Phosphoric Acid

-Wet process

- Furnace process

*** Blast furnace (up to 1938)**

*** Electric furnace (produce elemental P)**

- 40 Million tons of P_2O_5 after 2000 (projected)
- Use of H_3PO_4: DAP, MAP from 63% acid
- Phosphoric acid process can be classified according to the use of acid to decompose phosphatic rock : H_2SO_4, HNO_3 (Nitro phosphates), HCl.

Wet-Process Phosphoric Acid

Flourapatite

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 10nH_2O \rightarrow 10CaSO_4 \bullet nH_2O + 6H_3PO_4 + 2HF$$

where n = 0, 1/2, or 2, depending on the hydrate form in which the calcium sulfate crystallizes.

- Commercial processes:

Anhydrite	–	$CaSO_4$
Hemihydrate	–	$CaSO_4 \bullet \frac{1}{2}H_2O$
Dihydrate	–	$CaSO_4 \bullet 2H_2O$

Raw material

Table 11.14. Typical Analysis of Commercial Phosphate Rocks

Constituent	Range of Content, %	Average Content, %
P_2O_5	29-38	33
CaO	46-54	51.02
SiO_2	0.2-8.7	2.0
$Al_2O_3 + Fe_2O_3$	0.4-3.4	1.4
MgO	0.1-0.8	0.2
Na_2O	0.1-0.8	0.5
CO_2	0.2-7.5	4.5
F	2.2-4.0	3.7
Cl	0.0-0.5	<0.02
SO_3	0.0-2.9	1.0
$CaO:P_2O_5$ ratio	1.35-1.70	1.5

- Hydrate formation is controlled by temperature and acid concentration

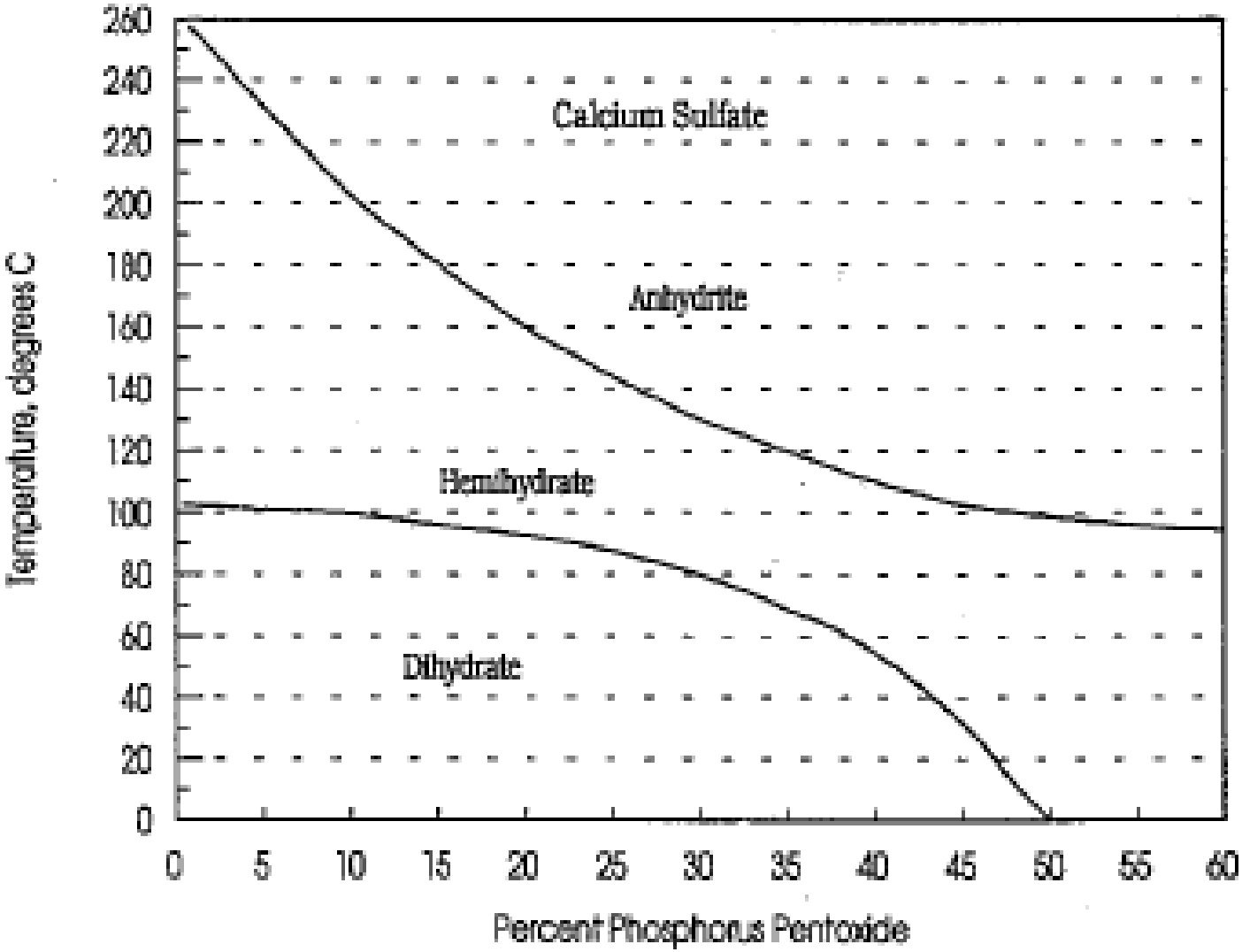


Figure 11.12. Dependence of Calcium Sulfate Crystallization on Temperature and P_2O_5 Concentration.

Table 11.13. Types of Commercial Processes

Crystal form(s)	Separation Steps[a]	Concentration of Acid, % P_2O_5	Reactor Temperature, °C	Recrystallizer Temperature, °C
Dihydrate	1	26-32	70-85	–
Hemihydrate	1	40-50	85-100	–
Hemihydrate-dihydrate	1	26-30	90-100	50-60
Hemihydrate-dihydrate	2	40-50	90-100	50-65
Dihydrate-hemihydrate	2	35-38	65-70	90-100

a. Filtration or centrifuging steps.

Dihydrate process

1. Selecting phosphate rock.
2. Selecting source of sulfuric acid.
3. Receiving and storing raw materials.
4. Grinding and otherwise preparing the rock.
5. Reacting the phosphate rock and sulfuric acid.
6. Filtering to separate phosphoric acid from gypsum.
7. Concentrating and clarifying the phosphoric acid.
8. Sludge treatment.

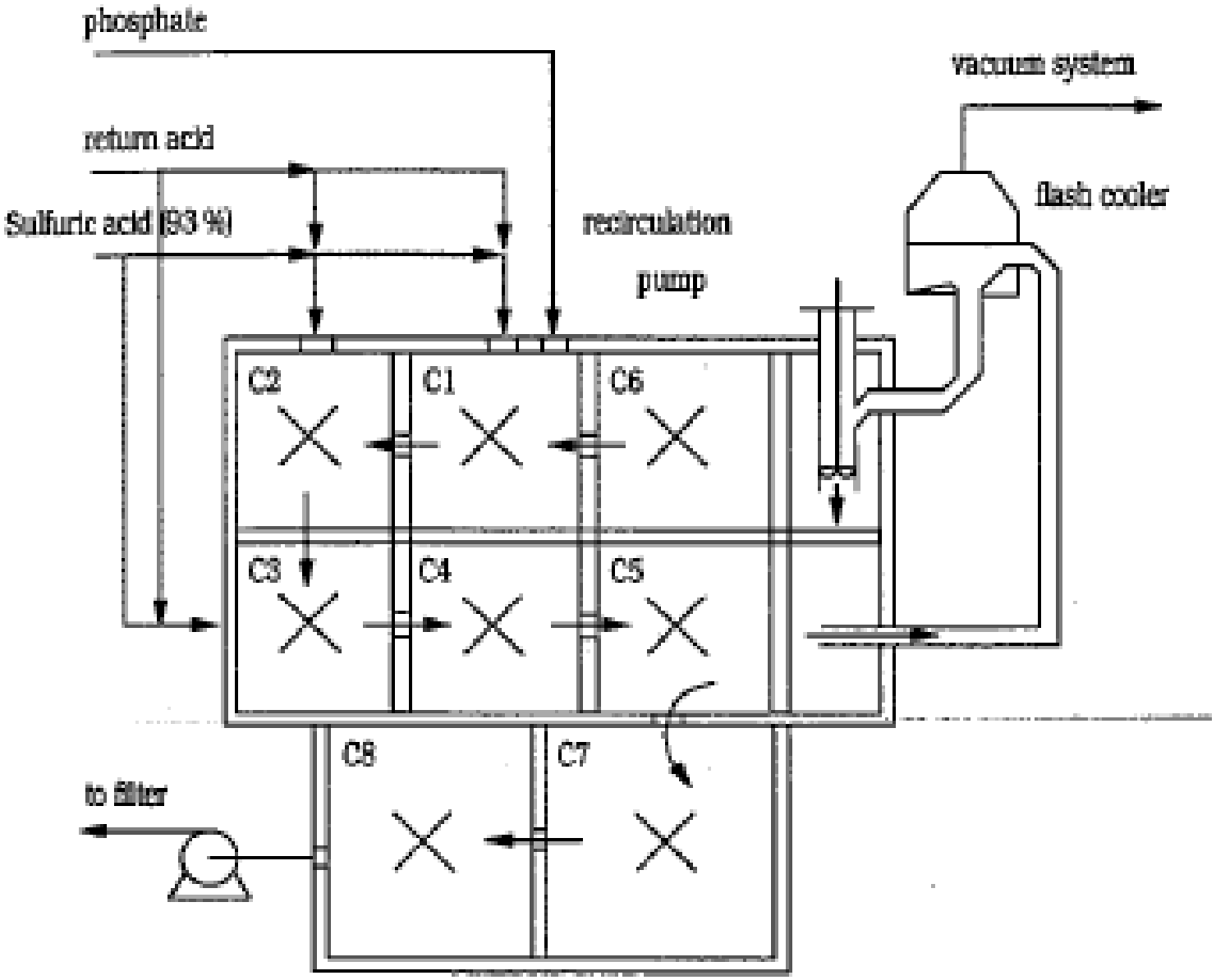


Figure 11.13. Reaction Section in the Prayon Mark IV Process.

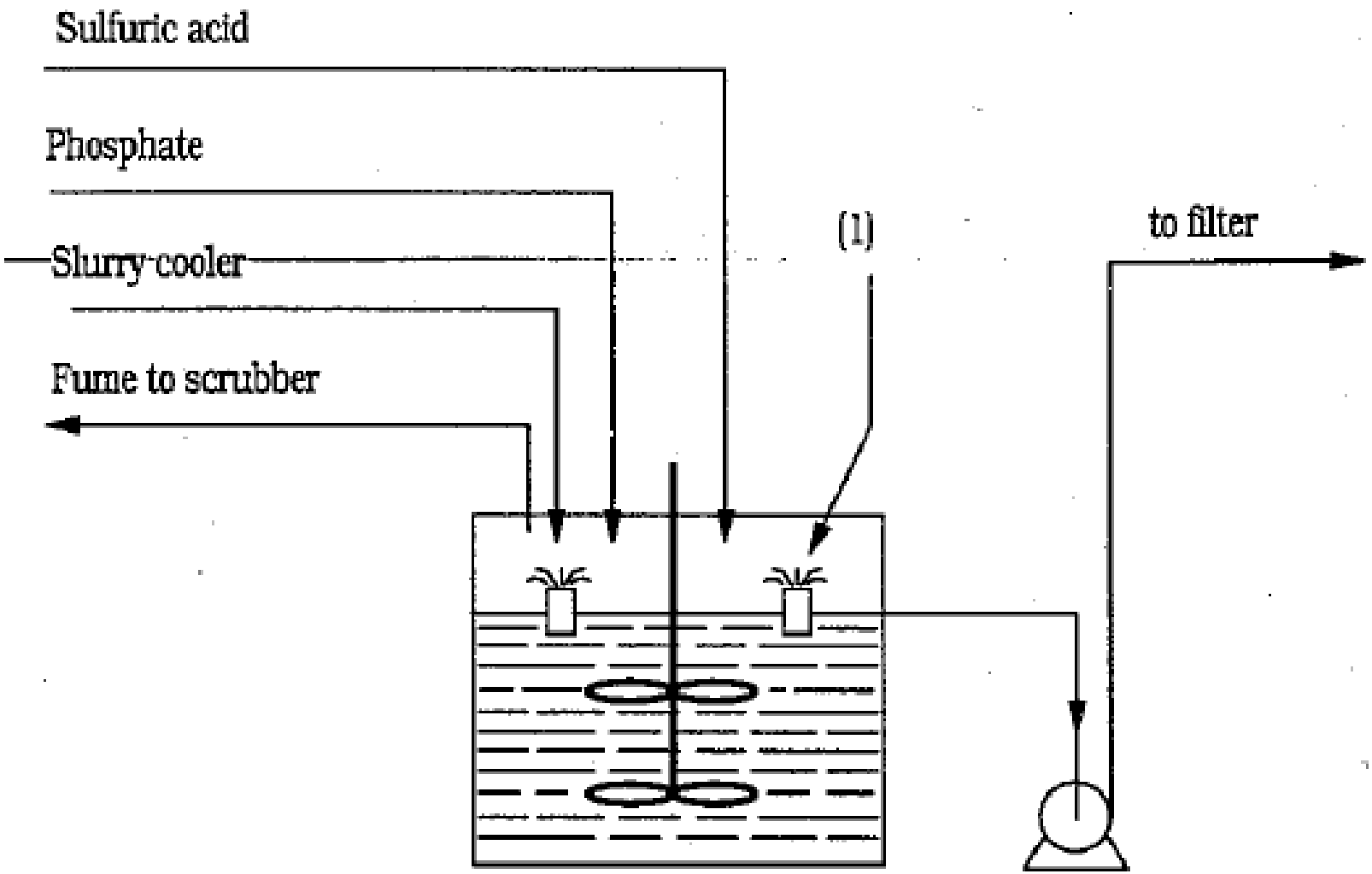


Figure 11.14. Rhone Poulenc Phosphoric Acid Reaction System.

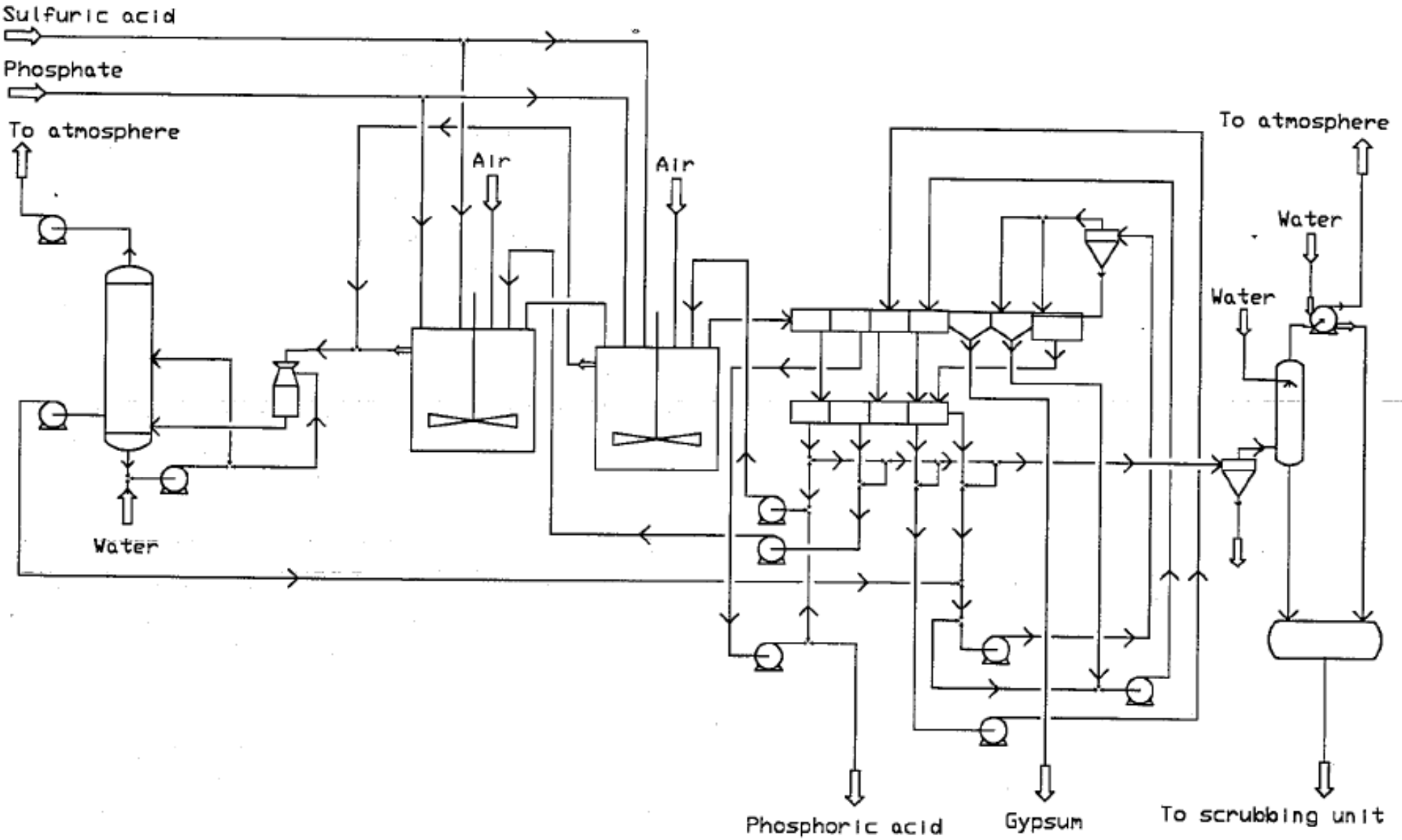
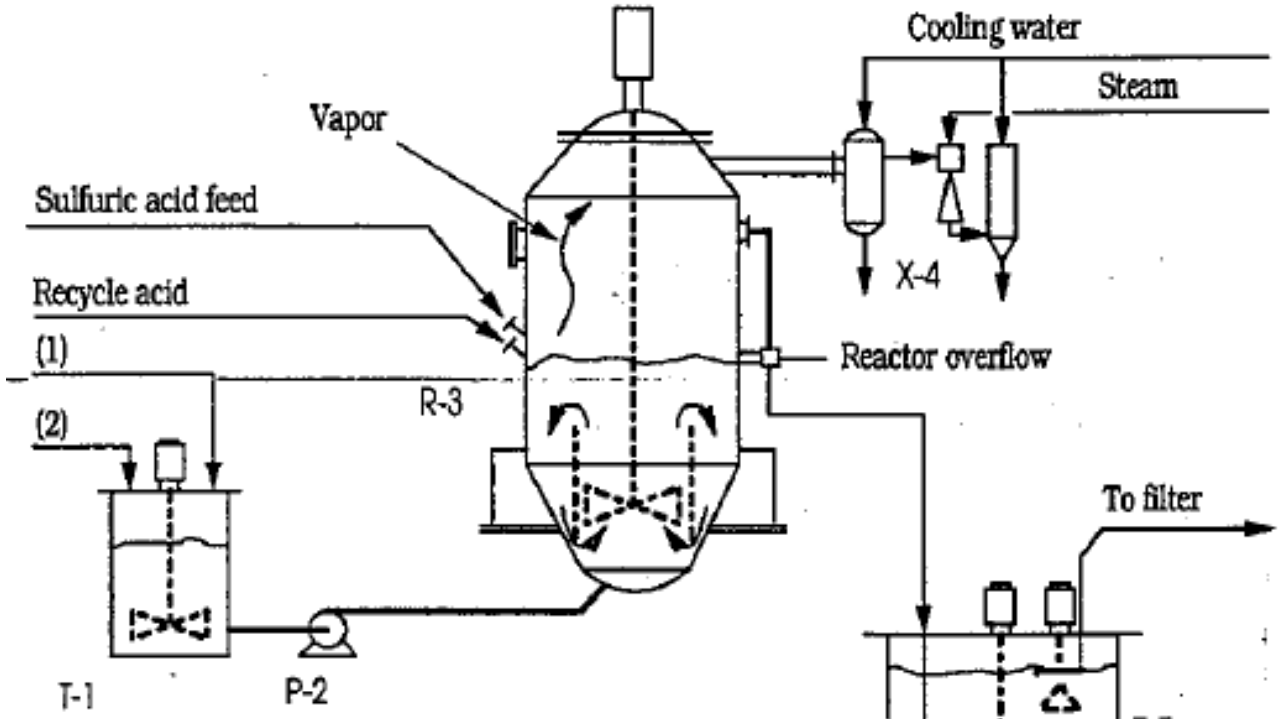


Figure 11.15. The Rhone-Poulenc Speichim DIPLO Phosphoric Acid Process.



Legend:

T-1 Rock slurry premix tank

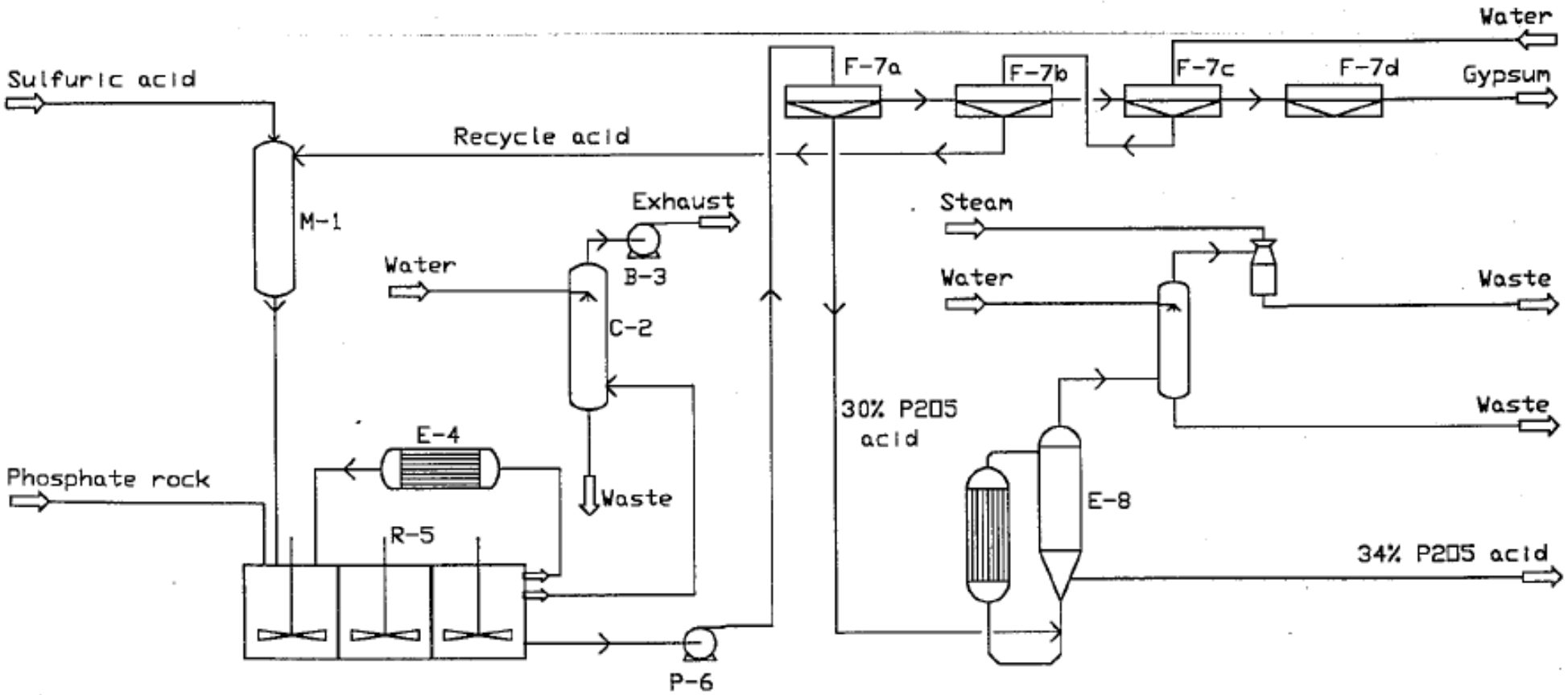
P-2 Pump

R-3 Raytheon isothermal reactor

X-4 Vacuum system

T-5 Filter feed tank

Figure 11.18. The Raytheon Isothermal Reactor.



Legend:
M-1 Mixer
C-2 Scrubber
B-3 Exhaust blower
E-4 Vacuum cooler
R-5 Reactors
P-6 Pump
F-7a - F-7d Pan filter
E-8 Vacuum evaporator

Figure 11.21. Typical Wet-Process Phosphoric Acid Plant.

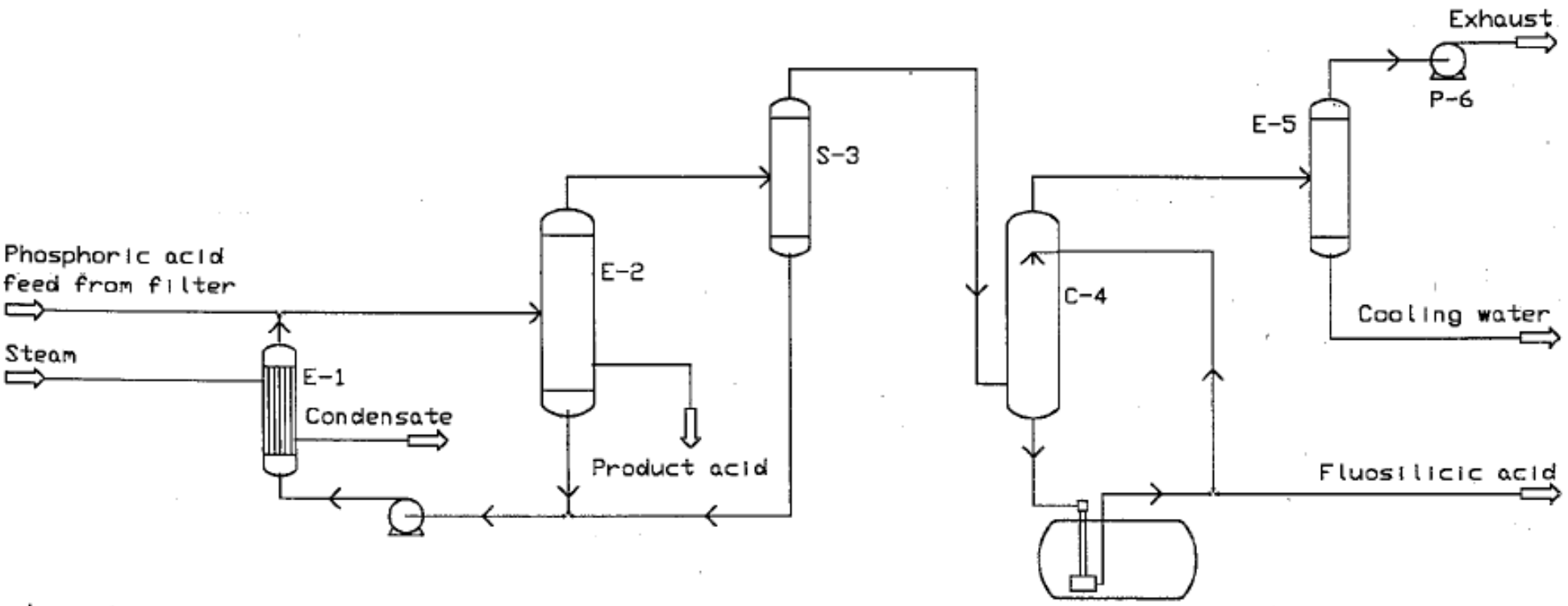


Figure 11.22. Typical Phosphoric Acid Concentration Unit.

Hemi-hydrate process

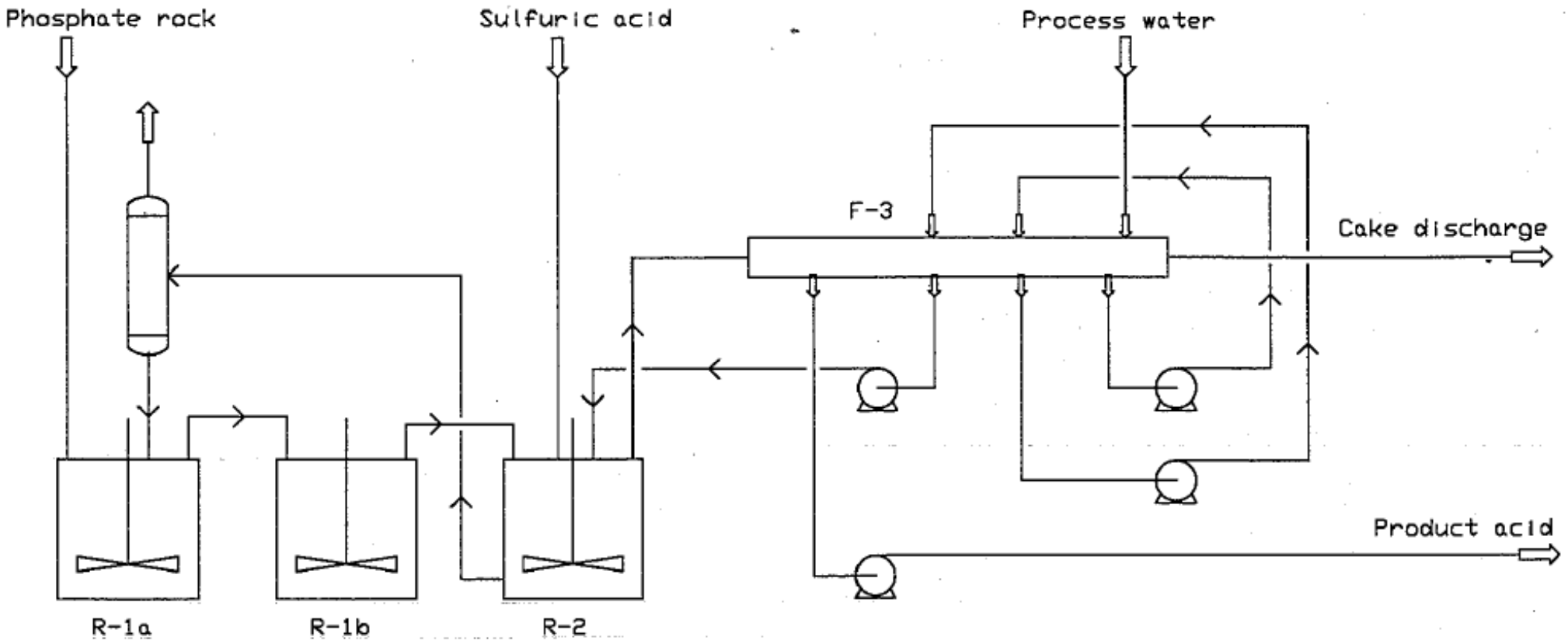


Figure 11.23. The Hydro HH Process.

Hemi-Di-hydrate process

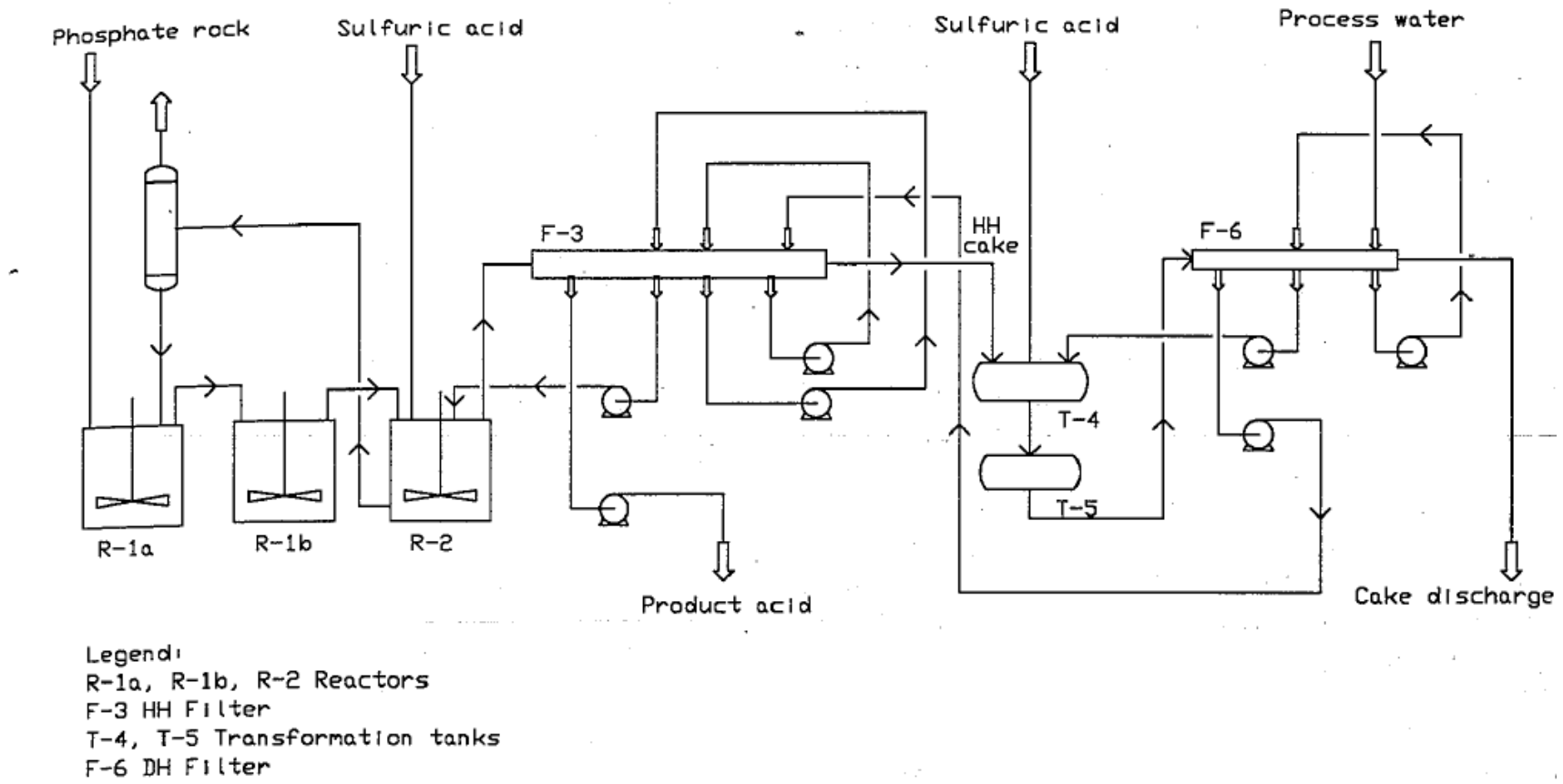


Figure 11.24. Nissan "C" Hemihydrate-Dihydrate Process.

Process/Features	Dihydrate (DH)	Hemihydrate (HH)	Hemidihydrate (HDH)
P_2O_5 efficiency, %	96.5	93.0	98.5
Phosphate rock	All grade sedimentary and igneous	Selected, coarser grinding acceptable	Igneous not suitable, coarser grinding acceptable
Rock feed	Dry or wet	Only dry	Dry or moist
Reactor system	Multi-compartment with separate sections for attack and digestion	As for DH with high and low temperature attack zones	Two-reactor system: and 1. as for HH 2. for recrystallization HH to DH
Unit capacity, tpd P_2O_5	Up to 1,800	Up to 1,300	Up to 1,300
Filter acid strength, % P_2O_5	29	42	45
Quality: acid and phosphogypsum	Standard	Acid of high purity	Gypsum of high purity

Super phosphoric acid

- Phosphoric acid when concentrated above 54% P_2O_5 forms super phosphoric acid (SPA).
- Advantages:

$$2H_3PO_4 + \text{Heat} \rightarrow H_4P_2O_7 + H_2O\ (g)$$

$$H_3PO_4 + H_4P_2O_7 + \text{Heat} \rightarrow H_5P_3O_{10} + H_2O\ (g)$$

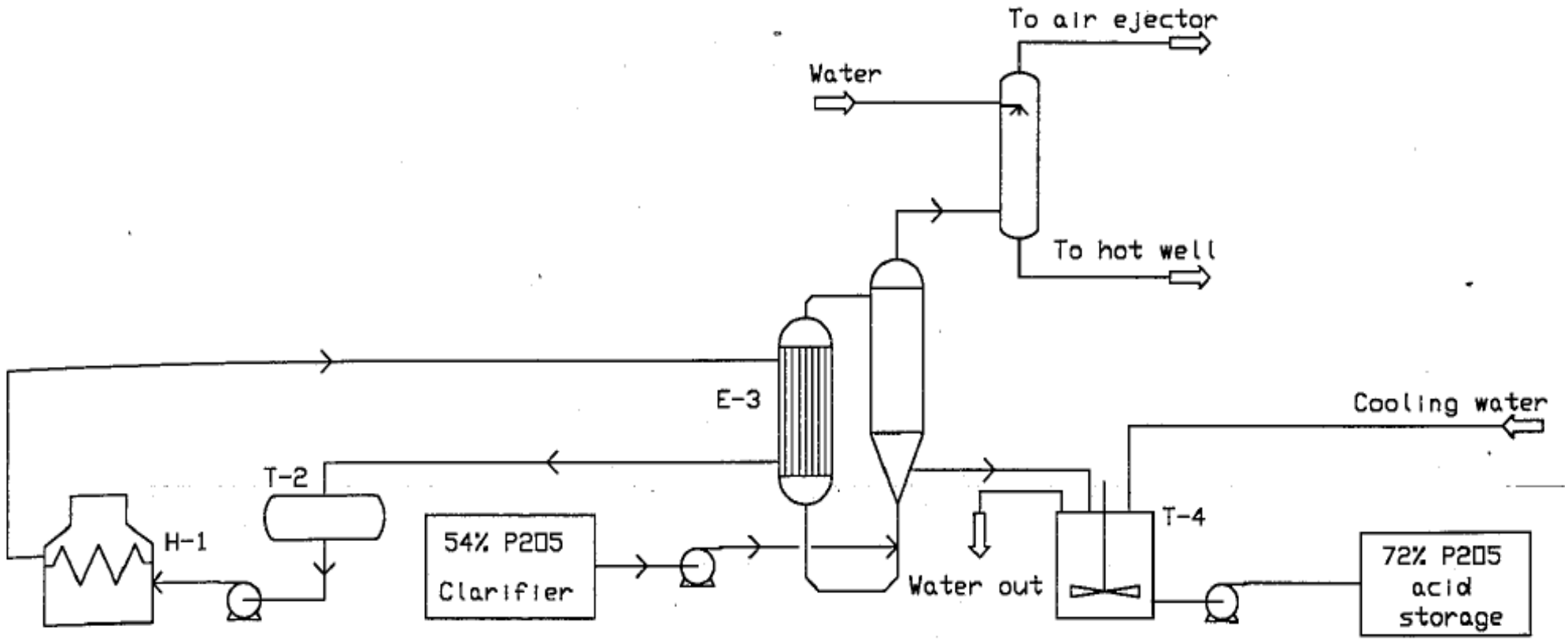
a. Savings in freight per unit of P_2O_5 compared with 54% acid.

b. Sludge is eliminated. The polyphosphoric acids sequester most common impurities; however, in some acids, titanium or magnesium pyrophosphates may precipitate.

c. Superphosphoric acid is much less corrosive than acid of lower concentrations.

d. Superphosphoric acid is suitable for production of clear liquid fertilizers (ammonium polyphosphate solutions) because the polyphosphate sequesters impurities that otherwise would precipitate upon ammoniation.

e. Superphosphoric acid is suitable for production of clear liquid fertilizers with micronutrients because of the ability to sequester metal ions.



Legend:
H-1 Dowtherm heater or steam boiler
T-2 Surge tank
E-3 F.c. evaporator
T-4 Cooling tank

Figure 11.25. Swenson System for Wet-Process Superphosphoric Acid.

PHOSPHATE FERTILIZERS

Triple super phosphate (TSP)

- Most highly concentrated straight phosphate fertilizer containing about 44-48% available P_2O_5 and 40-45% water soluble P_2O_5.
- Simplicity, low technical skill requirement and small investment (also for SSP)

TSP has three main disadvantages:

- The total nutrient content is lower than that of ammonium phosphates.
- Its acidic character may cause deterioration of some types of bags (hemp and paper).
- It is not well suited for blending with urea because of reactions that cause deterioration of physical condition.

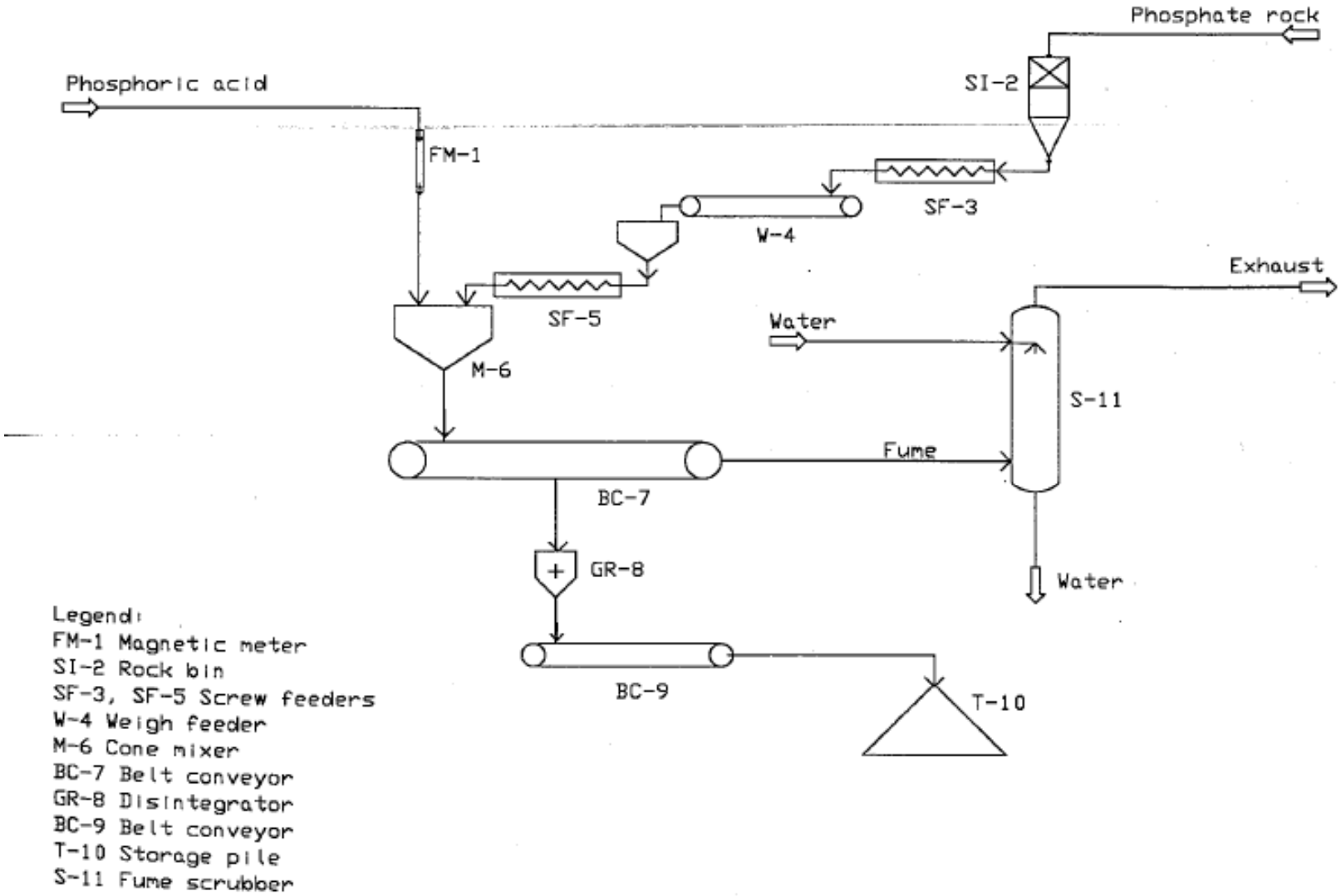
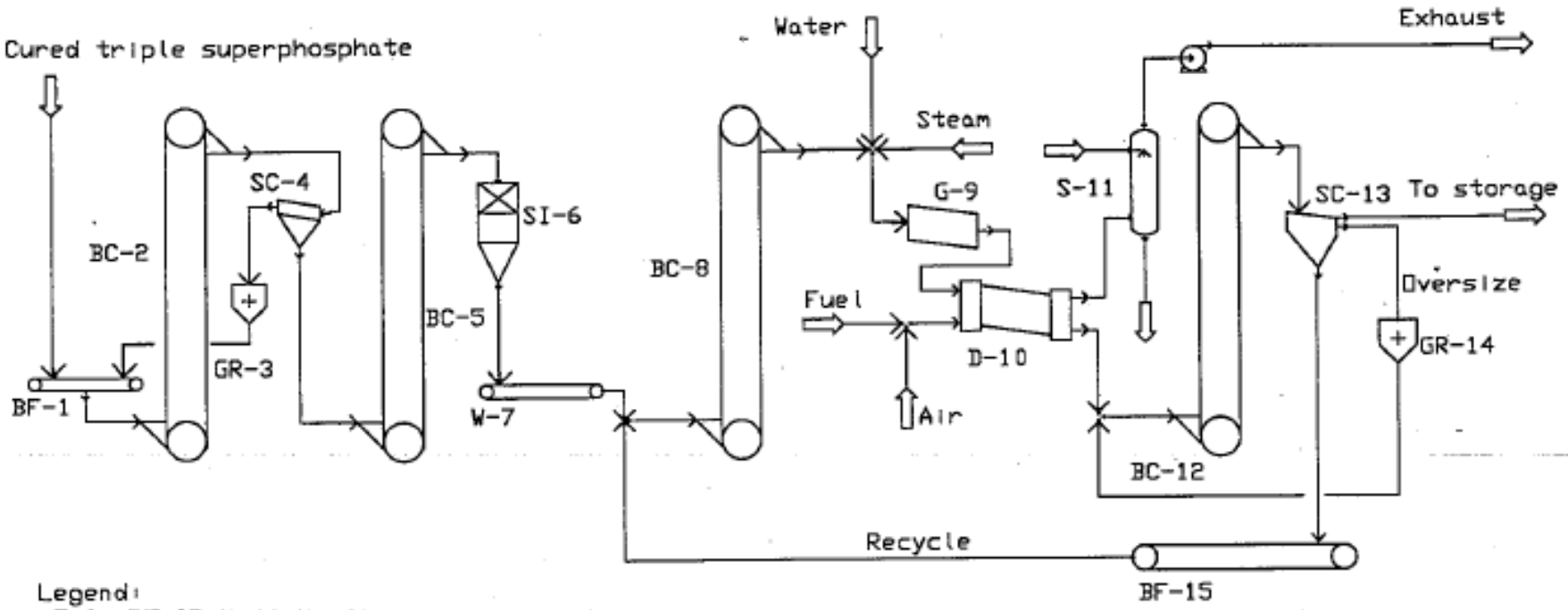


Figure 12.1. Manufacture of Run-of-Pile Triple Superphosphate.



Legend:
BF-1, BF-15 Belt feeders
BC-2, BC-5, BC-8, BC-12 Bucket elevators
GR-3, GR-14 Crushers
SC-4, SC-13 Screens
SI-6 Surge hopper
W-7 Weigh feeder
G-9 Granulator
D-10 Dryer
S-11 Fume scrubber

Figure 12.2. Granulation of Cured Run-of-Pile Triple Superphosphate.

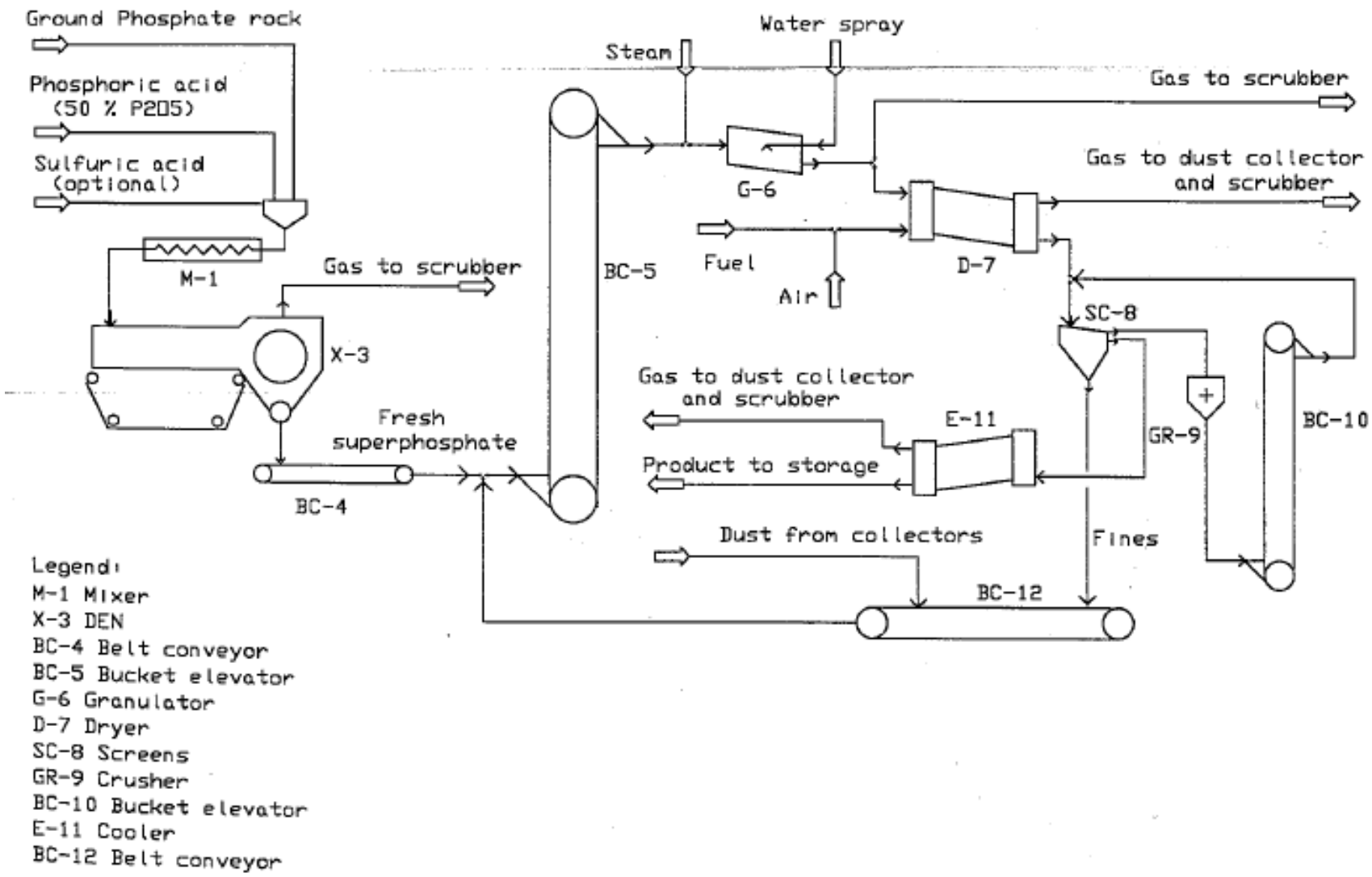


Figure 12.3. Ex-Den Granulation of TSP.