Materials and Energy Balance

Heat Balance in Pyrometallurgical Processes

Procedure in Calculating a Heat Balance

1. Work out the complete stoichiometry of the reactions and materials balance
2. Denote the temperatures at which all materials enter and leave the system
3. Fix and specify the basis of the heat balance (quantity throughout the process), reference temperature and reference state for water and other substances
4. Calculate the sensible heat for each input and output material
5. Calculate heats of reaction for the quantities of all the chemical reactions
6. Calculate if present, heats required to bring input materials up to the reference states
7. Calculate if present, heat supplied electrically or by other means from the surroundings
8. List and add input and output items, finding heat loss by the difference

Heat Balance in Roasting

Oxidation reactions occurring during roasting processes to convert metal sulphides to oxides are highly exothermic

Fuel is seldomly used and the sulphide ores that enter the furnace convert to oxides and flue gases which take the liberated heat as their sensible heat

Products are raised from 298 to an elevated temperature which can be calculated by making the heat balance

Heat Input = Heat Output = $(H_T - H_{298})_{products}$

Since there is no fuel in the roasting process, the final temperature of the products can not be controlled by arrangement of the amount of combusting material

The temperature attained by the products is calculated in a similar way to the calculation of flame temperature

Flame temperature

The maximum temperature the gaseous products can reach upon proceeding of an exothermic reaction is called the flame temperature

The furnace is considered as adiabatic for no heat loss to the surroundings and maximum flame temperature

$$aA(s)(T_1) + bB(g)(T_2) \xrightarrow{\Delta H_T} cC(g)(T_3) + dD(g)(T_3)$$

$$aA(s)(298) + bB(g)(298) \xrightarrow{\Delta H_3} cC(l)(298) + dD(g)(298)$$

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = -\Delta H_4 - \Delta H_5$$

$$\Delta H_4 = c\left[\int_{298}^{T_{m(C)}} C_{P(C(l))} dT + \Delta H_{v(C)} + a\int_{T_{m(C)}}^{Tflame} C_{P(C(g))} dT\right] = c(H_{Tflame} - H_{298})_{C(g)}$$

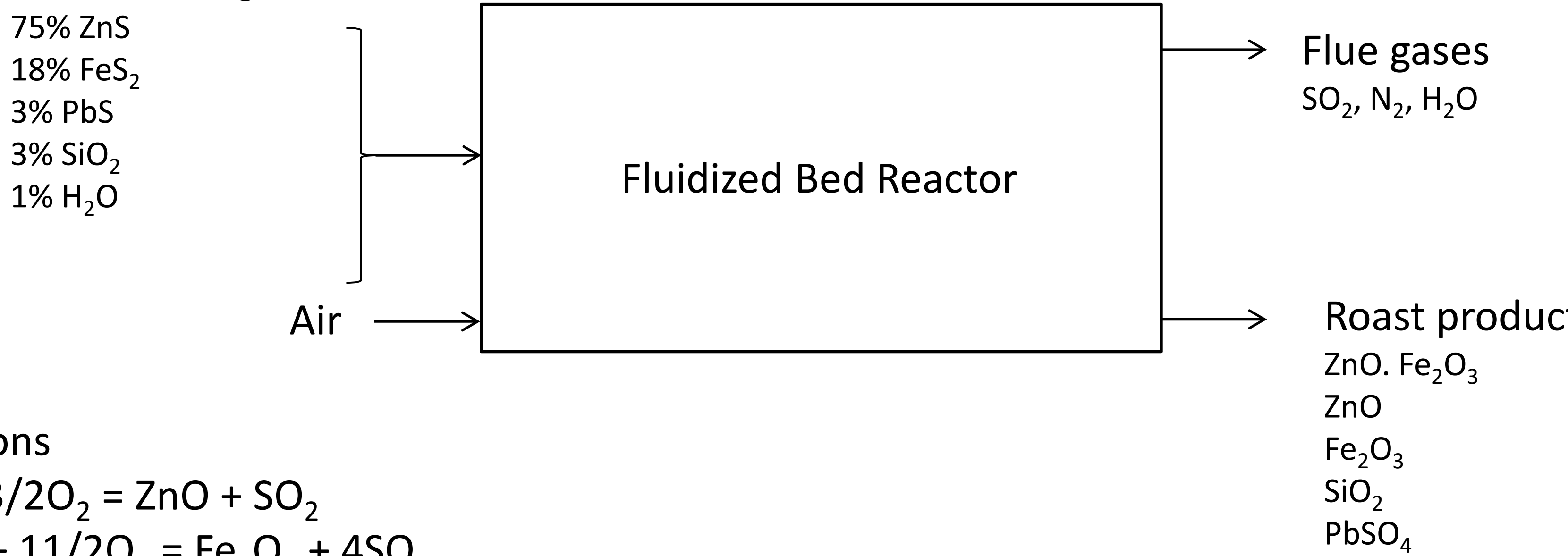
$$\Delta H_5 = d\int_{298}^{T_{Tflame}} C_{P(D(g))} dT = d(H_{Tflame} - H_{298})_{D(g)}$$

Roasting furnace analysis

Zinc concentrate of the following composition is roasted in a fluidized bed reactor with stoichiometric amount of air. During roasting 80% of total iron charged forms $ZnO.Fe_2O_3$
Find the bed temperature when 10% heat input is lost to the surroundings

Rational Analysis wt%					
Material	ZnS	FeS_2	PbS	SiO_2	H_2O
Zinc concentrate	75	18	3	3	1

Basis 1000 kg of zinc concentrate



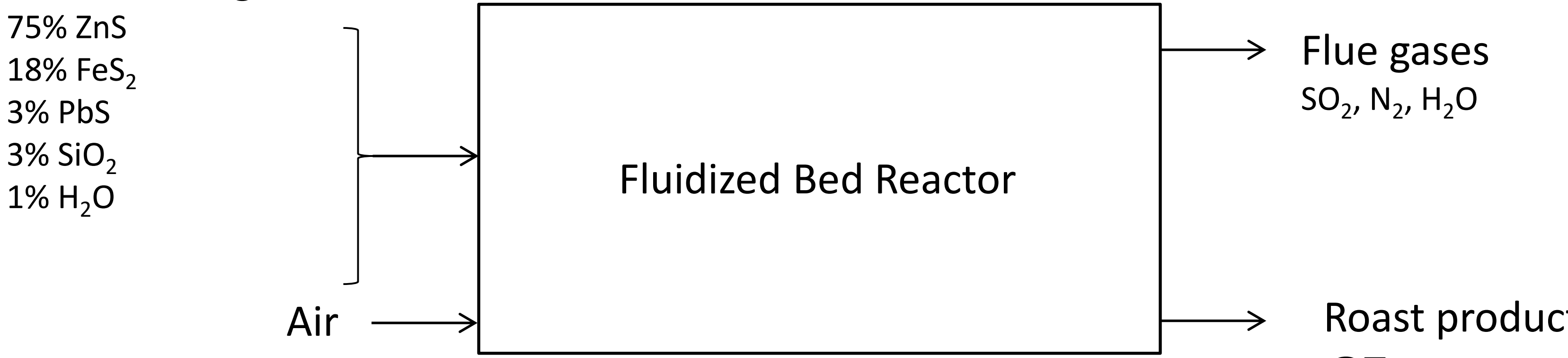
Reactions

$ZnS + 3/2O_2 = ZnO + SO_2$

$2FeS_2 + 11/2O_2 = Fe_2O_3 + 4SO_2$

$PbS + 2O_2 = PbSO_4$

Basis 1000 kg of zinc concentrate @298 K



@T

$ZnO.\ Fe_2O_3$

ZnO

Fe_2O_3

SiO_2

$PbSO_4$

Reactions

$ZnS + 3/2O_2 = ZnO + SO_2$

$2FeS_2 + 11/2O_2 = Fe_2O_3 + 4SO_2$

$PbS + 2O_2 = PbSO_4$

Material balance gives:

Concentrate content			Roast product content	Gas content
ZnS	7.732 kg-moles	$ZnS + 3/2O_2 = ZnO + SO_2$	ZnO 7.732 kg-moles	SO_2 7.732 mol
FeS_2	2.045 kg-moles	$2FeS_2 + 11/2O_2 = Fe_2O_3 + 4SO_2$	Fe_2O_3 1.0225 moles	SO_2 4.090 mol
PbS	0.126 kg-moles	$PbS + 2O_2 = PbSO_4$	$PbSO_4$ 0.126 moles	
SiO_2	0.500 kg-moles		SiO_2 0.500 kg-moles	
H_2O	0.555 kg-moles		H_2O 0.555 kg-moles	

Oxygen consumed

$$7.732*3/2 + 1.0225*11/2 + 0.121*2 = 17.464 \text{ kg-moles}$$

Nitrogen in the off-gas

$$17.464/0.21*0.79 = 65.698 \text{ kg-moles}$$

Some ZnO is tied up with Fe_2O_3 as $ZnO.Fe_2O_3$

Fe tied up with ZnO = 0.8*1.0225 = 0.818 kg-moles, 0.818 kg-moles Fe_2O_3 in 0.818 mol $ZnO.Fe_2O_3$

Free Fe_2O_3 in roast product = (1.0225-0.818) = 0.204 kg-moles

0.818 kg-moles ZnO in 0.818 mol $ZnO.Fe_2O_3$

Free ZnO in roast product = 7.732-0.818 = 6.914 kg-moles

Roast product content

ZnO	6.914 kg-moles
Fe_2O_3	0.204 kg-moles
$ZnO.Fe_2O_3$	0.818 kg-moles
$PbSO_4$	0.126 kg-moles
SiO_2	0.500 kg-moles

Flue gas content

SO_2	11.822 kg-moles
N_2	65.698 kg-moles
H_2O	0.555 kg-moles

Heat balance

Heat Input

Sensible heats of input materials (0)

Heats evolved in exothermic reactions

Heat Output

Sensible heats of output materials

Heats absorbed in endothermic reactions (0)

Heat loss to the surroundings (10% heat input)

Heat Input

Sensible heats of input materials (0)

Heats evolved in exothermic reactions

Heat Output

Sensible heats of output materials

Heats absorbed in endothermic reactions (0)

Heat loss to the surroundings (10% heat input)

Heats evolved in reactions

$ZnS + 3/2O_2 = ZnO + SO_2$ $\Delta H = -105950$ kcal/kg-mole ZnO

$2FeS_2 + 11/2O_2 = Fe_2O_3 + 4SO_2$ $\Delta H = -292600$ kcal/kg-mole Fe_2O_3

$PbS + 2O_2 = PbSO_4$ $\Delta H = -197000$ kcal/kg-mole $PbSO_4$

$ZnO + Fe_2O_3 = ZnO.Fe_2O_3$ $\Delta H = -4750$ kcal/kg-mole $ZnO.Fe_2O_3$

Total heat liberated = (-105950 *6.914)+(-292600*1.0225)+(-197000*0.126)+(-4750*0.818)

= -1138938 kcal

10% of heat input is lost to the surroundings = -113894 kcal

Heat available for raising the temperature of the products = -1025044 kcal

Sensible heats of output materials

ZnO $6.914*H_T-H_{298} = 6.914*(11.71T+0.61*10^{-3}T^2+2.18*10^5/T-4277)$

Fe_2O_3 $0.204*H_T-H_{298} = 0.204*(31.75T+0.88*10^{-3}T^2-8446)$

$ZnO.Fe_2O_3$ $0.818*H_T-H_{298} = 0.818*(27.78T+8.86*10^{-3}T^2-9044)$

$PbSO_4$ $0.126*H_T-H_{298} = 0.126*(10.96T+15.5*10^{-3}T^2-4.20*10^5/T-3327)$

SiO_2 $0.5*H_T-H_{298} = 0.5*(14.41T+0.97*10^{-3}T^2-4455)$

H_2O $0.555*H_T-H_{373} = 0.555*(7.30T+1.23*10^{-3}T^2-2286)$ + $0.555*\Delta H_m = 0.555*(11170)$

SO_2 $11.822*H_T-H_{298} = 11.822*(11.04T+0.94*10^{-3}T^2+1.84*10^5/T-3992)$

N_2 $65.698*H_T-H_{298} = 65.698*(6.83T+0.45*10^{-3}T^2+0.12*10^5/T-2117)$

Sensible heats of output materials

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N_2 $65.698*H_T-H_{298}= 65.698*(6.83T+0.45*10^{-3}T^2+0.12*10^5/T-2117)$

Total Heat Output = $623.13T+49.83*10^{-3}T^2-197018$

Heat available for raising the temperature of the products = -1025044 kcal

$623.13T+49.83*10^{-3}T^2-197018 = -1025044$

$49.83*10^{-3}T^2+623.13T-1222062 = 0$

$$T= \frac{-b\pm\sqrt{b^2-4ac}}{2a}$$

a= $49.83*10^{-3}$, b= 623.13, c= -1222062

<u>T = 1723.6 K</u>

The rate of roasting reactions are low due to the solid state of the sulphide concentrates
Extra oxygen is supplied by the excess air which considerably increases the rate of oxidation
Consider the same process with the use of 20% excess air

The flue gas content

SO_2	11.822 kg-moles
N_2	65.698 kg-moles + 65.698*0.2 = 78.84 kg-moles
O_2	65.698*0.2/0.79*0.21 = 3.49 kg-moles
H_2O	0.555 kg-moles

Increase in the total heat output

$65.698*0.2*H_T\text{-}H_{298}(N_2) + 3.49*H_T\text{-}H_{298}(O_2) = 118.73T + 14.12*10^{-3}T^2 - 34730$

Total heat output = $723.76T + 56.55*10^{-3}T^2\text{-}228495$

Available heat = -1025044 kcal

$56.55*10^{-3}T^2 + 723.76T - 1253539 = 0$

<u>T = 1545 K</u>

If 40% excess air was used to increase the oxidation rate,

Increase in the total heat output

$65.698*0.4*H_T\text{-}H_{298}(N_2) + 6.98*H_T\text{-}H_{298}(O_2) = 2*(118.73T + 14.12*10^{-3}T^2 – 34730)$

So, $63.36*10^{-3}T^2 + 824.32T - 1284995 = 0$

<u>T=1407 K</u>

Materials for the construction of the furnace may change due only to use of excess air

Heat Balance in Ironmaking

Consider an iron blast furnace charged with iron ore, limestone and coke for 20-day period to produce 507 tons pig iron per day

Rational Analysis wt%								
Material	Fe_2O_3	SiO_2	MnO	Al_2O_3	H_2O	C	CaO	CO_2
Limestone							56.25	43.75
Coke					4.8	95.2		

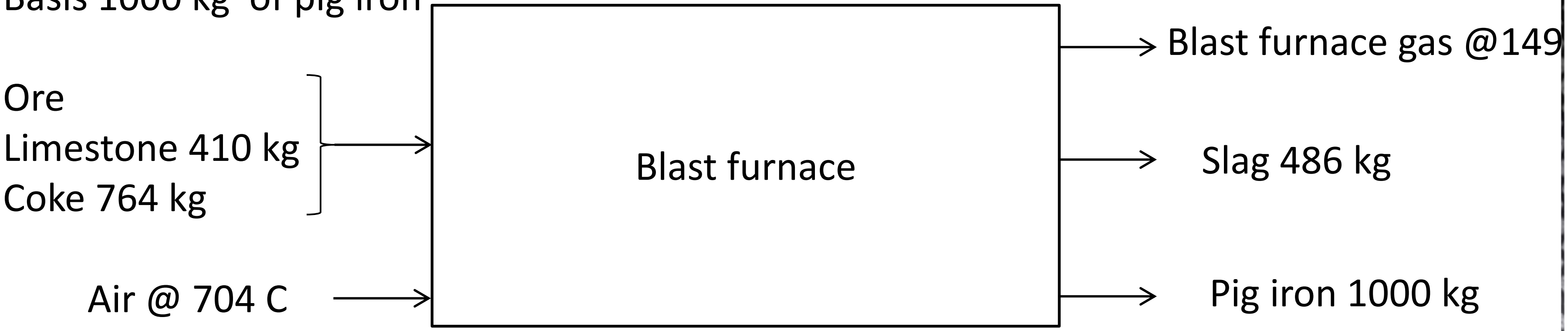
Air is blown through tuyeres at 704 C, the charge, flux and coke are at 25 C, gases leave at 149 C

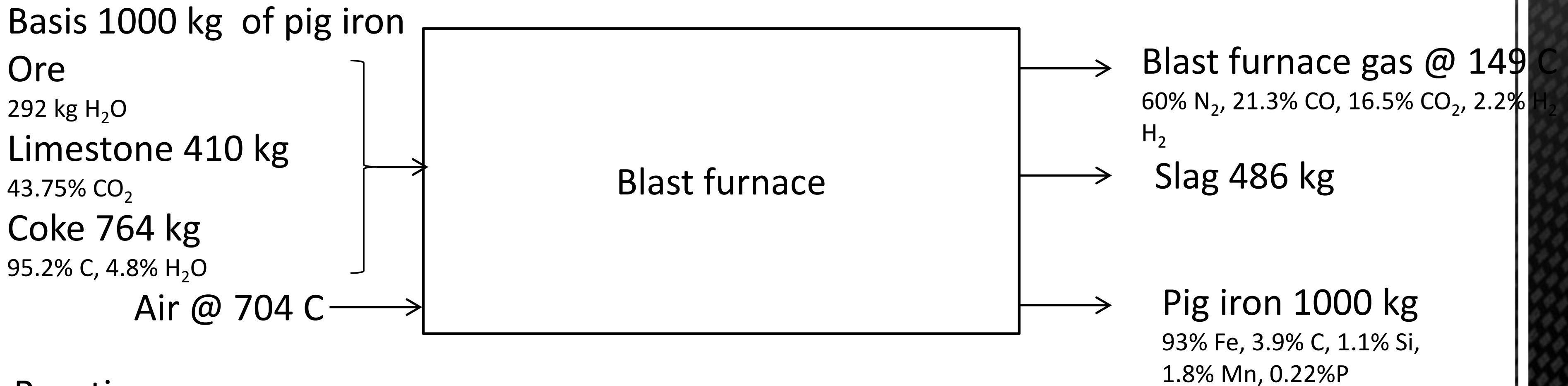
Moisture of 292 kg in one charge per ton of pig iron is added

The ultimate analysis of the pig iron gives 93% Fe, 3.9% C, 1.1% Si, 1.8% Mn, 0.22%P

The rational analysis of flue gases on dry basis gives 60% N_2, 21.3% CO, 16.5% CO_2, 2.2% H_2

Basis 1000 kg of pig iron





Reactions

$Fe_2O_3 + 3CO = 2Fe + 3CO_2$

$CaCO_3 = CaO + CO_2$

$C + 1/2O_2 = CO$

$P_2O_5 + 5C = \underline{2P} + 5\ CO$

$CO_2 + C = 2CO$

$H_2O(l) = H_2O(g)$

$SiO_2 + 2C = \underline{Si} + 2CO$

$MnO + C = \underline{Mn} + CO$

$CO_2 + C = 2CO$

$H_2O + C = CO + H_2$

$C = \underline{C}$

<u>Material Balance</u>

C balance is solved to find the quantity of top gases

C in coke + C in limestone = C in pig iron + C in top gas

Dry weight of C in coke = 764*95.2/100 = 727.33 kg

C in limestone = 410*43.75/100*12/44 = 48.92 kg

C in pig iron = 1000*3.9/100 = 39 kg

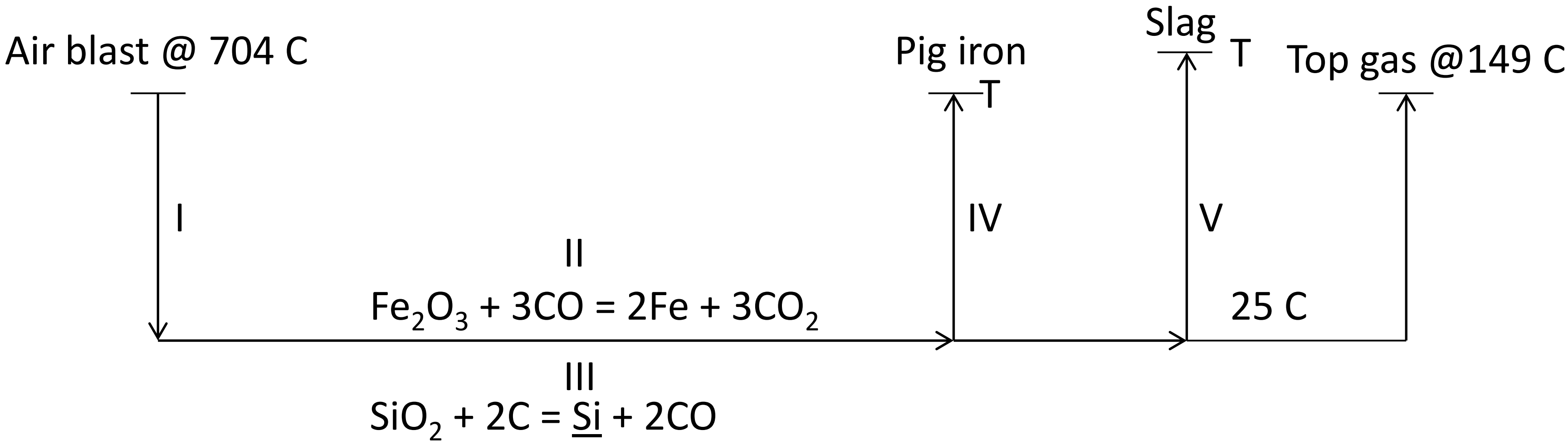
C in top gas = 727.33 + 48.92 – 39 = 733.58 kg = 64.8 kg-atom

C in top gas = 723.66 + 48.92 – 39 = 733.58 kg = 64.8 kg-atom
The top gas contains 16.5 CO_2 and 21.3% CO on dry basis
Dry top gas contains in total = 64.8/(0.165+0.213) = 171.43 kg-moles

Therefore on a dry basis the top gas contains:
CO_2 = 171.43 *16.5/100 = 28.29 kg-moles
CO = 171.43 *21.3/100 = 36.51 kg-moles
H_2 = 171.43 *2.2/100 = 3.77 kg-moles
N_2 = 171.43 *59.9/100 = 102.69 kg-moles
In addition the top gas contains H_2O from moisture in the charge and coke
H_2O = 292/18 + 764*4.8/100 = 16.22 + 36.67 = 52.89 kg-moles

N_2 balance is solved to find the quantity of air blast
N_2 in air = N_2 in top gas
= 102.69 kg-atoms
O_2 in air = 102.69*21/79 = 27.3 kg-atoms
Total air blast = 129.99 kg-atoms

Heat balance diagram



I – Sensible heat in the air blast
II – Heat evolution by the exothermic reactions
III – Heat absorption by the endothermic reactions
IV – Sensible heat in pig iron
V – Sensible heat in slag
VI – Sensible heat in top gas

I + II = III + IV + V + VI + heat loss

Material and heat balances in the reactions

$Fe_2O_3 + 3CO = 2Fe + 3CO_2$ Exothermic Rxn, ΔH= -6300 kcal/kg-mole

Kg-atom Fe in pig iron = 2/3 kg-mole CO = 2/3 kg-mole CO_2 produced Total heat evolved = -6300*24.91*1/3 = -52311 kcal

Kg-mole CO = 3/2*100*(92.99/100)/56 = 24.91 kg-moles

$SiO_2 + 2C = \underline{Si} + 2CO$ Endothermic Rxn, ΔH= 146200 kcal/kg-mole

Kg-atom C = kg-mole CO = 2*kg-atom Si in pig iron Heat absorbed by reduction = 146200*0.79/2 = 57749 kcal

= 2*1000*(1.1/100)/28 = 0.79 kg-moles

$CaCO_3 = CaO + CO_2$ Endothermic Rxn, ΔH= 42500 kcal/kg-mole

Kg-mole CO_2 = kg-mole $CaCO_3$ Heat absorbed by decomposition = 42500*4.08 = 173400 kc

= 410*(43.75/100)/44 = 4.08 kg-moles

$MnO + C = \underline{Mn} + CO$ Endothermic Rxn, ΔH= 62400 kcal/kg-mole

Kg-atom C = kg-mole CO = kg-atom Mn in pig iron Heat absorbed by reduction = 62400*0.33 = 20592 kcal

= 1000*(1.8/100)/55 = 0.33 kg-moles

$C + 1/2O_2 = CO$ Exothermic Rxn, ΔH= -29600 kcal/kg-mole C

Kg-atom C = kg-mole CO produced = 2*kg-mole O_2 consumed Total heat evolved = -29600*54.6 = -1616160 kcal

=2*27.3 = 54.6 kg-moles

$P_2O_5 + 5C = \underline{2P} + 5\ CO$ Endothermic Rxn, ΔH= 212000 kcal/kg-mole

Kg-atom C = kg-mole CO = 5/2*kg-atom P in pig iron Heat absorbed by reduction = 212000*0.17/5 = 7208 kcal

=5/2*1000*(2.1/100)/31 = 0.17 kg-moles

$CO_2 + C = 2CO$ Endothermic Rxn, ΔH= 38000 kcal/kg-mole

Kg-atom CO = 2*kg-atom C = 2*kg-atom CO_2 Heat absorbed by conversion = 38000*3.5 = 133000 kcal

Kg-atom C = kg-atom in coke – kg-atom in C in pig iron – kg-atom C consumed in all reactions

= 727.33/12 – 1000*(3.9/100)/12 – (48.8 + 0.33 + 0.79 + 0.17 + 3.77) = 3.5 kg-atom

3.5 kg-moles CO_2 consumed, 7 kg-moles CO produced

$H_2O + C = CO + H_2$
Kg-mole H_2O = kg-atom H_2 in the top gas
= 3.77 kg-moles

$H_2O(l) = H_2O(g)$
Kg-mole H_2O = 52.89 kg-moles

Endothermic Rxn, ΔH= 28200 kcal/kg-mole
Heat absorbed by decomposition = 28200*3.77 = 106314 kca

Endothermic Rxn, ΔH_v = 9756 kcal/kg-mole
Heat absorbed by evaporation = 9756*52.89 = 515995 kcal

<u>Total heat evolution by 2 exothermic reactions</u>

$C + 1/2O_2 = CO$	-1616160 kcal
$Fe_2O_3 + 3CO = 2Fe + 3CO_2$	-52311 kcal
	-1668471 kcal

<u>Total heat absorption by 7 endothermic reactions</u>

$SiO_2 + 2C = \underline{Si} + 2CO$	57749 kcal
$CaCO_3 = CaO + CO_2$	173400 kcal
$MnO + C = \underline{Mn} + CO$	20592 kcal
$P_2O_5 + 5C = \underline{2P} + 5\ CO$	7208 kcal
$CO_2 + C = 2CO$	133000 kcal
$H_2O + C = CO + H_2$	106314 kcal
$H_2O(l) = H_2O(g)$	515995 kcal
	1014258 kcal

There is excess heat of 654213 kcal that is available to take the products to a higher temperature
There is also heat evolution from the sensible heat in the air blast at 704 C:

O_2
H_{977}-H_{298}= 5235.3 kcal/kg-mole
Sensible heat = -5235.3*27.3 = -142923.7 kcal

N_2
H_{977}-H_{298}= 4951.8 kcal/kg-mole
Sensible heat = -4951.8*102.69 = -508500 kcal

Total heat input = Heat evolution from reactions + Sensible heat in the air blast
= - 1668471 -651424 kcal
= <u>-2319895 kcal</u>

Sensible heat in the products:

Sensible heat in pig iron:
It is estimated that 1 kg of pig iron carries about 284 kcal of sensible heat from the furnace
H_T-H_{298}= 284 kcal/kg
Heat absorption = 284*1000 = 284000 kcal

Sensible heat in slag:
It is estimated that 1 kg of slag carries about 500 kcal of sensible heat from the furnace
H_T-H_{298}= 500 kcal/kg
Heat absorption = 500*486 = 243000 kcal

Sensible heat in top gas:
Top gas leaves the furnace at 149 C

CO_2 = 28.29 kg-moles	H_{422}-H_{298}= 1181.6 kcal/kg-mole	Heat absorbed = 1181.6*28.29 = 33427.5
CO = 36.51 kg-moles	H_{422}-H_{298}= 865.1 kcal/kg-mole	Heat absorbed = 865.1*36.51= 31584.8
H_2 = 3.77 kg-moles	H_{422}-H_{298}= 859.0 kcal/kg-mole	Heat absorbed = 859.0*3.77= 3238.4
N_2 = 102.69 kg-moles	H_{422}-H_{298}= 865.1 kcal/kg-mole	Heat absorbed = 865.1*102.69= 88837.12
H_2O = 52.89 kg-moles	H_{422}-H_{298}= 1007.6 kcal/kg-mole	Heat absorbed = 1007.6*52.89=53292

Total sensible heat in top gas = 210379.8 kcal

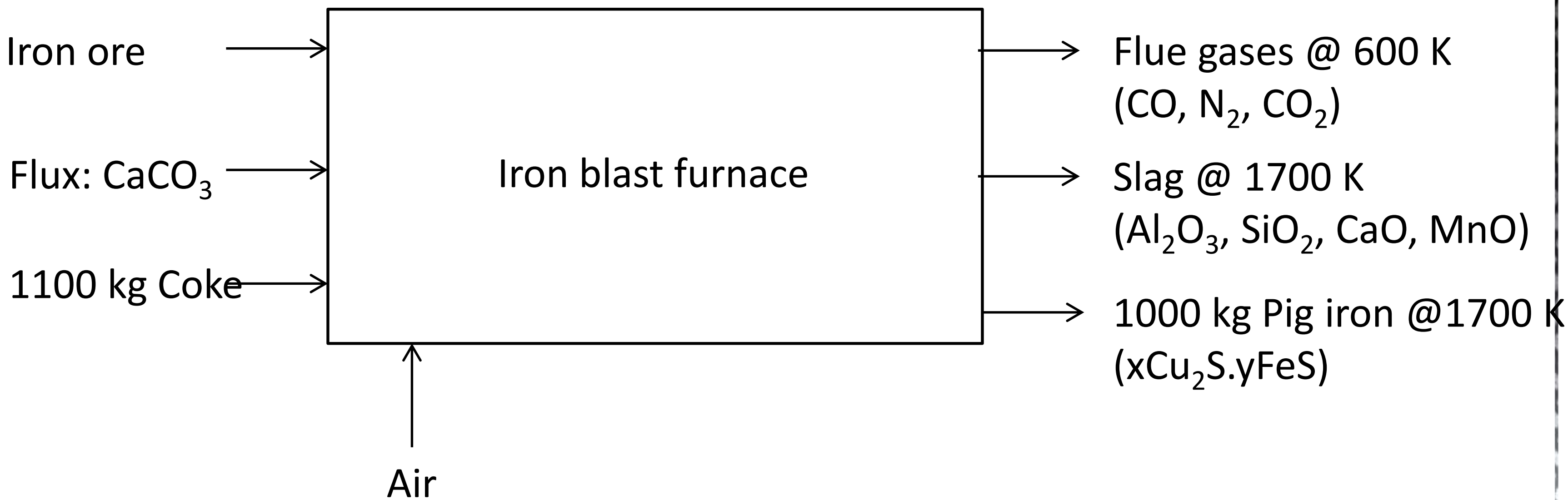
Total sensible heat in the products = 737379.8 kcal
Total heat absorption from the reactions = 1014258 kcal
Total heat output = 1751638 kcal
Heat loss = Total heat input – Total heat output = 2319895 – 1751638 = 568257 kcal
Thermal efficiency = (Total heat input – Heat loss)/ Total heat input) = 75.51%

Iron Smelting Analysis

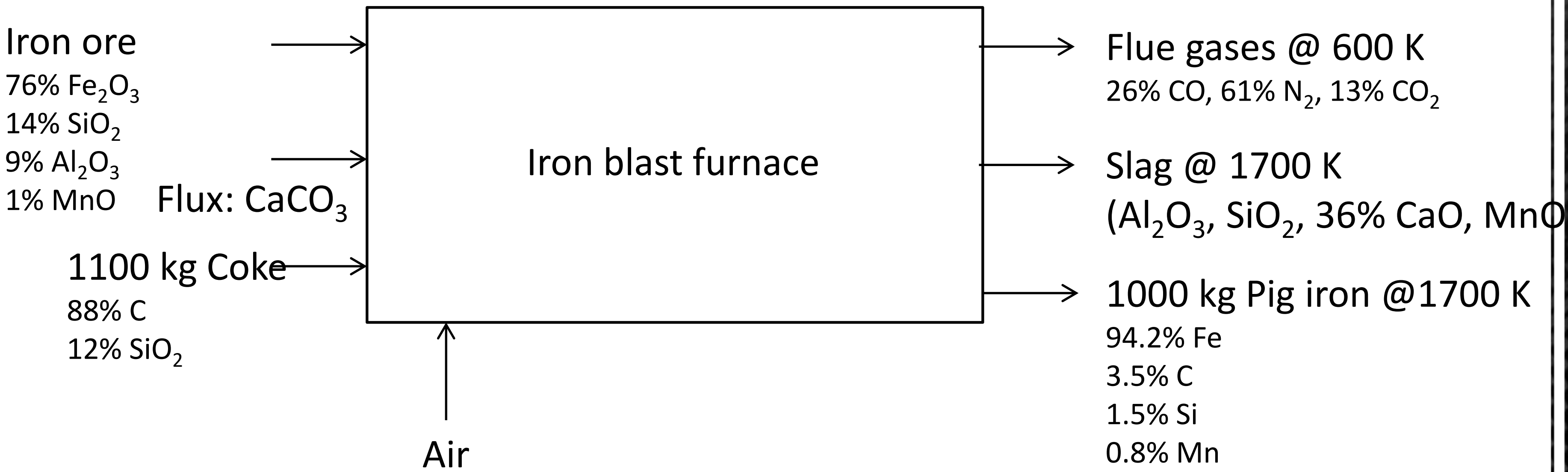
An iron blast furnace produces pig iron of composition 94.2% Fe, 3.5% C, 1.5% Si, 0.8% Mn. The burden of blast furnace consists of the following materials. Limestone is pure $CaCO_3$ and is converted to CaO that makes up 36% of the slag. The analysis of exit gas is given as 26% CO, 13% CO_2 and 61% N_2; assume no loss of iron in slag.

Rational Analysis wt%					
Material	Fe_2O_3	SiO_2	Al_2O_3	MnO	C
Iron ore	76	14	9	1	
Coke		12			88

Reactions: $CaCO_3 = CaO + CO_2$, $C + ½ O_2 = CO$, $Fe_2O_3 + 3CO = 2Fe + 3CO_2$, $SiO_2 + 2CO = Si + 2CO_2$



Iron Smelting Analysis



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Basis 1000 kg Pig iron

<u>Material balance</u>

Fe in ore = Fe in pig iron

(76/100)*(112/160)*X = 1000*(94.2/100) = 942 kg

Iron ore = X = 1771 kg

Si in slag = Si in ore + Si in coke - Si in pig iron

= 1771*(14/100)*(28/60) + 1100*(12/100)*(28/60) – 1000*(1.5/100) = 162.31 kg

SiO_2 in slag = 162.31*(60/28) = 347.81 kg

Mn in slag = Mn in ore – Mn in pig iron

= 1771*(1/100)*(55/71) – 1000*(0.8/100) = 5.72 kg

MnO in slag = 5.72*(71/55) = 7.38 kg

Al_2O_3 in slag = Al_2O_3 in ore = 1771*(9/100) = 159 kg

Slag composition

36% CaO

347.81 kg SiO_2

159 kg Al_2O_3

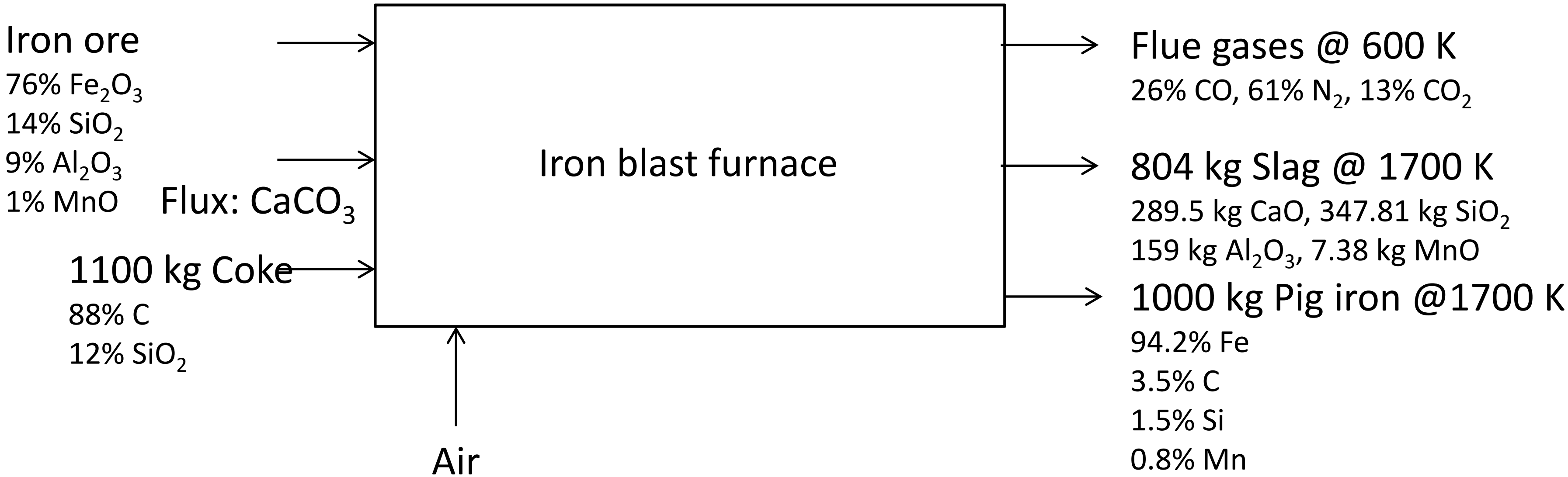
7.38 kg MnO

514.58 kg = 64%

CaO amount = 289.5 kg

Slag amount = 804 kg

Iron Smelting Analysis



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Basis 1000 kg Pig iron

Material balance

CaO in limestone = CaO in slag = 289.5 kg

$CaCO_3$ in limestone = 298.5*(100/56) = 533 kg

C in flux + C in coke = C in pig iron + C in flue gases

C in flue gases = 533/100 + 1100*(88/100)/12 - 1000*(3.5/100)/12 = 83.1 kg-atoms

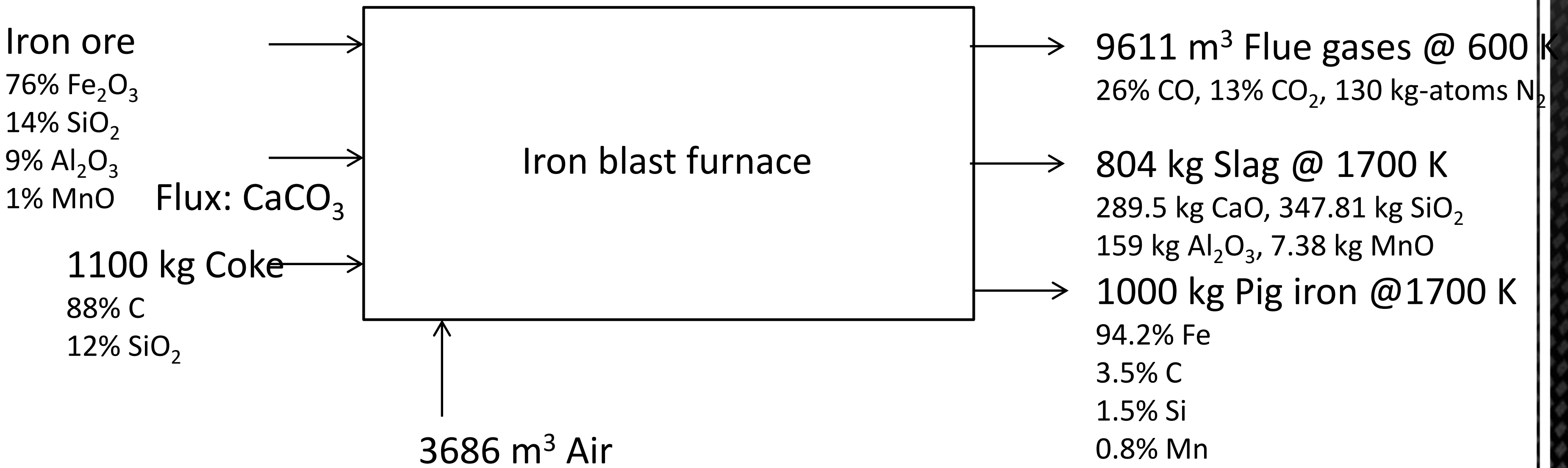
Total flue gas = 83.1*(100/39) = 213.1 kg-moles = 213.1*22.4*(600/298) = 9611 m^3

N_2 in flue gases = 213.1*(61/100) = 130 kg-atoms

N_2 in air = 130 kg-moles

O_2 in air = 130*(21/79) = 34.55 kg-moles

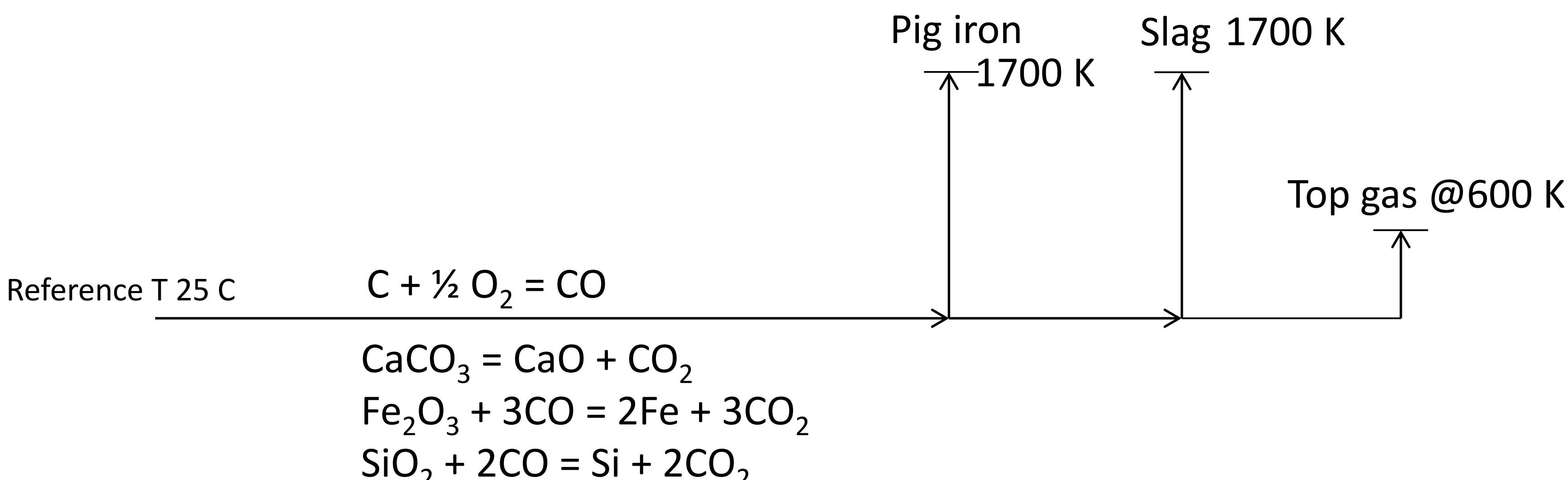
Iron Smelting Analysis



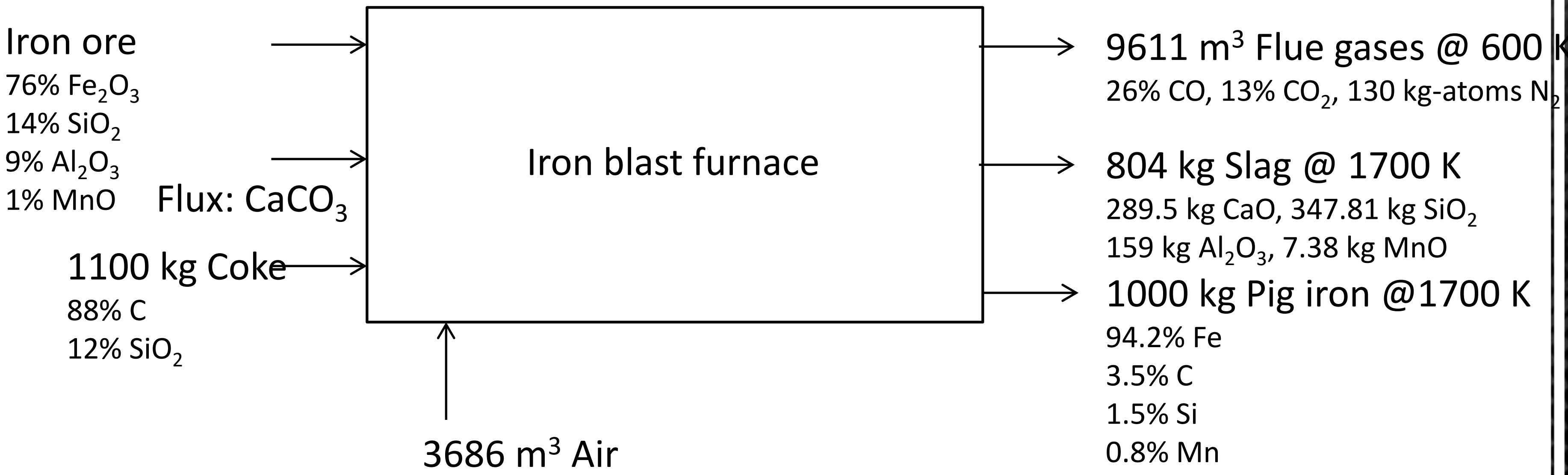
Reactions: $CaCO_3 = CaO + CO_2$, $C + \frac{1}{2} O_2 = CO$, $Fe_2O_3 + 3CO = 2Fe + 3CO_2$, $SiO_2 + 2CO = Si + 2CO_2$

Basis 1000 kg Pig iron

<u>Heat balance</u>



Iron Smelting Analysis



Reactions: $CaCO_3 = CaO + CO_2$, $C + ½ O_2 = CO$, $Fe_2O_3 + 3CO = 2Fe + 3CO_2$, $SiO_2 + 2CO = Si + 2CO_2$

Basis 1000 kg Pig iron

<u>Heat balance</u>

Exothermic reactions

$C + ½ O_2 = CO$ ΔH = -26400 kcal/kg-mole CO

C in coke = 81 kg-atoms

Heat of formation of 81 kg-moles CO = -26400*81 = 2138400 kcal

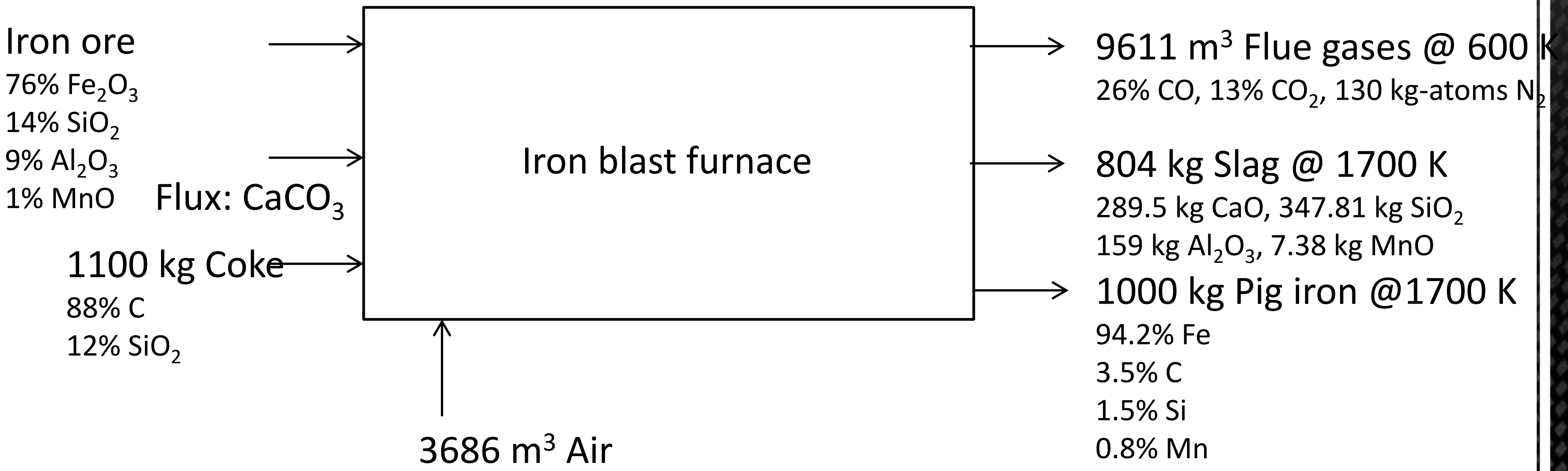
Endothermic reactions

$CaCO_3 = CaO + CO_2$ ΔH = 42500 kcal/kg-mole $CaCO_3$

CaO in slag = 289.5/56 = 5.17 kg-moles

Heat of decomposition of 5.17 kg-moles $CaCO_3$ = 42500*5.17 = 219725 kcal

Iron Smelting Analysis



Endothermic reactions

$Fe_2O_3 + 3CO = 2Fe + 3CO_2$ ΔH = 117273 kcal/kg-mole Fe_2O_3

Fe_2O_3 in ore = 1771*(76/100) = 1346 kg = 8.41 kg-moles

Heat of reduction of 8.41 kg-moles Fe_2O_3 = 117273*8.41 = 986266 kcal

$SiO_2 + 2CO = Si + 2CO_2$ ΔH = 152600 kcal/kg-mole SiO_2

Si in pig iron = 15 kg = 0.54 kg-atoms

Heat of reduction of 0.54 kg-moles SiO_2 = 152600*0.54 = 79400 kcal

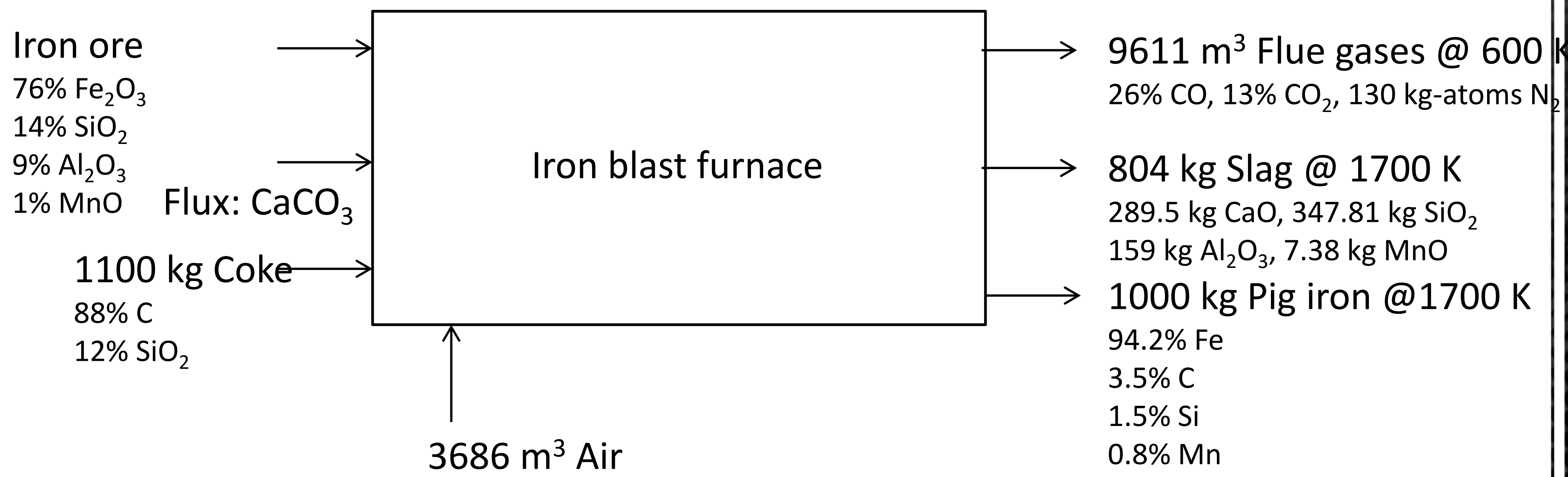
$CO_2 + C = 2CO$ ΔH = 41600 kcal/kg-mole

CO_2 reduced = CO_2 produced – CO_2 in flue gases

= 5.17 + 25.23 + 1.08 – 27.7 = 3.78 kg-moles

Heat of reduction of 3.78 kg-moles CO_2 = 41600*3.78 = 157248 kcal

Iron Smelting Analysis

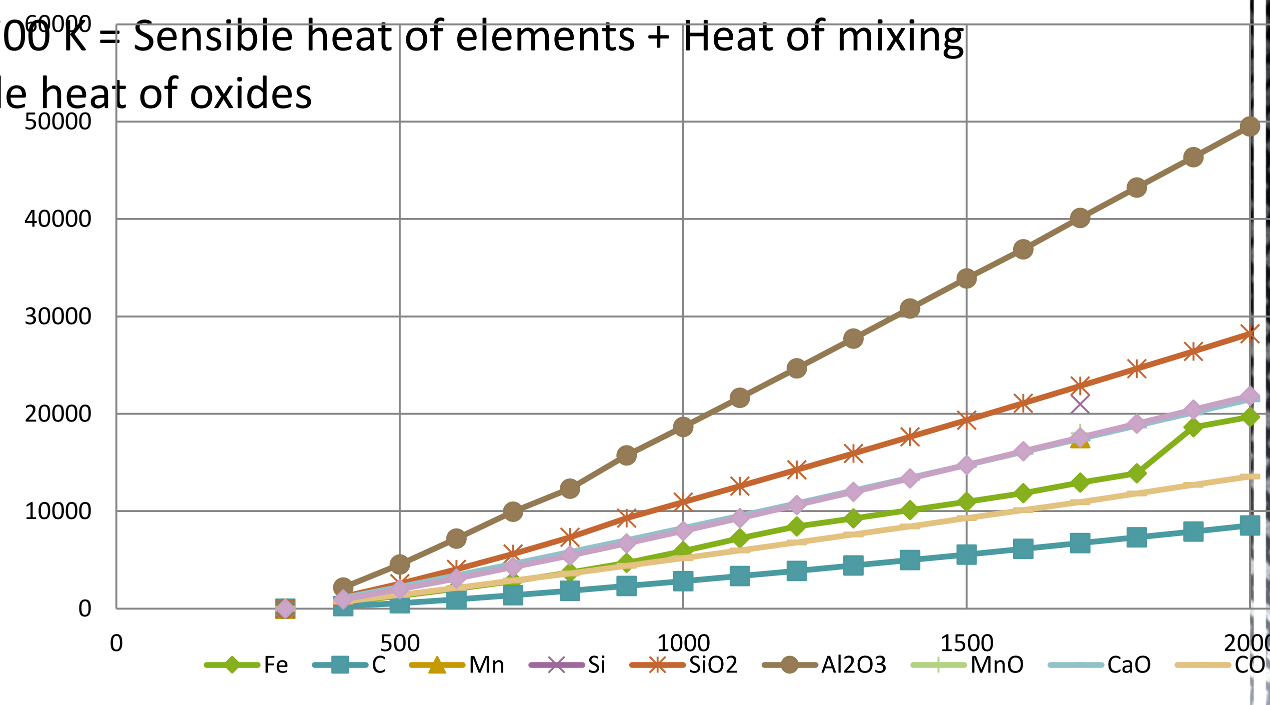


<u>Heat outputs</u>

Heat content of pig iron at 1700 K = Sensible heat of elements + Heat of mixing

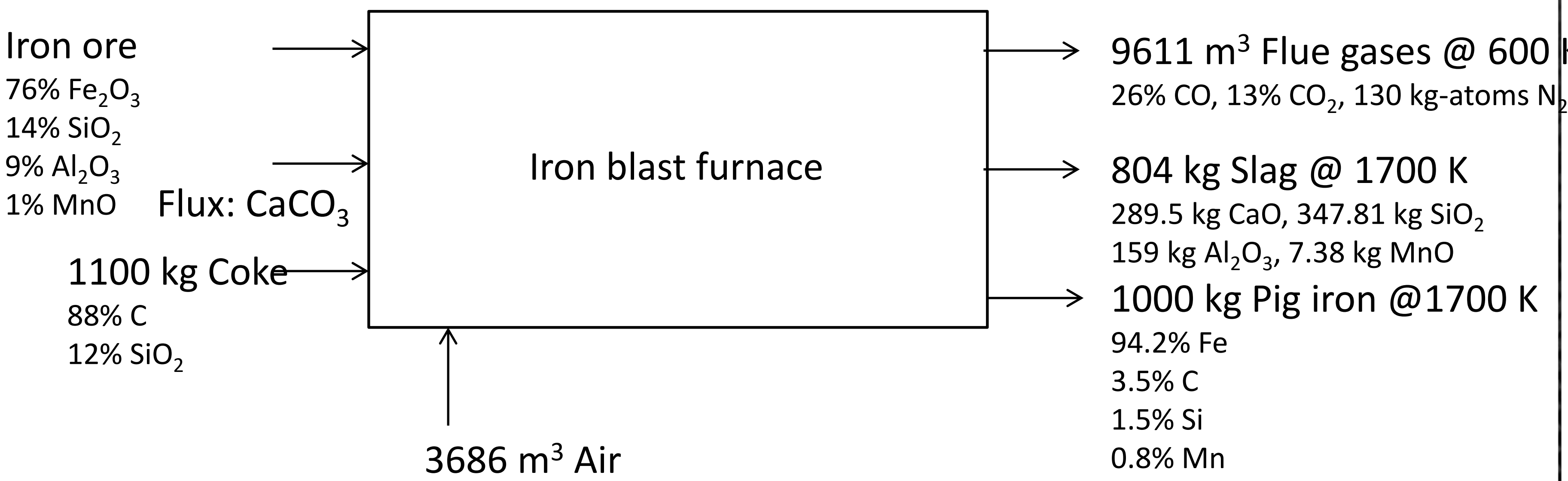
Heat content of slag = Sensible heat of oxides

Sensible heat in flue gases



Pig iron ΔH_m= 7500 kcal/ton

Iron Smelting Analysis



Heat balance

Heat Input

Heat evolution from exothermic reactions

2138400 kcal

Heat Output

Heat evolution from endothermic reactions

1442639 kcal

Heat content in pig iron

254134 kcal

Heat content in slag

244979 kcal

Sensible heat in flue gases

479180 kcal

A heat deficit of 282532 kcal