Materials and Energy Balance

Charge Calculations in Pyrometallurgical Processes

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, off-gas

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/cm³ Density of slag is around 2.8-3 g/cm³

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

Matte Smelting

Advantages of matte smelting

- Low melting point of matte so that less amount of thermal energy is required by converting
 the metal of the ore in the form of sulphide and then extracting the metal
 e.g. melting point of Cu₂S and FeS is around 1000 degrees Celsius
- Cu₂S which is contained in the matte, does not require any reducing agent It is converted to oxide by blowing oxygen
- Matte smelting is beneficial for extraction of metal from sulphide ore, particularly when sulphide ore is associated with iron sulphide which forms eutectic point with Cu and Ni

The grade of the matte is defined as the copper grade of matte A matte of 40 percent means, it has 40% copper, so matte is always given in terms of copper, because it is used to produce copper not iron

Slag in matte smelting is mixture of oxides e.g. in smelting of copper ore concentrate the slag may contain SiO_2 , Al_2O_3 , calcium oxide, Fe_2O_3 , Fe_3O_4

The desirable properties of slag are low viscosity, solubility, low melting point

Typical reactions in Cu matte smelting:

$$6\text{CuO} + 4\text{FeS} = 3\text{ Cu}_2\text{S} + 4\text{FeO} + \text{SO}_2$$
 or if the O₂ pressure is high
$$6\text{CuO} + 4\text{FeS} = 2\text{CuSO}_4 + 2\text{FeS}$$

$$2\text{CuSO}_4 + 2\text{FeS} = \text{Cu}_2\text{S} + 2\text{FeO} + 3\text{SO}_2$$

$$\text{Cu}_2\text{O} + \text{FeS} = \text{Cu}_2\text{S} + \text{FeO}$$

Oxygen has greater affinity for iron than copper:

$$10\text{Fe}_2\text{O}_3 + \text{FeS} = 7\text{Fe}_3\text{O}_4 + \text{SO}_2$$

 $3\text{Fe}_3\text{O}_4 + \text{FeS} = 10\text{FeO} + \text{SO}_2$

In the ideal condition matte contains only Cu₂S and FeS, plus little amount of Fe₃O₄ if oxygen dissolved

Higher oxides of iron are difficult to remove by the slag Roasting has to be controlled in order to minimize the formation of Fe_2O_3 or Fe_3O_4 , which may enter the matte during smelting

Off-gas consists of SO₂, nitrogen, oxygen if excess amount of air is used and sometimes SO₃ depending on the reaction

If fuel is used, CO and CO₂ may also be present depending upon the state of combustion

Flash Smelting

Conventionally smelting is carried out in reverberatory furnaces, fired with coal or oil Nowadays reverberatory furnaces are being replaced by flash smelting furnaces that have bee developed in recent years

The advantages of flash smelting is that it combines both converting and smelting, whereas in the reverberatory furnace the ore has to be smelted first and then it is transferred to reverberatory furnace for converting purposes

The reason for this combination is the economical processing of large amount of sulphur dioxide that is created especially in roasting

Collecting the concentrated off-gas from flash smelting and converting to H₂SO₄ is much more feasible

Other advantages of flash smelting:

- Very fine particles of ore concentrates are injected, so the reaction is extremely rapid and very high temperatures are created
- Heat generated is sufficient to carry out the smelting

Examples – In a copper ore, chalcopyrite (CuFeS₂) is 34%, pyrite (FeS₂) is 30% and SiO₂ is 36%

- a) Determine the % Cu and % gangue in the ore
- b) What % Fe in the ore concentrate is to be removed to make 40% matte? Consider Cu₂S
- c) If only excess S is eliminated in the ore concentrate, what is the composition of the resulting matte?

$$AW_{Cu} = 64$$
, $AW_{Fe} = 56$, $AW_{S} = 32$

a- ore =
$$Cu_2S$$
 + gangue
% $Cu = 34 * (64/184) = 11.83 %$
Gangue = $100 - 11.83 * (160/128) = 85.21 %$, % $Cu_2S = 14.78 %$

$$b - \frac{40}{100} = \frac{11.83\%}{14.78\% + \% FeS}$$

$$0.4(14.78+\% FeS) = 11.83$$
, % FeS = 14.795 after removal of FeO, % Fe = 14.795*(56/88) = 9.415 Initial % Fe = $34*(56/184)+30*(56/120) = 24.35$ % Fe to be removed = $24.35 - 9.415 = 14.935$ %

c – CuFeS₂ decomposes according to the reaction 2CuFeS₂ = Cu₂S + 2FeS + S FeS₂ decomposes according to the reaction FeS₂ = FeS + S % FeS = 24.35*(88/56) = 38.26 % Matte grade =
$$\frac{\% Cu}{\% Cu_2S + \% FeS}$$
 * 100 = 22.2 %

Examples – A copper matte may be represented as mCu₂S.nFeS with no fixed values of m and Calculate m and n for a matte grade of 38 %

$$0.38 = \frac{Amount \ of \ Cu}{Amount \ of \ Cu_2S + Amount \ of \ FeS}$$

$$= \frac{160m * 128/160}{160m + 88n}$$

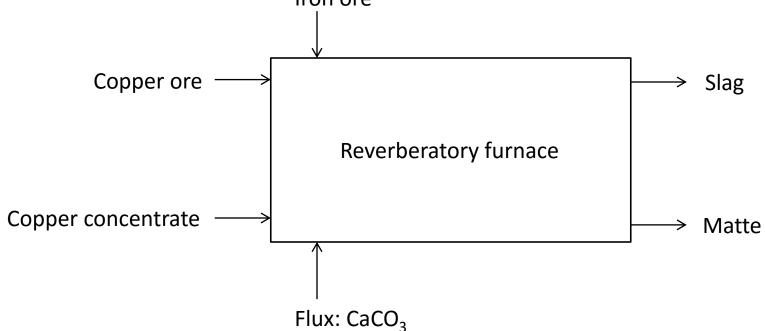
$$60.8m + 33.44n = 128m$$

$$\frac{m}{n} = \frac{33.44}{67.2} \approx 0.5$$

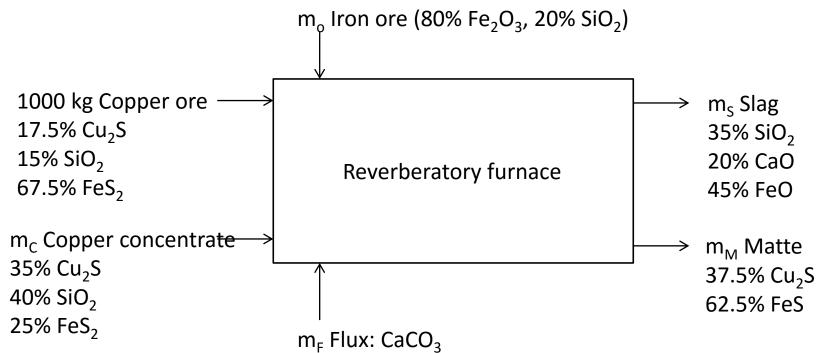
Matte may be represented as Cu₂S.2FeS or 2Cu₂S.4FeS or 3Cu₂S.6FeS

Example – Copper ore is smelted in a reverberatory furnace together with a copper concentrate. The fluxes are pure CaCO₃ and iron ore

Rational Analysis wt%						
Material	Cu ₂ S	FeS ₂	SiO ₂	Fe ₂ O ₃		
Copper ore	17.5	67.5	15			
Copper concentrate	35	25	40			
Iron ore			20	80		
Iron ore	-					



Reaction: $CaCO_3 = CaO + CO_2$

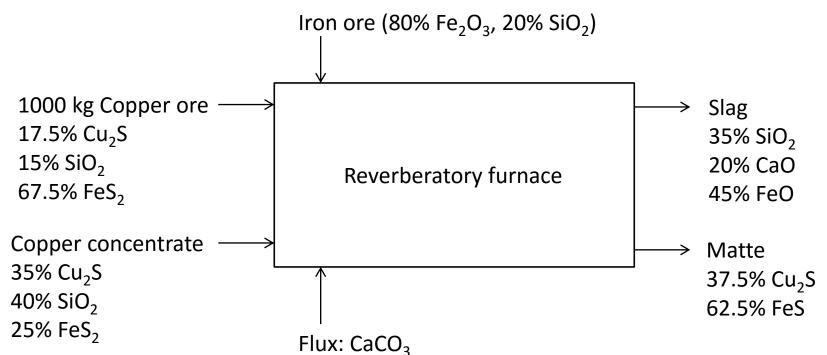


Reaction: $CaCO_3 = CaO + CO_2$

DOF analysis

5 unknown labeled variables (m_C , m_o , m_F , m_S m_S ,)

- + 2 independent chemical reactions
- 7 independent molecular species balances (Cu₂S, FeS₂, SiO₂, Fe₂O₃, CaCO₃, CaO, FeO)
- 0 other equation relating unknown variables
- = 0 degrees of freedom

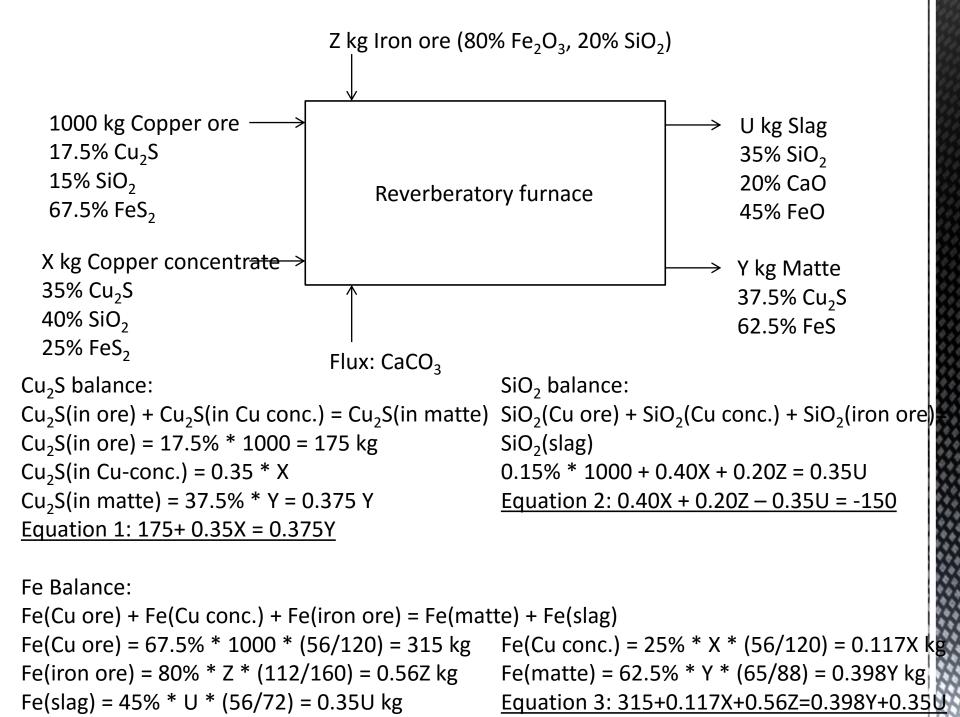


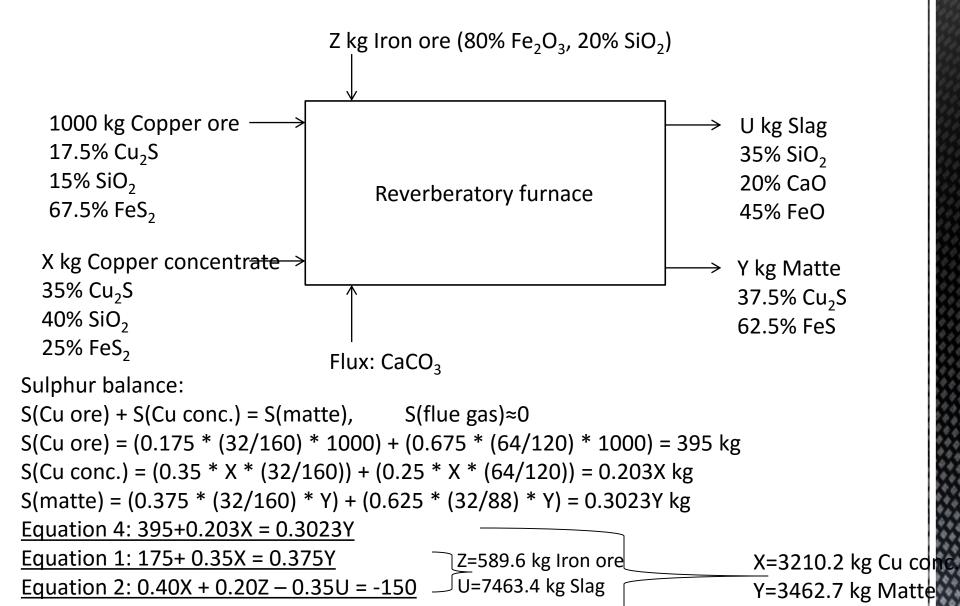
Reaction: $CaCO_3 = CaO + CO_2$

Calculate the quantities of concentrate, iron ore and flux in order to smelt 1000 kg ϕ copper ore and obtain a matte grade of 30% Cu and a slag with the composition 35% SiO₂ , 20 CaO, 45% FeO

Let X be the quantity of Cu concentrate
Let Y be the quantity of matte
Let Z by the quantity of iron ore
Let U be the quantity of slag

Four equations are needed to solve for the four variables X, Y, Z, U





CaO in slag: 20% * 7463.4 = 1492.7 kg CaO, $1492.7 * (100/56) = 2665.5 \text{ kg CaCO}_3$

Equation 3: 315+0.117X+0.56Z=0.398Y+0.35U

Converting

Liquid metal or matte coming from the smelting furnace with impurities is converted to high purity metal in oxidizing environments

Either steady air, blown air or blown oxygen are utilized to oxidize the gangue species Gangue oxide minerals are removed with the initially forming slag

Inputs – Pig iron, cast iron for steel converting, Cu-Fe matte for copper converting, flux, air Outputs – Slag, steel or blister copper, off-gas

Furnaces used

Hearths

Puddling furnaces

Cementation furnaces

Bessemer furnaces

Open Hearth furnaces

Basic oxygen furnaces

Electric arc furnaces

Converting Pig Iron

Wrought or worked iron was the main malleable iron used in rails and structures until large scale, commercial production of steel

It contained low amount of carbon (0.04 to 0.08%) and was worked by hand into bars and various shapes due to its malleability

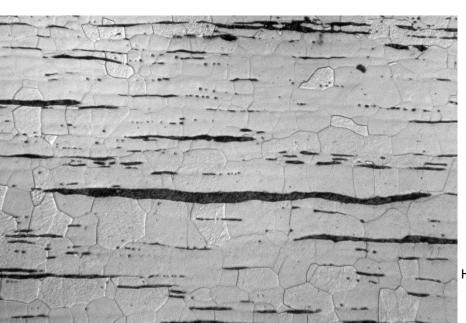
Slag up to 2% is mixed in its microstructure in the form of fibrous inclusions like wood Pig iron and cast iron were initially converted to wrought iron in hearths in ancient times then in puddling furnaces during 18th century

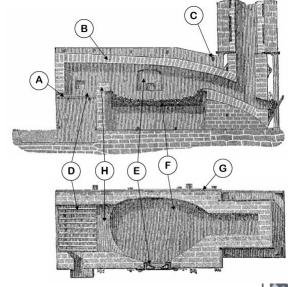
In these processes the charge was heated to melting temperature by burning charcoal and oxidized by air

Puddling process involves manually stirring the molten pig iron, which decarburizes the iron.

As the iron is stirred, globs of wrought iron are collected into balls by the stirring rod and those

are periodically removed by the puddler





Horizontal (lower) and vertical (upper) cross-sections of a single puddling furnace.

A. Fireplace grate; B. Firebricks; C. Cross binders; D. Fireplace; E. Work door;

F. Hearth; G. Cast iron retaining plates; H. Bridge wall

Commercial production of low carbon, low impurity steel was limited to inefficient and expensive process of adding carbon to carbon-free wrought iron between 17th and 19th centuries

The manufacturing process, called cementation process, consisted of heating bars of wrought iron in a furnace in between powdered charcoal layers at about 700° C for about a week Carbon slowly diffuses into iron and dissolves in the iron, raising the carbon percentage Steel obtained from this process is called "blister steel" due to the blister-like marks formed or the surface due to the evolved gases during the manufacturing process

Up to 3 tons of coke was burnt for each ton of steel produced
The fuel and labor costs resulted in a small scale
production of steel that was about 8 times more expensive

The Bessemer process reduced the time needed to make steel of this quality to about half an hour while only requiring coke to melt the pig iron initially

The Bessemer process - Henry Bessemer patented the process in 1855

The process is carried on in a large ovoid steel container lined with clay or dolomite

The capacity of a converter is from 8 to 30 tons of molten iron

The key principle is removal of impurities from the iron by oxidation with air being blown through the molten iron

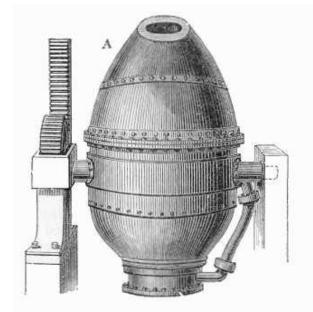
The oxidation process removes impurities such as silicon, manganese, and carbon as oxides These oxides either escape as gas or form a solid slag

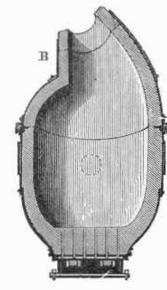
The oxidation also raises the temperature of the iron mass and keeps it molten

The refractory lining of the converter also plays a role in the conversion—the clay lining is used in the acid Bessemer, in which there is low phosphorus in the raw material

Dolomite, limestone or magnesite are used when the phosphorus content is high in the basic Bessemer







Once the converter is charged with molten pig iron, a strong thrust of air is blasted across the molten mass for about 20 minutes through tuyeres provided at the bottom of the vessel

The conversion process called the "blow" is typically completed in around twenty minutes

During this period the progress of the oxidation of the impurities is judged by the appearance of the flame issuing from the mouth of the converter since there is not enough time to make material analyses

The blow may be interrupted at certain periods to avoid the oxidation of certain impurities

Required amount of flux is added at the beginning of each period to produce the slag of desired composition and amount

At the end of the process all traces of the silicon, manganese, carbon, phosphorus and sulphur are oxidized, leaving the converter with pure iron

In order to give the steel the desired properties, other impurities can be added to the molten steel when conversion is complete



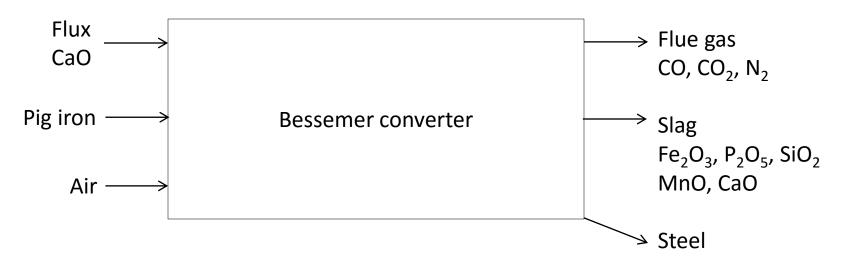
Steel converter analysis

A basic pneumatic steel converter is charged with 25 tons of pig iron containing various impurities

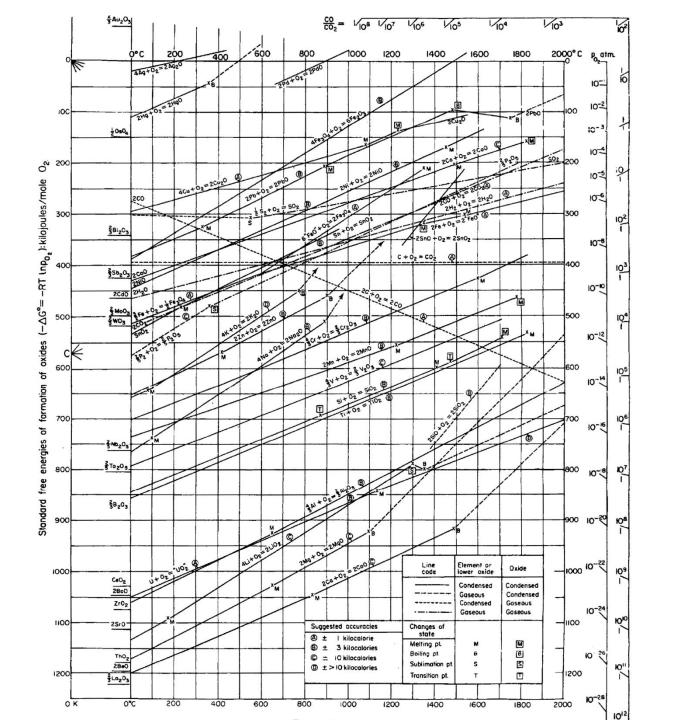
In addition to the removal of all of the C, Si, Mn and P, iron equivalent to 5% of the weight of charged iron oxidizes at a constant rate throughout the bessemerizing operation Enough lime is added to obtain a slag containing 35% CaO

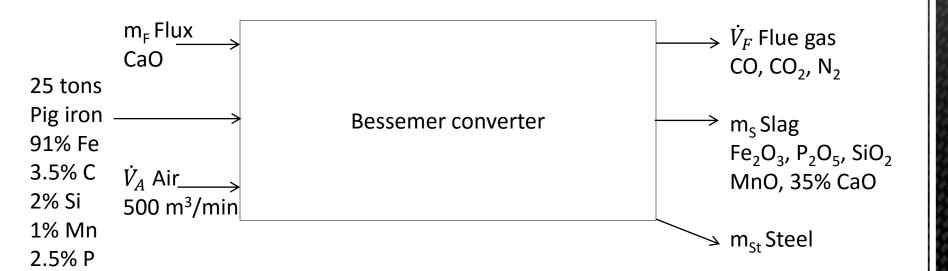
2/3 of the carbon in steel oxidizes to CO and 1/3 goes to CO₂

Air compressor delivers air at a rate of 500 m³/min for specific periods of time



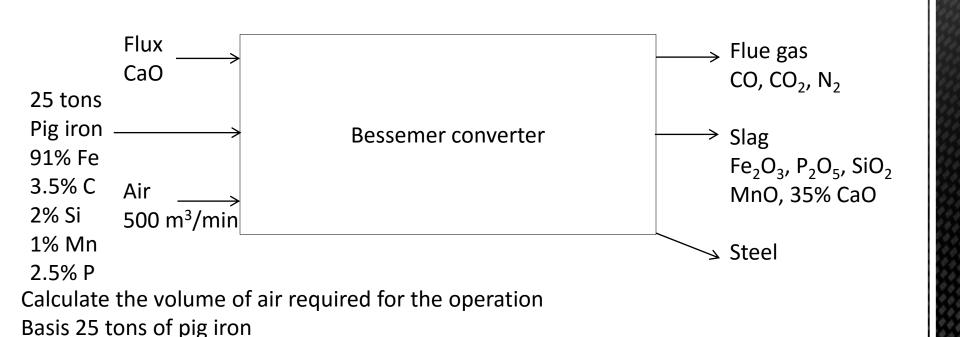
Ultimate Analysis wt%						
Material	Fe	С	Si	Mn	Р	
Pig iron	91	3.5	2	1	2.5	





DOF analysis

- 12 unknown labeled variables (\dot{V}_A , \dot{V}_F , m_F, m_S, m_{St}, X_{Fe2O3}, X_{P2O5}, X_{SiO2}, X_{MnO}, X_{CO}, X_{CO2}, X_{N2})
- + 6 independent chemical reactions
- 14 independent molecular species balances (Fe, C, Si, Mn, P, SiO₂, Fe₂O₃, CaO₁, MnO, P₂O₅, CO₂, N₂, O₂)
- 4 other equation relating unknown variables ($X_{Fe2O3} + X_{P2O5} + X_{SiO2} + X_{MnO} = 0.65$, $X_{CO} + X_{CO2} + X_{ND} = 0.65$) Fe oxidizes, 1/3 C oxidizes to CO2)
- = 0 degrees of freedom



 $n_{02} = (5/4) * n_p = 25.201 \text{ kg-mole}$



Calculate the volume of air required for the operation Basis 25 tons of pig iron

Total O₂ used during Si, Mn, C, P oxidation = 93.94 kg-mole

Considering small amount of Fe oxidizing in all steps:

$$n_{Fe}$$
 = 1137.5/56 = 20.312 kg-atom
2Fe + 3/2 O_2 = Fe₂ O_3
 n_{O2} = (¾)* n_{Fe} = (¾)*20.312 = 15.23 kg-mole

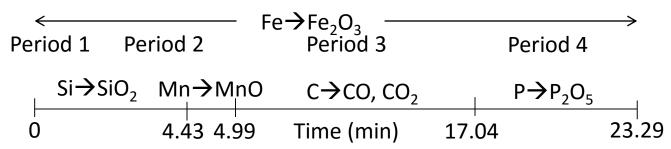
Total O_2 used = 2.273 + 17.857 + 24.306 + 24.306 + 25.201 + 15.23 = 109.17 kg-mole O_2 Volume of air required = (109.17/0.21) * 22.4 = 11644.8 m³/25 ton of Pig iron Total blowing time = 11644.8/500 = 23.29 minutes

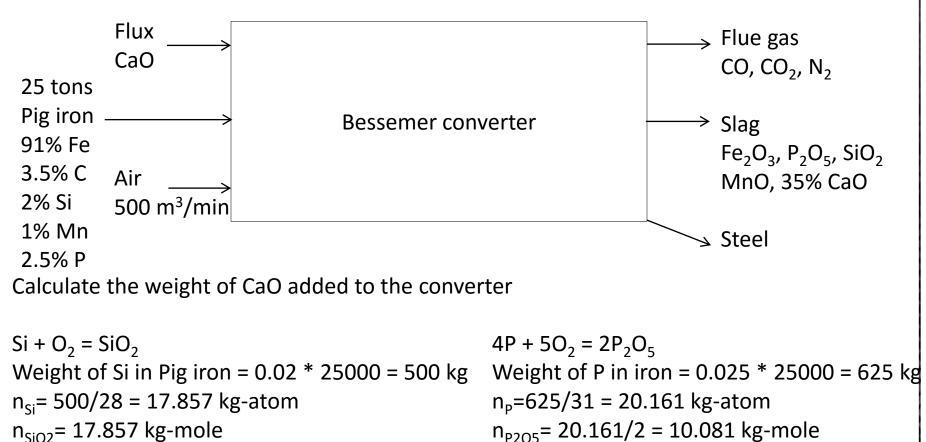


Calculate the durations of each blowing period

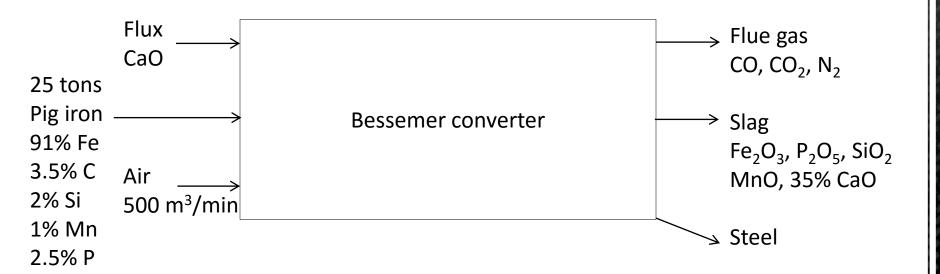
Total
$$O_2$$
 used = $2.273 + 17.857 + 24.306 + 24.306 + 25.201 + 15.23 = 109.17 kg-mole $O_2$$

Volume of air required for period 1= $(2.273/0.21) * 22.4 = 242.45 \text{ m}^3/500 \text{ kg Si}$ Volume of air required for period 2= $(17.857/0.21) * 22.4 = 1904.75 \text{ m}^3/250 \text{ kg Mn}$ Volume of air required for period 3= $(48.162/0.21) * 22.4 = 5137.3 \text{ m}^3/878 \text{ kg C}$ Volume of air required for period 4= $(25.201/0.21) * 22.4 = 2688.1 \text{ m}^3/625 \text{ kg P}$ Volume of air distributed in all periods= $(15.23/0.21) * 22.4 = 1624.5 \text{ m}^3/1138 \text{ kg Fe}$ Total blowing time = 11644.8/500 = 23.29 minutes





MnO + SiO₂ + P₂O₅ + Fe₂O₃ = 4450.6 kg, 35% CaO= (4450.6/0.65)*0.35 = 2396.5 kg CaO in slag



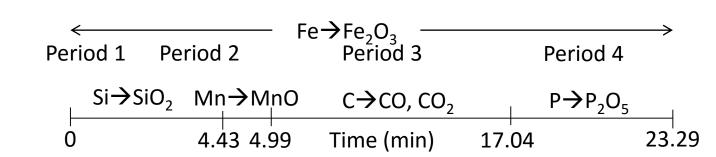
Calculate the weight and composition of the slag

Component	Weight (kg)	Weight %
SiO ₂	1071.4	15.64%
MnO	322.7	4.71 %
P_2O_5	1431.5	20.90%
Fe ₂ O ₃	1625	23.75%
CaO	2396.5	35.00%
Total	6848	100.00%



Calculate the weight of CaO added to the converter in each blowing period

Total CaO added as flux = 2396.5 kg CaO



CaO consumed each minute = 2396.5/23.29 = 102.9 kgCaO consumed in period 1 = 102.9 * 4.43 = 455.8 kgCaO consumed in period 2 = 102.9 * 0.56 = 58.02 kgCaO consumed in period 3 = 102.9 * 11.95 = 1229.4 kgCaO consumed in period 4 = 102.9 * 6.25 = 643.3 kg

Copper converting

- Liquid matte from the smelting process is oxidized in a bessemer or basic oxygen furnace by blowing air or oxygen
- The difference between steel converting and copper converting is that the value mineral Cu₂S is oxidized as well in the latter process

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

FeS₂ in the matte is oxidized initially due to its higher oxidation free energy Excess S in the matte may also oxidize preferentially prior to reduction of copper

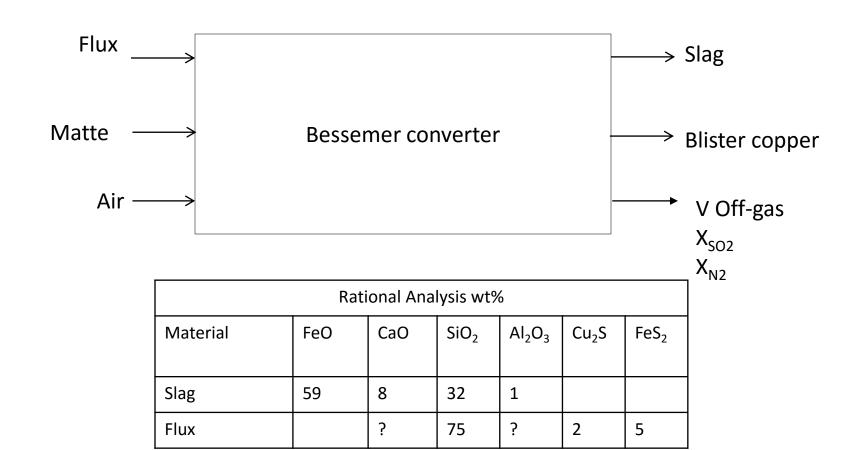
Blowing, fluxing and slagging may be done periodically due to convenience Flux is commonly added in batches due to the high amount of charge material and the limited space of furnaces

The amount of flux batches and blowing rate affects the time taken to produce slag in periods

SO₂ on the surface of the copper evaporate and form blisters on the solidifying copper Blister copper purity is around 99% and electrolysis treatment is needed to obtain pure copper Converted blister copper is considered as 100% pure for convenience in material balance

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 m³/minute



Air is blown at a rate of 100 m³/minute



9 unknown labeled variables (m_s , m_{bc} , V, X_{Fe} , X_S , X_{CaO} , X_{Al2O3} , X_{SO2} , X_{N2})

- 4 independent atomic species balances that are involved in the reactions (Cu, Fe, S, O)
- 4 molecular balances on independent nonreactive species (N₂, CaO, SiO₂, Al₂O₃)
- 3 other equation relating unknown variables ($X_{Fe} + X_S = 0.66$, $X_{CaO} + X_{Al2O3} = 0.18$, $X_{SO2} + X_{N2} = 1$)
- = -2 degrees of freedom!

Air is blown at a rate of 100 m³/minute 3000 kg Flux \rightarrow Slag 59% FeO, 8 CaO 75% SiO₂ >>> 32% SiO₂, 1% Al₂O₃ 2% Cu₂S 5% FeS₂ Bessemer converter Blister copper 40 tons Matte-34% Cu Air V Off-gas 100 m³/min X_{SO2} Calculate the time of each partial blow X_{N2}

$$Cu_2S$$
 in matte = 40000 * 0.34 * (160/128) = 17000 kg, FeS=23000 kg

Let X be the weight of slag Let Y be the weight of FeS oxidized in one blow

$$75\% * 3000 = 0.32 X$$
 (56/88) * Y + 5% * 3000 * (56/120) = 59% * 7031 * (56/72)

$$X = 7031 \text{ kg}$$
 $Y = 4963 \text{ kg} = 56.4 \text{ kg-moles}$

Oxygen required for 1 blow:

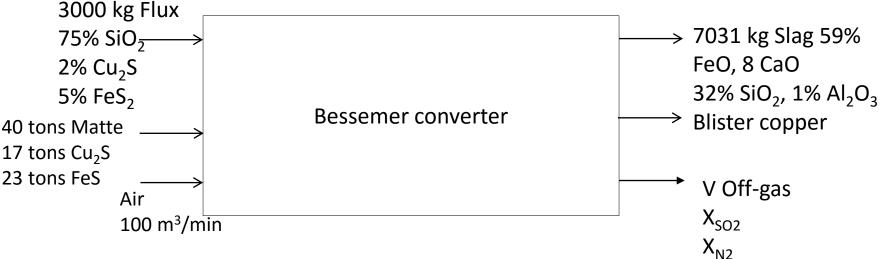
$$FeS + 3/2O_2 = FeO + SO_2$$
 $FeS_2 + 5/2O_2 = FeO + 2SO_2$

$$O_2$$
 required = 56.4 * (3/2) = 84.6 kg-moles O_2 required = 1.25 * (5/2) = 3.125 kg-moles

Total O₂ required = 87.725 kg-moles

Time for 1 blow =
$$\left(\frac{87.725}{0.21}\right) * \left(\frac{22.4}{100}\right) = 93.57$$
 minutes

Air is blown at a rate of 100 m³/minute



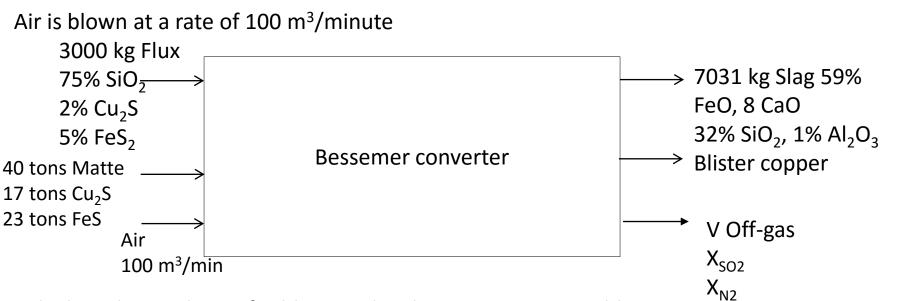
Calculate the number of partial blows and the weight of flux to be added for the last partial blow to completely remove FeO in the slag

Time for 1 blow =
$$\left(\frac{87.725}{0.21}\right) * \left(\frac{22.4}{100}\right) = 93.57$$
 minutes

The weight of FeS oxidized in one blow = 4963 kg = 56.4 kg-moles

Number of partial blows = 23000/4963 = 4.63 \approx 5

FeS oxidized in the 5th blow = 23000 - (4*4963) = 3148 kg Let Z be the amount of flux batch added in the last period O_2 balance: (3148/88)*(3/2) + (0.05Z/120)*(5/2) = 87.725*3148/4963 Z= 1903 kg



Calculate the total time for blowing the charge to convert to blister copper

Blow

Period (min)

93.57

93.57

93.57

 $Cu_2S + O_2 = Cu(1) + SO_2$

Total $Cu_2S = 17000/160 = 108$ kg-moles, Total O_2 required = 108 kg-moles Total air required = (108/0.21) * 22.4 = 11520 m³, Time required to convert Cu = 115.2 minutes Total time of operation = 546.88 minutes