Materials and Energy Balance

Heat Balance in Pyrometallurgical Processes II

Heat Balance in Matte Smelting

Sulphide ores are oxidized in matte smelting which results in evolution of a large amount of heat due to the exothermic nature of the oxidation reactions

SO_2 produced and inert N_2 that are present as flue gases take a large portion of the heat input as their sensible heats, minimizing their amount helps achieve high thermal efficiency

Use of fuel as an external heat source is often not necessary and heating of the oxidizing air is a more energy efficient way to overcome heat deficits

Matte Smelting Analysis

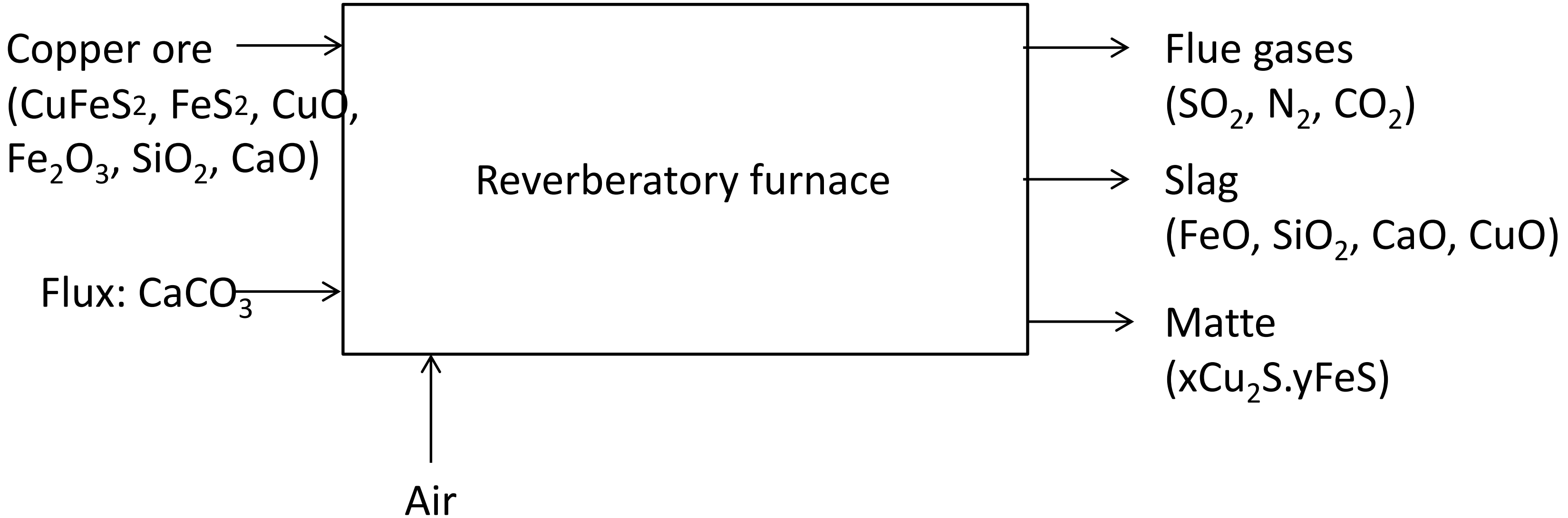
Copper ore of the following composition is smelted in a copper reverberatory furnace at a rate of 1000 tons/day. Pure $CaCO_3$ that is equal to 20% of ore is added as flux. All the sulphur eliminated in the furnace is oxidized to SO_2. Matte obtained is equal to 22% of the ore mixture and its grade is 39%. The flue gases leave the furnace at 1150 C and contain 3.6% SO_2

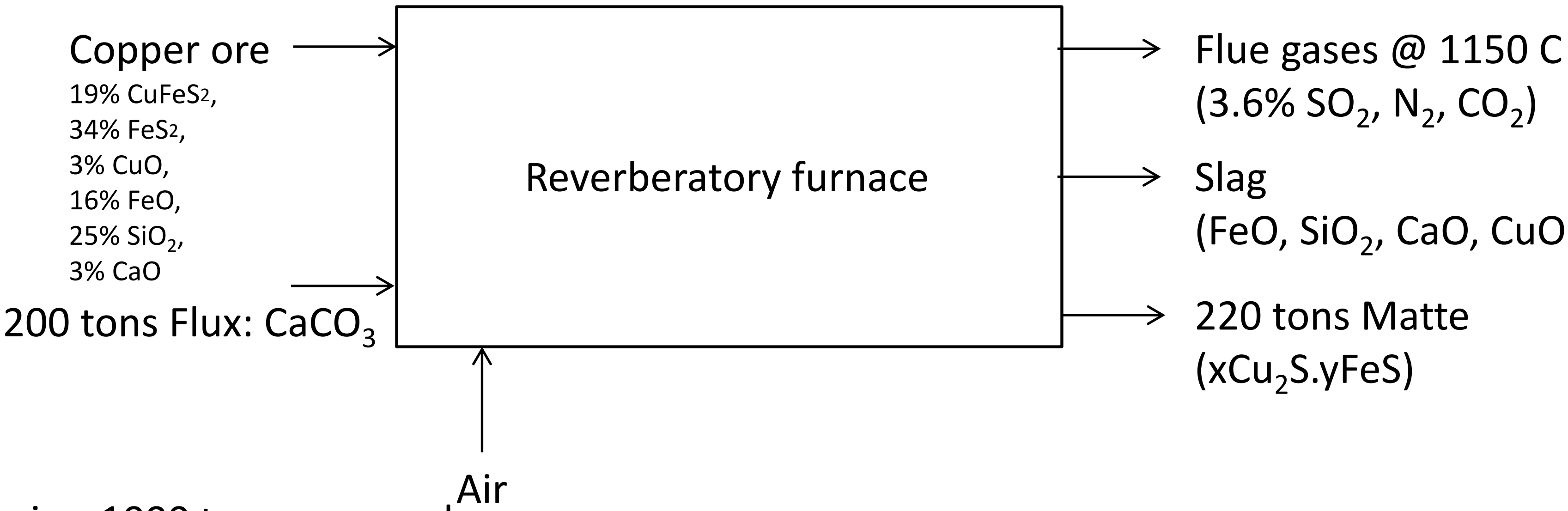
Rational Analysis wt%						
Material	$CuFeS_2$	FeS_2	CuO	FeO	SiO_2	CaO
Copper ore	19	34	3	16	25	3

Reactions: $CaCO_3 = CaO + CO_2$

$S + O_2 = SO_2$

$Fe + ½ O_2 = FeO$, $Cu + ½ O_2 = CuO$





Basis – 1000 tons ore per day

Reactions: $CaCO_3 = CaO + CO_2$

$S + O_2 = SO_2$

$Fe + ½ O_2 = FeO$, $Cu + ½ O_2 = CuO$

<u>Material balance</u>

Cu in matte = 220*(39/100) = 85.8 tons Cu, 85.8*(160/128) = 107.25 tons Cu_2S

FeS in matte = 220 – 107.25 = 112.75 tons, 112.75*(56/88) = 71.75 tons Fe

Fe in ore = Fe in matte + Fe in slag

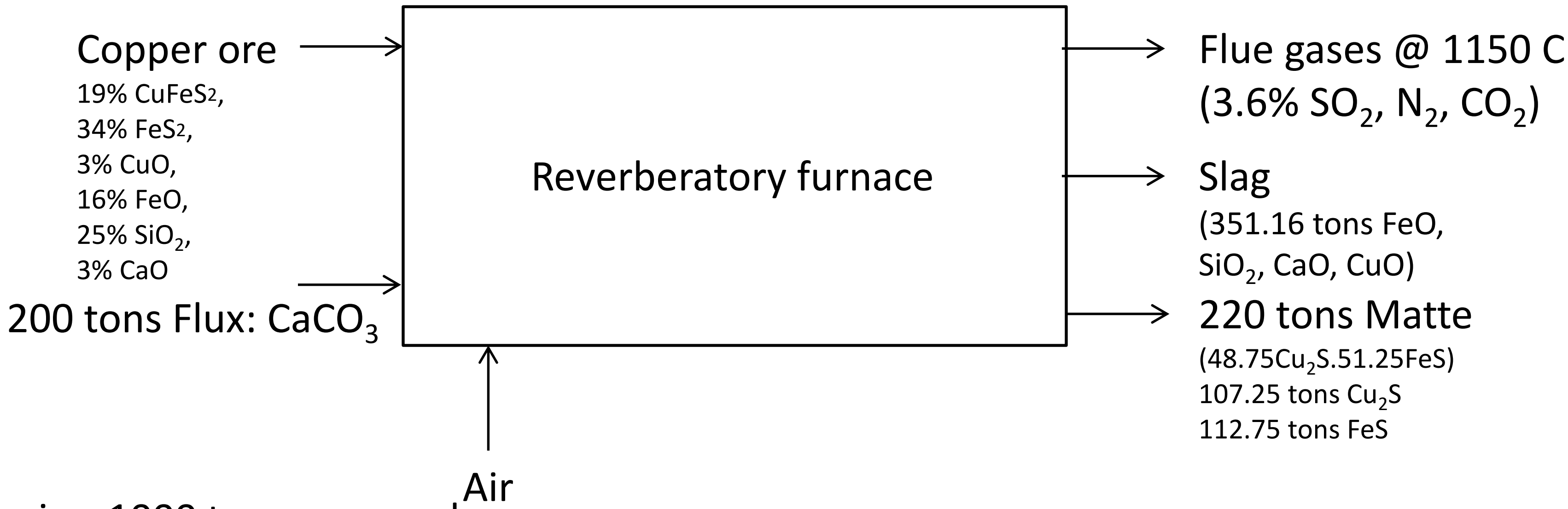
Fe in ore = 1000*(19/100)*(56/184) + 1000*(34/100)*(56/120) + 1000*(16/100)*(56/74)

= 57.826 + 158.667 + 121 = 337.49 tons

Fe in slag = Fe in ore – Fe in matte

= 337.49 – 71.75 = 265.74 tons

FeO in slag = 265.74*(74/56) = 351.16 tons



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$Fe + ½ O_2 = FeO$, $Cu + ½ O_2 = CuO$

Material balance

SiO_2 in ore = SiO_2 in slag

1000*(25/100) = 250 tons SiO_2

CaO from $CaCO_3$ + CaO from ore = CaO in slag

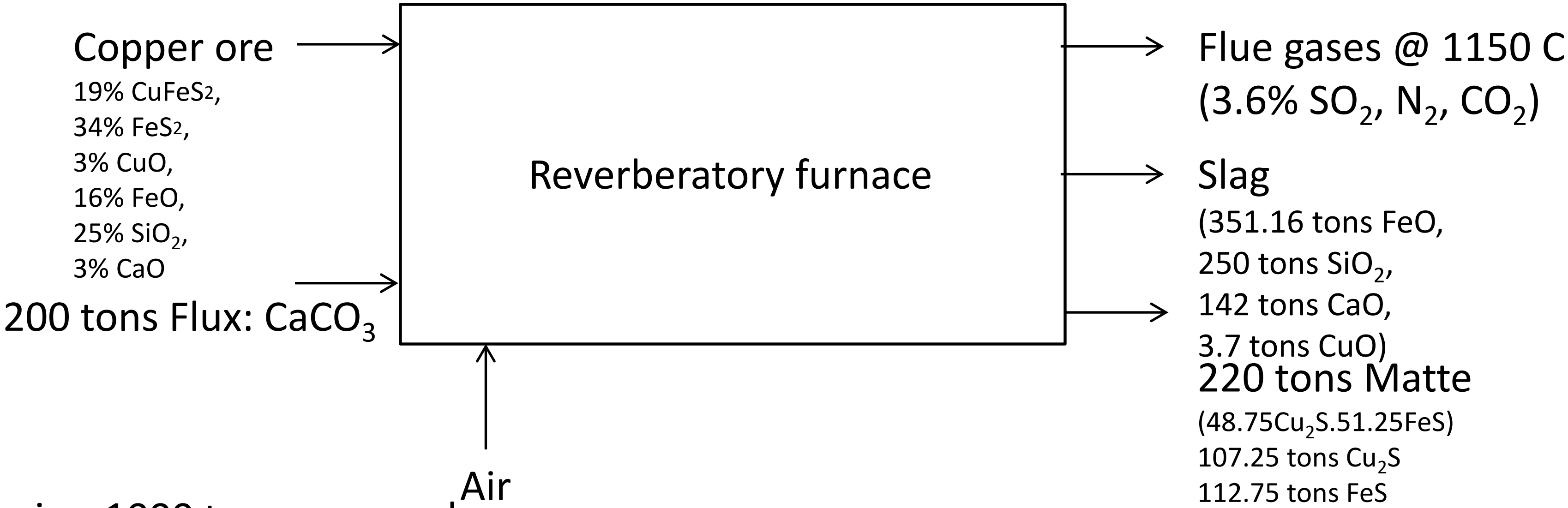
CaO from $CaCO_3$ = 1000*(20/100)*(56/100) = 112 tons CaO

CaO from ore = 1000*(3/100) = 30 tons CaO

CaO in slag = 112 + 30 = 142 tons

Cu in slag = Cu in ore – Cu in matte

= 1000*(19/100)*(64/184) + 1000*(3/100)*(64/82) – 220*(39/100) = 3.70 tons



Basis – 1000 tons ore per day

Reactions: $CaCO_3 = CaO + CO_2$

$S + O_2 = SO_2$

$Fe + ½\ O_2 = FeO$, $Cu + ½\ O_2 = CuO$

Material balance

S in ore = S in matte + S in flue gases

S in ore = 1000*(19/100)*(64/184) + 1000*(34/1000)*(64/120) = 247.42 tons

S in matte = 107.25*(32/160) + 112.75*(32/88) = 62.45 tons

S in flue gases = 247.42 – 62.45 = 184.97 tons = 184.97/32 = 5780.31 kg-atom S

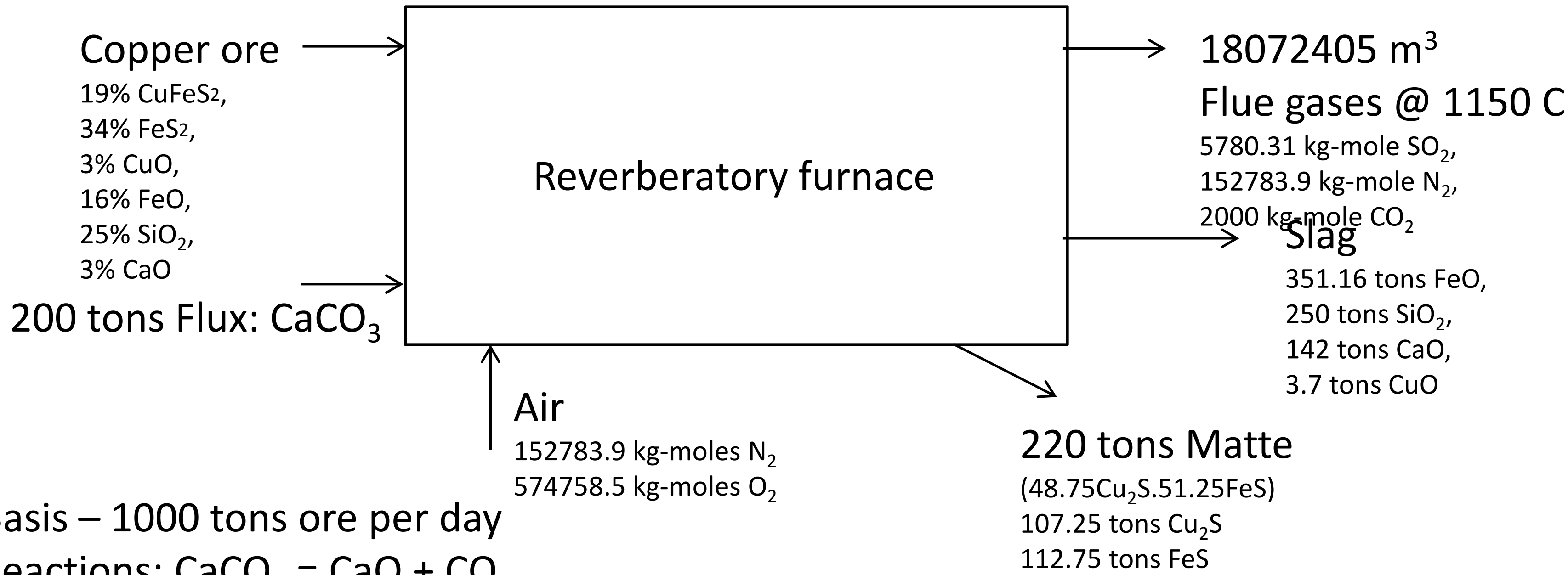
$S + O_2 = SO_2$ produces 5780.31 kg-mole SO_2 = 5780.31*22.4*(1423/273) = 674903.1 m^3

Total volume of flue gases = 674903.1*(96.4/3.6) = 18072405 m^3= 160564.2 kg-moles

CO_2 in $CaCO_3$ = CO_2 in flue gases

$CaCO_3 = CaO + CO_2$ produces 200000/100 = 2000 kg-moles CO_2

N_2 in flue gases = 160564.2 – 5780.31 – 2000 = 152783.9 kg-moles



Basis – 1000 tons ore per day

Reactions: $CaCO_3 = CaO + CO_2$

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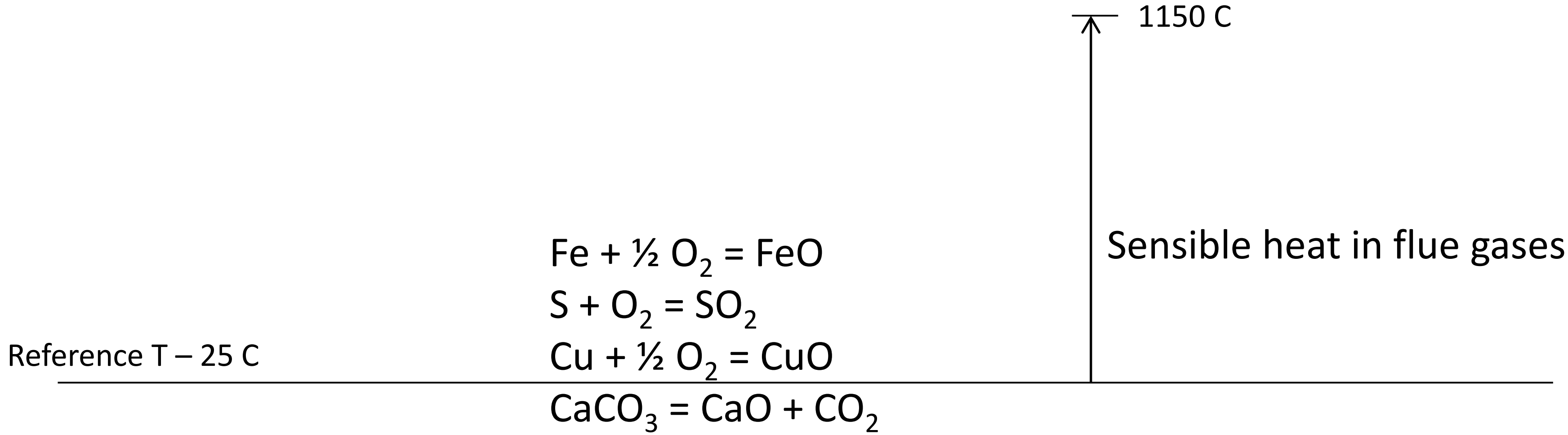
$Fe + ½\ O_2 = FeO$, $Cu + ½\ O_2 = CuO$

<u>Heat balance</u>



Reverberatory furnace

Copper ore
19% $CuFeS_2$,
34% FeS_2,
3% CuO,
16% FeO,
25% SiO_2,
3% CaO

200 tons Flux: $CaCO_3$

Air
152783.9 kg-moles N_2
574758.5 kg-moles O_2

18072405 m^3
Flue gases @ 1150 C
5780.31 kg-mole SO_2,
152783.9 kg-mole N_2,
2000 kg-mole CO_2

Slag
351.16 tons FeO,
250 tons SiO_2,
142 tons CaO,
3.7 tons CuO

220 tons Matte
($48.75Cu_2S.51.25FeS$)
107.25 tons Cu_2S
112.75 tons FeS

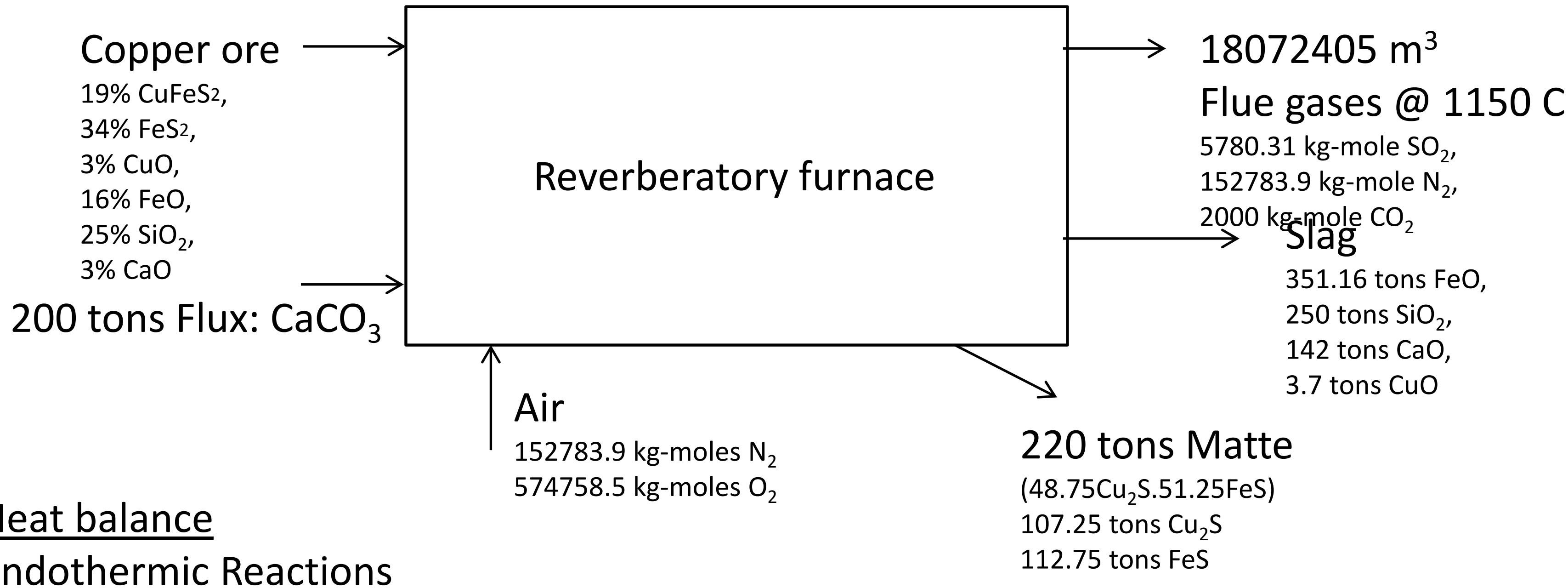
Heat balance

Exothermic Reactions

Fe + ½ O_2 = FeO   ΔH = -64700 kcal/kg-mole FeO
Fe from sulphides = 216.49 tons = 3865.9 kg-atom
Heat of formation of 3865.9 kg-moles FeO = -64700*3865.9 = -250123730 kcal

Cu + ½ O_2 = CuO   ΔH = -37100 kcal/kg-mole CuO
Cu in slag = 3.7 tons = 57.81 kg-atoms
Heat of formation of 57.81 kg-moles CuO = -2144335 kcal

S + O_2 = SO_2 ΔH = -70960 kcal/kg-mole SO_2
SO_2 in flue gases = 5780.31 kg-moles
Heat of formation of 5780.31 kg-moles SO_2 = -410170798 kcal
Total heat evolution from reactions = -662438863 kcal



Heat balance

Endothermic Reactions

$CaCO_3 = CaO + CO_2$ $\Delta H = 42500$ kcal/kg-mole $CaCO_3$

$CaCO_3$ in flux = 200 tons = 2000 kg-moles

Heat of decomposition of 2000 kg-moles $CaCO_3$ = 42500*2000 = 85000000 kcal

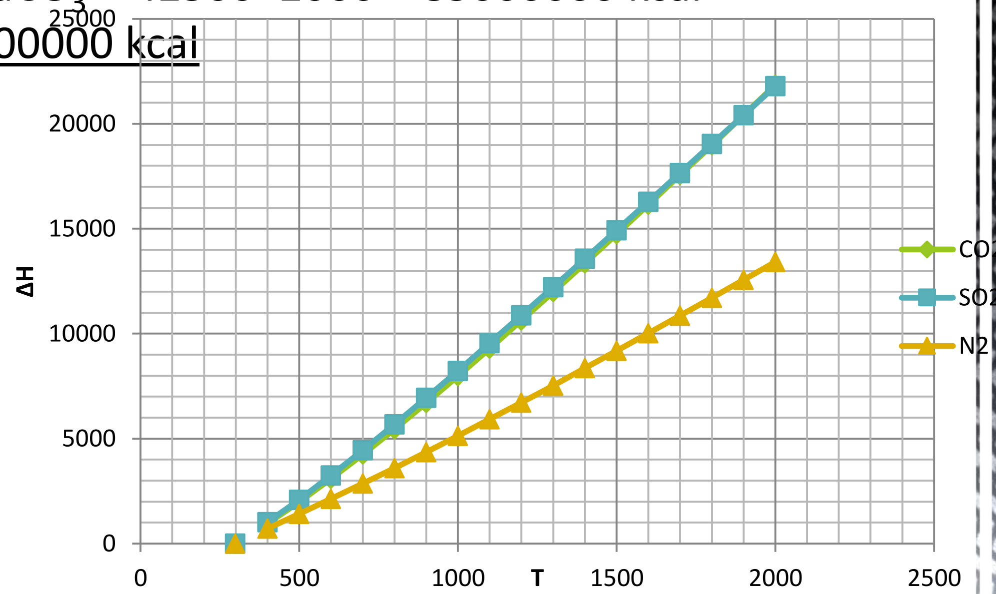
Total heat absorption from reactions = 85000000 kcal

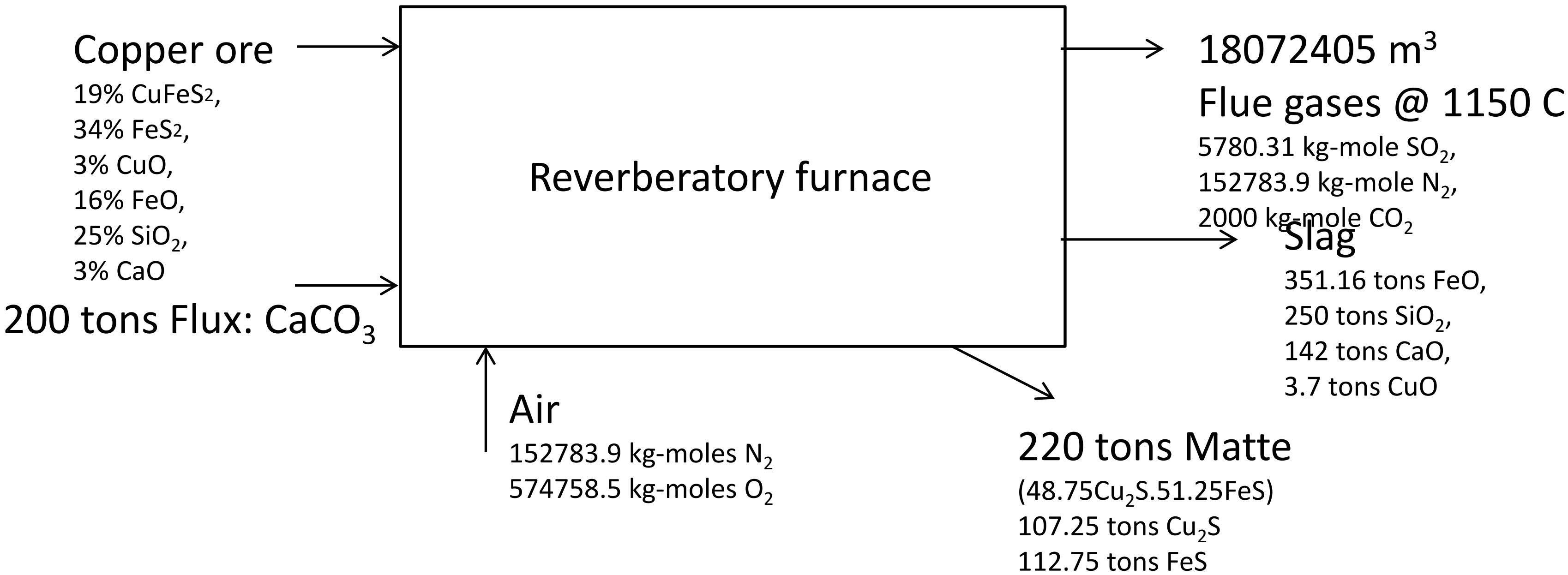
Sensible Heat in Flue Gases

For 5780.31 kg-moles SO_2

For 152783.9 kg-moles N_2

For 2000 kg-moles CO_2





<u>Heat balance</u>

Heat Input

Heat evolution from exothermic reactions

662438863 kcal

Heat Output

Heat absorption from endothermic reactions

85000000 kcal

Sensible heat in flue gases

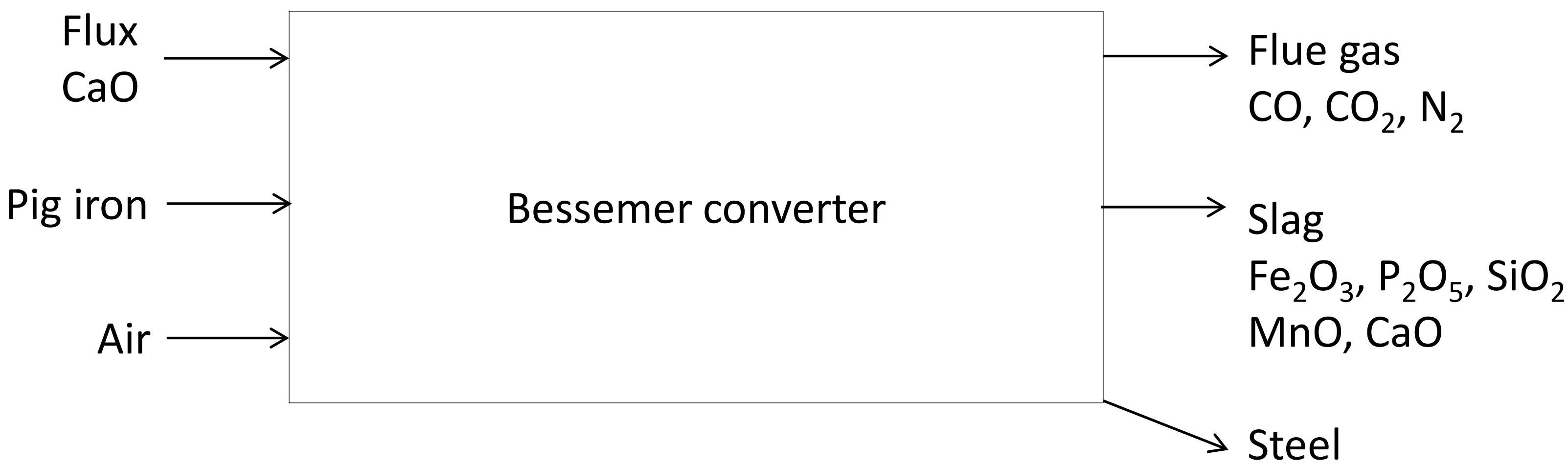
1413077644 kcal

A heat deficit of 835638781 !

Best solution : Heat the air to a high temperature

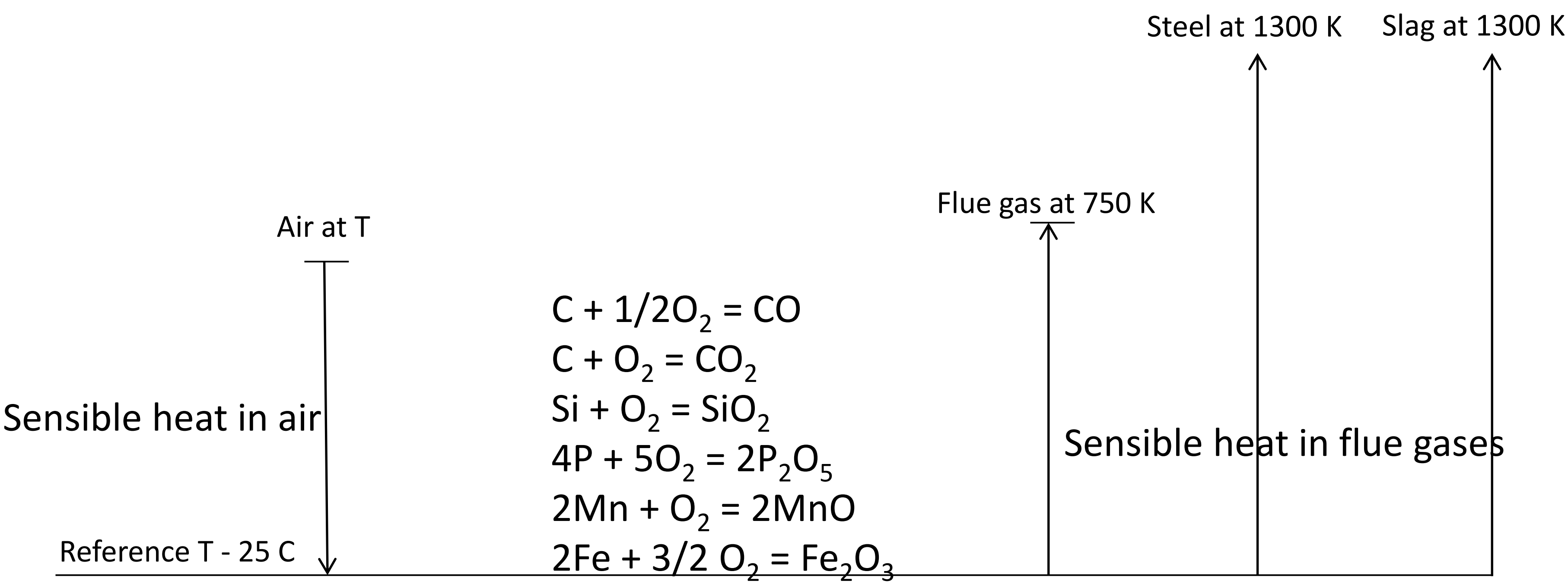
Steel converter analysis

A basic pneumatic steel converter is charged with 25 tons of pig iron with the given composition
In addition to the removal of all of the C, Si, Mn and P, iron equivalent to 5% of the weight of charged iron oxidizes at a constant rate throughout the bessemerizing operation
Enough lime is added to obtain a slag containing 35% CaO
2/3 of the carbon in steel oxidizes to CO and 1/3 goes to CO_2
Air compressor delivers air at a rate of 500 m^3/min for specific periods of time
Should air blowing into the furnace be heated, to what temperature?



Ultimate Analysis wt%					
Material	Fe	C	Si	Mn	P
Pig iron	91	3.5	2	1	2.5

Heat balance



$C + 1/2O_2 = CO$

$C + O_2 = CO_2$

$Si + O_2 = SiO_2$

$4P + 5O_2 = 2P_2O_5$

$2Mn + O_2 = 2MnO$

$2Fe + 3/2\ O_2 = Fe_2O_3$

<u>Heat balance</u>

Exothermic reactions

$C + 1/2O_2 = CO$ $\quad\Delta H = -26400$ kcal/kg-mole CO

$C + O_2 = CO_2$ $\quad\Delta H = -94400$ kcal/kg-mole CO

$2Fe + 3/2\ O_2 = Fe_2O_3$ $\quad\Delta H = -196500$ kcal/kg-mole Fe_2O_3

$Si + O = SiO_2$ $\quad\Delta H = -205400$ kcal/kg-mole SiO_2

$2P + 5/2\ O_2 = P_2O_5$ $\quad\Delta H = -360000$ kcal/kg-mole P_2O_5

$Mn + ½\ O_2 = MnO$ $\quad\Delta H = -91991$ kcal/kg-mole MnO

2396.5 kg
Flux
CaO

25 tons
Pig iron
91% Fe
3.5% C
2% Si
1% Mn
2.5% P

520 kg-moles
Air
500 m^3/min

Bessemer converter

Flue gas @ 750 K
48.61 kg-moles CO
24.31 kg-moles CO_2
411 kg-moles N_2

6847 kg Slag @ 1300 K
1625 kg Fe_2O_3
1431.5 kg P_2O_5
1071.4 kg SiO_2
322.7 kg MnO
2396.5 kg CaO

21612.5 kg Steel @ 1300 K

<u>Heat balance</u>

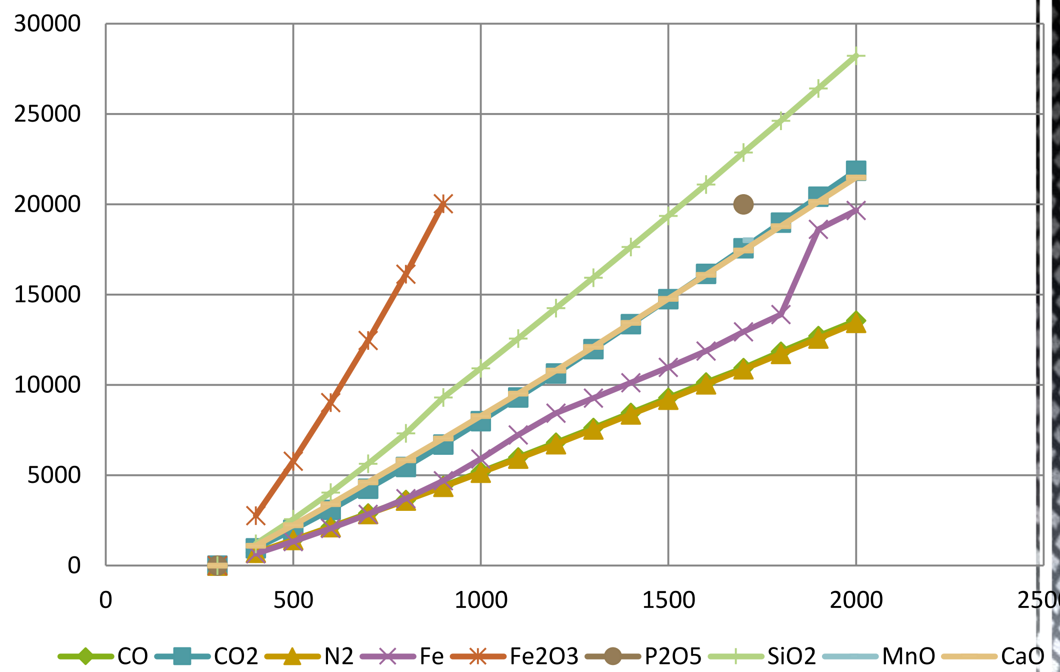
Endothermic reactions

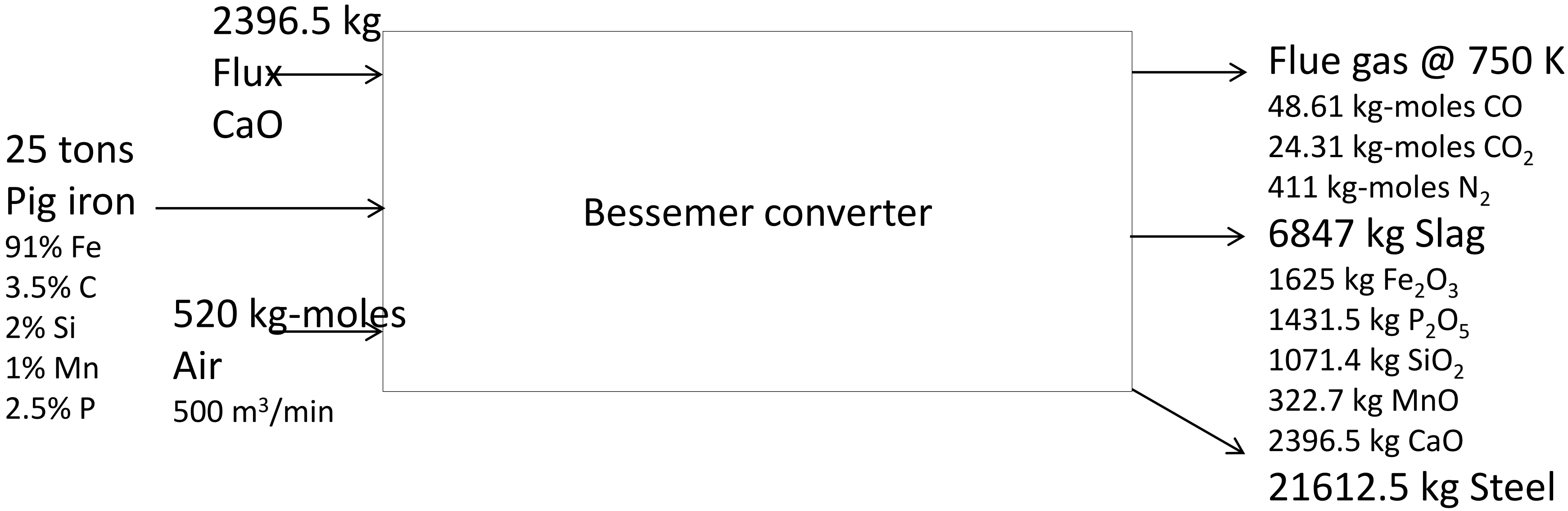
Flux is already decomposed to CaO

Heat content in the steel

Heat content in the slag

Sensible heat in flue gases





Heat Input

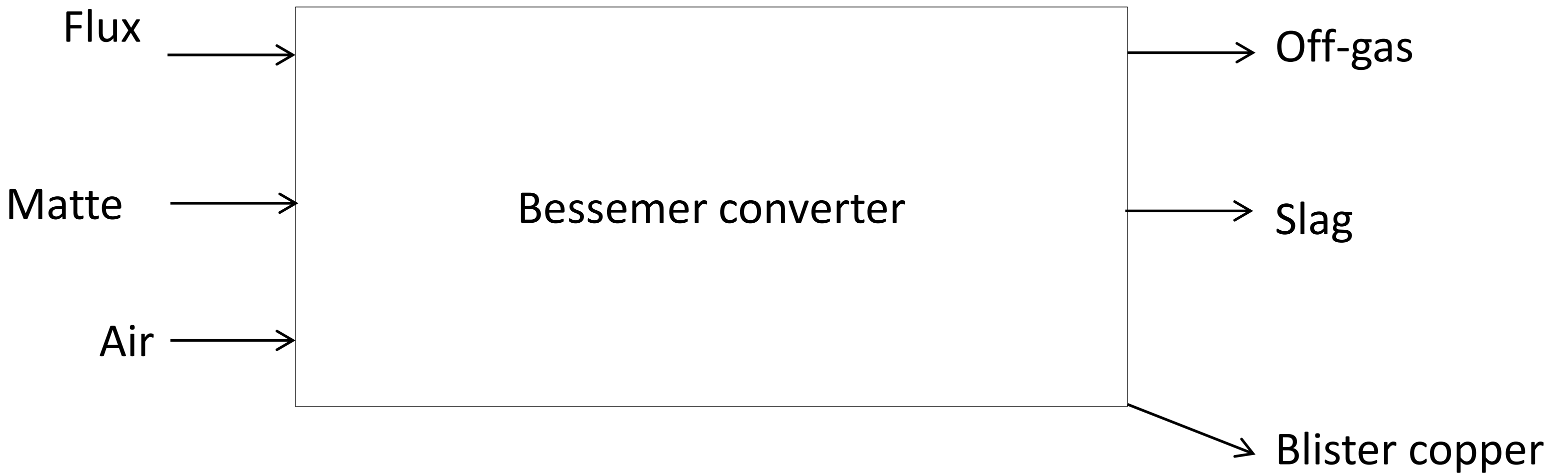
Heat evolution from exothermic reactions

Heat Output

Sensible heat in flue gases

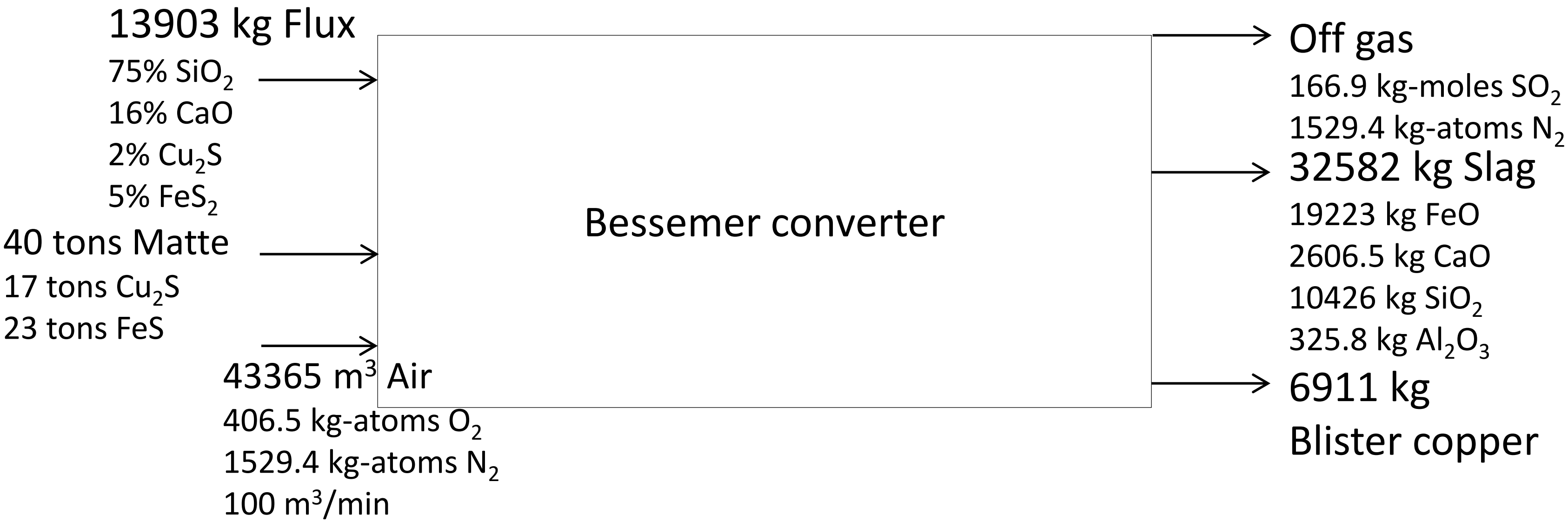
Copper converter analysis

40 tons of matte carrying 34% Cu is charged in a bessemer converter
The flux is added in batches of 3000 kg, the converter is blown after each addition to obtain slag of the given composition
Blister copper is produced after the removal of slags formed using partially added fluxes
Air is blown at a rate of 100 m^3/minute



Rational Analysis wt%						
Material	FeO	CaO	SiO_2	Al_2O_3	Cu_2S	FeS_2
Slag	59	8	32	1		
Flux		16	75	2	2	5

Air is blown at a rate of 100 m^3/minute



Blow	Period (min)
1	93.57
2	93.57
3	93.57
4	93.57
5	59.40

Total time to remove Fe in the matte and flux completely = 431.68 minutes

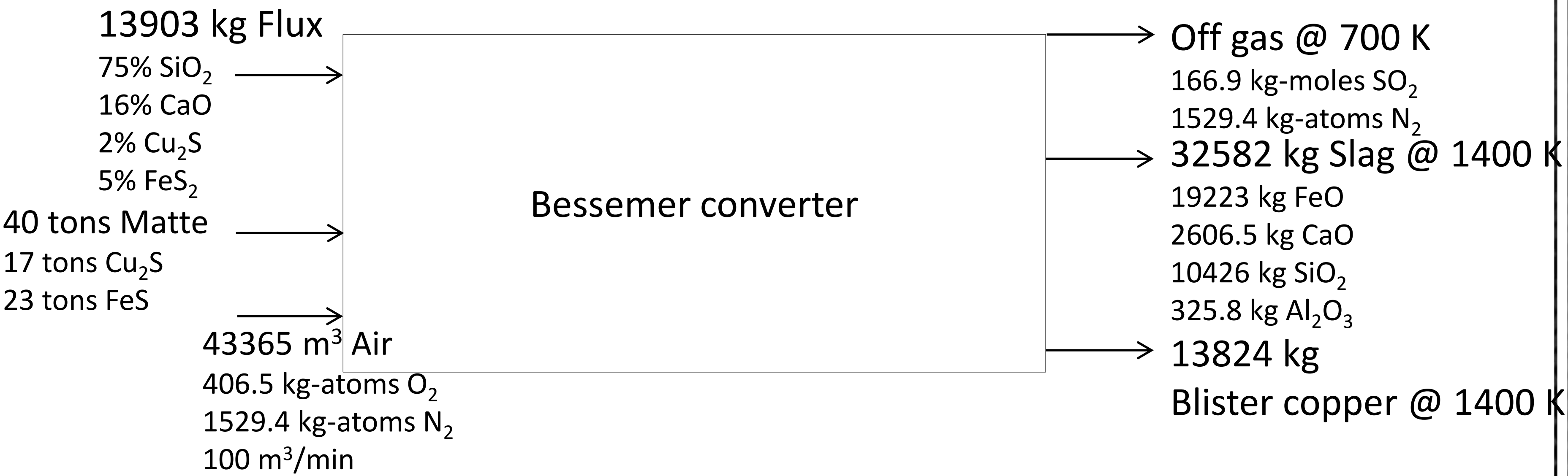
$$Cu_2S + O_2 = Cu(l) + SO_2$$

Total Cu_2S = 17000/160 = 108 kg-moles, Total O_2 required = 108 kg-moles

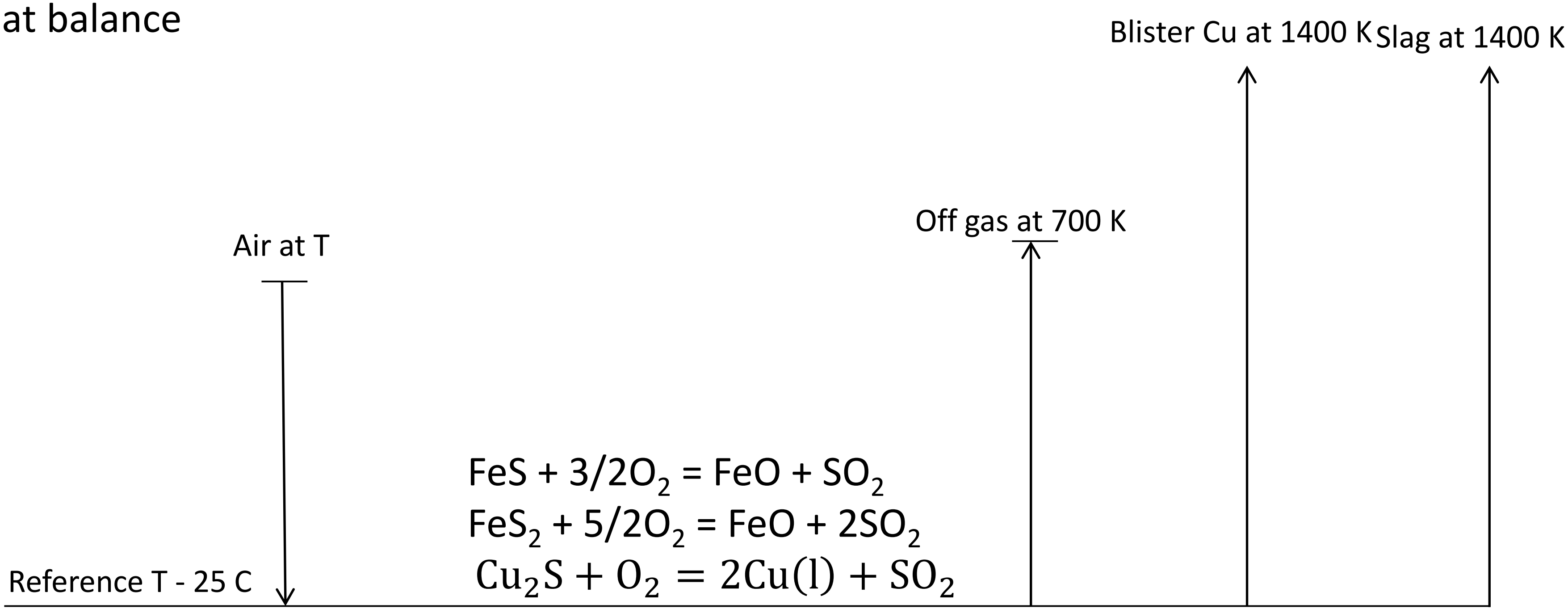
Total air required = (108/0.21) * 22.4 = 11520 m^3, Time required to convert Cu = 115.2 minutes

Total time of operation = 546.88 minutes

Air is blown at a rate of 100 m^3/minute

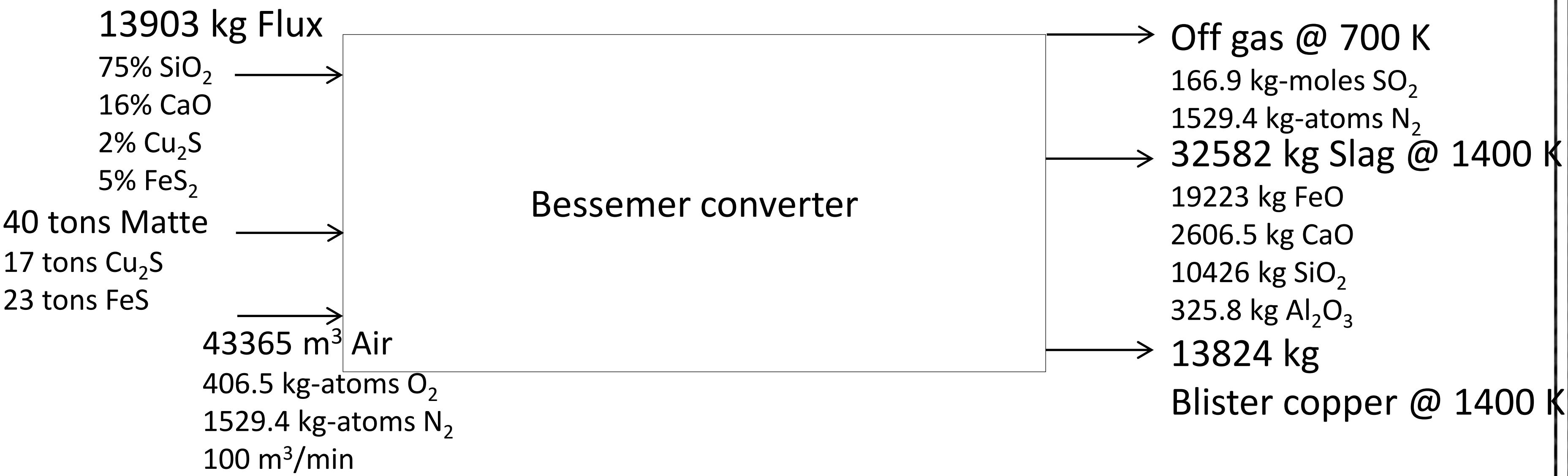


Heat balance



$$FeS + 3/2O_2 = FeO + SO_2$$
$$FeS_2 + 5/2O_2 = FeO + 2SO_2$$
$$Cu_2S + O_2 = 2Cu(l) + SO_2$$

Air is blown at a rate of 100 m^3/minute



Heat balance

Exothermic reactions

$FeS + 3/2O_2 = FeO + SO_2$ ΔH = -135660 kcal/kg-mole FeO

$FeS_2 + 5/2O_2 = FeO + 2SO_2$ ΔH = -206620 kcal/kg-mole FeO

$Cu_2S + O_2 = 2Cu(l) + SO_2$ ΔH = -31000 kcal/kg-mole Cu_2S

Air is blown at a rate of 100 m^3/minute

13903 kg Flux
75% SiO_2
16% CaO
2% Cu_2S
5% FeS_2

40 tons Matte
17 tons Cu_2S
23 tons FeS

43365 m^3 Air
406.5 kg-atoms O_2
1529.4 kg-atoms N_2
100 m^3/min

Bessemer converter

Off gas @ 700 K
166.9 kg-moles SO_2
1529.4 kg-atoms N_2

32582 kg Slag @ 1400 K
19223 kg FeO
2606.5 kg CaO
10426 kg SiO_2
325.8 kg Al_2O_3

13824 kg
Blister copper @ 1400 K

Heat balance
Endothermic reactions
CaO is added as flux, no decomposition reaction

Heat content in blister copper

Heat content in the slag

Sensible heat of off gas