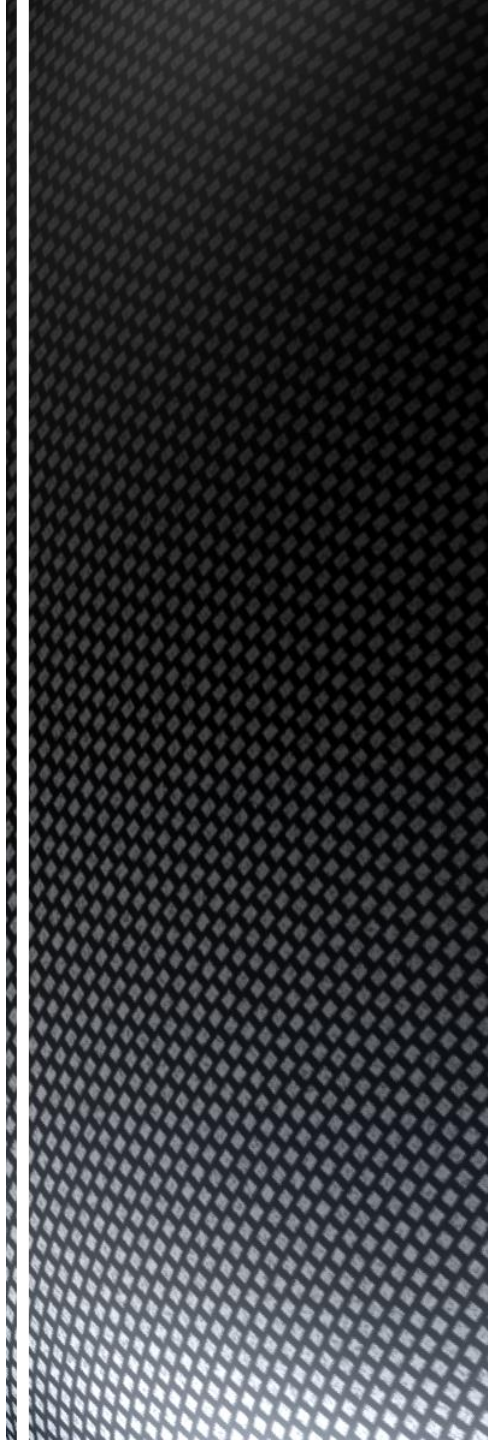# Materials and Energy Balance

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 Al_2O_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 CO_2 in the flue gases can be thought to originate from the reactions and air is simply O_2 and N_2

Charge calculation problems

Hints for effective material balance problem solving:
1 – Read the question to understand the process, materials and unknowns
2 – Draw a diagram
3 – Define a base
4 – Write down the independent equations and relations
5 – Perform degree of freedom analysis
6 – Do stoichiometric and materials balance calculations
7 – 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*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

Reacting Gaseous Mixture

T, P → Flue gases
CO_2
SO_2
H_2O
N_2

Air = O_2, N_2
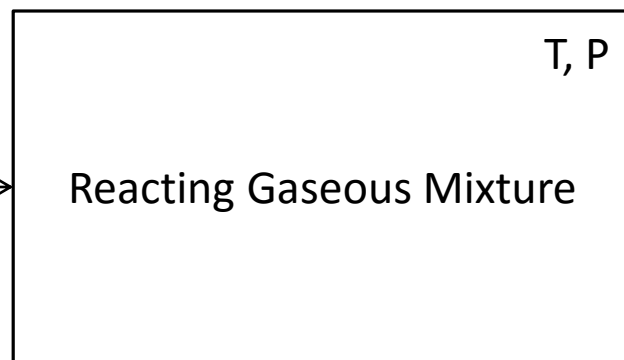
Chemical reactions
$C + O_2 = CO_2$
$H_2 + 1/2O_2 = H_2O$
$S + O_2 = SO_2$
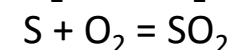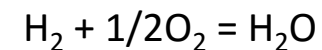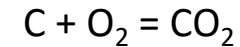
Degree of freedom analysis

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

Reacting Gaseous Mixture

T, P

V_G Flue gases
X_{CO2} CO_2
X_{SO2} SO_2
X_{H2O} H_2O
X_{N2} N_2

V_A Air
21% O_2, 79% N_2

Chemical reactions
$$C + O_2 = CO_2$$
$$H_2 + 1/2O_2 = H_2O$$
$$S + O_2 = SO_2$$
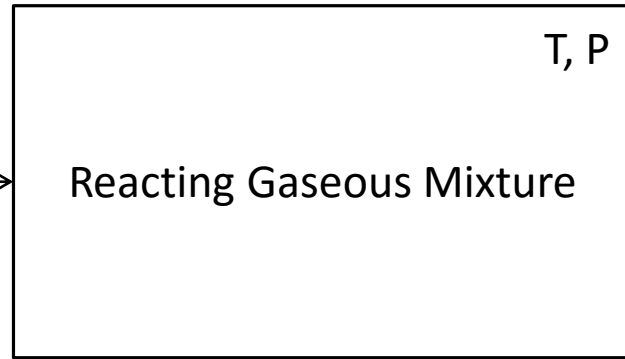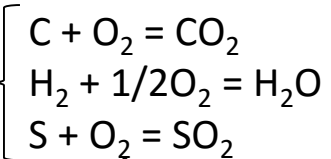
Material balance type – Initial input + generation = Final output + consumption

6 unknown labeled variables (V_A,V_G, X_{CO2}, X_{H2O}, X_{SO2}, X_{N2})

- 4 independent atomic species balances that are involved in the reactions (C, H, S, O)

- 1 molecular balances on independent nonreactive species (N_2)

- 1 other equation relating unknown variables (X_{CO2} + X_{H2O} + X_{SO2} + X_{N2} =1)

= 0 degrees of freedom

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

Reacting Gaseous Mixture

STP → V_G Flue gases
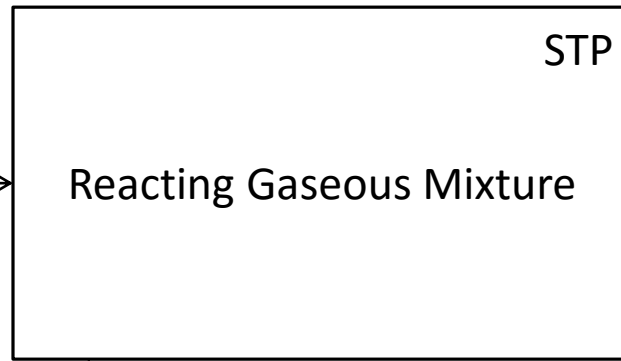X_{CO2} CO_2
X_{SO2} SO_2
X_{H2O} H_2O
X_{N2} N_2

V_A Air
21% O_2, 79% N_2

Chemical reactions $\begin{cases} C + O_2 = CO_2 \\ H_2 + 1/2 O_2 = H_2O \\ S + O_2 = SO_2 \end{cases}$
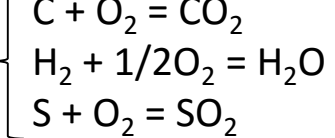
Calculate the volume of air necessary for complete combustion

Stoichiometry calculation

n_C = 850/12 = 70.83 kg-atom $\longrightarrow$ C + O_2 = CO_2 O_2 consumption = 70.83 kg-mole
n_{H2} = 50/2 = 25 kg-mole $\longrightarrow$ H_2 + 1/2O_2 = H_2O O_2 consumption = 12.5 kg-mole
n_S = 20/32 = 0.625 kg-atom $\longrightarrow$ S + O_2 = SO_2 O_2 consumption = 0.625 kg-mole
n_O = 70/16 = 4.375 kg-atom n_{O2} = 2.1875 kg-mole O_2 input from coal= 2.1875 kg-mole

O_2 input from air= 81.7675 kg-mole

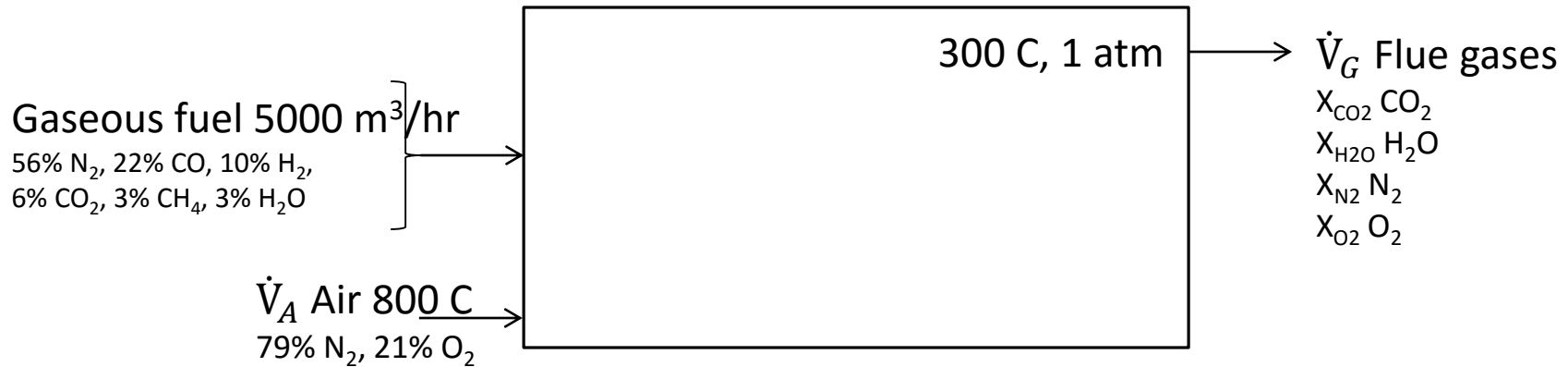O_2 balance – Input + generation (0) = output (0) + consumption

Volume of air = $\dfrac{81.7675*22.4}{0.21} = 8721 \ m^3$ per 1000 kg coal

Excess reactants

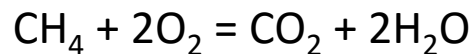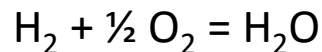5000 m³ of regenerator gas of following composition is used to heat an open hearth furnace at 300 C per hour:

Rational Analysis wt%						
Material	CO	CO_2	H_2	CH_4	H_2O	N_2
Gaseous fuel	22	6	10	3	3	56

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

Gaseous fuel 5000 m³/hr
56% N_2, 22% CO, 10% H_2,
6% CO_2, 3% CH_4, 3% H_2O

$\dot{V}_A$ Air 800 C
79% N_2, 21% O_2

300 C, 1 atm

$\dot{V}_G$ Flue gases
X_{CO2} CO_2
X_{H2O} H_2O
X_{N2} N_2
X_{O2} O_2

Combustion reactions
$CO + 1/2\ O_2 = CO_2$
$H_2 + \frac{1}{2}\ O_2 = H_2O$
$CH_4 + 2O_2 = CO_2 + 2H_2O$

Degree of freedom analysis

Gaseous fuel 5000 m³/hr
56% N_2, 22% CO, 10% H_2,
6% CO_2, 3% CH_4, 3% H_2O

$\dot{V}_A$ Air 800 C
79% N_2, 21% O_2

300 C, 1 atm

$\dot{V}_G$ Flue gases
X_{CO2} CO_2
X_{H2O} H_2O
X_{N2} N_2
X_{O2} O_2
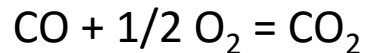
Combustion reactions   Material balance type – input + generation = output + consumption
$CO + 1/2\ O_2 = CO_2$
$H_2 + ½\ O_2 = H_2O$
$CH_4 + 2O_2 = CO_2 + 2H_2O$
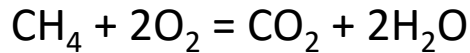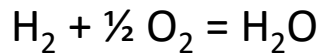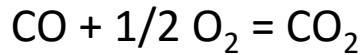
6 unknown labeled variables ($\dot{V}_A$, $\dot{V}_G$, X_{CO2}, X_{H2O}, X_{O2}, X_{N2})
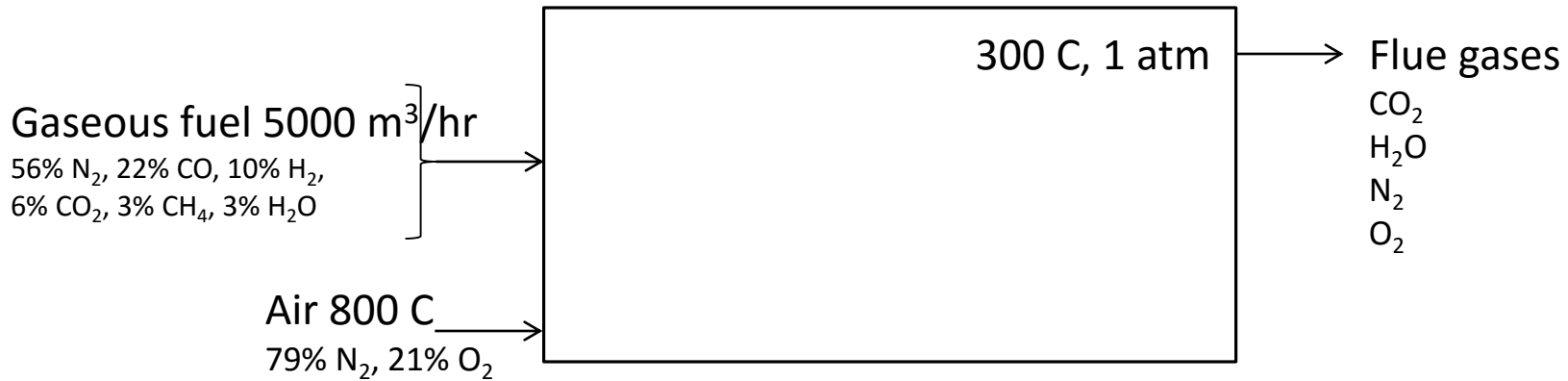
+ 3 independent chemical reactions

- 7 independent molecular species balances (CO, H_2O, H_2, CO_2, CH_4, O_2, N_2)

- 2 other equation relating unknown variables ($X_{CO2} + X_{H2O} + X_{O2} + X_{N2}$ =1, $\frac{1}{6} * 0.21 * \dot{V}_A = \dot{V}_G * X_{O2}$)

= 0 degrees of freedom

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

Gaseous fuel 5000 m³/hr
56% N_2, 22% CO, 10% H_2,
6% CO_2, 3% CH_4, 3% H_2O

Air 800 C
79% N_2, 21% O_2

300 C, 1 atm → Flue gases
CO_2
H_2O
N_2
O_2

Calculate the volume of air required to burn 1 m³ of regenerator gas per hour, then scale up

Basis: 1 m³/hr of regenerator gas

Gas composition @ 300 C
0.22 m³ CO
0.10 m³ H_2
0.03 m³ CH_4
0.06 m³ CO_2
0.03 m³ H_2O
0.56 m³ N_2

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

$$P_1 = P_2 = 1 \; atm$$

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

Gas composition @ 0 C
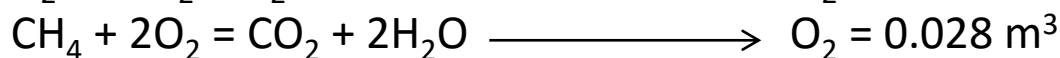CO = 0.22*(273/573) = 0.105 m³
H_2 = 0.10*(273/573) = 0.048 m³
CH_4 = 0.03*(273/573) = 0.014 m³
CO_2 = 0.06*(273/573) = 0.028 m³
H_2O = 0.03*(273/573) = 0.014 m³
N_2 = 0.56*(273/573) = 0.267 m³

O_2 requirements from combustion reactions
CO + 1/2 O_2 = CO_2 → O_2 = 0.0525 m³
H_2 + ½ O_2 = H_2O → O_2 = 0.024 m³
CH_4 + 2O_2 = CO_2 + 2H_2O → O_2 = 0.028 m³
Total O_2 = 0.1045 m³

Volume of O_2 at STP = 0.1045 m³
Volume of O_2 at 800 C = 0.412 m³
Theoretical air volume = 0.421/0.21
= 1.96 m³
Real air volume = 1.96*1.2 = 2.35 m³

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

Gaseous fuel 5000 m³/hr
56% N_2, 22% CO, 10% H_2,
6% CO_2, 3% CH_4, 3% H_2O

11750 m³/hr Air 800 C
79% N_2, 21% O_2

300 C, 1 atm → 4985 m³/hr
Flue gases
CO_2 14.8%
H_2O 9.1%
N_2 74.0%
O_2 2.1%

Calculate the composition of flue gases

Basis: 1 m³ of regenerator gas

Gas composition @ STP
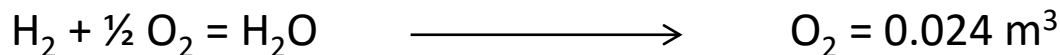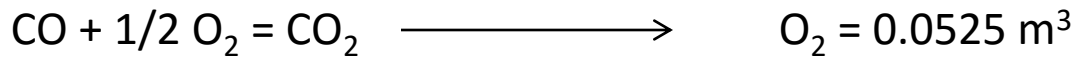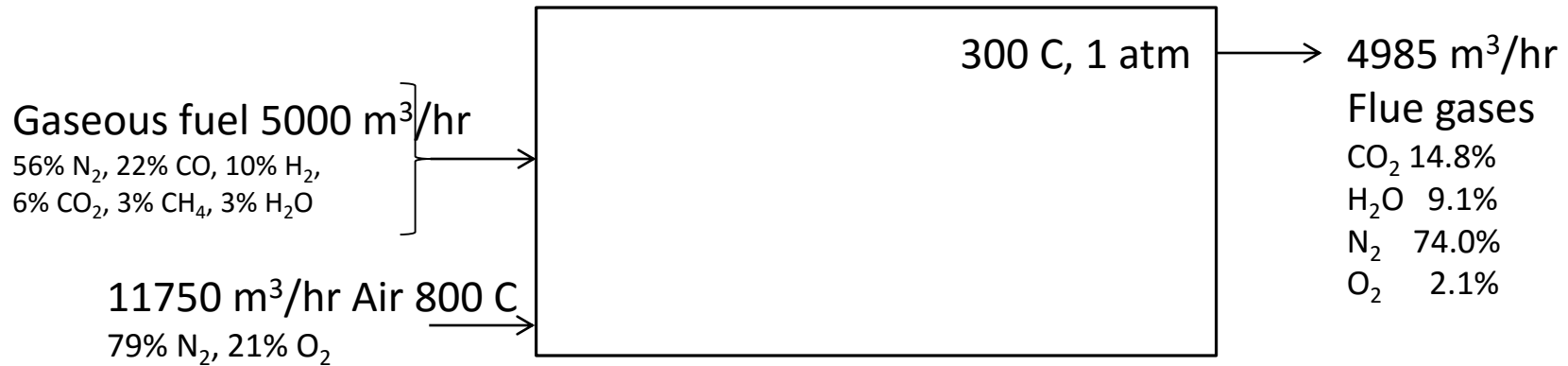$CO = 0.22*(273/573) = 0.105$ m³
$H_2 = 0.10*(273/573) = 0.048$ m³
$CH_4 = 0.03*(273/573) = 0.014$ m³
$CO_2 = 0.06*(273/573) = 0.028$ m³
$H_2O = 0.03*(273/573) = 0.014$ m³
$N_2 = 0.56*(273/573) = 0.267$ m³

Air composition @ STP
$O_2 = 0.1045*1.2 = 0.1255$ m³
$N_2 = 0.1255*(79/21) = 0.472$ m³

Flue gas composition
$CO_2 = CO_{2(combustion1)} + CO_{2(combustion3)} + CO_{2(gas)} = 0.105 + 0.014 + 0.028 = 0.147$ m³ / 14.8%
$H_2O = H_2O_{(combustion2)} + H_2O_{(combustion3)} + H_2O_{(gas)} = 0.048 + 0.028 + 0.014 = 0.090$ m³ / 9.1%
$N_2 = N_{2(gas)} + N_{2(air)} = 0.267 + 0.472 = 0.739$ m³ / 74.0%
$O_2 = O_{2(air)} - O_{2(combustion1,2,3)} = 0.1255 - 0.1045 = 0.021$ m³ / 2.1%

Nitriding Gas Treatment

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

Rational Gas Analysis wt%		
Material	NH_3	H_2
Incoming gas	10	90
Outlet gas	7	93

3000 ml/hr
Gas input at ~~500 C~~→
90% H_2, 10% NH_3

500 C, 1 atm

Fe $\underline{N}$

$\dot{V}_G$ Gas output
93% H_2, 7% NH_3

Reactions
$NH_3 = \frac{1}{2} N_2 + 3/2\ H_2$
$\frac{1}{2} N_2 = \underline{N}$
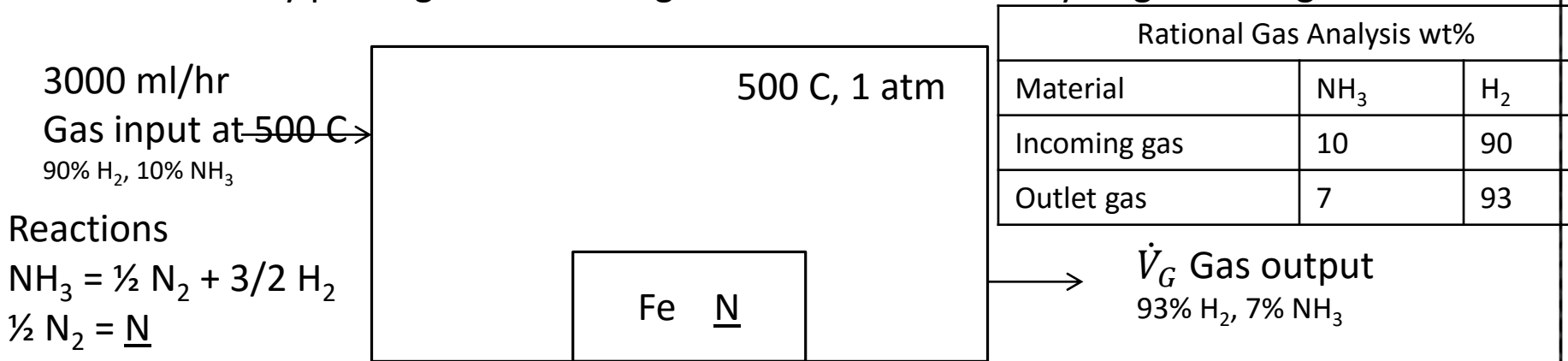
Calculate the amount of nitrogen, in gram/hr, that the iron picks up from the gas flowing in at a rate of 50 ml/min at 500 C

DOF analysis   Material balance type – Input + generation - output - consumption = accumulation

2 unknown labeled variables ($\dot{V}_G$, $\dot{m}_{N2}$)
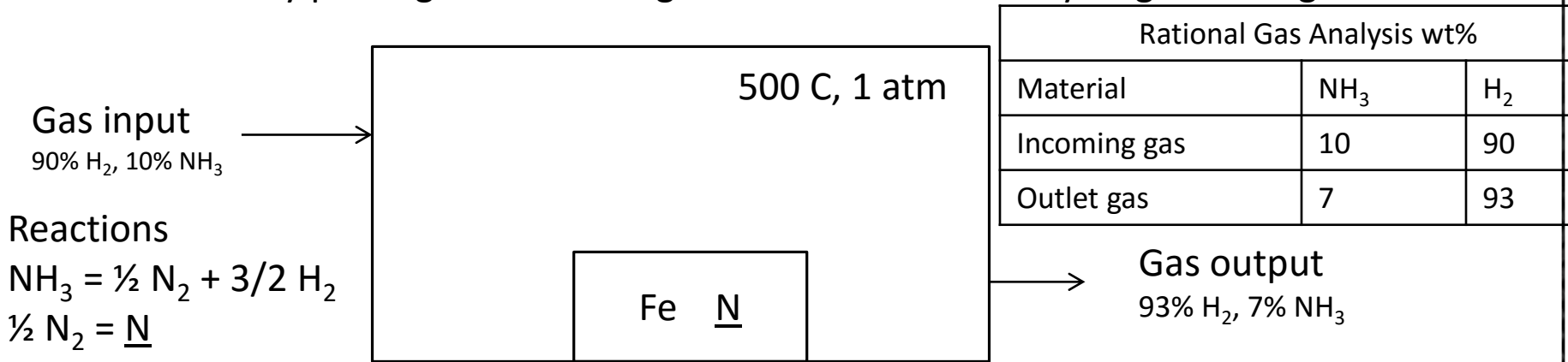
+ 2 independent chemical reactions

- 3 independent molecular species balances (NH_3, H_2, N_2)

- 1 other equation relating unknown variables (PV=m/MW*RT)

= 0 degrees of freedom

Nitriding Gas Treatment

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

500 C, 1 atm

Gas input
90% H_2, 10% NH_3

Reactions
$NH_3 = \frac{1}{2} N_2 + \frac{3}{2} H_2$
$\frac{1}{2} N_2 = \underline{N}$

Fe $\underline{N}$

Gas output
93% H_2, 7% NH_3

Rational Gas Analysis wt%		
Material	NH_3	H_2
Incoming gas	10	90
Outlet gas	7	93

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_3 = 300 ml NH_3 = (300-x) ml   where x is volume of consumed NH_3
H_2 = 2700 ml H_2 = (2700+3/2x) ml where 3/2x is the volume of generated H_2
Total = 3000 ml   Total = 3000+1/2x
%NH_3 = 7/100 = (300-x)/(3000+x/2)   volume of consumed NH_3, x = 86.96 ml/hr

$NH_3 = \frac{1}{2} N_2 + \frac{3}{2} H_2$ ⟶ N_2 generated per hour = 1/2x = ½*86.96 = 43.48 ml
$\frac{1}{2} N_2 = \underline{N}$ ⟶ N consumed in steel = 14 g/11200 ml N_2 = 0.5475 g $\underline{N}$ / 43.48 ml N_2

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_2O 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
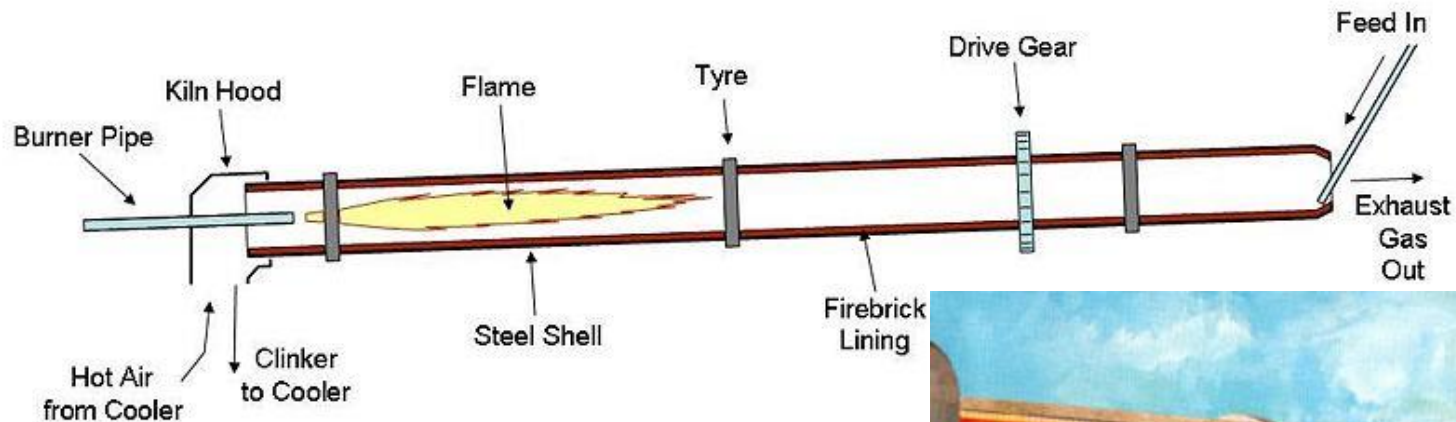
Other commercial uses of rotary kiln is cement and the removal of water from alumina
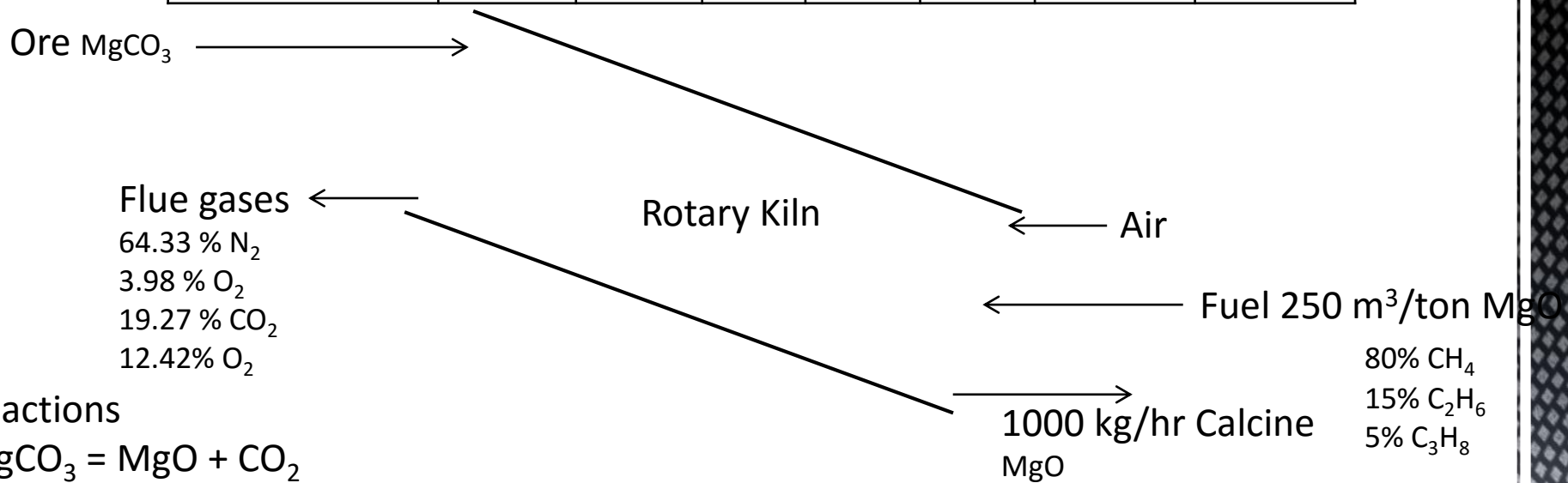
Calcination furnace analysis

Magnesium carbonate is decomposed to make MgO and CO_2 by heating in a rotary kiln, using as fuel a natural gas
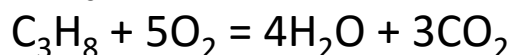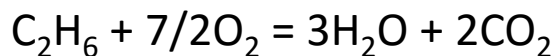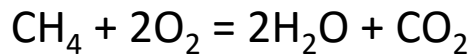
CO_2 formed by decomposition of magnesium carbonate mixes with the products of combustion to form the flue gas product

Fuel consumption is 250 m^3/ton MgO at STP
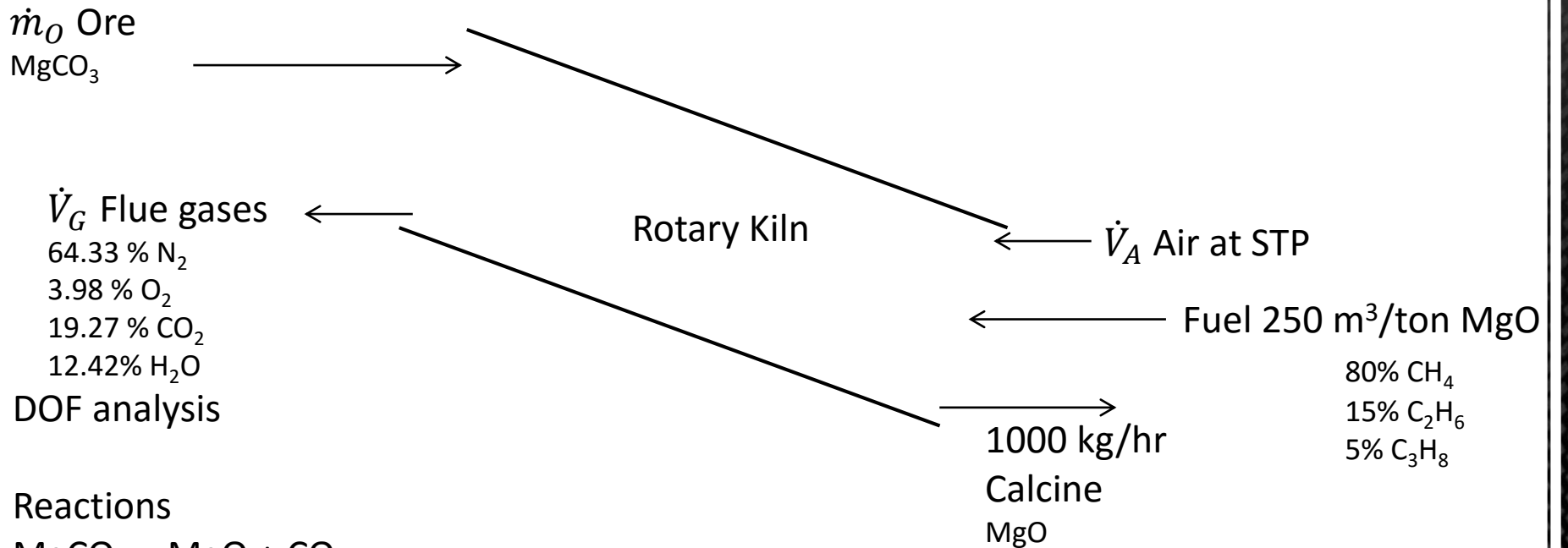
Rational Gas Analysis wt%							
Material	CH_4	C_2H_6	C_3H_8	CO_2	N_2	O_2	H_2O
Natural gas	80	15	5				
Flue gas				19.27	64.33	3.98	12.42

Ore $MgCO_3$ ⟶

Flue gases ⟵   Rotary Kiln   ⟵ Air
64.33 % N_2
3.98 % O_2 ⟵ Fuel 250 m^3/ton MgO
19.27 % CO_2
12.42% O_2 80% CH_4
                                                                         15% C_2H_6
Reactions   1000 kg/hr Calcine   5% C_3H_8
$MgCO_3 = MgO + CO_2$ MgO
$CH_4 + 2O_2 = 2H_2O + CO_2$
$C_2H_6 + 7/2O_2 = 3H_2O + 2CO_2$
$C_3H_8 + 5O_2 = 4H_2O + 3CO_2$

$\dot{m}_O$ Ore
MgCO$_3$

$\dot{V}_G$ Flue gases

   64.33 % N$_2$

   3.98 % O$_2$

   19.27 % CO$_2$

   12.42% H$_2$O

DOF analysis

Rotary Kiln

$\dot{V}_A$ Air at STP

Fuel 250 m^3/ton MgO

   80% CH$_4$

   15% C$_2$H$_6$

   5% C$_3$H$_8$

1000 kg/hr

Calcine

MgO

Reactions

MgCO$_3$ = MgO + CO$_2$

CH$_4$ + 2O$_2$ = 2H$_2$O + CO$_2$ Material balance type – Input + generation = Output + consumption

C$_2$H$_6$ + 7/2O$_2$ = 3H$_2$O + 2CO$_2$

C$_3$H$_8$ + 5O$_2$ = 4H$_2$O + 3CO$_2$

3 unknown labeled variables ($\dot{V}_A$, $\dot{V}_G$, $\dot{m}_O$)

+ 4 independent chemical reactions

- 9 independent molecular species balances (MgCO$_3$, MgO, H$_2$O, C$_3$H$_8$, C$_2$H$_6$, CO$_2$, CH$_{4,}$ O$_2$, N$_2$)

- 1 other equation relating unknown variables (E $* 0.21 * \dot{V}_A = \dot{V}_G * 0.0398$)

= -3 degrees of freedom!

Basis 1000 kg/hr of MgO

Ore $\longrightarrow$

$MgCO_3$

$\dot{V}_G$ Flue gases

Rotary Kiln $\longleftarrow$ Air 3687 m^3

64.33 % N_2

3.98 % O_2

19.27 % CO_2

12.42% H_2O

$\longleftarrow$ Fuel 250 m^3/ton MgO

$\longrightarrow$ Calcine

1000 kg MgO

80% CH_4

15% C_2H_6

5% C_3H_8

Calculate the air consumption in m^3 per ton of MgO produced per hour

Reactions

$MgCO_3 = MgO + CO_2$

$CH_4 + 2O_2 = 2H_2O + CO_2$

$C_2H_6 + 7/2O_2 = 3H_2O + 2CO_2$

$C_3H_8 + 5O_2 = 4H_2O + 3CO_2$
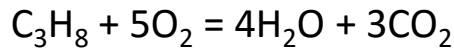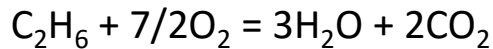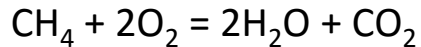
CO_2 balance

kg-mole MgO = $1000/MW_{MgO}$ = 25 kg-mole = CO_2 from $MgCO_3$

kg-mole CH_4 = 250*(80/100) = 200 m^3/ton MgO = 8.93 kg-mole CH_4
= 8.93 kg-mole CO_2

kg-mole C_2H_6 = 250*(15/100) = 37.5 m^3/ton MgO = 1.67 kg-mole C_2H_6
= 2*1.67 kg-mole C_2H_6 = 3.34 kg-mole CO_2

kg-mole C_3H_8 = 250*(5/100) = 12.5 m^3/ton MgO = 0.56 kg-mole C_3H_8
= 3*0.56 kg-mole C_3H_8 = 1.68 kg-mole CO_2

Total kg-mole CO_2 = 25 + 8.93 + 3.34 + 1.68 = 38.95 kg-mole

Total flue gas = 38.95*(100/19.27) = 202.155 kg-mole

Total N_2 = 202.155*(64.33/100) = 130.04 kg-mole N_2

Since N_2 in air = N_2 in flue gas, Air consumption = 130.04*(100/79) = 164.6 kg-mole air/ ton MgO
= 164.6*22.4 = 3687 m^3 (STP) / ton MgO

Basis 1000 kg of MgO
Ore
$MgCO_3$

Flue gases
202.155 kg-mole
64.33 % N_2
3.98 % O_2
19.27 % CO_2
12.42% H_2O

Rotary Kiln

Air 3687 m^3

Fuel 250 m^3/ton MgO

Calcine
1000 kg MgO

80% CH_4
15% C_2H_6
5% C_3H_8

Calculate the percent excess air

Excess O_2 = 202.155*(3.98/100) = 8.055 kg-mole
Excess air = 8.055*(100/21) = 38.36 kg-mole
% Excess air = (38.36/(164.6-38.36))*100 = 30.38

Theoretical air = 164.6-38.36 = 126.24 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
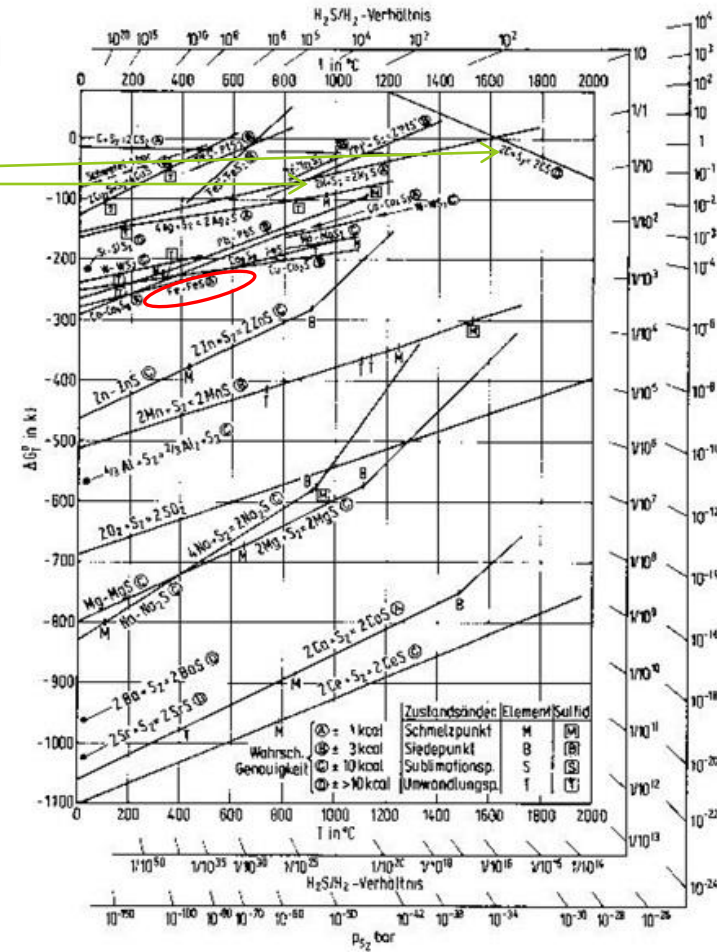
Roasting is carried out below the melting point of the components of the ore
By virtue of this, the roast product is in solid state in addition to the solid ore concentrate

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

Byproducts of roasting are rich in 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 sulphurious gases are used to produce H_2SO_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_2S = -18950 kilocalories per kg mole
ZnS = -44000 kilocalories per kg mole
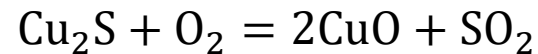FeS_2 = -35500 kilocalories per kg mole
CuO = -37100 kilocalories per kg mole
SO_2 = -70940 kilocalories per kg mole
SO_3 = -93900 kilocalories per kg mole
CO_2 = -94450 kilocalories per kg mole
CO = -26840 kilocalories per kg mole

$$Cu_2S + O_2 = 2CuO + SO_2$$

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. $PbS + O_2 = PbSO_4$ and 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. $2NaCl + MS + 2O_2 = Na_2SO_4 + MCl_2$ direct chlorination
$4NaCl + 2MO + S_2 + 3O_2 = 2Na_2SO_4 + 2MCl_2$ indirect chlorination

Roasting furnace analysis

Pyrometallurgical extraction of ores rich in CuS, FeS$_2$, 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	Cu	Fe	Zn	SiO$_2$	S	CaO, Al$_2$O$_3$, etc	SO$_2$	SO$_3$	O$_2$, N$_2$
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$_2$O$_3$ and ZnO

Basis 1000 kg of copper ore

Ore
4% ZnS
6% CuS
25% FeS$_2$
20% SiO$_2$
11.4% CaO, Al$_2$O$_3$, etc
33.6% S

Air →
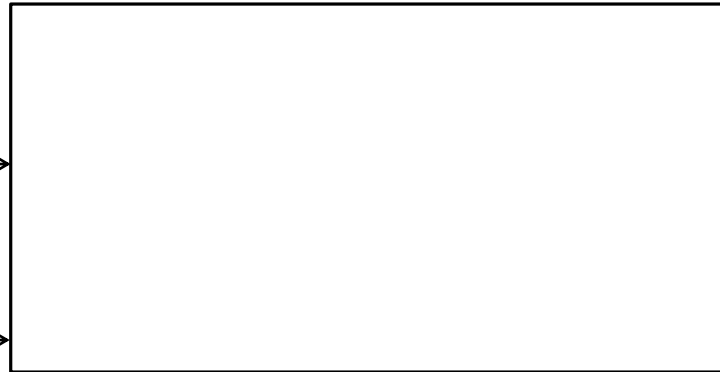
Flue gases
2.5% SO$_2$
0.4% SO$_3$
O$_2$, N$_2$

Calcine
ZnO
CuO
Fe$_2$O$_3$
SiO$_2$
CaO, Al$_2$O$_3$
→ Leaching

Reactions

$$CuS + 3/2 O_2 = CuO + SO_2$$
$$2FeS_2 + 11/2 O_2 = Fe_2O_3 + 4SO_2$$
$$ZnS + 3/2 O_2 = ZnO + SO_2$$
$$SO_2 + 1/2 O_2 = SO_3$$
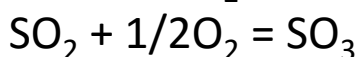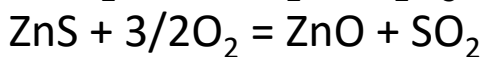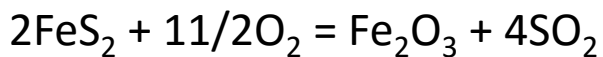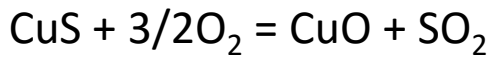
1000 kg Ore
4% Zn
6% Cu
25% Fe
20% SiO_2
11.4% CaO, Al_2O_3, etc
33.6% S

V_A Air at ~~STP~~ →
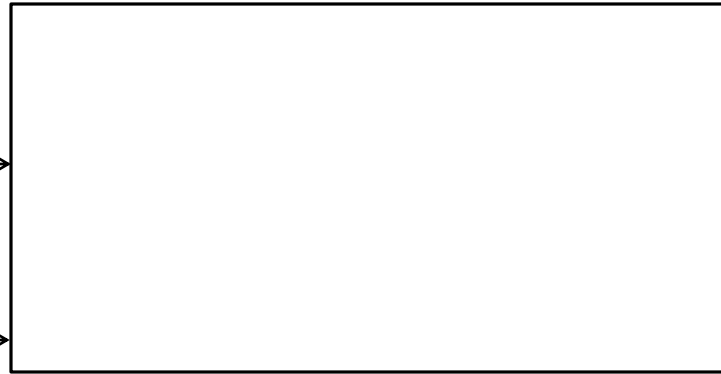
V_G Flue gases
2.5% SO_2
0.4% SO_3
X_{O2} O_2
X_{N2} N_2

m_c Calcine
X_{ZnO} ZnO
X_{CuO} CuO ⎤
X_{Fe2O3} Fe_2O_3⎦ →Leaching
X_{SiO2} SiO_2
$X_{CaO, Al2O3,etc}$ CaO, Al_2O_3, etc

Reactions
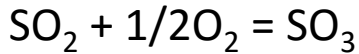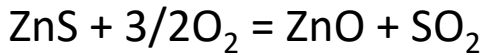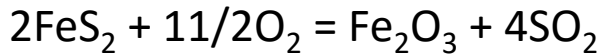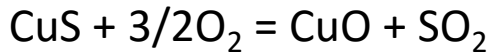
$CuS + 3/2O_2 = CuO + SO_2$
$2FeS_2 + 11/2O_2 = Fe_2O_3 + 4SO_2$
$ZnS + 3/2O_2 = ZnO + SO_2$
$SO_2 + 1/2O_2 = SO_3$ Material balance type – Input + generation = output + consumption

DOF analysis

10 unknown labeled variables (V_A, V_G, m_c, X_{ZnO}, X_{CuO}, X_{Fe2O3}, X_{SiO2}, $X_{CaO, Al2O3,etc}$, X_{O2}, X_{N2})

- 5 independent atomic species balances that are involved in the reactions (Zn, Cu, Fe, S, O)

- 3 molecular balances on independent nonreactive species (N_2, CaO, SiO_2)

- 2 other equations relating unknown variables ($X_{O2} + X_{N2} = 0.971$, $X_{ZnO} + X_{CuO} + X_{Fe2O3} + X_{SiO2} + X_{CaO}$ = 1)

= 0 degrees of freedom

Basis 1000 kg of copper ore
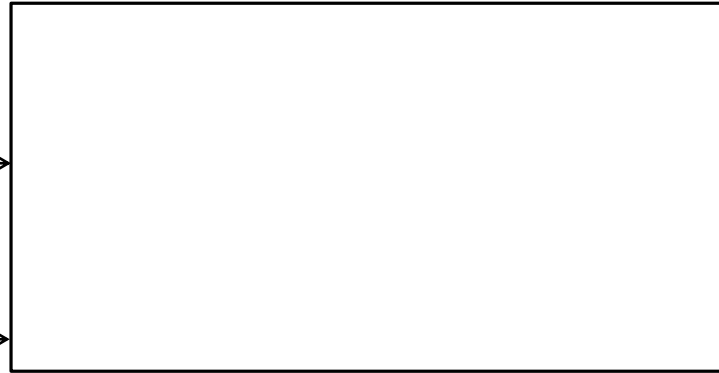
Ore
4% Zn as ZnS
6% Cu as CuS
25% Fe as FeS_2
20% SiO_2
11.4% CaO, Al_2O_3, etc
33.6% S

Air →

Flue gases
2.5% SO_2
0.4% SO_3
O_2, N_2

Calcine
ZnO SiO_2] Leaching →
CuO   CaO, Al_2O_3
Fe_2O_3

Calculate the weight and approximate analysis of the calcine resulting from roasting 1 ton ore

Base: 1000 kg ore

Input 1000 kg			Output		
Cu	60 kg		CuO	60*(80/64) =	75 kg
Fe	250 kg		Fe_2O_3	250*(160/112) =	357 kg
Zn	40 kg		ZnO	40*(81/65) =	50 kg
SiO_2	200 kg		SiO_2		200 kg
CaO, Al_2O_3, etc	114 kg		CaO, Al_2O_3, etc		114 kg
S	336 kg				
Total	1000kg		Total solids		796 kg

Analysis of calcine
CuO = (75/796)*100 = 9.4% Fe_2O_3 = (357/796)*100 = 44.9%
ZnO = (50/796)*100 = 6.3% SiO_2 = (200/796)*100 = 25.1%
Others (CaO, Al_2O_3, 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_2
114 kg CaO, Al_2O_3, etc
336 kg S

Air →
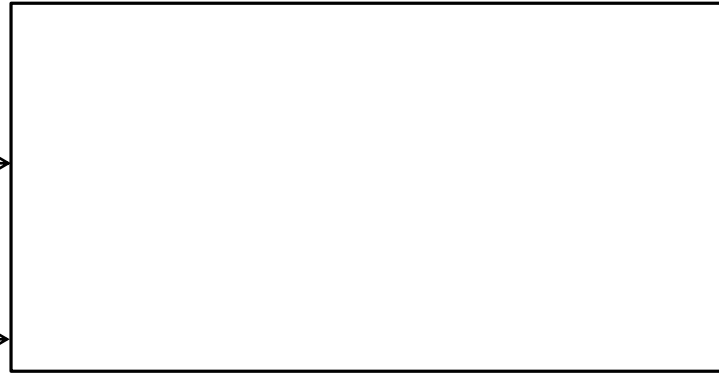
Flue gases
2.5% SO_2
0.4% SO_3
O_2, N_2

Calcine
ZnO SiO_2 Leaching
CuO   CaO, Al_2O_3 →
Fe_2O_3

Calculate the volume of flue gases per ton of ore

Reactions

$CuS + 3/2O_2 = CuO + SO_2$ ⟶ $V_{SO2} = 22.4 * 1 * \left(\frac{60*\frac{96}{64}}{96}\right) = 21 \ m^3$

$2FeS_2 + 11/2O_2 = Fe_2O_3 + 4SO_2$ ⟶ $V_{SO2} = 22.4 * 4 * \left(\frac{250*\frac{120}{112}}{120}\right) = 200 \ m^3$

$ZnS + 3/2O_2 = ZnO + SO_2$ ⟶ $V_{SO2} = 22.4 * 1 * \left(\frac{40*\frac{97}{65}}{97}\right) = 14 \ m^3$

$235 \ m^3$

$SO_2 + 1/2O_2 = SO_3$ ⟶ $V_{SO2} = (235 - x) \ m^3$, $V_{SO3} = x \ m^3$
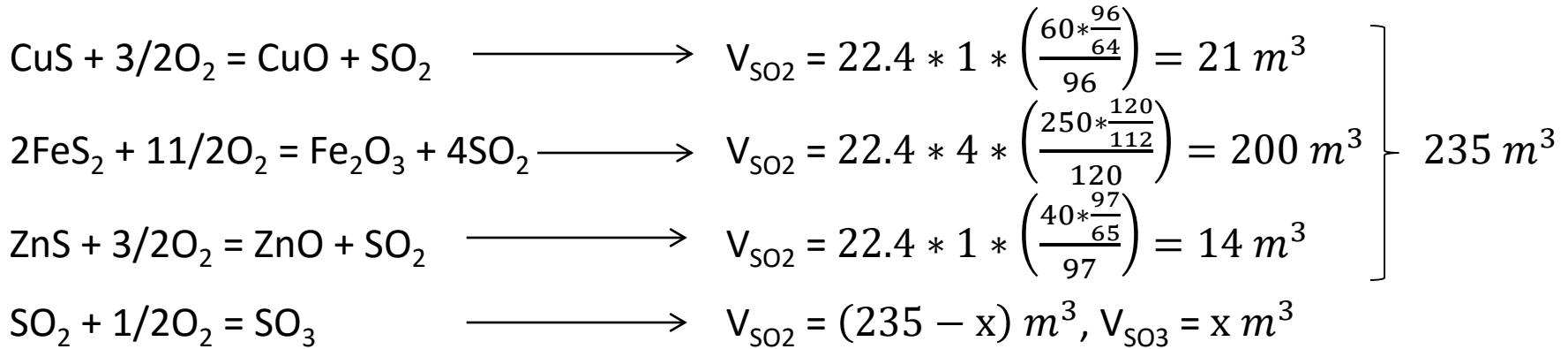
%SO_2 = 2.5/100 = (235-x)/$V_{fluegas}$

%SO_3 = 0.4/100 = (x/$V_{fluegas}$)

$V_{fluegas}$ = 8103.5 m^3, V_{SO3} = x = 32.4 m^3, V_{SO2} = 202.6 m^3

Basis 1000 kg of copper ore

Ore
40 kg Zn
60 kg Cu
250 kg Fe
200 kg SiO_2
114 kg CaO, Al_2O_3, etc
336 kg S

Air ⟶

Flue gases 8103.5 m^3
SO_2 202.6 m^3
SO_3 32.4 m^3
O_2, N_2 7868.5 m^3
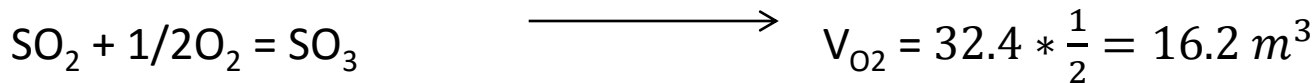
Calcine
ZnO SiO_2 Leaching
CuO   CaO, Al_2O_3
Fe_2O_3
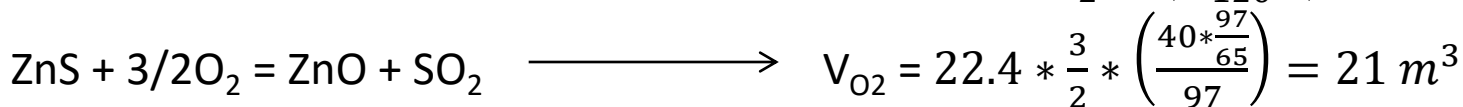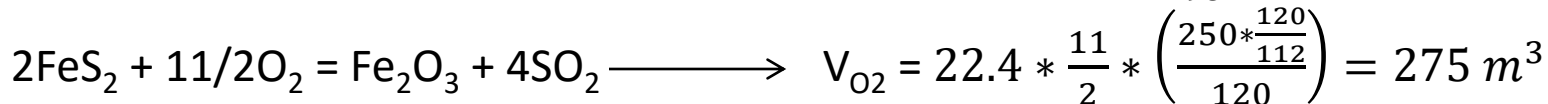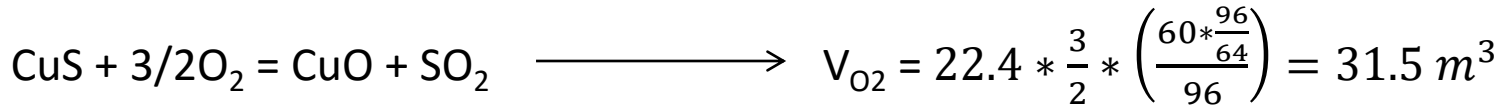
Calculate the volume roasting air, percent excess and the composition of the flue gases

Roasting reactions   Volume of O_2 consumed

CuS + 3/2O_2 = CuO + SO_2 ⟶ V_{O2} = $22.4 * \frac{3}{2} * \left(\frac{60*\frac{96}{64}}{96} \right) = 31.5\ m^3$

2FeS$_2$ + 11/2O_2 = Fe_2O_3 + 4SO_2 ⟶ V_{O2} = $22.4 * \frac{11}{2} * \left(\frac{250*\frac{120}{112}}{120} \right) = 275\ m^3$

ZnS + 3/2O_2 = ZnO + SO_2 ⟶ V_{O2} = $22.4 * \frac{3}{2} * \left(\frac{40*\frac{97}{65}}{97} \right) = 21\ m^3$ 343.7 m^3

SO_2 + 1/2O_2 = SO_3 ⟶ V_{O2} = $32.4 * \frac{1}{2} = 16.2\ m^3$

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

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

$$V_{O2+N2} = V_{air-th} + V_{excess} - V_{O2consumed}$$
$$7868.5 = 1636.67 + 1636.67 * y - 343.7$$
$$y = 4.02, V = 1636.67 + 1636.7 * 4.02 = 8216.07\ m^3$$
$$V_{O2excess} = 8216.07 * 0.21 - 343.7 = 1381.67\ m^3, V_{N2} = 8216.07 * 0.79 = 6490.69\ m^3$$

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. Cu_2S 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
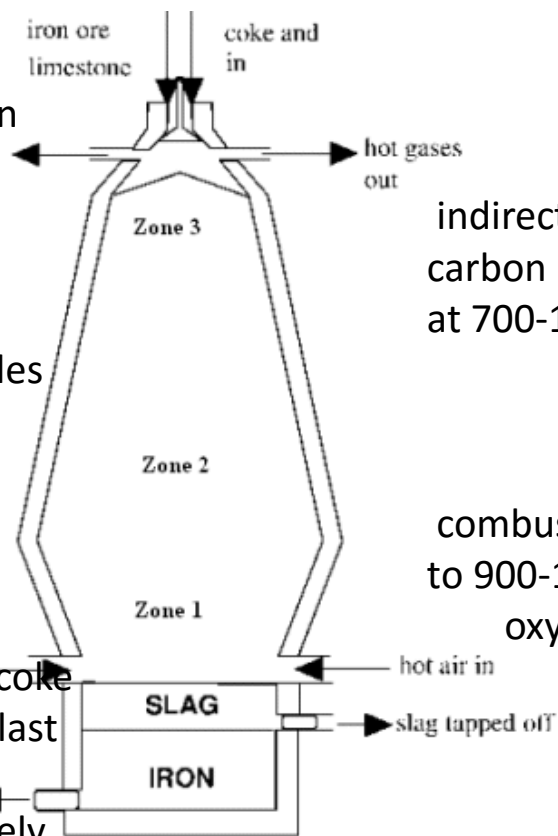The process is continuous with raw materials being regularly charged to the top of the furnace and molten iron and slag being tapped from the bottom of the furnace at regular intervals

iron ore limestone coke and in

hot gases out

Zone 3

Zone 2

Zone 1

hot air in

SLAG

slag tapped off

IRON

iron tapped

free moisture is driven off from the burden materials and hydrates and carbonates are disassociated

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

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

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

$$C + (O_2 + 3.76N_2) = CO_2 + 3.76N_2$$
$$CO_2 + 3.76N_2 + C = 2CO + 3.76N_2$$
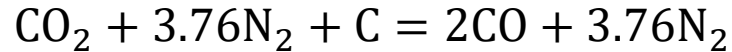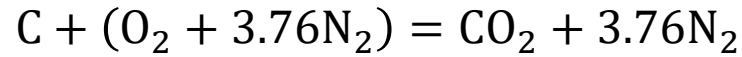
Upward gas rising consists of CO, CO_2 and nitrogen

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

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + CO = 3FeO + CO_2$$
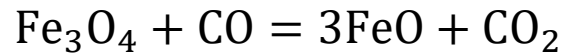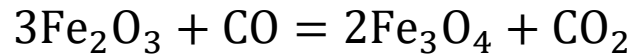
whereas, the reaction $FeO + CO = Fe + CO_2$ requires high concentration of CO
So it occurs near the middle of the furnace where the concentration of CO is high
At around 900 C, the equilibrium concentration of CO in the CO-CO_2 mixture is around 65 to 70 percent for FeO to be able to reduce to iron
Some iron oxide is also reduced directly by 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_2O_3	SiO_2	MnO	Al_2O_3	H_2O	C	$CaCO_3$
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^3 of flue gas is produced
The rational analysis of flue gases gives 58% N_2, 26% CO, 12% CO_2, 4% H_2O

Basis 1000 kg of pig iron
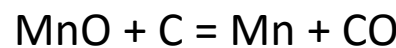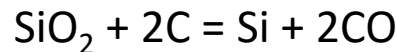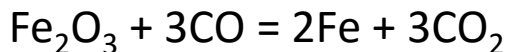
Ore 1750 kg
Limestone 500 kg
Coke

Air
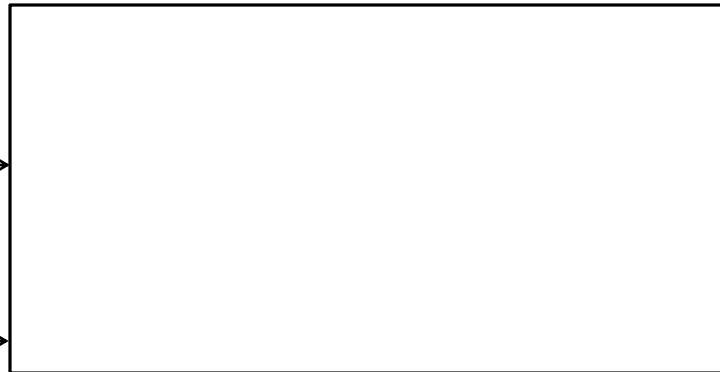
Blast furnace gas 4200m^3

Slag

Pig iron 1000 kg

Reactions

$Fe_2O_3 + 3CO = 2Fe + 3CO_2$
$CaCO_3 = CaO + CO_2$
$C + 1/2O_2 = CO$

$SiO_2 + 2C = Si + 2CO$
$MnO + C = Mn + CO$
$CO_2 + C = 2CO$
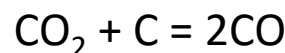
Basis 1000 kg/hr of pig iron

Ore 1750 kg/hr

80% Fe_2O_3, 12% SiO_2, 1% MnO,
3% Al_2O_3, 4% H_2O

Limestone 500 kg/hr

95% $CaCO_3$, 1% H_2O, 4% SiO_2

Coke $\dot{m}_C$

10% SiO_2, 90% C

Air $\longrightarrow$

Blast furnace gas 4200m^3

58% N_2, 26% CO, 12% CO_2, 4% H_2O

Slag $\dot{m}_S$

Fe_2O_3, SiO_2, MnO, Al_2O_3, CaO

Pig iron 1000 kg

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

Reactions

$Fe_2O_3 + 3CO = 2Fe + 3CO_2$ $SiO_2 + 2C = Si + 2CO$

$CaCO_3 = CaO + CO_2$ $MnO + C = Mn + CO$

$C + 1/2O_2 = CO$ $CO_2 + C = 2CO$

$C + O_2 = CO_2$
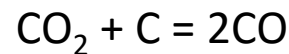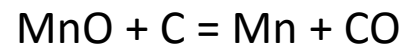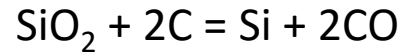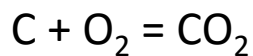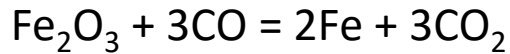
DOF analysis

8 unknown labeled variables ($\dot{V}_A$, $\dot{m}_C$, $\dot{m}_S$, X_{Fe2O3}, X_{SiO2}, X_{MnO}, X_{Al2O3}, X_{CaO})

+ 7 independent chemical reactions

- 14 independent molecular species balances (Fe_2O_3, SiO_2, MnO, Al_2O_3, H_2O, $CaCO_3$, C, CO, CO_2, O_2, N_2, Mn, Si, Fe)

- 1 other equation relating unknown variables (X_{Fe2O3} + X_{SiO2} + X_{MnO} + X_{Al2O3} + X_{CaO} = 1)

= 0 degrees of freedom

Basis 1000 kg of pig iron

Ore 1750 kg

80% Fe_2O_3, 12% SiO_2, 1% MnO, 3% Al_2O_3, 4% H_2O

Limestone 500 kg

95% $CaCO_3$, 1% H_2O, 4% SiO_2

Coke

10% SiO_2, 90% C

Air $\longrightarrow$

Blast furnace gas 4200m^3

58% N_2, 26% CO, 12% CO_2, 4% H_2O

Slag

Pig iron 1000 kg

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

Reactions

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2 \qquad\qquad SiO_2 + 2C = Si + 2CO$$
$$CaCO_3 = CaO + CO_2 \qquad\qquad\qquad MnO + C = Mn + CO$$
$$C + 1/2 O_2 = CO \qquad\qquad\qquad\qquad CO_2 + C = 2CO$$
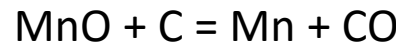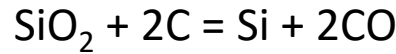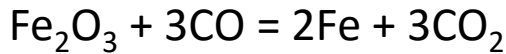
Calculate the quantity of coke used per ton of pig iron

Carbon balance:

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

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

0.075x + 4.75 = 3.333 + 71.25,   x= 69.833/0.075=931 kg coke per ton of pig iron

Calculate the air consumption per ton of pig iron

N_2 balance:

$N_{2(air)} = N_{2(flue\ gas)}$ = 4200*0.58 = 2436 m^3,   Air consumption = 2436*(100/79) = 3083.5m^3

Basis 1000 kg of pig iron

Ore 1750 kg

80% Fe_2O_3, 12% SiO_2, 1% MnO, 3% Al_2O_3, 4% H_2O

Limestone 500 kg

95% $CaCO_3$, 1% H_2O, 4% SiO_2

Coke

10% SiO_2, 90% C

Air →

Blast furnace gas 4200m^3

58% N_2, 26% CO, 12% CO_2, 4% H_2O

Slag

Fe_2O_3, SiO_2, MnO, Al_2O_3, CaO

Pig iron 1000 kg

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

Calculate the composition of the slag

Fe_2O_3 balance:

$Fe_2O_{3(ore)} = Fe_2O_{3(pig\ iron)} + Fe_2O_{3(slag)}$

$1750*0.8 = 0.938*1000*(160/112) + Fe_2O_{3(slag)}$, $Fe_2O_{3(slag)}=1400-1340= 60$ kg

SiO_2 balance:

$SiO_{2(ore)} + SiO_{2(limestone)} + SiO_{2(coke)} = SiO_{2(pig\ iron)} + SiO_{2(slag)}$

$1750*0.12 + 500*0.04 + 931*0.1 = 0.012*1000*(60/28) + SiO_{2(slag)}$, $SiO_{2(slag)}=210+20+93.1-25.7$

$=297.4$ kg

MnO balance:

$MnO_{(ore)} = MnO_{(pig\ iron)} + MnO_{(slag)}$

$1750*0.01 + 0.01*1000*(71/55) + MnO_{(slag)}$

$MnO_{(slag)} = 17.5 - 12.9 = 4.6$ kg

Al_2O_3 balance:

$Al_2O_{3(ore)} = Al_2O_{3(slag)} = 1750*0.03 = 52.5$ kg

CaO balance:

$CaO_{(limestone)} = CaO_{(slag)} = 500*(56/100)*0.95 = 266$ kg

Total slag composition:

Fe_2O_3	60 kg	8.82%
SiO_2	297.4 kg	43.70%
MnO	4.6 kg	0.67%
Al_2O_3	52.5 kg	7.71%
CaO	266 kg	39.10%
Total	680.5 kg	