Comprehensive Waste Management Project

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Objective:

Detailed waste management plan for the **phosphoric acid production process (wet process)**, integrating process optimization, material and energy balances, life cycle assessment (LCA), product carbon footprint (PCF) assessment, and cost-benefit analysis.

1. Industry & Process:

Chemical manufacturing Industry : Phosphoric Acid production through wet process

2. Process Flow and Material/Energy Balances:

- **Process Flow Diagram (PFD) :**

  Reactions:

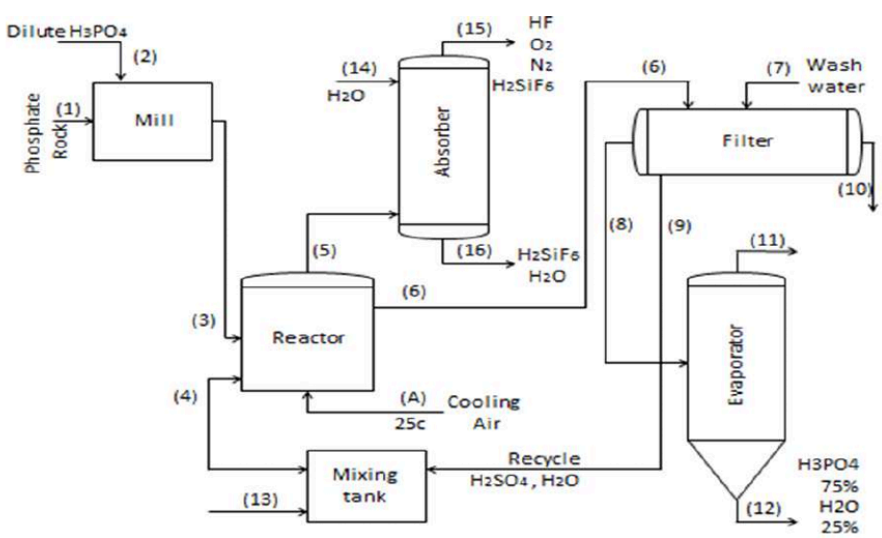
  i. Main Reaction

  $$Ca_3(PO4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4).2H_2O \text{.........(1)}$$

  ii. Side Reaction

  $$CaF_2 + H_2SO_4 + 2H_2O \rightarrow 2HF + CaSO_4.2H_2O \text{.......................(2)}$$

  $$6HF + SiO_2 \rightarrow H_2SiF_4 + 2H_2O \text{...(3)}$$



- **Material Balance :**

  Assumptions

  ~ H_3PO_4 Production = 1000 ton/day = 10^6 kg/day = 42000 kg/hr = 429 kmol/hr

Yield = 95%, Conc of H_2SO_4 = 94%, H_2SO_4 Excess = 15%

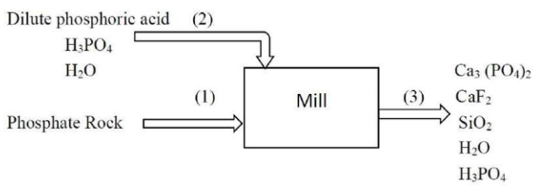
~ Product stream = 42000/0.75 = 56000 kg/hr

~ H_2O Stream = 0.25 x 56000 = 14000 kg/hr

~ From Reaction (1) : $Ca_3(PO_4)_2$ = 0.5 x 429 kmol/hr = 214.5 kmol/hr = 66.5 kg/hr

~ Since Yield = 95%, Feed $Ca_3(PO_4)_2$ = 429/0.95 = 451.5 kmol/hr = 140000 kg/hr

a) Around Mill:



Stream - 1 : Phosphate Rock Composition [$Ca_3(PO_4)_2$ (75%), CaF_2 (20%) , SiO_2 (5%)]

$Ca_3(PO_4)_2$ = 140000 kg/hr; CaF2 = 0.2*187000 = 37400 kg/hr

SiO2 = 0.05*187000 = 9350 kg/hr

Stream - 2 : Dilute Phosphoric Acid [H_2O (85%), H_3PO_4 (15%)] = 0.5 x 187000 = 93500 kg/hr (Considering dil H_3PO_4 : Phosphate Rock = 1:2)

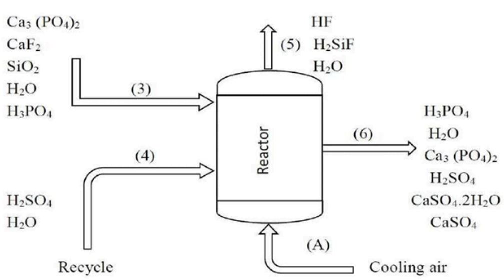
H_2O = 93500 * 0.85 = 79500 kg/hr; H_3PO_4 = 93500 * 0.15 = 14000 kg/hr

Composition	Stream-1	Stream-2	Stream-3
$Ca_3(PO_4)_2$	140000		140000
CaF_2	37400		37400
SiO_2	9350		9350
H_2O		79500	79500
H_3PO_4		14000	14000

Mass In : 140000+37400+9350+79500+14000 = 280250

Mass out : 140000+37400+9350+79500+14000 = 280250

b) Around Reactor:



H_3PO_4 production = 429 kmol/hr

Reaction 1:

$Ca_3(PO_4)_2$ reacted = 429/2 = 214.5 kmol/hr

Unreacted $Ca_3(PO_4)_2$ = 452-214.5 = 237.5 kmol/hr

H_2SO_4 reacted = 3/2 * 429 = 643.5 kmol/hr

H_2O reacted = 6/2 * 429 = 1287 kmol/hr

$CaSO_4.2H_2O$ produced = 3/2 * 429 = 643.5 kmol/hr

Reaction 2:

In CaF_2 = reacted CaF_2 = 480 kmol/hr Reacted

H_2SO_4 = 480 kmol/hr

Produced HF = 2 * 480 = 960 kmol/hr

Produced $CaSO_4$ = 480 kmol/hr

Reaction 3:

In SiO_2 = reacted SiO_2 = 156 kmol/hr

Reacted HF = 6 * 156 = 936 kmol/hr

Produced H_2SiF_6 = 156 kmol/hr

Produced H_2O = 2 * 156 = 312 kmol/hr

Stream 4:

Total H_2SO_4 reacted = 643.5 + 480 = 1123.5 kmol/hr = 110000 kg/hr

Excess H_2SO_4 = 15% → 0.15 = (in−reacted)/in =0.15 = (in−110000)/110000

In = 126630 kg/hr

Non reacted H_2SO_4 = 126630 - 110000 = 16530 kg/hr

H_2SO_4 concentration 94%: 126630/0.94 = 134700 kg/hr

H_2SO_4 = 126630 kg/hr

H_2O = 134700 – 126600 = 8100 kg/hr

Stream 6:

H_3PO_4 = 42000 + 14000 = 56000 kg/hr

H_2O = 79500 + 8100 + 5600 – 23130 = 70000 kg/hr

$Ca_3 (PO_4)_2$ = 73600 kg/hr

$CaSO_4.2H_2O$ = 110700 kg/hr

H_2SO_4 = 16500 kg/hr

$CaSO_4$ = 65250 kg/hr

Stream 5:

H_2SiF_6 = 22450 kg/hr

H_2O = assume 50% of H_2O from stream 6 is vaporized: 0.5 * 70000 = 35000 kg/hr

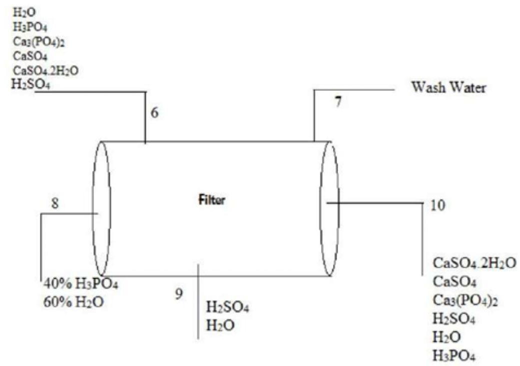
HF = produced – reacted = 960 – 936 = 24 kmol/hr = 480 kg/hr

Cooling air stream: 79% Nitrogen, 21% Oxygen

Mass In : Stream 3 + Stream 4 = 140000 + 37400 + 9350 +79500 + 14000 + 8100 + 126630 = 414980 kg/hr

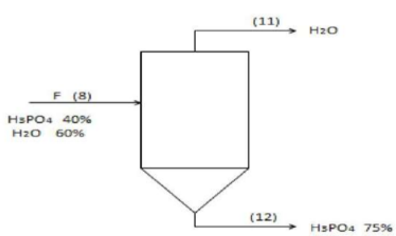
Mass Out : Stream 5 + Stream 6 = 35000 + 22450 + 73600 + 35000 + 56000 + 16500 + 110700 + 65250+480 = 414980 kg/hr

c) Around Filter:



<u>Stream 10</u>: H3PO4 = 14000 kg/hr
<u>Stream 8</u>: H3PO4 = 56000 – 14000 = 42000 kg/hr
Total stream 8 = 42000/0.4 = 105000 kg/hr
H2O in stream 8 = 0.6 * 105000 = 63000 kg/hr
(Assuming 1.5% of H2SO4 & H2O goes with gypsum for easy filtration)
H2SO4 in stream 10 = 16500 * 0.015= 247.5 kg/hr
H2SO4 in stream 9 = 16500 – 247.5 = 16252.5 kg/hr
H2O in stream 10 = 35000 * 0.015 = 525 kg/hr
(Since Stream 9 recycles back to the reactor and the acid conc needs to be at 94%)
Total stream 9 = $H2SO/$ 0.94 = 16252.5/0.94 = 17290 kg/hr
H2O in stream 9 = 17290 * 0.06 = 1037.5 kg/hr
H2O in stream 7 = -35000 + 63000 + 525 + 1037.5 = 29562.5 kg/hr
Mass In : Stream (6+7) = 73600 + 35000 + 16500 + 56000 + 110700 + 65250 + 29562.5 = 386612.5 kg/hr
Mass Out : Stream (8+9+10) = 63000 + 42000 + 1037.5 + 16252.5 + 73600 + 525 + 247.5 + 14000 + 110700 + 65250 = 386612.5 kg/hr

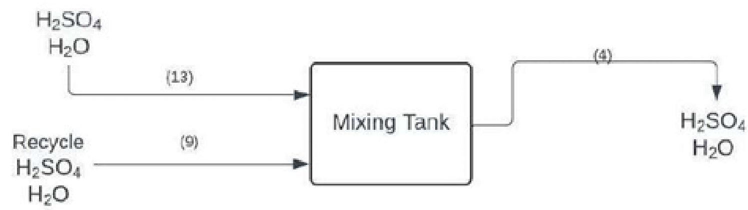
d) Around Evaporator:



Stream 8(F) composition: H3PO4 = 42000 kg/hr, H2O = 63000 kg/hr
Material balance on H3PO4:
0.4 * F = 0.75 * Stream 12
0.4 * 105000 = 0.75 * Stream 12
Stream 12 = 56000 kg/hr
H2O in Stream 12 = 0.25 * 56000 = 14000 kg/hr
H2O in Stream 11 = 63000 – 14000 = 49000 kg/hr
Mass In : Stream 8 = 42000 + 63000 = 105000 kg/hr

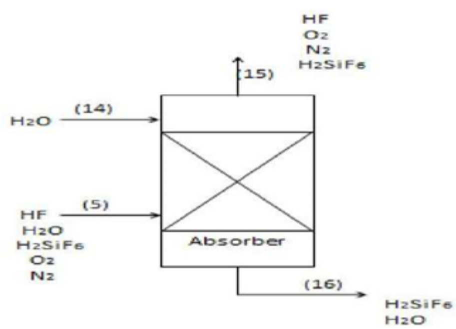
Mass Out : Stream (11+12) = 49000 + 14000 + 42000 = 105000 kg/hr

e) Around Mixing Tank:



Stream 4: H2SO4 = 126630 kg/hr, H2O = 8100 kg/hr
Stream 9: H2SO4 = 16252.5 kg/hr, H2O = 1037.5 kg/hr
Stream 13: H2SO4 = 126630 – 16252.5 = 110377.5 kg/hr , H2O = 8100 – 1037.5 = 7062.5 kg/hr
Mass In : 16252.5 + 1037.5 + 110377.5 + 7062.5 = 134730 kg/hr
Mass Out : 126630 + 8100 = 134730 kg/hr

f) Around Absorber:



Assume 99% recovery: H2SiF6 in stream 16 = 0.99 * 22450 = 22225.5 kg/hr
H2SiF6 in stream 15 = 22450 – 22225.5 = 224.5 kg/hr
(Assuming the amount of water in stream 16 made H2SiF6 into 15%)
Total stream 16 = 22225.5 0.15 = 148170 kg/hr
H2O in stream 16 = 0.85 * 148170 = 125944.5 kg/hr
H2O in stream 14 = 125944.5 – 35000 = 90944.5 kg/hr
Mass In : 22450 + 35000 + 480 + 90944.5 = 148874.5
Mass Out : 224.5 + 480 + 22225.5 + 125944.5 = 148874.5 kg/hr

- **Energy Balance :**

a) Around Reactor :

Operating Conditions : T = 75-80℃, P = 1 atm, T_{ref} = 25℃
Heat In = Heat Out

$\sum mC_p \Delta T + \sum n\Delta H_{reaction} = Q + \text{Latent Heat}$; where
$\Delta H_{reaction} = \sum \Delta H^f_{products} - \sum \Delta H^f_{reactants}$

b) Around Evaporator :

Heat In = Heat Out, $T_{ref} = 72℃$
m CpH3PO4 dT + m CpH2O dT + Q = m CpH2O dT + m ʎH2O + m CpH3PO4 dT + m CpH2O dT

3. Identify Waste Streams:

- **Waste Streams (liquid, solid & gases) :**

Stream	Physical State	Component
Stream (10)	Solid (S)	Gypsum ($CaSO_4.2H_2O$)
	Liquid (L)	H_2SO_4
Stream (15)	Gas (G)	HF
Stream (16)	Liquid (L)	H_2SiF_6

- **Current Handling/Disposal Methods :**

a) Gypsum Disposal - Disposed in Land / Sea
b) H_2SO_4 - Neutralized before disposal
c) HF - Wet Scrubbing
d) H_2SiF_6 - Used in Water Fluoridation

4. Propose Optimization Strategies:

- **Process improvements to reduce waste generation / increase resource efficiency :**

a) Absorber Gas Recovery Enhancement:

  - Upgrade absorber design with multi-stage scrubbing and pH-controlled water/alkali solution.
  - Improve packing material and residence time for better absorption efficiency.

Metrics	Before	After
HF loss in gas (kg/hr)	~ 480	< 480
H_2SiF_6 recovery efficiency (%)	~ 70-75%	>95%
Revenue from H_2SiF_6	Medium	High

b) Reactor Cooling Optimization:

- Use **heat exchangers** to recover thermal energy from reactor cooling air and preheat incoming feed (Stream 2 or 3).

Parameter	Before	After
Cooling Energy Loss	High	Reduced
Energy Recovery	None	Significant
Overall Efficiency	Moderate	Improved

5. Conduct Life Cycle Assessment (LCA) and Product Carbon Footprint (PCF):

Goal & Scope Definition:

- **Objective:** Calculate GWP (kg CO_2-eq) and PCF (kg CO_2-eq/kg H_3PO_4).
- **Functional Unit:** 1 ton (1000 kg) of phosphoric acid produced.
- **System Boundary:** Cradle-to-gate (raw material extraction to product output).

Life Cycle Inventory (LCI)

Inputs	Stage	Outputs(Emissions/Products/Wastes)
- Phosphate rock ($Ca_3(PO_4)_2$, CaF_2, SiO_2) - Sulfur (for H_2SO_4 production)	Raw Material Extraction	- CO_2 from mining equipment - Particulate matter (dust)
- Sulfur → H_2SO_4 (via combustion + contact process) - Water	Material Processing	- SO_2, trace H_2SO_4 vapors - Heat and electricity use emissions
- Phosphate rock - H_2SO_4 - Dil. H_3PO_4 - H_2O	Reaction (Reactor)	- H_3PO_4 (product) - Gypsum (solid) - HF (gas) - Heat loss
- Air (cooling) - Absorbent water	Gas Absorption	H_2SiF_6 (captured) - Uncaptured HF (fugitive)
- Energy (filtration)	Filtration	- Recovered H_3PO_4 - Gypsum ($CaSO_4.2H_2O$) with traces of H_2SO_4
- Steam (energy input)	Evaporation / Concentration	- Concentrated H_3PO_4 (75%) - Water vapor (released or recycled)
- Process water - Recycled H_2SO_4 stream	Waste Handling / Recycling	- Treated effluents - Potential emissions (HF, H_2SiF_6) if not fully captured
- Electricity - Cooling water	Utilities & Energy	- CO_2 from grid electricity - Thermal losses

- Steam (boilers)		- Cooling water discharge

Life Cycle Impact Assessment (LCIA) & Baseline & Optimized Scenario

Impact Category	Description	Baseline Scenario	Optimized Scenario	Improvement
Global Warming Potential (GWP)	Total greenhouse gas emissions (CO_2-eq) from energy use, sulfur combustion, etc.	High (due to fossil-based energy use)	Medium (with energy recovery)	15–25%
Acidification Potential	Emissions of SO_2, NO_x, HF affecting soil and water acidity	High (SO_2, HF release)	Lower (HF capture, gas scrubbing)	40–60%
Eutrophication Potential	Nutrient-rich wastewater discharge causing algal blooms	Moderate (H_3PO_4, H_2SO_4 traces in effluent)	Low (better wastewater control)	30–50%
Photochemical Ozone Creation Potential (POCP)	VOCs, NO_x, HF reacting with sunlight to create smog	Low	Very Low	10–20%
Human Toxicity Potential	Emissions of HF, H_2SO_4 aerosols, and H_2SiF_6 impacting human health	High (if gases not controlled well)	Low (with absorber and scrubbing)	60–80%
Water Consumption	Total freshwater used in process cooling, dilution, scrubbing	High (especially cooling air water)	Medium (recycling of water streams)	30–40%

Product Carbon Footprint (PCF) (Optimized Scenario)

Stage	Carbon Intensity	Optimizations & Impacts
Phosphate Rock Mining	Medium	Same as baseline
Sulfuric Acid Production	Medium	Partial recycling of acid stream; lower virgin acid requirement
Reaction & Filtration	Medium	No change in chemistry, but better temperature control reduces loss
Gas Handling & Scrubbing	Low	High-efficiency absorbers with >95% H_2SiF_6 capture
Evaporation	Medium	Heat integration using reactor waste heat reduces steam consumption

Waste Handling	Low-to-Medium	Lower volume of waste, potential valorization of H_2SiF_6 as by-product
Electricity Use (Auxiliary)	Medium-Low	Process integration reduces pumping and reprocessing loads

6. Perform a Cost-Benefit Analysis:

Component	Baseline Scenario	Optimized Scenario	Cost (₹/year)	Benefit (₹/year)	Remarks
1. Absorber Gas Recovery	70–75% H_2SiF_6 recoveryHF loss: ~480 kg/hr	>95% H_2SiF_6 recoveryHF loss: <50 kg/hr	₹25–30 lakhs (CapEx)	₹60–70 lakhs	H_2SiF_6 market value ₹30–40/kg
2. HF Emission Control	Wet scrubbing (partial capture)	Advanced scrubbing (multi-stage)	Included above	₹5–10 lakhs	Reduced environmental fines, safer work conditions
3. Heat Recovery (Reactor Cooling)	No recoveryHeat lost in air cooling	heat exchangers for feed preheating	₹20 lakhs (CapEx)	₹30–40 lakhs	Saves steam/fuel for preheating feed
4. H_2SO_4 Recovery from Filter	1.5% acid loss (~247.5 kg/hr) with gypsum	Acid stream recovery (94% H_2SO_4)	₹5 lakhs (O&M)	₹15–20 lakhs	Reduces fresh acid demand and disposal
5. Evaporator Optimization	Direct steam evaporation	Heat-integrated evaporator system	₹15 lakhs (CapEx)	₹20–25 lakhs	Energy efficiency, lower evaporation cost
6. Gypsum Valorization	Land/sea disposal (₹500–₹1000/ton)	Potential use in cement/fertilizer industry	₹5 lakhs (logistics)	₹10–15 lakhs	Gypsum ~110700 kg/hr = ~950 T/day
7. Regulatory Compliance Benefit	Moderate risk of fines & penalties	Enhanced control of HF, H_2SiF_6, H_2SO_4 emissions	—	₹5–10 lakhs (avoided cost)	Non-monetary but important
8. Carbon Savings	Higher emissions → higher PCF	Lower PCF via optimization	—	₹5–10 lakhs (carbon credit potential)	0.1–0.2 tCO_2e per ton of acid saved

References :

PRODUCTION OF PHOSPHORIC ACID

Fluorine recovery in the fertilizer industry - a review. - Fluoride Action Network

Economic Analysis of Phosphoric Acid Extraction