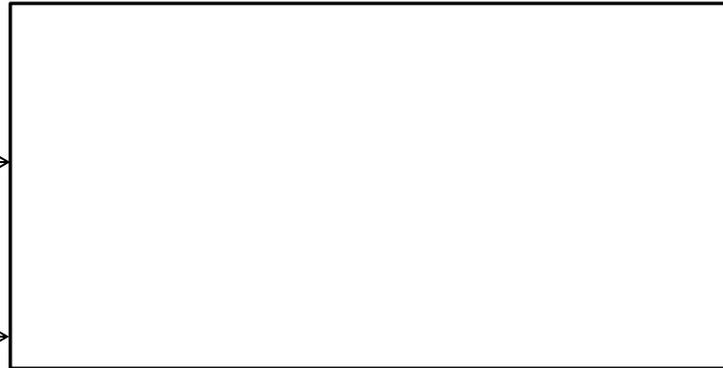
Copper, iron and zinc of the ore oxidize to CuO, Fe<sub>2</sub>O<sub>3</sub> and ZnO

Basis 1000 kg of copper ore

Ore

4% Zn as ZnS  
6% Cu as CuS  
25% Fe as FeS<sub>2</sub>  
20% SiO<sub>2</sub>  
11.4% CaO, Al<sub>2</sub>O<sub>3</sub>, etc  
33.6% S

Air



Flue gases

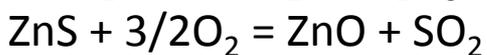
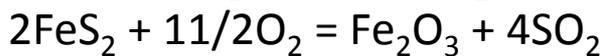
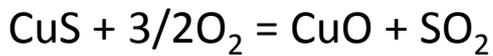
2.5% SO<sub>2</sub>  
0.4% SO<sub>3</sub>  
O<sub>2</sub>, N<sub>2</sub>

Calcine

ZnO  
CuO  
Fe<sub>2</sub>O<sub>3</sub>  
SiO<sub>2</sub>  
CaO, Al<sub>2</sub>O<sub>3</sub>

Leaching

Reactions

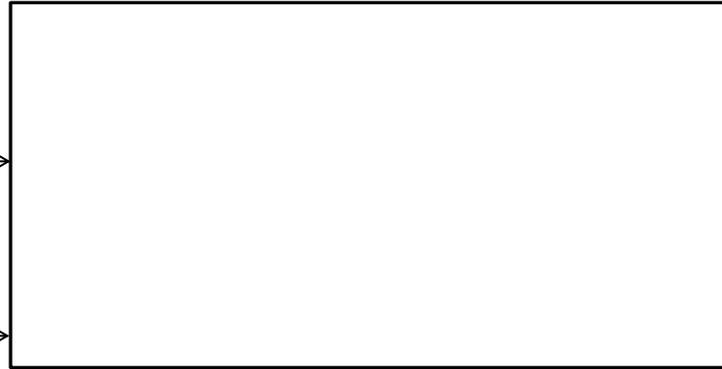


Basis 1000 kg of copper ore

Ore

- 4% Zn as ZnS
- 6% Cu as CuS
- 25% Fe as FeS<sub>2</sub>
- 20% SiO<sub>2</sub>
- 11.4% CaO, Al<sub>2</sub>O<sub>3</sub>, etc
- 33.6% S

Air



Flue gases

- 2.5% SO<sub>2</sub>
- 0.4% SO<sub>3</sub>
- O<sub>2</sub>, N<sub>2</sub>

Calcine

- ZnO SiO<sub>2</sub>
- CuO CaO, Al<sub>2</sub>O<sub>3</sub>
- Fe<sub>2</sub>O<sub>3</sub>

Leaching

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
SiO <sub>2</sub>	200 kg
CaO, Al <sub>2</sub> O <sub>3</sub> , etc	114 kg
S	336 kg
<hr/> Total	<hr/> 1000kg

Output

CuO	60*(80/64) =	75 kg
Fe <sub>2</sub> O <sub>3</sub>	250*(160/112) =	357 kg
ZnO	40*(81/65) =	50 kg
SiO <sub>2</sub>		200 kg
CaO, Al <sub>2</sub> O <sub>3</sub> , etc		114 kg
<hr/> Total solids	<hr/>	<hr/> 796 kg

Analysis of calcine

CuO = (75/796)\*100 = 9.4%      Fe<sub>2</sub>O<sub>3</sub> = (357/796)\*100 = 44.9%

ZnO = (50/796)\*100 = 6.3%      SiO<sub>2</sub> = (200/796)\*100 = 25.1%

Others (CaO, Al<sub>2</sub>O<sub>3</sub>, etc) = (114/796)\*100 = 14.3%

Basis 1000 kg of copper ore

Ore

40 kg Zn

60 kg Cu

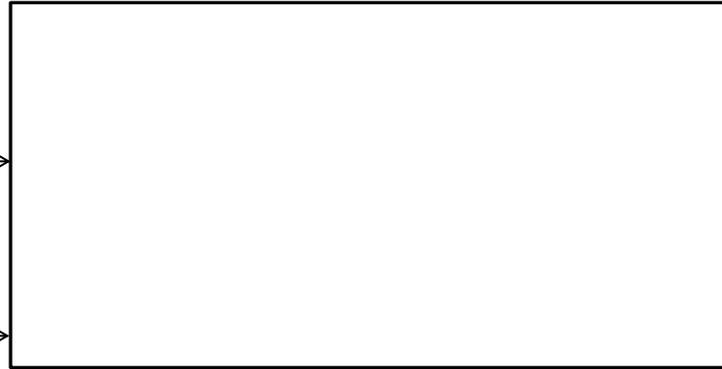
250 kg Fe

200 kg SiO<sub>2</sub>

114 kg CaO, Al<sub>2</sub>O<sub>3</sub>, etc

336 kg S

Air



Flue gases

2.5% SO<sub>2</sub>

0.4% SO<sub>3</sub>

O<sub>2</sub>, N<sub>2</sub>

Calcine

ZnO SiO<sub>2</sub>

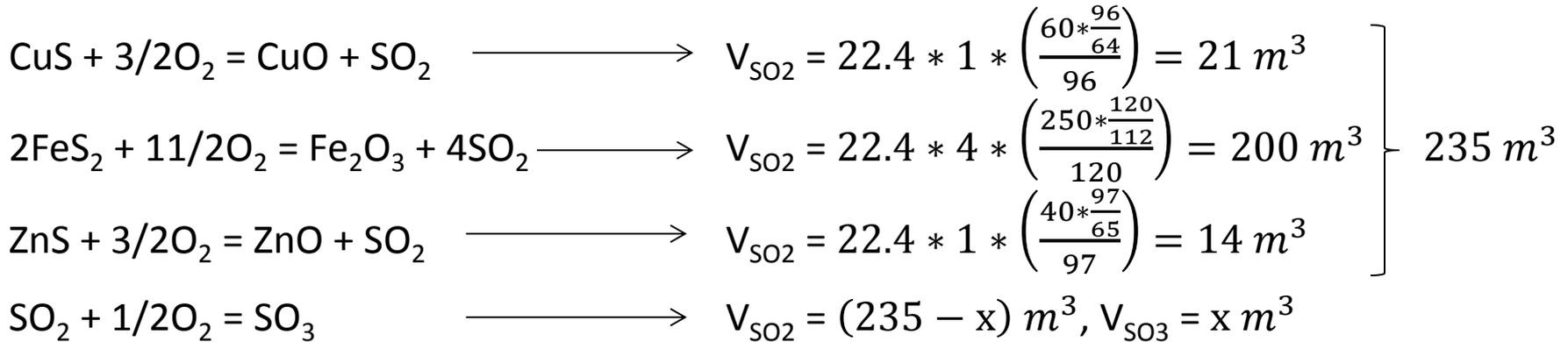
CuO CaO, Al<sub>2</sub>O<sub>3</sub>

Fe<sub>2</sub>O<sub>3</sub>

Leaching

Calculate the volume of flue gases per ton of ore

Reactions



$$\% \text{SO}_2 = 2.5/100 = (235-x)/V_{\text{fluegas}}$$

$$\% \text{SO}_3 = 0.4/100 = (x/V_{\text{fluegas}})$$

$$V_{\text{fluegas}} = 8103.5 \text{ m}^3, V_{\text{SO}_3} = x = 32.4 \text{ m}^3, V_{\text{SO}_2} = 202.6 \text{ m}^3$$

Basis 1000 kg of copper ore

Ore

40 kg Zn

60 kg Cu

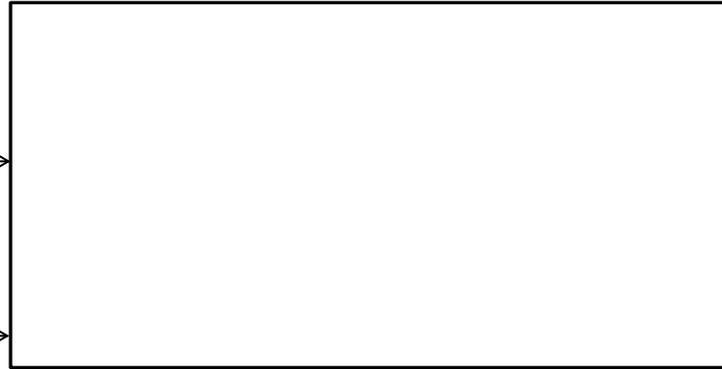
250 kg Fe

200 kg SiO<sub>2</sub>

114 kg CaO, Al<sub>2</sub>O<sub>3</sub>, etc

336 kg S

Air



Flue gases 8103.5 m<sup>3</sup>

SO<sub>2</sub> 202.6 m<sup>3</sup>

SO<sub>3</sub> 32.4 m<sup>3</sup>

O<sub>2</sub>, N<sub>2</sub> 7868.5 m<sup>3</sup>

Calcine

ZnO SiO<sub>2</sub>

CuO CaO, Al<sub>2</sub>O<sub>3</sub>

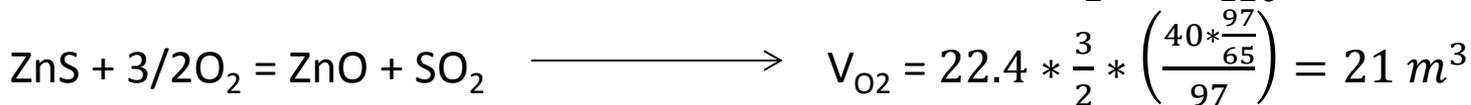
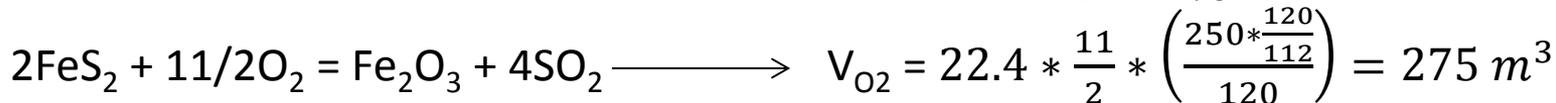
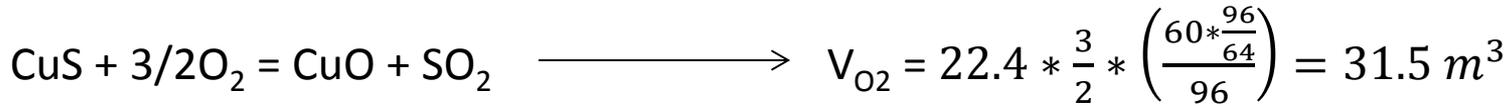
Fe<sub>2</sub>O<sub>3</sub>

Leaching

Calculate the volume roasting air, percent excess and the composition of the flue gases

Roasting reactions

Volume of O<sub>2</sub> required



343.7 m<sup>3</sup>

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<sub>2</sub>+N<sub>2</sub> balance in order to obtain actual air V

$$V_{\text{O}_2+\text{N}_2} = V_{\text{air-th}} + V_{\text{excess}} - V_{\text{O}_2\text{consumed}}$$

$$7868.5 = 1636.67 + 1636.67 * y - 343.7$$

$$y = 4.02, V = 1636.67 + 1636.7 * 4.02 = 8216.07 \text{ m}^3$$

$$V_{\text{O}_2\text{excess}} = 8216.07 * 0.21 - 343.7 = 1381.67 \text{ m}^3, V_{\text{N}_2} = 8216.07 * 0.79 = 6490.69 \text{ m}^3$$

## 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.  $\text{Cu}_2\text{S}$  and  $\text{FeS}$

When metal is separated as liquid, it is called reduction smelting

e.g. Ironmaking

Density of liquid metal or matte is around  $5\text{-}5.5 \text{ g/cm}^3$

Density of slag is around  $2.8\text{-}3 \text{ g/cm}^3$

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

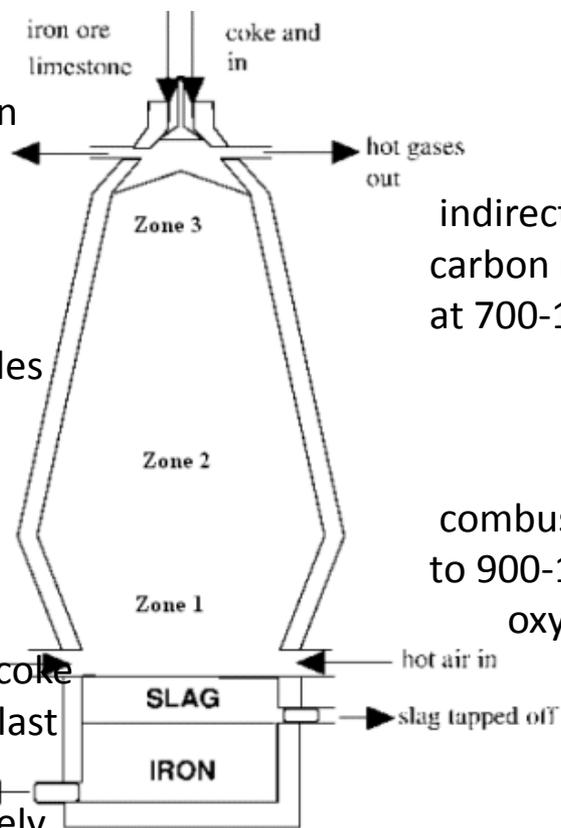
The process is continuous with raw materials being regularly charged to the top of the furnace and molten iron and slag being tapped from the bottom of the furnace at regular intervals

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



indirect reduction of the iron oxides by carbon monoxide and hydrogen occurs at 700-1,000 C

combustion air that is preheated to 900-1,300 C and often enriched with oxygen is blown into the furnace

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  $>300\text{ }^{\circ}\text{C}$  - 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

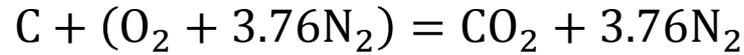
In any counter current heat and mass exchange reactor, which consists of gas and solid, the permeability of the bed and the distribution of the burden are very important issues

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<sub>2</sub> at the tuyere level because of availability of oxygen

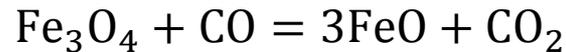
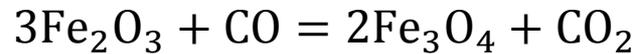


Upward gas rising consists of CO, CO<sub>2</sub> and nitrogen

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



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<sub>2</sub> 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

Rational Analysis wt%							
Material	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MnO	Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	C	CaCO <sub>3</sub>
Ore	80	12	1	3	4		
Limestone		4			1		95
Coke		10				90	

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 m<sup>3</sup> of flue gas is produced

The rational analysis of flue gases gives 58% N<sub>2</sub>, 26% CO, 12% CO<sub>2</sub>, 4% H<sub>2</sub>O

Basis 1000 kg of pig iron

Ore 1750 kg

Limestone 500 kg

Coke

Air

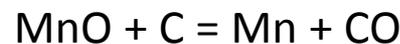
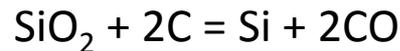
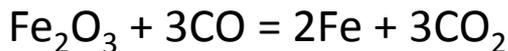


Blast furnace gas 4200 m<sup>3</sup>

Slag

Pig iron 1000 kg

Reactions



Basis 1000 kg of pig iron

Ore 1750 kg

80% Fe<sub>2</sub>O<sub>3</sub>, 12% SiO<sub>2</sub>, 1% MnO,  
3% Al<sub>2</sub>O<sub>3</sub>, 4% H<sub>2</sub>O

Limestone 500 kg

95% CaCO<sub>3</sub>, 1% H<sub>2</sub>O, 4% SiO<sub>2</sub>

Coke

10% SiO<sub>2</sub>, 90% C

Air

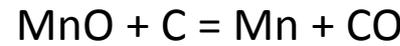
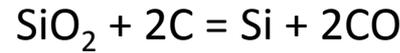
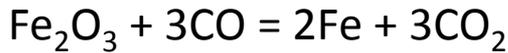


Blast furnace gas 4200m<sup>3</sup>  
58% N<sub>2</sub>, 26% CO, 12% CO<sub>2</sub>, 4% H<sub>2</sub>O

Slag

Pig iron 1000 kg  
93.8% Fe, 4% C, 1.2% Si, 1% Mn

Reactions



Calculate the quantity of coke used per ton of pig iron

Carbon balance:

$$C_{\text{coke}} + C_{\text{limestone}} = C_{\text{pig iron}} + C_{\text{flue gas}} \quad \text{let } x \text{ be the weight of coke}$$

$$\frac{0.9x}{12} + \frac{0.95 * 500 * 12/100}{12} = \frac{0.04 * 1000}{12} + \frac{4200 * 0.26}{22.4} + \frac{4200 * 0.12}{22.4}$$

$$0.075x + 4.75 = 3.333 + 71.25, \quad x = 69.833/0.075 = 931 \text{ kg coke per ton of pig iron}$$

Calculate the air consumption per ton of pig iron

N<sub>2</sub> balance:

$$N_{2(\text{air})} = N_{2(\text{flue gas})} = 4200 * 0.58 = 2436 \text{ m}^3,$$

$$\text{Air consumption} = 2436 * (100/79) = 3083.5 \text{ m}^3$$

Basis 1000 kg of pig iron

Ore 1750 kg

80% Fe<sub>2</sub>O<sub>3</sub>, 12% SiO<sub>2</sub>, 1% MnO,  
3% Al<sub>2</sub>O<sub>3</sub>, 4% H<sub>2</sub>O

Limestone 500 kg

95% CaCO<sub>3</sub>, 1% H<sub>2</sub>O, 4% SiO<sub>2</sub>

Coke

10% SiO<sub>2</sub>, 90% C

Air



Blast furnace gas 4200m<sup>3</sup>  
58% N<sub>2</sub>, 26% CO, 12% CO<sub>2</sub>, 4% H<sub>2</sub>O

Slag

Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MnO, Al<sub>2</sub>O<sub>3</sub>, CaO

Pig iron 1000 kg

93.8% Fe, 4% C, 1.2% Si, 1% Mn

Calculate the composition of the slag

Fe<sub>2</sub>O<sub>3</sub> balance:

$$\text{Fe}_2\text{O}_{3(\text{ore})} = \text{Fe}_2\text{O}_{3(\text{pig iron})} + \text{Fe}_2\text{O}_{3(\text{slag})}$$

$$1750 \cdot 0.8 = 0.938 \cdot 1000 \cdot (160/112) + \text{Fe}_2\text{O}_{3(\text{slag})}, \quad \text{Fe}_2\text{O}_{3(\text{slag})} = 1400 - 1340 = 60 \text{ kg}$$

SiO<sub>2</sub> balance:

$$\text{SiO}_{2(\text{ore})} + \text{SiO}_{2(\text{limestone})} + \text{SiO}_{2(\text{coke})} = \text{SiO}_{2(\text{pig iron})} + \text{SiO}_{2(\text{slag})}$$

$$1750 \cdot 0.12 + 500 \cdot 0.04 + 931 \cdot 0.1 = 0.012 \cdot 1000 \cdot (60/28) + \text{SiO}_{2(\text{slag})}, \quad \text{SiO}_{2(\text{slag})} = 210 + 20 + 93.1 - 25.7 = 297.4 \text{ kg}$$

MnO balance:

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

$$1750 \cdot 0.01 + 0.01 \cdot 1000 \cdot (71/55) + \text{MnO}_{(\text{slag})}$$

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

Al<sub>2</sub>O<sub>3</sub> balance:

$$\text{Al}_2\text{O}_{3(\text{ore})} = \text{Al}_2\text{O}_{3(\text{slag})} = 1750 \cdot 0.03 = 52.5 \text{ kg}$$

CaO balance:

$$\text{CaO}_{(\text{limestone})} = \text{CaO}_{(\text{slag})} = 500 \cdot (56/100) \cdot 0.95 = 266 \text{ kg}$$

Total slag composition:

Fe <sub>2</sub> O <sub>3</sub>	60 kg	8.82%
SiO <sub>2</sub>	297.4 kg	43.70%
MnO	4.6 kg	0.67%
Al <sub>2</sub> O <sub>3</sub>	52.5 kg	7.71%
CaO	266 kg	39.10%
<b>Total</b>	<b>680.5 kg</b>	