The Phosphorus Industry
History

- Phosphate containing materials used as early as 200 B.C by the Incas of Peru (guano and bird droppings)
- American Indians used fish and bones as source of fertilizer
- 1842 → patent treating bone ash with sulfuric acid
- Finely ground phosphate ores applied directly to soil not as effective as phosphates treated with sulfuric acid
# Table showing phosphate rock processing, products and by-products

<table>
<thead>
<tr>
<th>Process</th>
<th>Raw Materials and Reagents</th>
<th>Main Products and Derivatives</th>
<th>By-products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidulation</td>
<td>Phosphate rock, sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, ammonia, potassium chloride</td>
<td>Superphosphate, phosphoric acid (wet process), triple superphosphate, monoaammonium phosphate, diammonium phosphate, monopotassium phosphate</td>
<td>Fluorine compounds, vanadium, uranium (limited)</td>
</tr>
<tr>
<td>Electric-furnace reduction</td>
<td>Phosphate rock, siliceous flux, coke (for reduction), electrical energy, condensing water</td>
<td>Phosphorus, phosphoric acid, triple superphosphate, various Na, K, NH₄, Ca salts; phosphorus pentoxide and halides</td>
<td>Fluorine compounds, carbon monoxide, slag (for railroad ballast aggregate, fillers, etc.), ferrophosphorus, vanadium*</td>
</tr>
<tr>
<td>Calcium metaphosphate</td>
<td>Phosphate rock, phosphorus, air or oxygen, fuel</td>
<td>Calcium metaphosphate</td>
<td>Fluorine compounds</td>
</tr>
<tr>
<td>Calcination or defluorination</td>
<td>Phosphate rock, silica, water or steam, fuel</td>
<td>Defluorinated phosphate</td>
<td>Fluorine compounds</td>
</tr>
</tbody>
</table>

*Vanadium is present in appreciable quantities only in the western phosphates.
- Phosphorus rock called flourapatite or apatite (raw material)
- $\text{CaF}_2.3[\text{Ca}_3(\text{PO}_4)_2]$
Material Balances

- Based on the law of conservation of matter
- Mass (not volume, not moles) cannot be created or be destroyed
- Helps to identify what happens to all the chemicals in a process

\[
\text{INPUT} - \text{OUTPUT} = \text{ACCUMULATION}
\]

\[
I - O = A
\]

or

\[
I = O + A
\]
If there is no reaction in a system, then

\[
\text{mass in} = \text{mass out}
\]

I = O

But if there is a chemical reaction, then we must account for the formation of product chemicals and the use of feed chemicals

\[
\text{mass in} + \text{mass formed by reaction} = \text{mass out} + \text{mass consumed by the reaction}
\]
Mineral processing

Hydro-metallurgical extraction

Mining

Waste rocks

Phosphatic tailings

Apatite concentrate

Phosphogypsum process water

Phosphoric acid

Simplified flow diagram of phosphate mine and phosphoric acid plant

Taken from Mine Wastes, by Bernd G. Lottermoser, 2nd edition, Springer, pg 250
Fig. 16.2. Material balance flowsheet for Florida phosphate rock. Material flow in metric tons per year. (International Minerals and Chemical Corp.)
Energy Balance

- Total energy put in = total energy taken out

- Law of conservation of energy

- Take into account bond energies, energy required to heat reaction or produce steam

- Important for energy requirements of the plant → costing of plant process
Manufacture of Phosphoric Acid:
1. Wet Process

\[
\begin{align*}
\text{CaF}_2\cdot 3\text{Ca}_3(\text{PO}_4)_2 & + 10\text{H}_2\text{SO}_4 & + 20\text{H}_2\text{O} \\
\text{apatite} & & \text{sulfuric acid} \\
10\text{CaSO}_4\cdot 2\text{H}_2\text{O} & + 2\text{HF} & + 6\text{H}_3\text{PO}_4 \\
\text{gypsum} & & \text{phosphoric acid} \\
\text{Acid slurry that must be separated. How?}
\end{align*}
\]
Fig. 16.5. Wet-process phosphoric acid manufacture, using Bird-Prayon tilting-pan washing filters. The overall efficiency is 94 to 98 percent producing an acid of 30 to 32% P₂O₅ concentration.
\[
4\text{HF (g)} + \text{SiO}_2 (s) \rightarrow \text{SiF}_4 (g) + 4\text{H}_2\text{O (l)}
\]

from crude rock

- Is extremely toxic and corrosive therefore plant is lined with rubber or stainless steel

\[
\text{SiF}_4 (g) + 2\text{H}_2\text{O (l)} \rightarrow 2\text{H}_2\text{SiF}_6 + \text{SiO}_2
\]

Fluosilicic acid - used for fluoridation of drinking water and in preparation of fluosilicates
End product is usually black and contains a lot of impurities

HF \rightarrow \text{forms fluosilicic acid}

Suspended solids removed by settling

Dissolved impurities removed by solvent extraction:
- Use a partially miscible solvent into which the phosphoric acid is extracted leaving impurities behind.
- Back extract into water
Uranium recovery

- Uranium present in US phosphate rock
- Recovered by solvent extraction
- Energy value of the extracted uranium is 10 X greater than the amount of energy it takes to produce it → phosphate industry is also involved in producing energy
2. The Furnace or Thermal Process

- Raw materials are reacted in an electric furnace to produce elemental phosphorus

\[ \text{CaF}_2 \cdot 3[\text{Ca}_3(\text{PO}_4)_2] + 15\text{C} + 9\text{SiO}_2 \]

\[ \downarrow \]

\[ 9\text{CaSiO}_3 + \text{CaF}_2 + 6\text{P (g)} + 15\text{CO (g)} \]

- Slag for roads
- Used as fuel to prepare the furnace charge
\[ 4P + 5O_2 \rightarrow P_4O_{10} \quad \text{....oxidation} \]

\[ P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4 \]

high purity, used in the food industry, eg?

What is the most important requirement in this particular process?
Phosphoric Acid

- Produced as orthophosphoric acid, $H_3PO_4$
- Reactions with NaOH produces monosodium phosphate ($NaH_2PO_4$), disodium phosphate ($Na_2HPO_4$) and trisodium phosphate ($Na_3PO_4$)

Food Industry

$NaH_2PO_4 + NaHCO_3 \rightarrow CO_2 + Na_2HPO_4 + H_2O$
- **Detergent Industry**
- **Sodium tripolyphosphate (STPP) used in detergent powders**

![Chemical structure of sodium tripolyphosphate](image)

- Ionizes in solution to give a species that has 5 negative charges which reacts with Ca and Mg in hard water to soften it.

"Ionizes in solution to give a species that has 5 negative charges which reacts with Ca and Mg in hard water to soften it."
Fertilizers

- Supply nutrients to the soil for plant growth
- Plants take up $CO_2$ and $H_2O$ but in addition require 13 other essential elements

Macro-nutrients: N, P, K, Ca, Mg, S

Secondary nutrients: Cu, Zn, B, Mo, Cl, Fe, Mn

Trace elements or micro-nutrients
Fertilizers

- Calcium phosphates
- Ammonium phosphates
- Nitric phosphates
  - Normal superphosphates
  - Triple superphosphates
Fertilizers

Normal Superphosphates
- 30% monocalcium phosphate (MCP) $\text{CaH}_4(\text{PO}_4)_2$ or $\text{Ca(H}_2\text{PO}_4)_2$
- 10% dicalcium phosphate (DCP)
- 45% calcium sulfate
- 5% water
- 10% oxides of iron, silicon, aluminium and other impurities

$\text{CaF}_2.3\text{Ca}_3(\text{PO}_4)_2 + 7\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O} \rightarrow 3\text{CaH}_4(\text{PO}_4)_2\cdot\text{H}_2\text{O} + 2\text{HF}↑ + 7\text{CaSO}_4$

Triple superphosphates
Simplified flowchart for the manufacture of normal superphosphate

1. Phosphate rock prep
   - Ground phosphate rock storage

2. Mixing with acid
   - Water
   - 98% sulfuric acid
   - Fume scrubber
   - Exhaust
   - Slat conveyor
   - Disintegrator
   - Metering screw
   - Cone mixer
   - Weigh feeder

3. Curing & drying
   - Continuous den
   - Storage pile
   - 16-20% P₂O₅

4. Milling & bagging
   - Run-of-pile superphosphate

---

1. Phosphate rock prep
2. Mixing with acid
3. Curing & drying
4. Milling & bagging
Fertilizers

- Normal Superphosphates
- Triple superphosphates

- More concentrated fertilizer
- 45 to 46% of available \( P_2O_5 \) or 3 X the amount of regular superphosphate

\[
CaF_2 \cdot 3[Ca(PO_4)_2] + 14H_3PO_4 \rightarrow 10CaH_4(PO_4)_2 + 2HF\uparrow
\]
Fertilizers

- Calcium phosphates
- Ammonium phosphates
- Nitric phosphates

\[
\begin{align*}
\text{NH}_3 + \text{H}_3\text{PO}_4 & \rightarrow \text{NH}_4\text{H}_2\text{PO}_4 \\
2\text{NH}_3 + \text{H}_3\text{PO}_4 & \rightarrow (\text{NH}_4)_2\text{HPO}_4
\end{align*}
\]
Fertilizers

- Calcium phosphates
- Ammonium phosphates
- Nitric phosphates

\[
\text{CaF}_2 \cdot 3\text{[Ca(PO}_4\text{)}_2\text{]} + 14\text{HNO}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{CaH}_4(\text{PO}_4\text{)}_2 \cdot \text{H}_2\text{O} + 7\text{Ca(NO}_3\text{)}_2 + 2\text{HF} \uparrow
\]

OR

\[
\text{CaF}_2 \cdot 3\text{[Ca(PO}_4\text{)}_2\text{]} + 20\text{HNO}_3 \rightarrow 6\text{H}_3\text{PO}_4 + 10\text{Ca(NO}_3\text{)}_2 + 2\text{HF} \uparrow
\]

\[
\rightarrow 12\text{NH}_3 \rightarrow \text{CaHPO}_4 + 12\text{NH}_4\text{NO}_3 + 4\text{Ca(PO}_4\text{)}_2
\]
Fertilizers - Nitrogen

- Needed for stem and leave development in the early stages of plant growth

- $N_2$ unreactive - Why?

- Need to be fixed $\rightarrow NH_3$ or nitrate ion

- Haber process $(NH_3) \rightarrow$ convert to a salt, $NH_4NO_3$

- Ammonium $\rightarrow$ nitrates by nitrification bacteria

- N in the form of urea takes time to convert to the nitrate form as it must first hydrolyze to ammonium
Ammonia (NH₃) - contains about 81.8 % N
- if NH₃ used on its own, it can be injected directly into the irrigation system or the soil

- Urea (H₂NCONH₂) - contains about 46 % N
- relatively cheap
- highest content of N in solid fertilizer
- keep production of dimer called biuret, NH₂CONHCONH₂, low as it is not easily taken up by plants

http://www.canadianagri.ca/images/urea_g.jpg

http://aggie-horticulture.tamu.edu/syllabi/422/pics/nutr/biuret_t.jpg
14 MPa

\[ \text{CO}_2 + 2\text{NH}_3 \rightarrow \text{NH}_2\text{COONH}_4 \quad \Delta H = -155\text{MJ/kg.mol} \]

180 °C

\[ \text{NH}_2\text{COONH}_4 \leftrightarrow \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \quad \Delta H = +42\text{ MJ/kg.mol} \]

Simplified diagram of urea stripping plant
Ammonium nitrate (NH₄NO₃) - contains about 33.5% N

\[ \text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 \quad \Delta H = -4.9 \text{ kJ/mol} \]

- produced on site where NH₃ and HNO₃ produced
- major constituent of some types of explosives and government forbids its sale in the pure form
- mixed with lime and sold as LAN (limestone ammonium nitrate) < 28% N content
● Oklahoma bombing 1995

● truck bomb with a mixture of explosive grade ammonium nitrate fertilizer and fuel oil
Fertilizers - Potassium

- Essential for the formation of:
  a) Starch in potatoes
  b) Sugar in fruit
  c) Fibrous material in plants
- Measured as % $K_2O$ in fertilizers
- Available as natural deposits of $KCl$ (mined as a salt) & $K_2SO_4$ (occurs naturally as a double salt, $K_2SO_4.MgSO_4$)
Different crops require different grades of fertilizer.

Either N or K may be the component in larger quantity and P is generally present as 10 to 40% of the nitrogen requirement.

$2 + 3 + 2 = 7$

$22/7 = 3.15\%$

$\times 2 = 6.3\%$

$\times 3 = 9.4\%$

$2-3-2 \ (22)$

N P K

Refers to the total active ingredient.

Nitrogen as N, phosphorus as $P_2O_5$ & potassium as $K_2O$. 
<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>6.3 %</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>9.4 %</td>
</tr>
<tr>
<td>K₂O</td>
<td>6.3 %</td>
</tr>
</tbody>
</table>

If a trace element has been added, its symbol is written after the numerical code e.g., 2-3-2 (22) Zn - this means that Zn has been added.

Zn - necessary for soils for maize growing
Cu - depleted from soils where pineapples are grown
Mg - added to soils where green crops are grown → important for chlorophyll production
The Economics of Production

- Plant made up of various components:
  - Raw material
  - Energy
  - Labour
  - Laboratory services
  - Security
  - Fire services
  - Packaging
Fixed costs: (do not change with the amount of product made)
- Labour
- Maintenance
- Safety
- Laboratory services
- Management
- Depreciation (20 %)

Variable costs: (change with the amount of product made)
- Raw materials
- Energy
- Packaging
- Transport
- Licences & Patents

Return on capital
Example: A fertilizer manufacturing company, Growmore, has a start up capital of R 100 million and has the following costs:

<table>
<thead>
<tr>
<th>Cost (million R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labour</td>
</tr>
<tr>
<td>Depreciation</td>
</tr>
<tr>
<td>Raw materials</td>
</tr>
<tr>
<td>Energy</td>
</tr>
<tr>
<td>Return on capital</td>
</tr>
</tbody>
</table>

If the production capacity of the plant at 100 % is 500 000 tonnes of fertilizer, what should the fertilizer produced be sold at to cover all expenses?
Cost (million R)

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost (R million)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labour</td>
<td>5</td>
</tr>
<tr>
<td>Depreciation</td>
<td>20</td>
</tr>
<tr>
<td>Raw materials</td>
<td>50</td>
</tr>
<tr>
<td>Energy</td>
<td>10</td>
</tr>
<tr>
<td><strong>Subtotal</strong></td>
<td><strong>85</strong></td>
</tr>
<tr>
<td>Return on capital</td>
<td><strong>15</strong></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

Price per tonne = \(\frac{100,000,000}{500,000}\) = R 200