CHAPTER TWO

2.1 Material Balance

Main Reaction: -

$Ca_3 (PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4.\ 2H_2O)$ …….. (1)

Side Reactions:

$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$ …….. (2)

$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$ …….. (3)

Raw Materials:

- Phosphate Rock Analysis % by wt.

$Ca_3 (PO_4)_2$	75
CaF_2	20
SiO_2	5

- H_2SO_4 concentration 94%

Assumptions: -

- Production of H_3PO_4 =300 Ton/year =1000 Kg/day
- Year = 300day
- Some sulfuric acid (1-1.5) percent is allowed to go with gypsum to make it easily filterable.
- Excess of H_2SO_4 =15%
- Yield = 95%

Component	**M.wt**
H_3PO_4	98
H_2SO_4	98
SiO_2	60
CaF_2	78
H_2O	18
$Ca(PO_4)_2$	310
$CaSO_4$	136
$CaSO_4.2H_2O$	172
HF	20
H_2SiF_6	144
P_2O_5	142

Production of H_3PO_4 =1000 Kg/day = 42Kg/hr. = 0.428Kgmole/hr.

Stream of product = 42/0.75= 56Kg/hr.

H_2O= 56*0.25 = 14 Kg/hr.

From reaction (1)

Reacted of $Ca_3 (PO_4)_2$ = 1/2*0.428 = 0.214Kgmole/hr. = 66.34Kg/hr.

$$\text{Yield} = \frac{\text{product H3PO4}}{\text{feed Ca3(PO4)2}}$$

$Ca_3 (PO_4)_2$ feed = 0.428/0.95 = 0.45Kgmole/hr. = 139.5Kg/hr.

Feed steam = 139.5/0.75 = 186 Kg/hr.

CaF_2 = 0.2 * 186 = 37.2 Kg/hr.

SiO_2= 0.05 *186 = 9.3 Kg/hr.

Phosphate Rock, Kg/hr.

$Ca_3 (PO_4)_2$	139.5
CaF_2	37.2
SiO_2	9.3

2.1.1 Martial Balance on Mill: -

Dilute phosphoric acid stream

Phosphoric acid 15% wt.

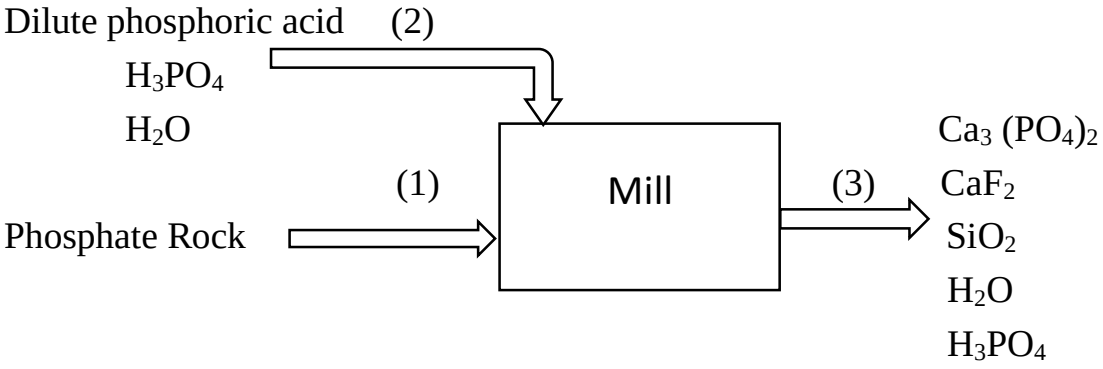
H_2O 85% wt.

Assume 50 Kg of dilute H_3PO_4 /100 Kg Phosphate Rock

186* 50/100 = 93 Kg /hr. (H_2O+H_3PO_4 dilute)

H_3PO_4 = 14 Kg/hr.

H_2O = 79 Kg /hr.



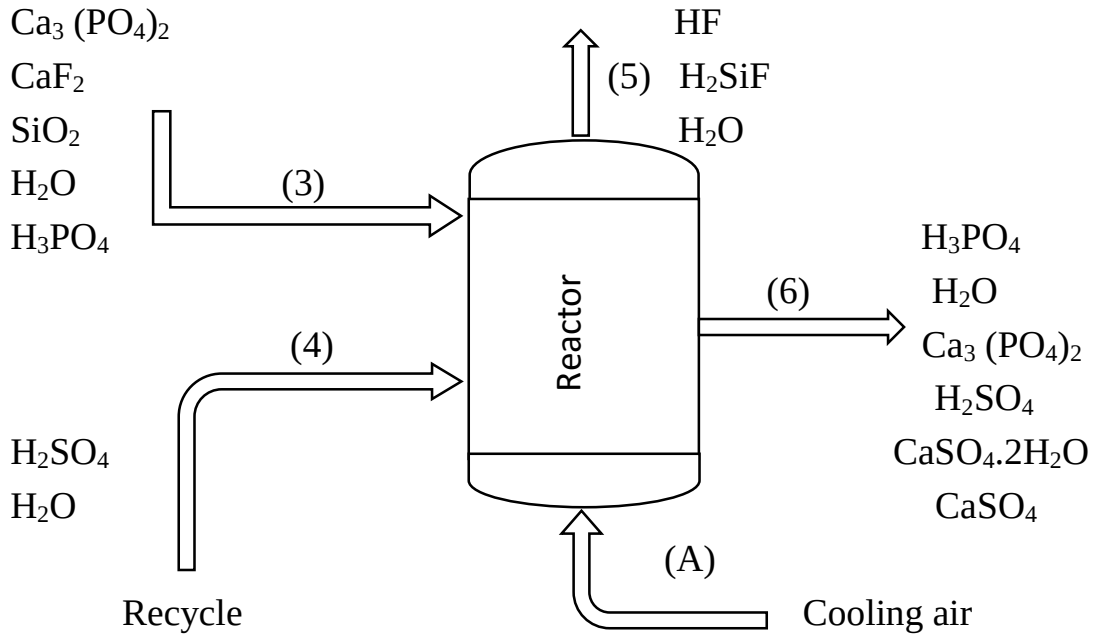
Composition	Stream 1	Stream 2	Steam 3
$Ca_3(PO_4)_2$	139.5		139.5
CaF_2	37.2		37.2
SiO_2	9.3		9.3
H_2O		79	79
H_3PO_4		14	14

Mass in = 139.5 + 37.2 +9.3 +79 +14 = 279 Kg /hr.

Mass out= 139.5 +37.2 +9.3+79+14 = 279 Kg/hr.

Mass in = Mass out = 279 Kg/hr.

2.1.2 Material Balance on Reactor:



Reactions:

$Ca_3 (PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4.2H_2O)$ ….. (1)

$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$ …… (2)

$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$ ….. (3)

H_3PO_4 product = 0.428 Kg mole/hr.

From Reaction (1)

$Ca_3 (PO_4)_2$ reacted = 0.428/2 =0.214 Kg mole /hr.

Out of $Ca_3 (PO_4)_2$ =in – req.

= 0.45 – 0.214 = 0.236 Kg mole/hr.

= 73.16Kg/hr.

Reacted of H_2SO_4 = 3/2 * 0.428 = 0.642 Kg mole/hr.

Reacted of H_2O = 6/2 * 0.428 = 1.284 Kg mole/hr.

Product of $CaSO_4.2H_2O$ = 3/2 * 0.428 = 0.642

From Reaction (2)

In CaF_2 = req. = 0.48 Kg mole/hr.

Reacted of H_2SO_4 = 0.48 Kg mole/hr.

Product of HF = 2 * 0.48 = 0.96 Kg mole/hr.

Product of $CaSO_4$ = 0.48 Kg mole/hr.

From Reaction (3)

In SiO_2= req.= 0.155kg.mole/hr.

Reacted of HF= 6*0.155= 0.93kg.mole/hr.

Product of H_2SiF_6= 0.155 kg.mole/hr.

Product of H_2O= 2*0.155= 0.31 kg.mole/hr.

Reacted of H_2SO_4= 0.48 + 0.642= 1.122 kg.mole/hr. = 109.96 kg /hr.

Excess%H_2SO_4= 0.15= $\frac{\text{In}-\text{req.}}{\text{req.}} = \frac{\text{In}-109.96}{109.96}$

In= 126.45 kg /hr.

Out of H_2SO_4= In – req. = 126.45 – 109.96= 16.45 kg/hr.

Stream (4)

$\frac{126.45}{0.94} = 134.53$ kg/hr

H_2SO_4 126.45 kg/hr.

H_2O 8.08 kg/hr.

Stream (6)

In + gen. = req. + out

H_3PO_4= 42 + 14= 56 kg/hr.

Out H_2O= In – req. = 79 + 8.08 + 5.58– 23.1

Out of H_2O= 69.56 kg.

Assume 45% from H_2O is vaporized

H_2O= 38.258kg/hr.

$Ca_3 (PO_4)_2$= 73.16 kg/hr.

$CaSO_2.2H_2O$= 101.4 kg/hr.

H_2SO_4= 16.45 kg/hr.

$CaSO_4$= 65.28 kg/hr.

Stream (5)

H_2SiF_6= 22.32 kg/hr.

H_2O= 31.302 kg/hr.

HF= In–req.= 0.96–0.93= 0.03kg.mole/hr.

HF= 0.6 kg/hr.

Cooling Air

79% N_2

21% O_2

Comp.	Stream(3)	Stream(4)	Stream(5)	Stream(6)	Stream(A)
$Ca_3(PO_4)_2$	139.5			73.16	
CaF_2	37.2				
SiO_2	9.3				
H_2O	79	8.08	31.302	38.258	
H_3PO_4	14			56	
H_2SO_4		126.45		16.45	
$CaSO_4.2H_2O$				110.4	
$CaSO_4$				65.28	
H_2SiF_6			22.32		
HF			0.6		
O_2			21		21
N_2			79		79

Mass in= 139.5+ 37.2+ 9.3 +79 +14+ 8.08+ 126.45+ 21+ 79

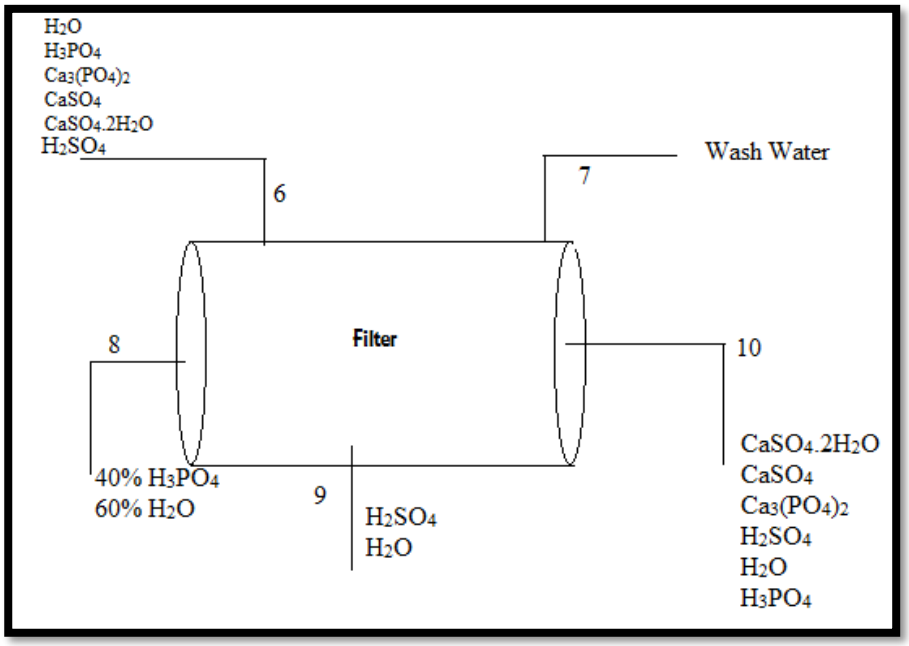
= 513.77 kg/hr.

Mass out= 31.302+ 22.32+ 0.6+ 21+79+73.16+ 38.258+ 56+ 16.45+110.4+65.28

= 513.77 kg/hr.

∴ Mass in= Mass out= 513.77 kg/hr.

2.1.3 Material Balance on Filter



Stream (8)

H_3PO_4= 42 kg/hr.

Stream (8) = $\frac{42}{0.4} = 105\ \frac{kg}{hr}$

H_2O= 0.6* 105= 63 kg/hr.

H_2SO_4 in stream (10) = 16.45* $\frac{1.5}{100} = 0.247$ kg/hr.

H_2SO_4 in stream (9) = 16.45–0.247= 16 .2 kg/hr.

H_2O in stream (10) = 38.258* $\frac{1.5}{100} = 0.574$ kg/hr.

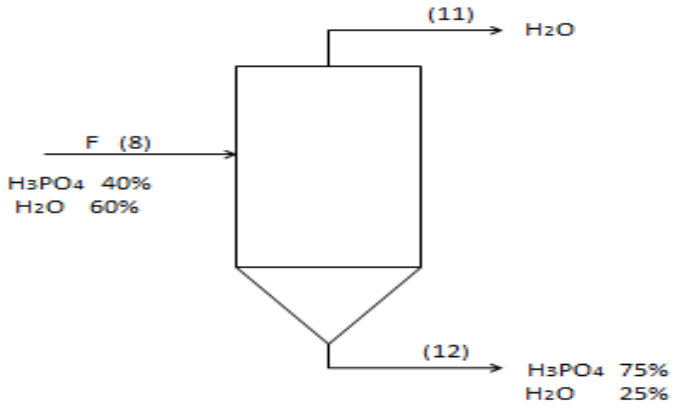
H_2O in stream (9) = 1.035 kg/hr.

H_2O in stream (7) = 0.574+ 1.035+ 63– 38.258 =26.35kg/hr.

H_3PO_4 in stream (10) = 14 kg/hr.

Comp.	Stream(6)	Stream(7)	Stream(8)	Stream(9)	Stream(10)
$Ca_3(PO_4)_2$	73.16				73.16
H_2O	38.258	26.35	63	1.035	0.574
H_2SO_4	16.45			16.2	0.247
H_3PO_4	56		42		14
$CaSO_4.2H_2O$	110.4				110.4
$CaSO_4$	65.28				65.28

2.1.4 Material Balance on Evaporator: -



M.B on H_3PO_4

IN = Out

0.4 F = 42 ⟶ F = 105 Kg/hr.

:. Stream (8)

H_3PO_4 = 42 Kg/hr.

H_2O = 63 Kg/hr.

:. H_2O in stream (11) = 63 – 14 = 49 Kg/hr.

Component	Stream (8)	Stream (11)	Stream (12)
H_3PO_4	42		42
H_2O	63	49	14

Mass In = 42 + 63 = 105 Kg/hr.

Mass Out = 49 + 42 + 14 = 105 Kg/hr.

:. Mass In = Mass Out = 105 Kg/hr.

2.1.5 Material Balance on Mixing Tank.

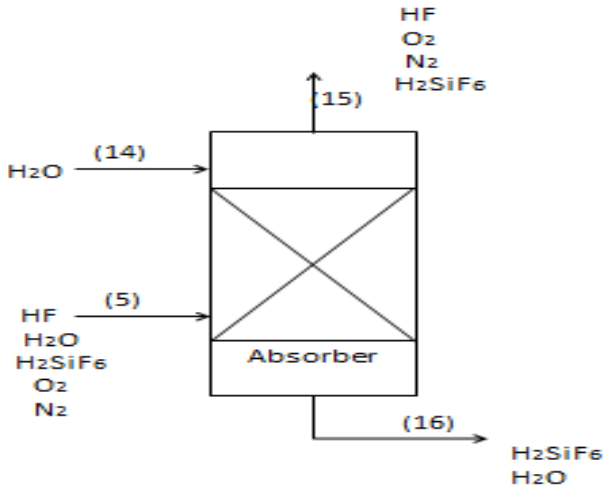
Component	Stream (9)	Stream (13)	Stream (4)
H_2SO_4	16.2	110.25	126.45
H_2O	1.035	7.045	8.08

Mass In = 16.2 + 1.035 + 110.25 + 7.045 = 134.53 Kg/hr.

Mass Out = 126.45 + 8.08 = 134.53 Kg/hr.

:. Mass In = Mass Out = 134.53 Kg/hr.

2.1.6 Material Balance on Absorber.



Recovery = 99%

$Y_2 = Y_1$ (1- recovery) = 0.202 (1- 0.99) = 0.002

$(Ls/Gs)_{min} = (y_1-y_2)/(y_1/m) = m[1-(y_2/y_1)]$

$m = (P_{H2SiF6} / P_T) = (418 mmHg/760 mmHg) = 0.55$

$(Ls/Gs)_{min} = 0.55 [1-(0.002/0.202)] = 0.544$

$(Ls/Gs)_{actual} = 1.5(Ls/Gs)_{min} = 0.816$

Gs = 100.6 Kg/hr.

Ls = 82 Kg/hr.

Comp.	Stream (5)	Stream (14)	Stream (15)	Stream (16)
HF	0.6		0.6	
H_2O	31.302	82		113.3
H_2SiF_6	22.32		0.223	22.097
O_2	21		21	
N_2	79		79	

Mass In = 0.6 + 31.302 + 22.32 + 21 + 79 + 82

= 236.22 Kg/hr.

Mass Out = 0.6 + 0.223 + 21 + 79 + 113.3 + 22.097 = 236.22 Kg/hr.

Mass In = Mass Out = 236.22

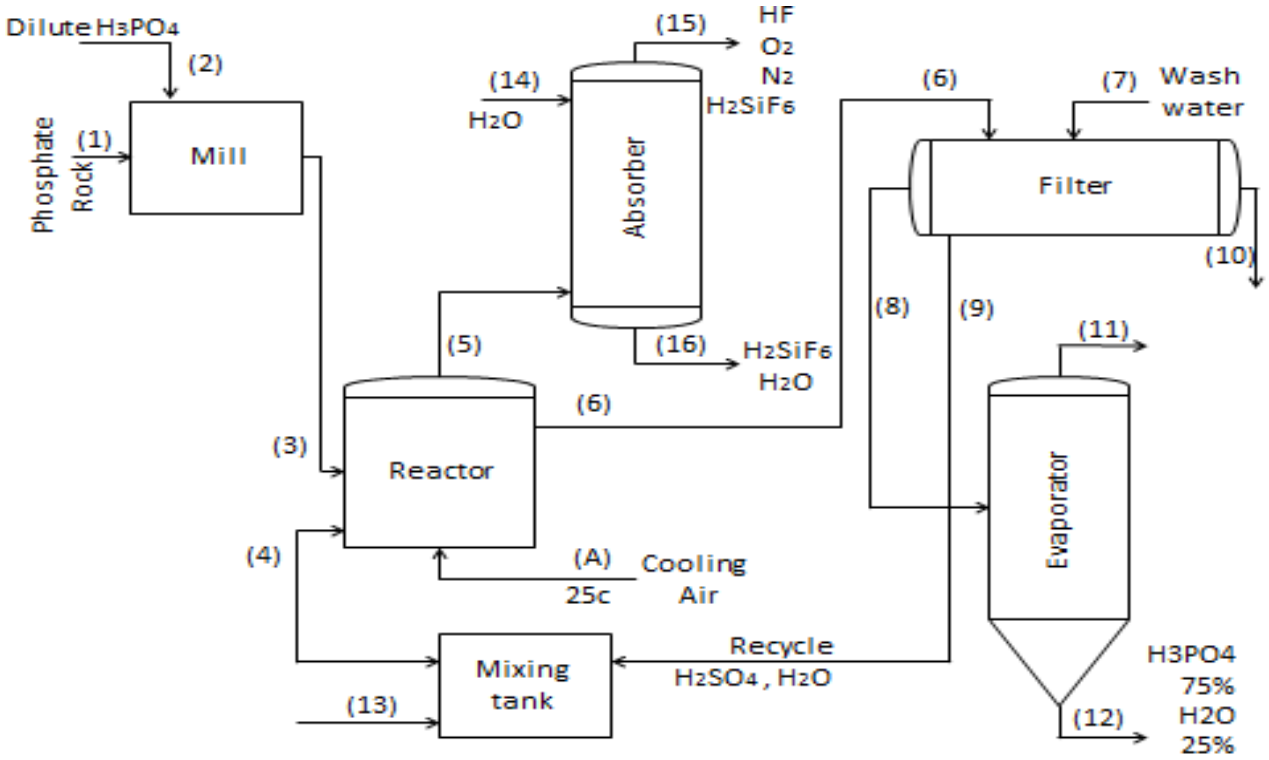
2.1.7 Over all Material Balance:

Stream Input		Stream Output	
Stream (1)	186	Stream (10)	263.66
Stream (2)	93	Stream (11)	49
Stream (A)	100	Stream (12)	56
Stream (13)	117.295	Stream (15)	100.823
Stream (7)	26.35	Stream (16)	135.397
Stream (14)	82		

Mass In = 604.88 & Mass Out = 604.88

:. Mass In = Mass Out = 604.88 Kg/hr.

2.1.8 General Diagram of Process.



2.2 Energy Balance

Table (1) Heat capacity of gases kJ/kg mole

Component	A	B	C	D
H_2O	32.243	$1.923*10^{-3}$	$1.055*10^{-5}$	$-3.596*10^{-9}$
O_2	28.106	$-3.68*10^{-6}$	$1.745*10^{-5}$	$-1.065*10^{-8}$
N_2	31.15	$-1.356*10^{-2}$	$2.679*10^{-5}$	$-1.168*10^{-8}$
HF	29.061	$6.611*10^{-4}$	$-2.032*10^{-6}$	$2.503*10^{-9}$

$\Delta H = m \int Cp\ \Delta T$

$\Delta H = m/M.wt\ [\int (A+BT+CT^2+DT^3)\ dT]$

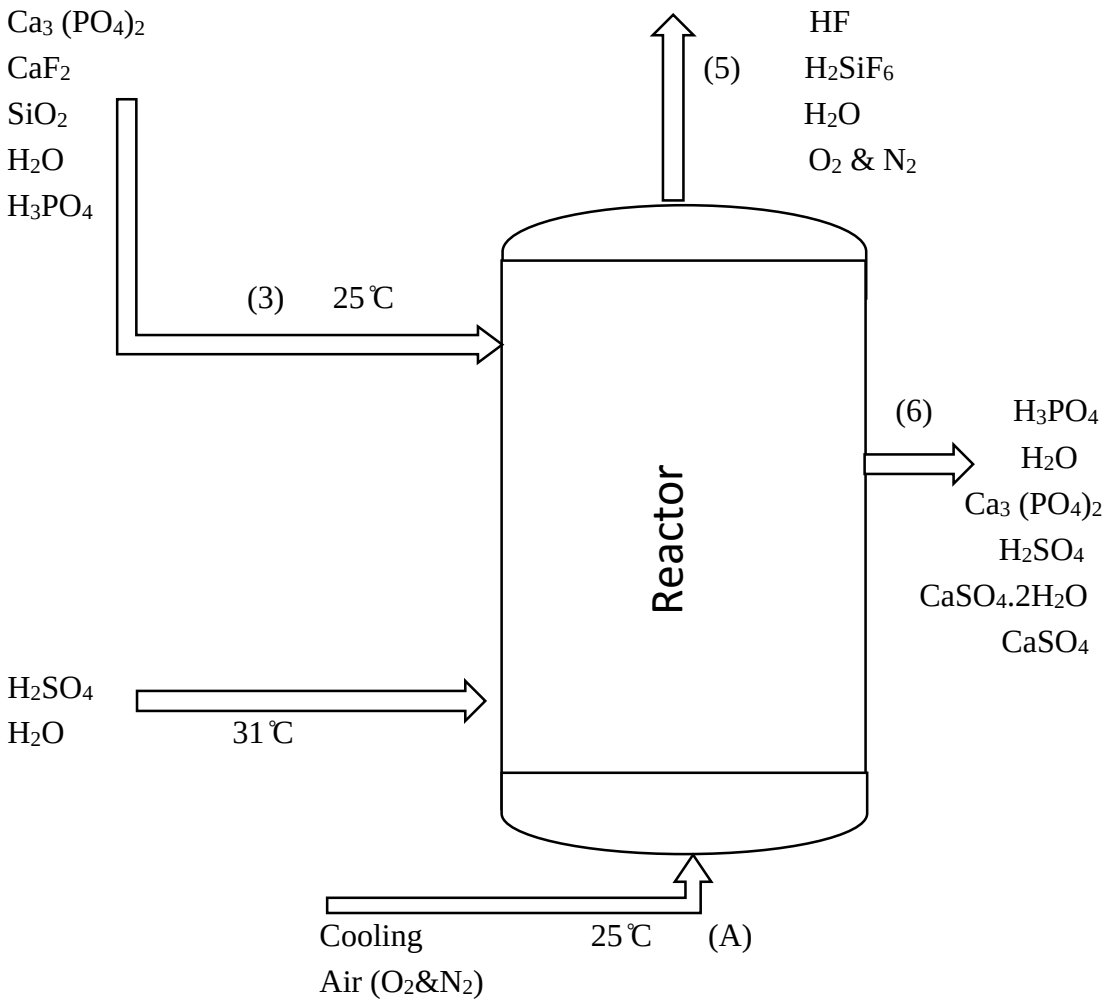
$\Delta H = n\ [A\ (T_2 - T_1) + B/2\ (T_2^2 - T_1^2) + C/3\ (T_2^3 - T_1^3) + D/4\ (T_2^4 - T_1^4)$

$Cp = A + BT + CT^2 + DT^3$ KJ/Kg mole. K

Table (2)

Comp.	TBP ˚C	Cp KJ/kg mole .C	ΔHF Kcal/kg mole. K
HF	20	47.3	-64.2
$Ca_3(PO_4)_2$		262.9	-988.9
H_2SiF_6		236.1	-267.8
$CaSO_4.2H_2O$		315.5	-483.06
$CaSO_4$		164.9	-346.67
CaF_2		92.1	-286.5
SiO_2	223	74.5	-203.4
H_2SO_4		167.4	-193.91
H_3PO_4		185.4	-306.2
H_2O	100	75.3	-68.32

2.2.1 Energy Balance on Reactor



Reaction:

$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4.2H_2O)$

$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$

$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$

Operating Conditions:

T = 75-80℃ , P = 1atm. , Liquid Phase

Heat in = heat out

$M\ Cp\ \Delta T_{Ca_3(PO_4)_2} + m\ Cp\ \Delta T_{CaF_2} + m\ Cp\ \Delta T_{SiO_2} + m\ Cp\ \Delta T_{H_2O} + m\ Cp \Delta T_{H_3PO_4} + m\ Cp\ \Delta T_{H_2SO_4}$

$+ m\ Cp\ \Delta T_{H_2O} + m\ Cp\ \Delta T_{O_2} + m\ Cp\ \Delta T_{H_2} + \Delta Hr° = m\ Cp\ \Delta T_{HF} + m\ Cp\ \Delta T_{H_2SiF_6} + mCp\Delta T_{H_2O}$

$+ m\ Cp\ \Delta T_{O_2} + m\ Cp\ \Delta T_{N_2} + m\ Cp\ \Delta T_{H_3PO_4} + m\ Cp\ \Delta T_{H_2O} + m\ Cp\ \Delta T_{Ca_3(PO_4)_2} + m\ Cp\ \Delta T_{H_2SO_4} +$

$m\ Cp\ \Delta T_{CaSO_4} + m\ Cp\ \Delta T_{CaSO_4.2H_2O} + Q + m\ \lambda_{H_2O}$

$T_{ref..} = 25C°$

$M\ Cp_{HF}\ \Delta T + m\ Cp_{H_2SiF_6}\ \Delta T + m\ Cp_{H_2O}\ \Delta T + m\ Cp_{O_2}\ \Delta T + m\ Cp_{N_2} \Delta T + m\ Cp_{H_3PO_4}\ \Delta T + m\ Cp_{H_2O}\ \Delta T + m\ Cp_{Ca3(PO4)_2} \Delta T + m\ Cp_{H_2SO_4} \Delta T + m\ Cp_{CaSO_4} \Delta T + m\ Cp_{CaSO_4.2H_2O} \Delta T + Q + m\ \lambda_{H_2O} = \Delta Hr° + m\ Cp_{H_2O}\ \Delta T + m\ Cp_{H_2SO_4} \Delta T$

We have three reactions:

$\Delta Hr° = -693.5$ Cal/g.mole $= -2901.5$ KJ/Kg.mole

$\Delta Hr_2° = 5.34$ Cal/g.mole $= 22.343$ KJ/Kg.mole

$\Delta Hr_3° = 184.16$ Cal/g.mole $= 770.5$ KJ/Kg.mole

$\Delta Hr° = 0.214 * (-2901.5) + 0.48 * 22.342 + 0.155 * 770.5$

$\Delta Hr° = -490.765$ KJ/Kg

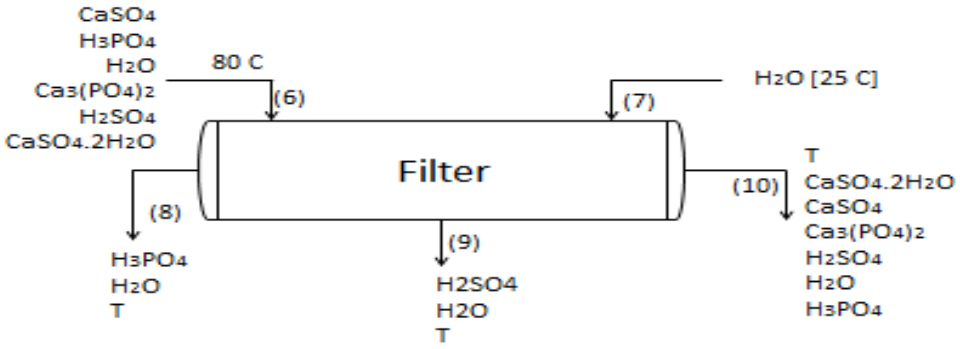
$$\frac{0.6}{20} * [29.061(353-298) + \frac{6.611 * x10^{-4}}{2} * (353^2 - 298^2) - \frac{2.032 * 10^{-6}}{3} * (353^3 - 298^3) + \frac{2.503 * 10^{-9}}{4} * (353^4 - 298^4)\ ] + \frac{31.302}{18}\Big[32.243\ (353-298) + \frac{1.923 * 10^{-3}}{2} * (353^2 - 298^2) + \frac{1.055 * 10^{-5}}{3}\ (353^3 - 298^3) - \frac{3.596 * 10^{-9}}{4} * (353^4 - 298^4)\Big] + \frac{22.32}{144} * [\ 0.67 * (353-298)]$$

$$+\frac{21}{32}[28.106\ (353-298)\ - \frac{3.68 * 10^{-6}}{2}\ (353^2 - 298^2) + \frac{1.745 * 10^{-5}}{3}\ (353^3 - 298^3) - \frac{1.065 * 10^{-8}}{4}\ (353^4 - 298^4)] + \frac{79}{28} * \Big[31.15\ (353-298) - \frac{1.356 * 10^{-2}}{2}\ (353^2 - 298^2) + \frac{2.679 * 10^{-5}}{3}\ (353^3 - 298^3) - \frac{1.108 * 10^{-8}}{4}\ (353^4 -$$

$$298^4) + \frac{56}{98} * 185.4\,(353 - 298) + \frac{38.258}{18} * 75.3\,(353 - 298) + \frac{73.16}{301} * 262.9\,(353 - 298) + \frac{16.45}{98} * 167.4\,(353 - 298) + \frac{16.45}{98} * 167.4\,(353 - 298) + \frac{110.4}{172} * 164.91\,(353 - 298) + \frac{65.28}{136} * 236.1\,(353 - 298)\Big] + Q + \frac{31.302}{18} * 40683 = -490.765 + \frac{8.08}{18} * 75.3\,(304 - 298) + \frac{126.45}{98} * 167.4\,(304 - 298)$$

Q = – 263273.7493 KJ/hr.

2.2.2 Energy Balance on Filter



Heat IN = Heat Out

m $Cp_{H_3PO_4}$ dT + m Cp_{H_2O} dT + m $Cp_{Ca_3(PO_4)_2}$ dT + m $Cp_{H_2SO_4}$ dT + m $Cp_{CaSO_4.2H_2O}$ dT + m Cp_{CaSO_4} dT + m Cp_{H_2O} dT = m $Cp_{H_3PO_4}$ dT + m Cp_{H_2O} dT + m $Cp_{H_2SO_4}$ dT + m Cp_{H_2O} dT + m Cp $_{CaSO_4.2H_2O}$ dT + m Cp $_{CaSO_4}$ dT + m Cp $_{Ca_3(PO_4)_2}$ dT + m Cp $_{H_2SO_4}$ dT + m Cp_{H_2O} dT + m Cp $_{H_3PO_4}$ dT

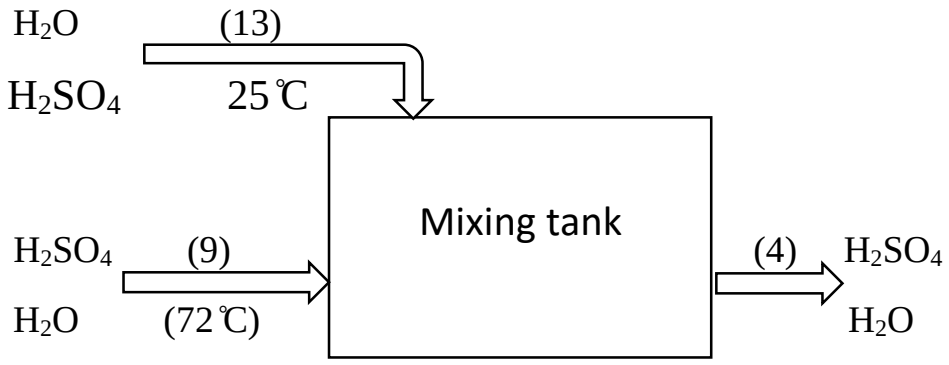
T_{ref} = T

m $Cp_{H_3PO_4}$ dT + m Cp_{H_2O} dT + m $Cp_{Ca_3(PO_4)_2}$ dT + m $Cp_{H_2SO_4}$ dT + m $Cp_{CaSO_4.2H_2O}$ dT + m Cp_{CaSO_4} dT + m Cp_{H_2O} dT = 0

>> [(56/98) * 185.4 + (38.258/18) * 75.3 + (73.16/310) * 262.9 + (16.45/98) * 167.4 + (110.4/172) * 315.5 + (65.28/136) * 164.9] {353 – T} + [26.35 * 4.184] {298 – T} = 0

T = 72 C°

2.2.3 Energy Balance on mixing tank:



Heat in = Heat out

m Cp $_{H2O}$ ΔT + m Cp $_{H2SO4}$ ΔT + m Cp $_{H2O}$ ΔT + m Cp $_{H2SO4}$ ΔT= m Cp $_{H2SO4}$ ΔT+ m Cp $_{H2O}$ ΔT

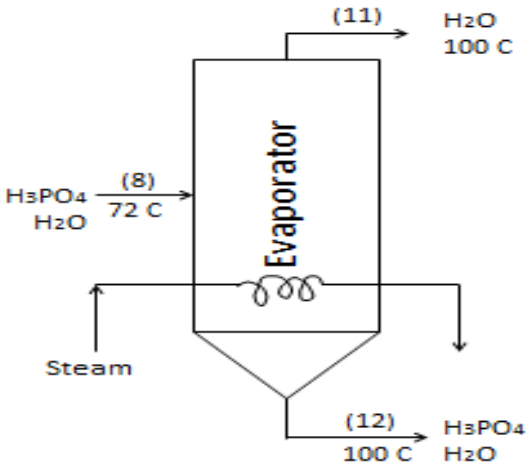
$T_{ref.}$ = T

m Cp $_{H2O}$ ΔT + m Cp $_{H2SO4}$ ΔT + m Cp $_{H2O}$ ΔT + m Cp $_{H2SO4}$ ΔT = 0

[1.035/18 *75.3 (345 – T) + 16.2/98 * 167.4 (345-T)] + [7.045/18 * 75.3 (298-T) + 110.25/98 * 167.4 (298 – T)] = 0

T= 31℃ = 304K

2.2.4 Energy Balance on Evaporator



Heat In = Heat Out

$m\ Cp_{H_3PO_4}\ dT + m\ Cp_{H_2O}\ dT + Q = m\ Cp_{H_2O}\ dT + m\ \lambda_{H_2O} + m\ Cp_{H_3PO_4}\ dT + m\ Cp_{H_2O}\ dT$

$T_{ref} = 72\ C°$

$Q = m\ Cp_{H_3PO_4}\ dT + m\ Cp_{H_2O}\ dT + m\ \lambda_{H_2O} + m\ Cp_{H_2O}\ dT$

Q = (42/98)*185.4*(373-345) + (14/18)*{4.184*(373-345) + (49/18)*32.243*(373-345) + (1.9238*10^-3/2)*(373^2-345^2) + (1.055*10^-5/3)*(373^3-345^3) – (3.596 * 10^-5 /4) *(373^4-345^4)} + (49/18)* 40683

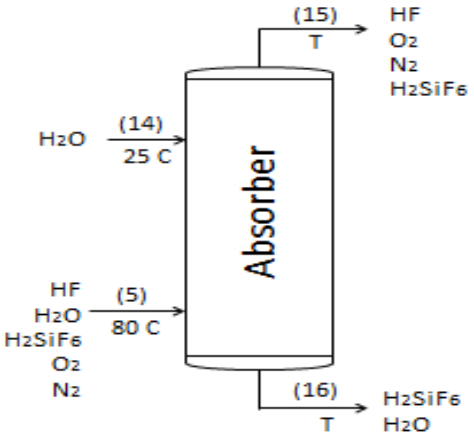
Q = 115665.33 KJ/hr.

This heat is supplied by sat. Steam 150 C°

$\lambda_s = 2113$ KJ/Kg.

$m_s = Q/\lambda_s = 115665.33/2113 = 55$ Kg/hr.

2.2.5 Energy Balance on Absorber



Heat In = Heat Out

m Cp_{H_2O} dT+m Cp_{HF} dT+m Cp_{H_2O} dT+m $ʎ_{H_2O}$+m $Cp_{H_2SiF_6}$ dT+m Cp_{O_2} dT+

m Cp_{N_2} dT = m Cp_{HF} dT + m Cp_{O_2} dT + m Cp_{N_2} dT+m $Cp_{H_2SiF_6}$ dT+m Cp_{H_2O} dT+ m $Cp_{H_2SiF_6}$ dT

T_{ref} = T

m Cp_{H_2O} dT+m Cp_{HF} dT+m Cp_{H_2O} dT+m $ʎ_{H_2O}$ + m Cp_{O_2} dT + m Cp_{N_2} dT+m $Cp_{H_2SiF_6}$ dT = 0

(82/18)*75.3*(298-T) + (0.6/20)*{29.06(353-T) + (6.611*10^-4/2)*(353^2-T^2) + (2.032*10^-6/3)*(353^3 – T^3) + (2.503*10^-9/4)*(353^4-T^4)} + (31.302/18)*{32.243(353-T) + (1.923*10^-3/2)* (353^2-T^2) + (1.055*10^-5/3)* (353^3 – T^3)

$-3.596* 10^{-9}/4 (353^4 – T^4)]$ + 31.302/18 * 40683 + 21/82

$[28.106(353-T) – 3.68*10^{-6}/2 (353^2 – T^2) + 1.745*10^{-5}/3 (353^3 – T^{3)} – 1.065*10^{-8}/4 (353^4 – T^4)]$ + 79/28 $[31.15 (353-T) – 1.35*10^{-2}/2 (353^2 – T^2) + 2.679*10^{-5}/3 (353^3 - T^3) – 1.108*10^{-8}/4 (353^4 – T^4)]$ + 22.32/144[0.67 *(353 – T)] =0

By trial and error

T = 60℃