PHOSPHORUS INDUSTRIES

PHOSPHORUS (P) IS A VITAL RESOURCE FOR SUSTAINING WORLD AGRICULTURE.

LECTURE 10

PHOSPHORUS - USES

- Phosphates are used to make special glass that is an important component of sodium lamps.
- Phosphorus is an essential nutrient for plants. It is, therefore, added to fertilizers.
- In the laboratory, two radioactive isotopes of phosphorus can be used as radioactive tracers.
- Calcium phosphate can be used to make fine china.
- The strikers for matchsticks are made from phosphorus. Flares and safety matches are also made from phosphorus.
- White phosphorus is used in incendiary bombs, smoke screens (such as smoke bombs) and tracer ammunition.

- Tributylphosphate, a compound of phosphorus, is used to extract uranium. This is called the Purex process.
- Phosphorus is an important component of DNA and RNA.
- Phosphorus is used in the production of steel.
- Sodium tripolyphosphate is used in laundry detergents in some parts of the world. It helps in the cleaning of clothes. However, some countries have banned them as it leads to the killing of fish when leaked into waterways.
- Other compounds of phosphorus are used in the manufacture of pesticides, food additives, toothpaste and fertilizers.

<table>
<thead>
<tr>
<th>Widely used compounds</th>
<th>Use</th>
</tr>
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<tbody>
<tr>
<td>Ca(H₂PO₄)₂·H₂O</td>
<td>Baking powder and fertilizers</td>
</tr>
<tr>
<td>Ca(H₂PO₄)₂·2H₂O</td>
<td>Animal food additive, toothpowder</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>Manufacture of phosphate fertilizers</td>
</tr>
<tr>
<td>PO₃</td>
<td>Manufacture of POC₃ and pesticides</td>
</tr>
<tr>
<td>POCl₃</td>
<td>Manufacturing plasticizer</td>
</tr>
<tr>
<td>P₄S₁₀</td>
<td>Manufacturing of additives and pesticides</td>
</tr>
<tr>
<td>Na₅P₂O₁₀</td>
<td>Detergents</td>
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</table>
PHOSPHATE ROCK

Phosphate rock (PR) is a globally accepted but imprecise term describing any naturally occurring geological material that contains one or more phosphate minerals suitable for commercial use.

Flourapatite admixed with various proportions of other compounds of Ca, F, Fe, Al, and Si.

Flourapatite: CaF₂·3Ca₃(PO₄)₂, an extremely insoluble compound, Ca₁₀F₂(PO₄)₆

PHOSPHATE ROCK PROCESSING

ACIDULATION: The process of treating a fertilizer source with an acid. The most common process is treatment of phosphate rock with an acid (or mixture of acids) such as sulfuric, nitric, or phosphoric acid.

PRODUCTS: Superphosphates, phosphoric acid, triple superphosphates, monoammonium phosphate, P₂O₅

ELECTRIC FURNACE REDUCTION: Phosphate rock is blended with coke (reducing agent) and silica.

Charged with electric current forming gaseous P, later condensed to liquid P.

PRODUCTS: P, P₂O₅

TABLE 1. World phosphate rock reserves, reserve bases, and production.

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>United States (U.S.)</td>
<td>1,300</td>
<td>4,960</td>
<td>47,937</td>
<td>50,039</td>
<td>51,023</td>
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<td>410</td>
<td>3,890</td>
<td>3,967</td>
<td>4,408</td>
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<td>230</td>
<td>230</td>
<td>23,142</td>
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<td>24,244</td>
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<td>200</td>
<td>4,417</td>
<td>4,188</td>
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<td>Jordan</td>
<td>100</td>
<td>630</td>
<td>5,492</td>
<td>5,896</td>
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<td>Kazakhstan</td>
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<td>2,424</td>
<td>551</td>
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<tr>
<td>Morocco and Western Sahara</td>
<td>6,800</td>
<td>23,100</td>
<td>22,369</td>
<td>22,922</td>
<td>23,142</td>
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<tr>
<td>Russia</td>
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<td>South Africa</td>
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<td>2,675</td>
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<td>Togo</td>
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<td>2,164</td>
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<tr>
<td>Tunisia</td>
<td>300</td>
<td>8,166</td>
<td>9,956</td>
<td>9,024</td>
<td>7,934</td>
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<tr>
<td>Other countries</td>
<td>1,100</td>
<td>2,800</td>
<td>10,019</td>
<td>11,130</td>
<td>11,920</td>
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<tr>
<td>World total (rounded)</td>
<td>12,000</td>
<td>36,780</td>
<td>104,362</td>
<td>106,566</td>
<td>149,872</td>
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</table>

Reserve and reserve base cost less than $20/ton and $30/ton, respectively. Cost includes capital, operating expenses, taxes, royalties, and a 15 percent return on investment, FOB mine.
SUPERPHOSPHATES

Product of the acidulation process:
$$\text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaH}_4(\text{PO}_4)_2 + 2\text{CaSO}_4 $$

monocalciumphosphate

$$\text{CaF}_2 + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 + HF $$

$$4\text{HF} + \text{SiO}_2 \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} $$

$$3\text{SiF}_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2\text{SiF}_6 $$

MANUFACTURE OF SUPERPHOSPHATE

Preparation of phosphate rock
Mixing with acid
Curing and drying of the slurry
Milling and bagging

TRIPLE SUPERPHOSPHATE

- A more concentrated fertilizer (in terms of $\text{P}_2\text{O}_5$ content) nearly 3X vs. superphosphate.
- $\text{PR} + 14\text{H}_3\text{PO}_4 \rightarrow 10 \text{Ca}(\text{H}_2\text{PO}_4)_2 + HF$
PHOSPHORIC ACID

Uses:
Fertilizers – 85%
Detergent materials – 5%
Animal feed – 5%
Food, beverages, etc 5%

PHOSPHORIC ACIDS - MANUFACTURE

WET PROCESS:
\[
\text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 + 4\text{H}_2\text{O} \rightarrow 2\text{H}_3\text{PO}_4 + 3\text{CaSO}_4
\]
Wet process phosphoric acid normally contains 26 to 30 percent $P_2O_5$. In most cases, the acid must be further concentrated to meet phosphate feed material specifications for fertilizer production. Depending on the types of fertilizer to be produced, phosphoric acid is usually concentrated to 40 to 55 percent $P_2O_5$ by using 2 or 3 vacuum evaporators.

Electric Furnace Phosphorus And Phosphoric Acid

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4 + 10CO \quad \Delta H = -3055 \text{ kJ}$$

Using elemental phosphorus:

$$4P + 5O_2 \rightarrow 2P_2O_5$$

$$P_4O_6 + 3H_2O \rightarrow 2H_3PO_4$$

PHOSPHORUS

ELECTRIC FURNACE REDUCTION:

$$3Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow CaSiO_3 + P_4 + 10CO$$
MANUFACTURE OF PHOSPHORIC ACID

THERMAL:
Raw materials for the production of phosphoric acid by the thermal process are elemental (yellow) phosphorus, air, and water. Thermal process phosphoric acid manufacture involves 3 major steps: (1) combustion, (2) hydration, and (3) demisting.

PHOSPHORUS

ELECTRIC FURNACE REDUCTION:
\[ 3\text{Ca}_3(\text{PO}_4)_2 + 6\text{SiO}_2 + 10\text{C} \rightarrow \text{CaSiO}_3 + P_4 + 10\text{CO} \]
SODIUM PHOSPHATES

Various forms:
Orthophosphates: MSP $\text{NaH}_2\text{PO}_4$
DSP $\text{Na}_2\text{HPO}_4$
TSP $\text{Na}_3\text{HPO}_4$

Manufactured from Phosphoric acid and Soda ash / caustic soda.

PYROPHOSPHATE / TRIPOLYPHOSPHATE

- Used as water softeners
- Tripolyphosphate: (STPP)
  $\text{NaH}_2\text{PO}_4 + 2\text{Na}_2\text{HPO}_4 \rightarrow \text{Na}_5\text{P}_3\text{O}_{10} + 2\text{H}_2\text{O}$
- Pyrophosphate: (TSP)
  $2\text{Na}_2\text{HPO}_4 \rightarrow \text{Na}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O}$

LECTURE 11
POTASSIUM INDUSTRIES
PHOSPHORUS (P) IS A VITAL RESOURCE FOR SUSTAINING WORLD AGRICULTURE.

USES:
- Used in the production of alloys (heat transfer)
- Manufacture of $\text{KO}_2$ in life support systems

Manufacture:
$\text{Na} + \text{KCl} \rightarrow \text{K} + \text{NaCl}$
POTASSIUM CHLORIDE

Uses:
Fertilizer

MANUFACTURE: TRONA PROCESS

POTASSIUM SULFATE

USES:
Fertilizers

Production:
\[ \text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4 \text{ (burkeite)} + \text{KCl} \]

POTASSIUM BISULFATE

USES:
Ceramics

Manufacture:
\[ \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightarrow 2\text{KHSO}_4 \]

POTASSIUM HYDROXIDE

Caustic Potash

Uses:
Production of other K salts (K_2CO_3, KMnO_4, etc)
KCl for liquid fertilizers
Pesticides and other chemicals

Manufacture: Electrolysis
POTASSIUM CARBONATE

Uses:
- pottery, soaps, adsorbent for acid gases

 Manufacture:
\[ \text{CO}_2 + 2\text{KOH} + \text{H}_2\text{O} \]

POTASSIUM PERMANGANATE

USES:
Laboratory oxidizing agents (an expensive oxidizing agent)

 Manufacture:
Passing \( \text{CO}_2 \) through a \( \text{KMnO}_3 \) solution
\[ \text{KMnO}_3 \text{ from } \text{MnO}_2 + \text{KOH} + \text{O}_2 \]

Potassium Bromide

Uses: photographic emulsions, photoengraving, Sedative,

 Manufacture:
\[ 3\text{Fe} + 4\text{Br}_2 \rightarrow \text{Fe}_3\text{Br}_8 \]
\[ \text{Fe}_3\text{Br}_8 + 4\text{K}_2\text{CO}_3 + 4\text{H}_2\text{O} \rightarrow 8\text{KBr} + 2\text{Fe(OH)}_3 + 4\text{CO}_2 \]