Phosphoric Acid

Table 6. The Linear Polyphosphoric Acids of General Formula H_{n+2}P_nO_{3n+1}^d

	Wt %						Number of dissociated hydrogen atoms	
Formula	P ₂ O ₅	Structure			Prefix	Strong	Weak	
H ₃ PO ₄	72.42 но-	о -Рон 				mono- (ortho)	1	2
H ₄ P ₂ O ₇	79.76 но-	O 	О -РОН 			di- (pyro)	2	2
H ₅ P ₃ O ₁₀	82.54 но-	OH OH	O O O O O O O O O O O O O O O O O O O	—он		tri- (tripoly)	3	2
H ₆ P ₄ O ₁₃	84.01 HO-	0 	O O -P-O-P- 		он	tetra-	4	2
$H_{n+2}P_nO_{3n+1}$	но-	ОН —Р—О—	OH OH OH	O P-O-	0 -РОН ОН	poly	n	2

Some Phosphoric acid uses

- Heavy duty alkaline cleaning products
- Laundry Detergents
- Emulsion polymerisation
- Textile auxiliaries
- Acid cleaners
- Metal working fluids
- Emulsifiers
- Wetting agents
- Dispersants
- Water based lubricants
- Intermediate for the synthesis of other anionic surfactants
- Coca cola

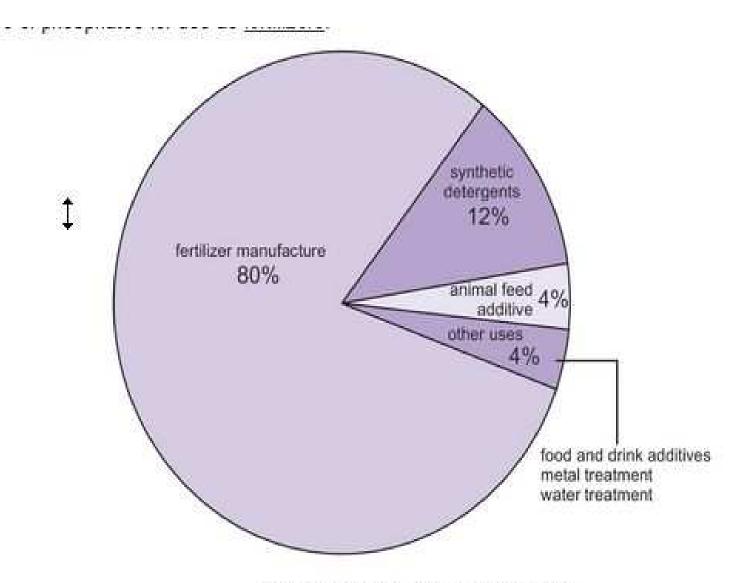
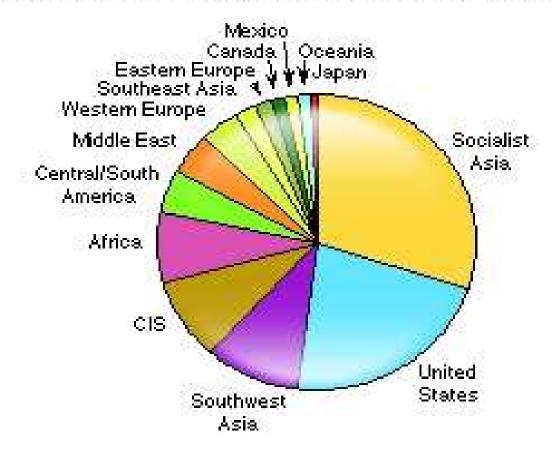
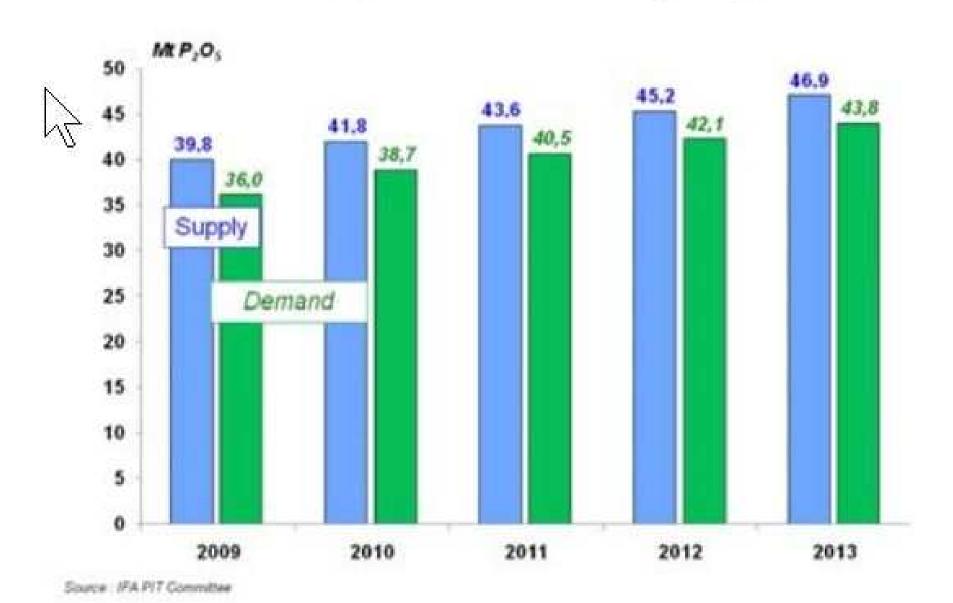


Figure 1 Uses of phosphoric acid.

World Consumption of Wet-Process Phosphoric Acid—2009



World Phosphoric Acid Supply/Demand



Production of Phosphoric acid

Chemical Reaction:

```
Ca (PO<sub>4</sub>)<sub>2</sub> + 3H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O -> 3CaSO<sub>4</sub> - 2H<sub>2</sub>O + 2H<sub>3</sub>PO<sub>4</sub>
```

Phos Rock + Sulphuric Acid + Water → Gypsum (hydrated) + Phosphoric Acid

aivided into three simplined steps.

1. The tricalcium phosphate constituent is converted to phosphoric acid and calcium sulfate.

$$Ca_3(FO_4)_2 + H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4$$
 (1)

2. The calcium fluoride constituent of the fluorapatite reacts with sulfuric acid to produce hydrogen fluoride and calcium sulfate.

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4 \tag{2}$$

3. The calcium carbonate constituent is converted to carbon dioxide and calcium sulfate.

$$CaCO2 + H2SO4 \rightarrow CO2 + CaSO4 + H2O$$
 (3)

The entire reaction between the major constituents and sulfuric acid is as follows:

$$Ca_{10}(PO_4)_6F_2\cdot CaCO_2 + 11H_2SO_4 \rightarrow 6H_3PO_4 + 11CaSO_4 + 2HF + H_2O + CO_2$$
 (4)

The hydrogen fluoride produced may react with silica to form silicon tetrafluoride, which then hydrolyzes to fluosilicic acid:

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \tag{5}$$

$$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2 \tag{6}$$

The CaSO, formed in the reactions can be in three stages of hydration: anhydrite, hemihydrate (sometimes called semihydrate), or di-

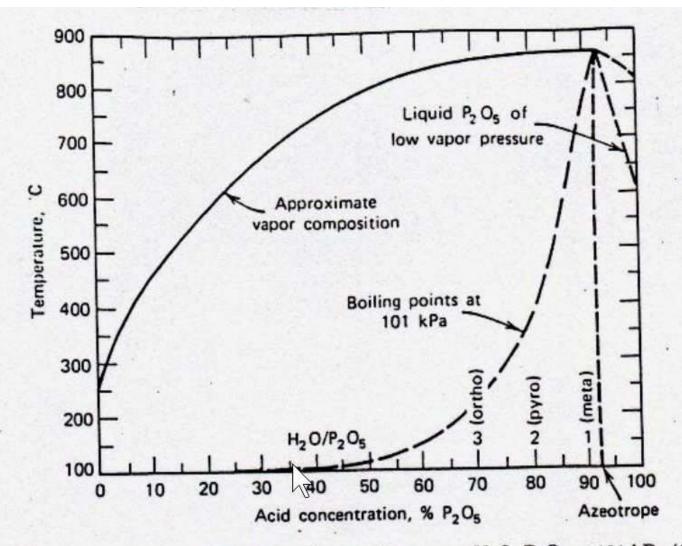
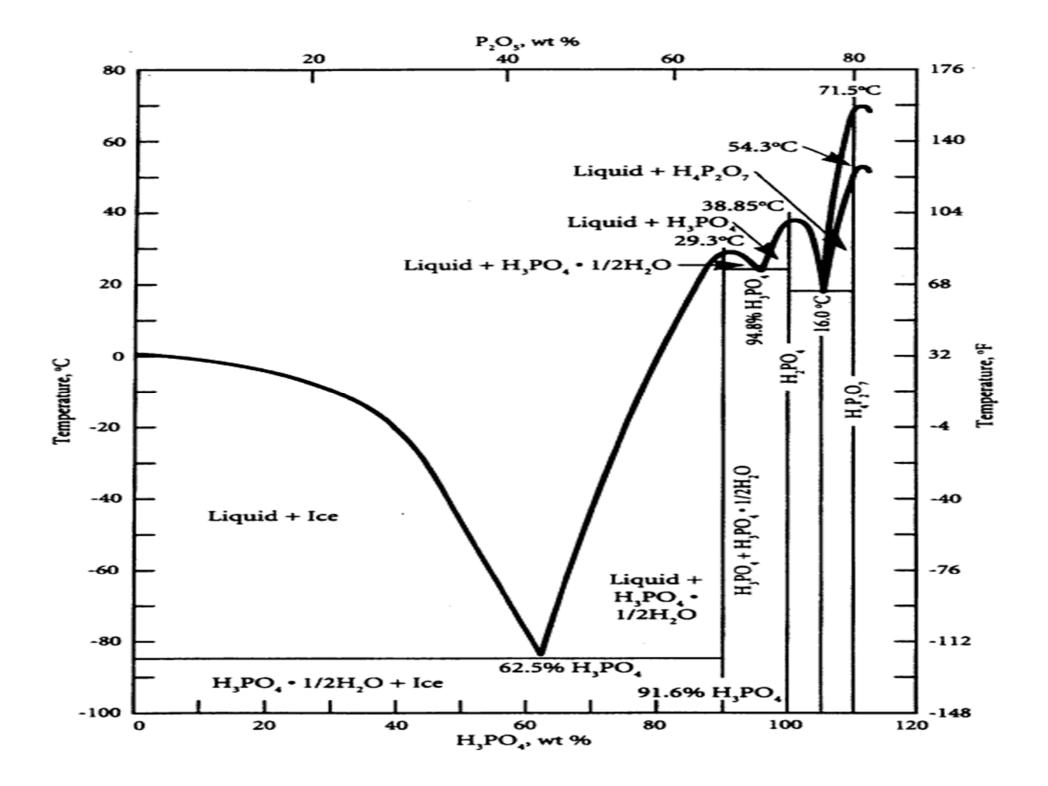
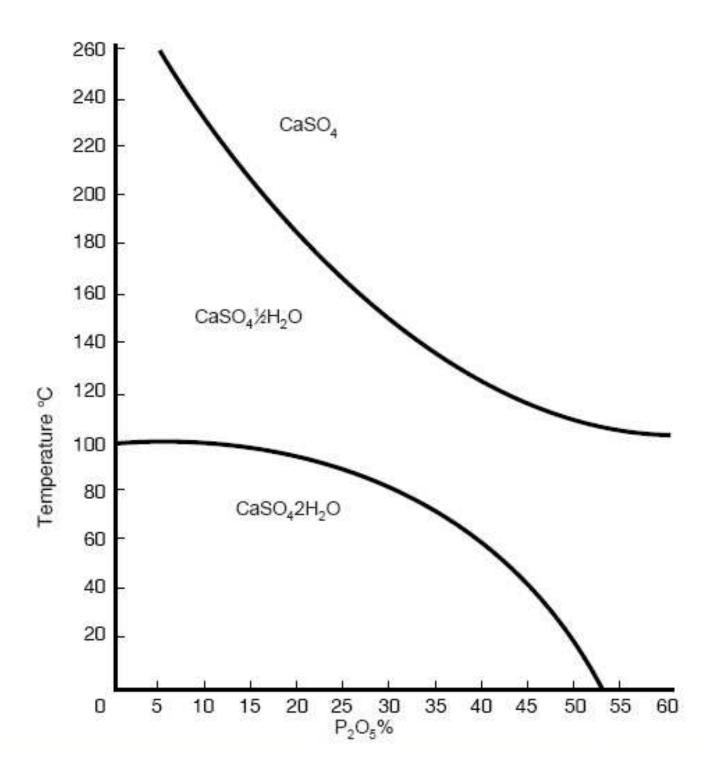


Figure 6. Temperature-composition diagram for system H₂O-P₂O₅ at 101 kPa (1 atm).

$$H_4P_2O_7 \rightleftharpoons H_3P_2O_7^- \rightleftharpoons H_2P_2O_7^{2-} \rightleftharpoons HP_2O_7^{3-} \rightleftharpoons P_2O_7^{4-}$$
 (11)
 $K_1 \simeq 10^{-1}$ $K_2 \simeq 1.5 \times 10^{-2}$ $K_3 \simeq 2.7 \times 10^{-7}$ $K_4 \simeq 2.4 \times 10^{-10}$



REACTION TEMPERATURE



'able 7. Comparison of Wet-Acid Processes and Products

		Operating temperature, °C		Acid con-	Acid impurity level vs	Suitability of calcium sulfate for	
ype of rocess	Principal developers	Extraction	Crystal conversion	centration, % P ₂ O ₅	dihydrate acid	wallboard or cement	Cyl
ihydrate	Prayon, Dorr and othersa	71-85	none	28-32		no	95
emihydrate	Fisons	91-99	none	45-50	ca same	no	91-94
nhydrite	Nordengren	102-238	none	40-50	lower	no no	91
ihydrate-	Central Glass of Japan Société					1,700	
hemihydrate	de Prayon Nissan, NKK Mitsubishi,	62–68	93–99	33-38	higher	yes	97
	Fisons,				depends		
	Singmaster			30-358	on process		
emihydrate-	Breyer/Heurty,				variation		
dihydrate	Dorr HYS	91-99	60-19	40-50d	can be lower	yes	96-98

Fig (5) Process Flow Diagram for Phosphoric Acid Manufacturing (Wet Process) Inputs Operations Outputs Grinding Dusts & Particulates Phosphate Rock Noise (work place) Washing Diluted Phosphoric Acid. Fluorides (HF, SiF4) and Reaction Strong Sulphuric Acid acid mist (to the scrubber) Acid fumes emissions Filtration Wastewaterrecycledto (Vacuum Pan reactor (rich in sulphuric Process Water filter) Wash water (recycled to Process Water Gypsum the reactor) Wash Fluoride emissions to air Wash water (recycled to Settling the reactor) Pond Fluoride emissions to air Gypsum Condensates Vacuum Evaporation Emissions (SiF4) ▼ Phosphoric Acid (54 %) Settling Solid wastes Extraction Solvent (n-butanol/isobutanol), ammonia and alkali Solid waste impurities Separation (metals, fluorine colloidal organic compounds) Back Extraction Water

Solvent Recovery

1

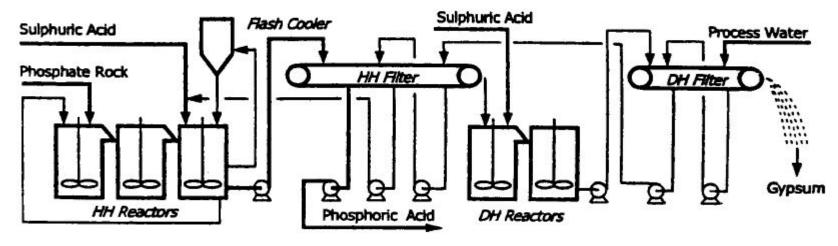


Fig. 23.12. Hydro fertilizer technology hemihydrate process.

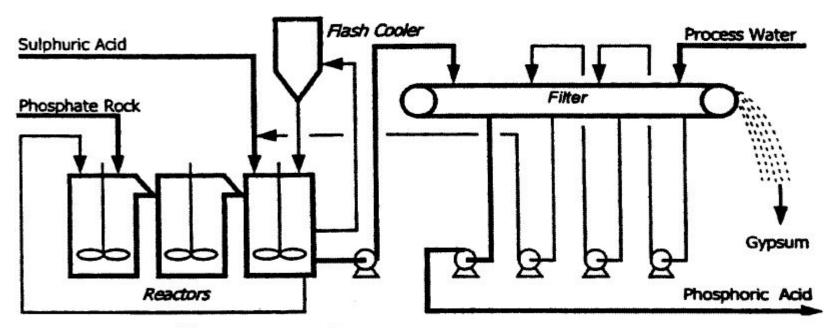


Fig. 23.13. Hydro fertilizer technology hemihydrate process.

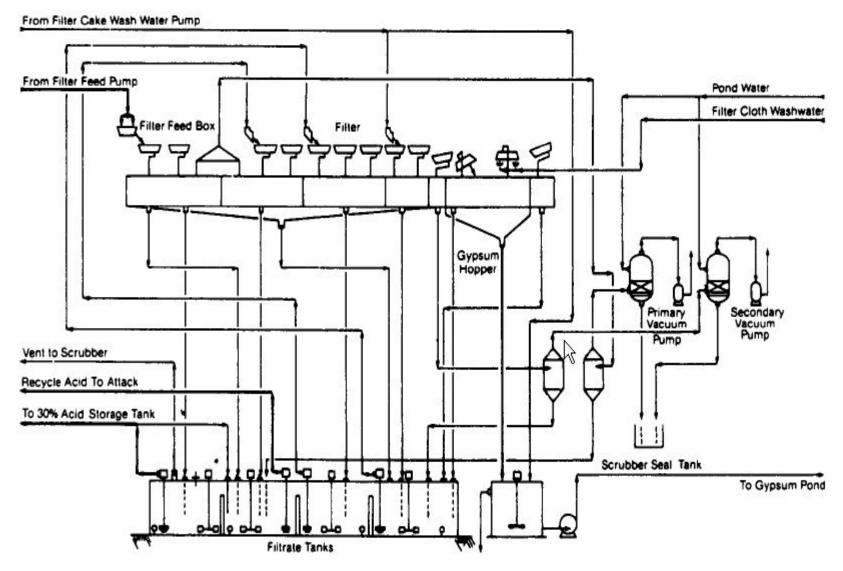


Fig. 23.14. Flow diagram of filtration section of a wet process phosphoric acid plant. (Prayon process, courtesy Davy Mckee Corp.)

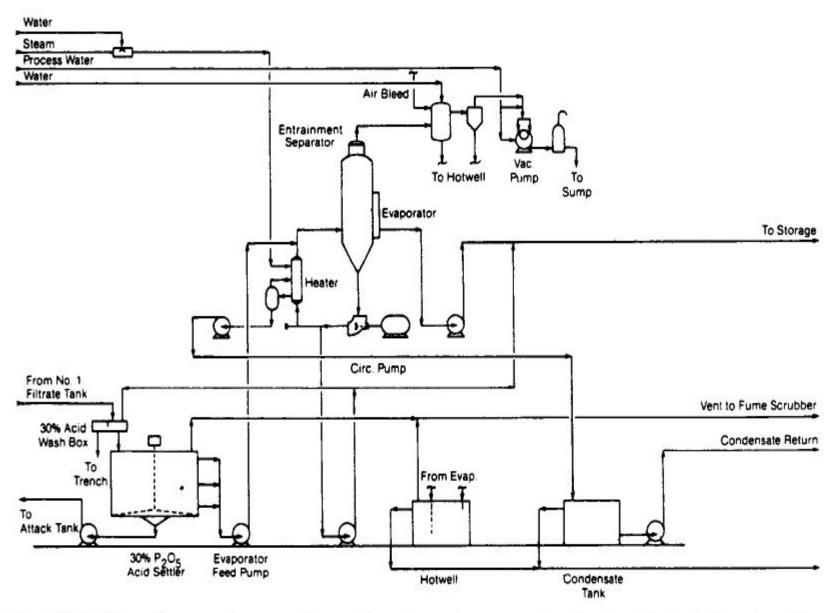


Fig. 23.15. Flow diagram of evaporation section of a wet process phosphoric acid plant. (Courtesy Davy Mckee Corp.)

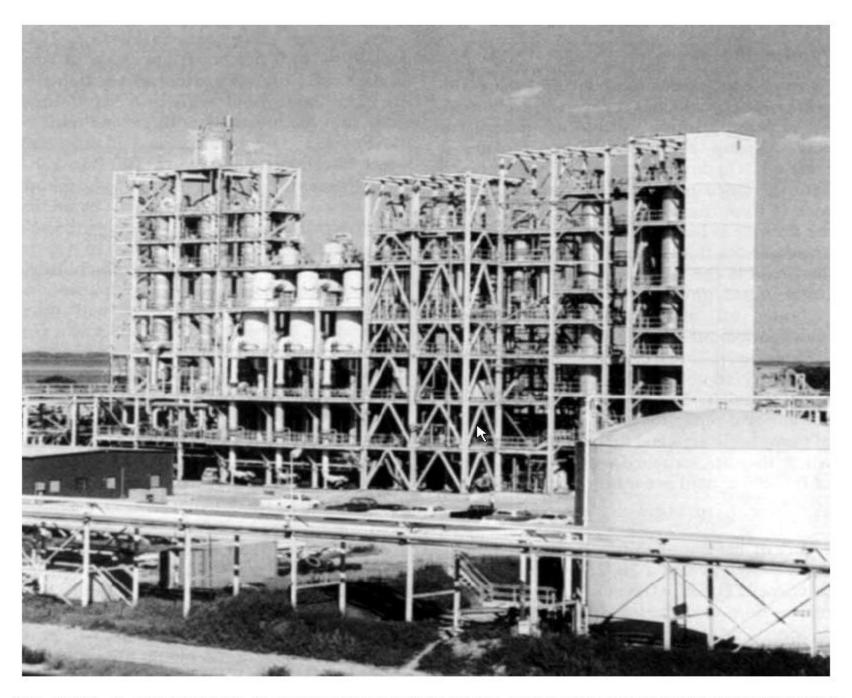


Fig. 23.16. Purified phosphoric acid plant for P.A. Partnership, Aurora, NC. (Courtesy P.A. Partnership and Jacobs Engineering.)

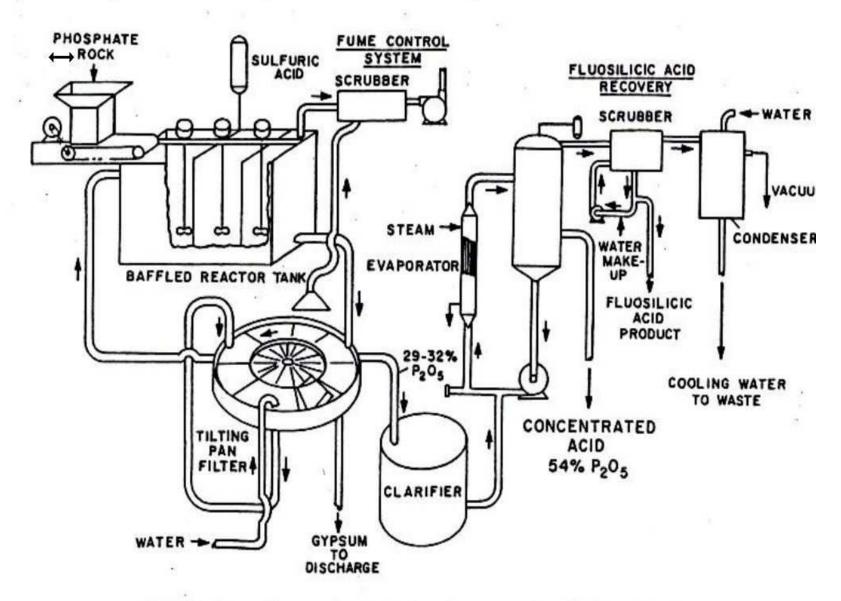


FIG. 3. Flow diagram for typical wet-process phosphoric acid plant.

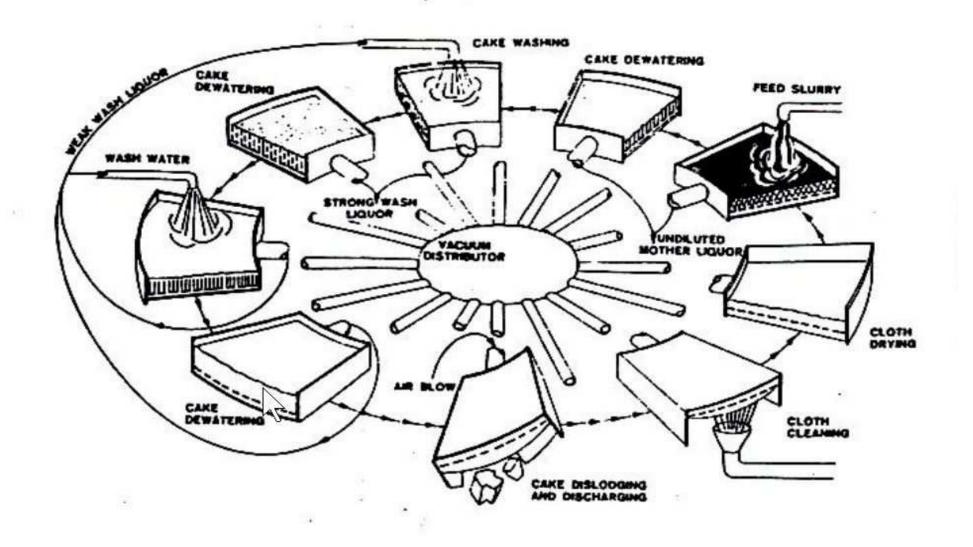
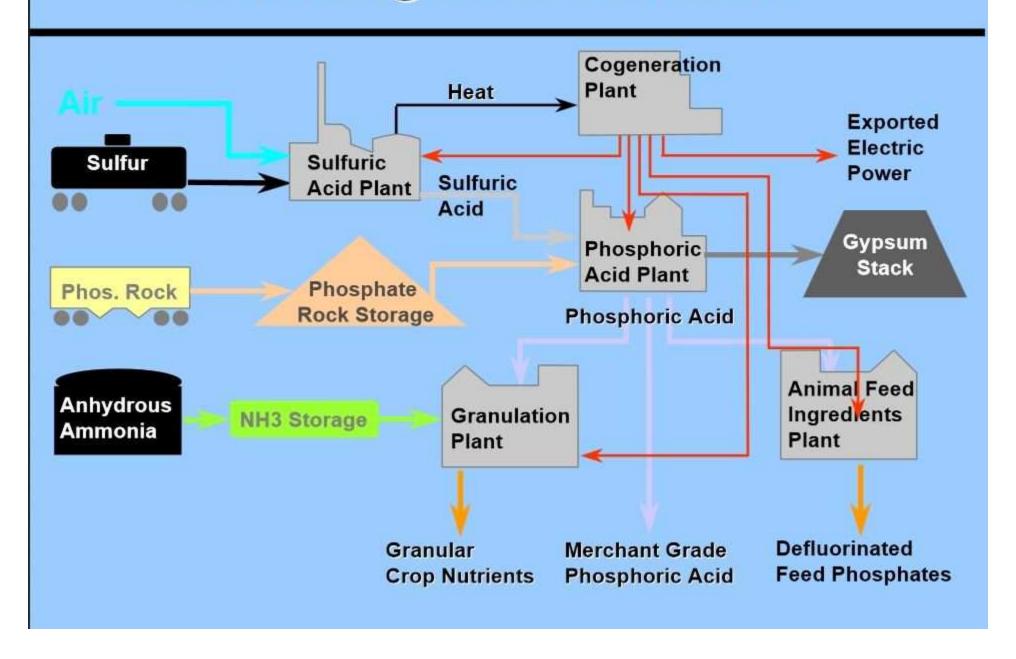


FIGURE 5. Operation of the Bird-Prayon Tilting-pan
Vacuum Filter

Processing Plant Flowsheet



Sulfuric acid process

Step 1 - Production of sulfur dioxide

$$S + O2 \rightarrow SO2 \Delta H = -300 kJ mol$$

Step 2 - Conversion to sulfur trioxide

SO2+1/2O2 →SO3 ∆H=-100 kJ mol

Step 3 - Absorption of SO3to form sulfuric acid

SO3+ H2O → H2SO4 △H= -200 kJ mol

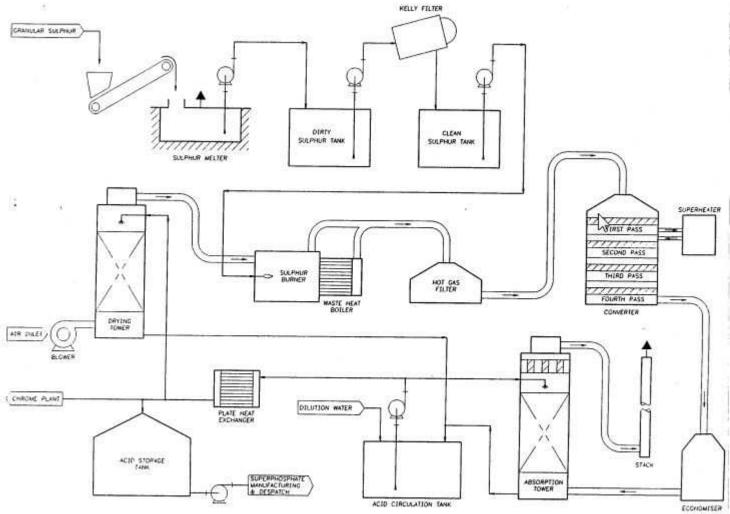


Figure 2 - Process flow diagram of the sulfuric acid plant

Superphosphates

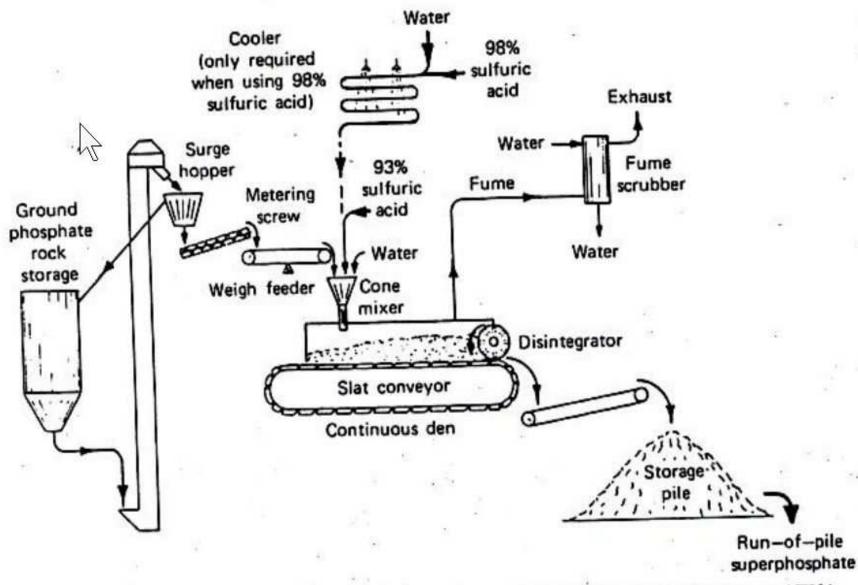


Figure 8 Continuous process for manufacture of normal superphosphate. Courtesy of TVA.

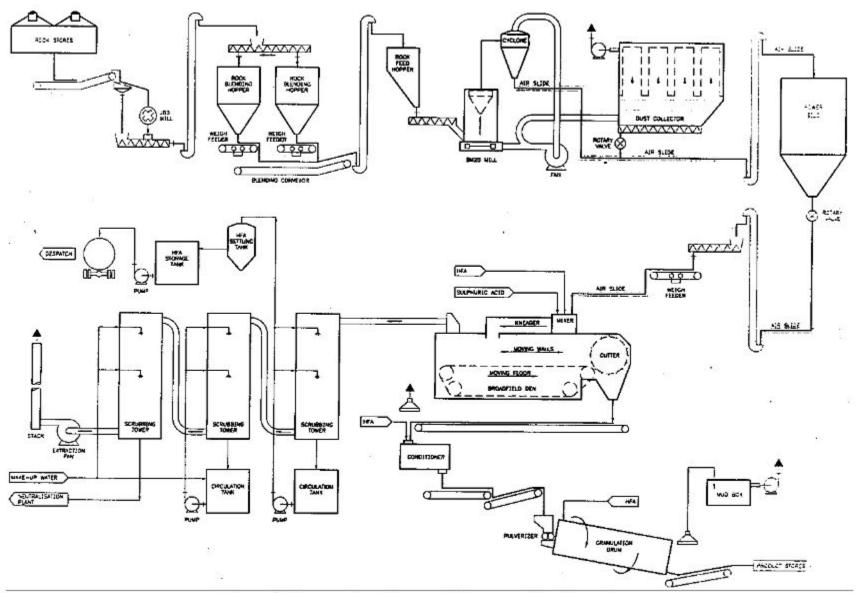
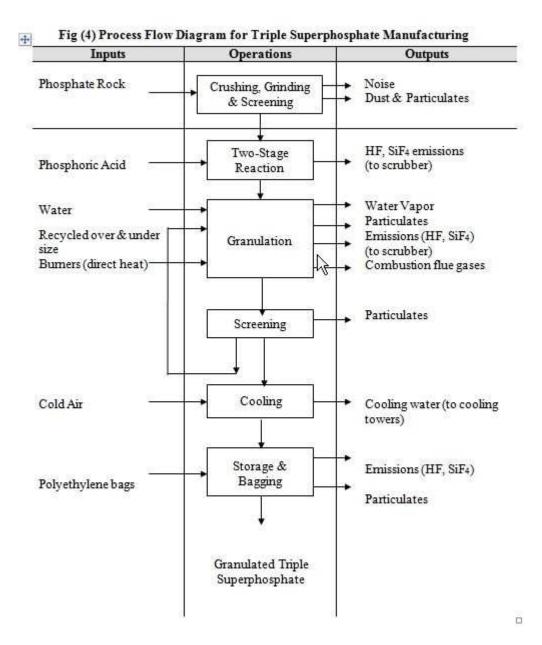


Figure 4 - Process flow diagram of the superphosphate plant



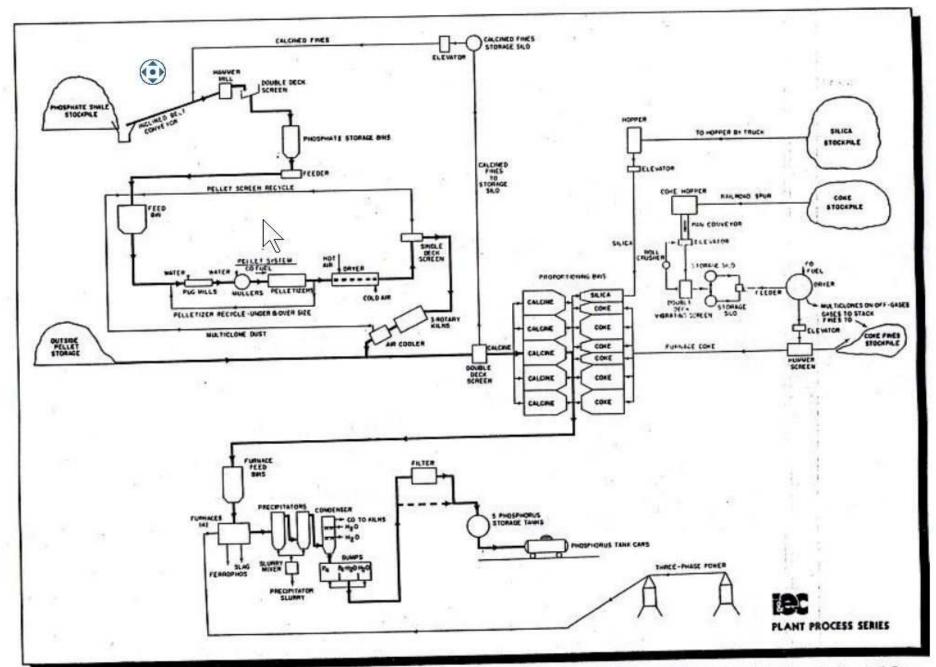
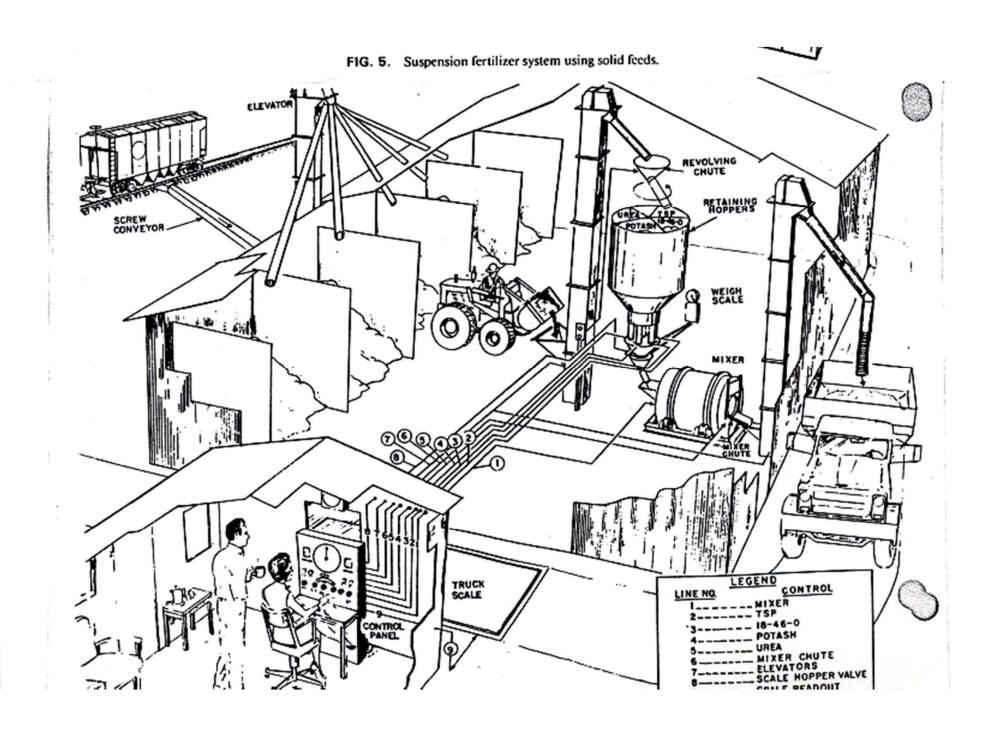


Figure 1. Flow sheet for production of elemental phosphorus by electric furnace by Westvaco Mineral Product Division, Food Machinery & Chemical Corp.



Phosphoric acid derivatives

- MCP Mono calcium phosphate
- DCP Di calcium phosphate
- MAP Mono ammonium phophate
- DAP- Di ammonium phosphate
- Sodium polyphosphates

Figure 2 – World Uranium Mined Production in 2006⁽³⁾

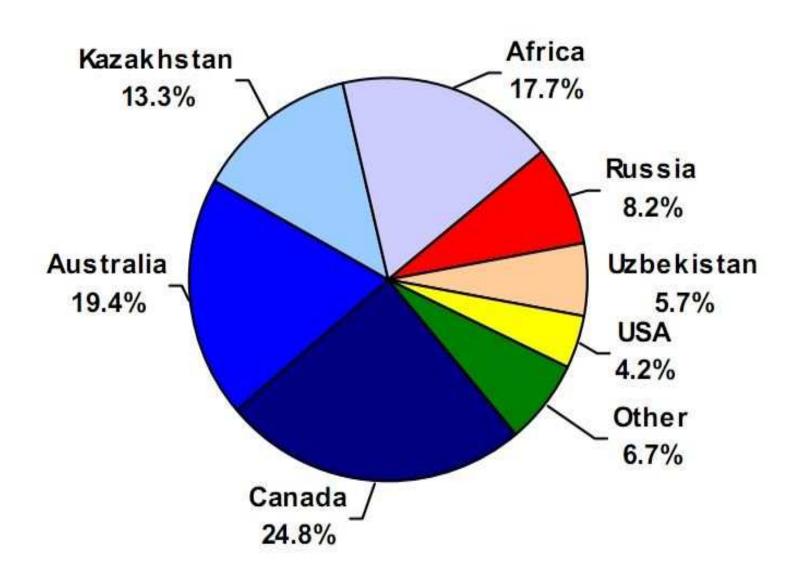
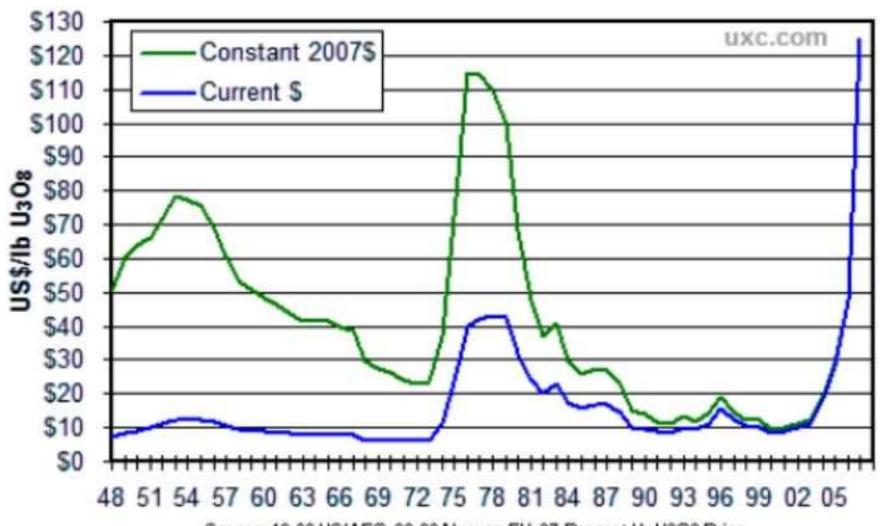


Figure 4 – History of U3O8 Spot Prices 1948-2007

Constant 2007 US\$ vs. Current US\$ Spot U308 Prices



Source: 48-68 US/AEC, 69-86 Nuexco EV, 87-Present Ux U308 Price

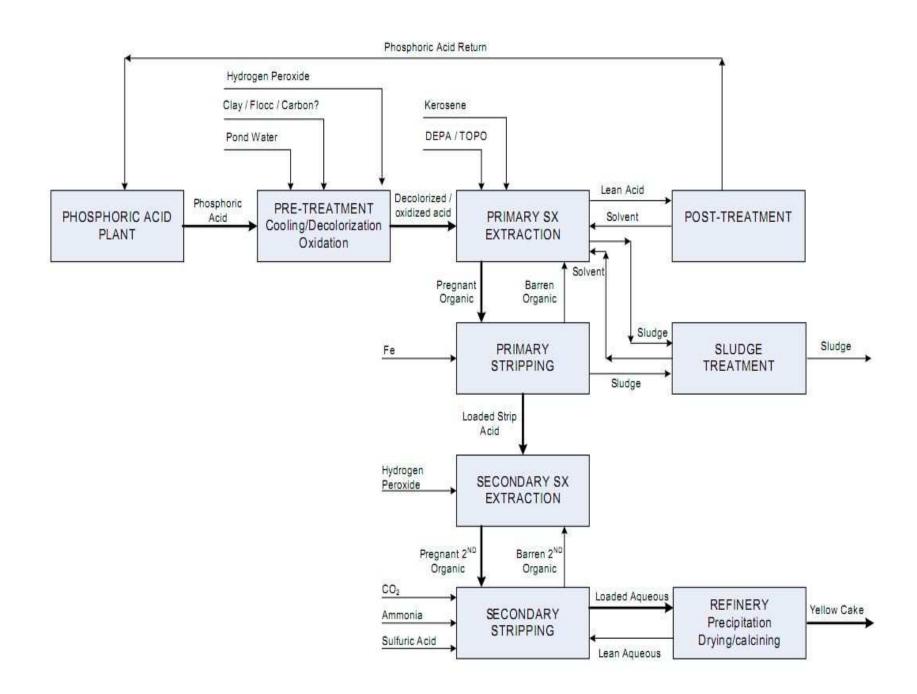
4 – Uranium Content of Selected World Phosphate Rock⁽⁴⁾

Country	Deposit	U	(ppn	1)
Algeria	Djebel Onk	25		
	Djebel Kouif	100	28	
Australia	Duchess	80	to	92
China	Undifferentiated	10	to	39
Egypt	Abu Tartur	40	to	120
Israel	Arad	150		
Jordan	Shidyia	46		
Morocco	Bucraa	70	to	80
	Khourigba	80	to	120
Peru	Sechura	47	to	80
Saudia Arabia		25	to	85
Senegal	Taiba	64	to	70
Syria	Khneifiss	75		
Tanzania	Minjingu	390		
Togo		77	to	110
Tunisia		12	to	88
USA	Central Florida	59		200

Table 5 – Past Uranium From Phosphoric Acid Projects

Company		Process	Capacity t/y P ₂ O ₅	Capacity lb/y U ₃ O ₈	Start	Close
Blockson	IL	Precipitation	100,000	80,000	1952	1961
IMC	FL	OPPA	100,000	80,000	1955	1961
IMC	FL	DEPA-TOPO	1,700,000	1,360,000	1980	1992
US Phosphoric Products (Gardinier)	FL	OPPA Revised	200,000 450,000	160,000 360,000	1955 1979	1961 1982
URC/WR Grace	FL	OPAP	330,000	264,000	1976	1980
WMC/Farmland	FL	DEPA-TOPO	450,000	360,000	1978	1981
Freeport/Agrico/IMC	LA	DEPA-TOPO	950,000	760,000	1978	1998
Freeport/Agrico/IMC	LA	DEPA-TOPO	540,000	432,000	1980	1998
CFI	FL	DEPA-TOPO	950,000	760,000	1980	1992
CFI	FL	DEPA-TOPO	600,000	480,000	1980	1985
ESI/Western Coop	Canada	OPAP DEPA-TOPO	110,000	88,000	1980	1981
Chemie Rupel	Belgium	DEPA-TOPO	140,000	112,000	1980	1998
China Phosphate	Taiwan	DEPA-TOPO	33,000	26,400	1981	1985
SOM	Iraq	DEPA-TOPO	90,000	72,000	1984	1991

Figure 3 – Typical SX Process Flow Diagram



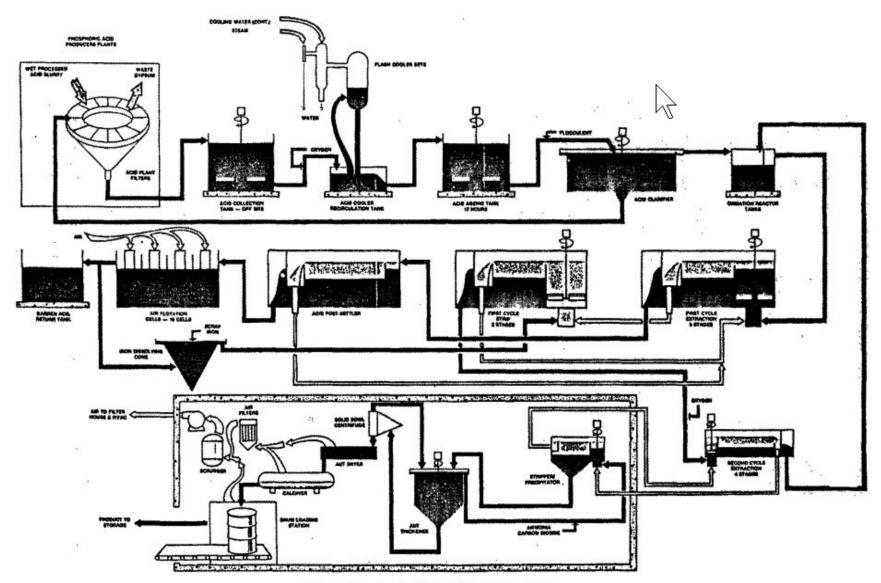


FIG. 1. Flow sheet of the DEHPA/TOPO process.