Phosphorus Fertilizer Production and Technology
Phosphorus (P) Cycling in Crop Production Systems
**P is Essential for Plant Nutrition**

- Taken up mostly as phosphate ($\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$)
- Involved in photosynthesis, energy transfer, cell division and enlargement
- Important in root formation and growth
- Improves the quality of fruit and vegetable crops
- Is vital to seed formation
- Improves water use
- Helps hasten maturity

![P deficient corn](image)
The Role of P as an Essential Nutrient for Animal Nutrition

- P is a major component of bones and teeth
- It is important for lactating animals
- P and calcium (Ca) are closely associated in animal nutrition
- It is essential for energy transfer and utilization
History of Phosphate Fertilizer

• Early sources were mostly animal based – bones, guano, manure
• Treatment of bones with acid to increase P solubility started early to mid 1800s
• Sulfuric acid treatment process of bones and P minerals (apatite) was patented in mid 1800s.
• Today most P fertilizer production is based on acidification of apatite from phosphate rock (PR)
Map of World P Resources

Source: IFDC
Phosphate Rock Reserves and Resources

• PR is a finite natural resource

• Reserves are generally defined as materials that can be economically produced at the present time using existing technology

• Resources include reserves and any other materials of interest that are not reserves

• Some have predicted that we are nearing “peak production” and that a scarcity of PR is looming

• An exhaustive review (IFDC, 2010) provides more details on global P reserves
PR Reserves and Resources

- Recent review by IFDC shows much larger world reserves than formerly estimated
- This table shows top five countries in order of reserve holdings based on IFDC estimates
- Based on this information, the world will not soon run out of PR

<table>
<thead>
<tr>
<th>Country</th>
<th>Mine production</th>
<th>USGS, 2010 est. reserves</th>
<th>IFDC est. reserves(^1) (product)</th>
<th>IFDC est. resources(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2008</td>
<td>2009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Morocco</td>
<td>25.0</td>
<td>24.0</td>
<td>5,700</td>
<td>51,000</td>
</tr>
<tr>
<td>China</td>
<td>50.7</td>
<td>55.0</td>
<td>3,700</td>
<td>3,700</td>
</tr>
<tr>
<td>United States</td>
<td>30.2</td>
<td>27.2</td>
<td>1,100</td>
<td>1,800</td>
</tr>
<tr>
<td>Jordan</td>
<td>6.3</td>
<td>6.0</td>
<td>1,500</td>
<td>900</td>
</tr>
<tr>
<td>Russia</td>
<td>10.4</td>
<td>9.0</td>
<td>200</td>
<td>500</td>
</tr>
<tr>
<td>Other countries</td>
<td>38.5</td>
<td>35.8</td>
<td>3,427</td>
<td>2,007</td>
</tr>
<tr>
<td><strong>World total (rounded)</strong></td>
<td><strong>161</strong></td>
<td><strong>158</strong></td>
<td><strong>16,000</strong></td>
<td><strong>60,000</strong></td>
</tr>
</tbody>
</table>

Estimated longevity in years based on 2008-09 average production level:

- **100** years
- **376** years

\(^1\)Reserves as usable or marketable product.
\(^2\)Resources as unprocessed PR of varying grades or concentrate.
Formation of Phosphate Rock Deposits

- Most (>80%) PR used in fertilizer production is sedimentary, but igneous deposits are also used.
- Sedimentary PRs were formed in continental shelf marine environments, and are thus taken from present or former continental margins.
- Igneous PR was formed mostly in shield areas and rift zones.
PR Mining Techniques

- Most phosphate rock is extracted through open pit mining techniques such as
  - Draglines
  - Bucket wheel excavators
  - Front end loader removal
Phosphate Rock Utilization Factors

• Concentrated (beneficiated) PRs are usually about 27% to 37% P$_2$O$_5$ (may be as low as ~23%)
• Low free carbonate content to avoid excess consumption of acid in phosphoric acid production
• Low Fe$_2$O$_3$, Al$_2$O$_3$, and MgO contents (below ~5%) to avoid formation of intermediate products
• Low Cl$^-$ content (<500 ppm) to prevent equipment corrosion
Ore Impurities and Beneficiation

• Initial removal of impurities from PR ore is called beneficiation
• Beneficiation of PR involves removal of materials such as sand, clay, carbonates, organics, and iron oxide
• Beneficiation may involve
  – Screening (wet or dry)
  – Washing
  – Hydrocyclones
  – Calcination
  – Flotation
  – Magnets
Ore Washing and Screening

- Separates oversize material (3 to 20 cm)
- Removes clays and other fines which result in a slurry of suspended waste called “slime”
- In areas without sufficient water, dry screening may be used
Ore Flotation

- Froth flotation requires deslimed feedstock
- The first step involves bubbling air through an anionic collector such as fatty acid
- Fine ore is passed through flotation cells, PR is attracted to the anionic collector, and rises with froth
- Floating apatite is thus separated from silica tailings by overflow or paddlewheels
Ore Calcination

- Is used at some locations to remove organic matter
- Organic matter is burned by passing ore through furnace
- Results in higher quality product
- Used where energy cost, especially natural gas, is low
Conversion of PR to Phosphoric Acid

• After beneficiation, PR is converted to phosphoric acid

• Two processes of phosphoric acid production
  – Wet (chemical) process
  – Electric furnace (thermal) process

• The majority of P fertilizer is produced by wet process
  – Reaction of PR with acid

• The most common acid used on wet process is sulfuric (although others such as nitric acid are also used)

• The two major feedstocks in P fertilizer manufacturing are PR and elemental S
Wet Process Phosphoric Acid Production
Wet Process Phosphoric Acid Production
Tailing Disposal

- Two major tailings produced in P fertilizer manufacture
  - Slime
  - Phosphogypsum
- Slime is produced by the separation of clay and other “fines” from PR
- Slime may be
  - placed in settling ponds
  - disposed of in the sea
  - placed in mined-out areas for reclamation
Tailing Disposal (Continued)

- Phosphogypsum (PG) is produced in the reaction of sulfuric acid with PR.
- Most PG is placed in stacks near the point of production.
- In some countries it is disposed of in the sea.
- Only a small percentage (~15%) of PG is reused in:
  - agricultural applications
  - cement retardant
  - construction materials
  - plaster board
- Where nitric acid is used to produce P fertilizer there is no gypsum byproduct.
Mine Land Reclamation

• Mineland is reclaimed after ore is removed
• Reclaimed land can be more productive than in the original state
• Revegetation and reestablishment of ecosystem and wildlife habitat are of utmost importance in reclamation efforts
P Fertilizer Sources – Dry Granular

• Ordinary or normal superphosphate (OSP or SSP)
  – Ca\((\text{H}_2\text{PO}_4)\)_2 \cdot \text{H}_2\text{O}
  – Low analysis (0-20-0-10S)
  – Simple to produce – results from reaction of PR with sulfuric acid
  – Oldest source – less popular than in the past

• Triple superphosphate (TSP)
  – First high analysis P fertilizer (0-46-0)
  – Results from reaction of PR with phosphoric acid
  – Production has declined since the 1980s in favor of ammoniated phosphates
P Fertilizer Sources – Dry Granular (Cont.)

- Diammonium phosphate (DAP)
  - Analysis, 18-46-0
  - Produced by reacting 2 moles ammonia with 1 mole of phosphoric acid
  - Worlds major dry P fertilizer

- Monoammonium phosphate (MAP)
  - Typical analysis, 11-52-0
  - Produced by reacting 1 mole ammonia with 1 mole of phosphoric acid
  - Lower quality PR can be used in production of MAP than DAP
P Fertilizer Sources – Dry Granular

- Simplified flowchart of granular P production

Phosphate Rock

+ $\text{H}_2\text{SO}_4$ + $\text{H}_2\text{SO}_4$ + $\text{HNO}_3$

SSP

Wet Process Acid

+ Ammonia + Phosphate Rock

DAP, MAP

TSP

CaSO$_4$$\cdot$XH$_2$O

Nitrophosphates

NPKs
P Fertilizer Sources – Fluid

• Superphosphoric acid
  – Used as feedstock in the production of liquid polyphosphate fertilizers
  – Produced by dehydration of phosphoric acid
  – Contains 68 to 70% \( P_2O_5 \)
  – Consists of mix of poly (20 to 35%) and orthophosphate

\[
\text{Phosphoric acid} + \text{Heat} \rightarrow \text{Pyrophosphoric acid, a polyphosphate} + \text{Water vapor}
\]
P Fertilizer Sources – Fluid (Cont.)

• Polyphosphates
  – Consist of a variety of polymers
  – Major polymer is pyrophosphate (two P molecules linked), but longer chained polyphosphates are also present
P Fertilizer Sources – Fluid (Cont.)

- Ammonium polyphosphate (APP)
  - Analysis 10-34-0 or 11-37-0
  - Major liquid P source
  - Mostly produced in TVA pipe reactor, introduced in 1972
  - Produced by reaction of superphosphoric acid, ammonia, and water
  - 70 to 75% of P is polyphosphate, the remainder is orthophosphate
  - Has good sequestering ability and storage characteristics
Suspending Fertilizers

- First introduced in the 1960s
- Consist of crystals suspended by gelled clay
- Analysis intermediate between solutions (polyphosphate) and granular
- Base materials commonly include anhydrous ammonia, MAP, water, attapulgite clay, and potash (KCl)
- Distressed products can often be used to produce suspensions
- Storage and application characteristics are poor relative to polyphosphates, thus they often require more management
Shipping and Storage
Phosphorus Fertilizer and the Soil

- Common commercial P fertilizers are highly (≥90%) water soluble
- Once dissolved in soils, orthophosphate is available for plant uptake
- Polyposphates in APP must be converted to orthophosphate for plant uptake.
- Conversion or hydrolysis of poly to ortho in soils happens readily and does not affect nutritional value
- P chemistry in soils is complex – P may become sparingly available to plants in some soils due to formation of less soluble products
Phosphorus Fertilizer Placement

• P fertilizer may be broadcast on the soil surface (liquid or dry) or it can be placed in a concentrated band.

• There may be advantages to banding, including:
  – Early crop growth enhancement
  – Concentration of P to minimize soil contact and reaction
  – Placement in the root zone
P Fertigation

• P fertilizer is sometimes applied with irrigation water, although not as commonly as N
• P fertigation requires special consideration of fertilizer properties and water chemistry
• It can cause system plugging and fouling by reacting with
  – Calcium
  – Magnesium
  – Ammonium
  – Iron
• Successful P fertigation requires careful planning!
High Yielding Crops Remove Large Amounts of P

Nutrients removed in crop harvest, including P, must eventually be replaced or production will suffer.

<table>
<thead>
<tr>
<th>Crop</th>
<th>Yield/A</th>
<th>Nutrient removal, lb P₂O₅/A</th>
<th>Yield, mt/ha</th>
<th>Nutrient removal, kg P₂O₅/ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maize</td>
<td>180 bu</td>
<td>80</td>
<td>11</td>
<td>90</td>
</tr>
<tr>
<td>Wheat</td>
<td>60 bu</td>
<td>30</td>
<td>4</td>
<td>34</td>
</tr>
<tr>
<td>Rice</td>
<td>70 cwt</td>
<td>45</td>
<td>7.8</td>
<td>50</td>
</tr>
<tr>
<td>Cotton</td>
<td>3 bales</td>
<td>35</td>
<td>1.6</td>
<td>39</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>8 tons</td>
<td>120</td>
<td>18</td>
<td>134</td>
</tr>
<tr>
<td>Potato</td>
<td>500 cwt</td>
<td>75</td>
<td>56</td>
<td>84</td>
</tr>
</tbody>
</table>
Phosphorus and the Environment

- Eutrophication – the natural aging of lakes or streams by nutrient enrichment
- Nutrient additions can accelerate the process
- P is often the limiting element
- Dissolved oxygen is depleted by excessive plant growth
- Best management practices (BMPs) can help minimize P runoff from fields

University of Manitoba

C+N Added

C+N+P Added (blue-green algae)
Summary

- Phosphorus is essential for healthy plants and animals
- Most P fertilizer comes from reacting PR with sulfuric, phosphoric or nitric acid
- Many excellent granular, liquid, and suspension P fertilizers are available for specific needs
- Addressing the need for P fertilizer is part of a complete and balanced crop nutrition program
- BMPs help ensure minimal environmental impacts from P fertilizer
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