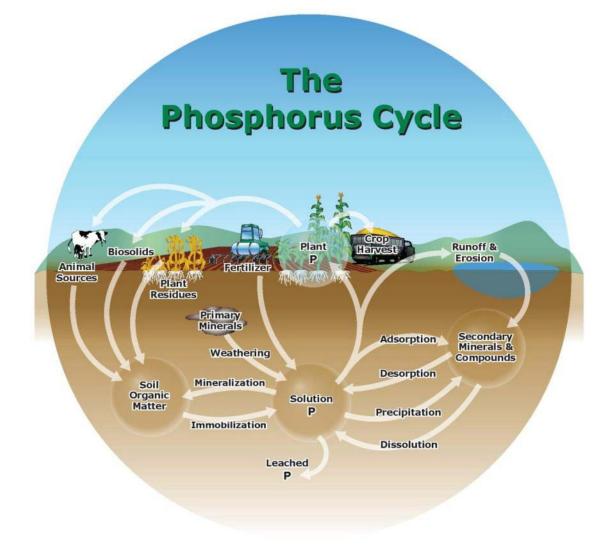


# Phosphorus Fertilizer Production and Technology

#### Phosphorus (P) Cycling in Crop Production Systems





### **P** is Essential for Plant Nutrition

- Taken up mostly as phosphate (H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup>)
- 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





### 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)

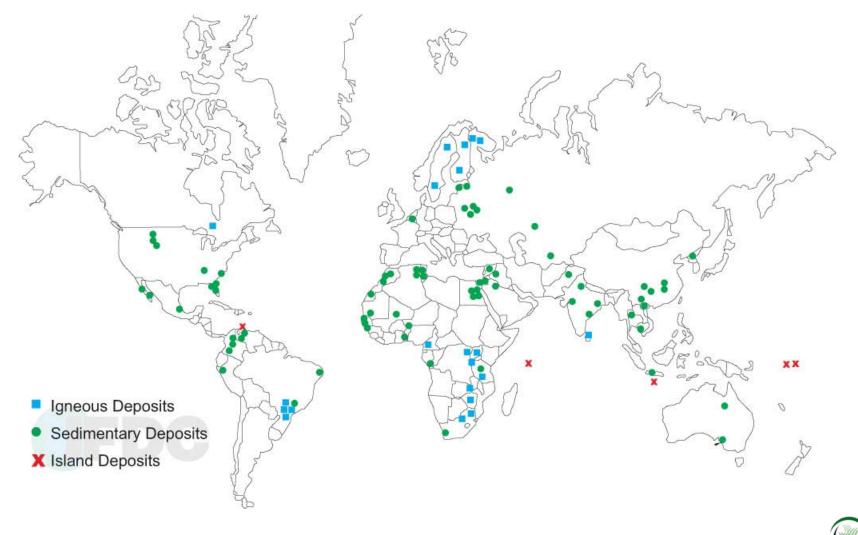




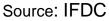




#### Map of World P Resources



IPNI



#### 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

| Country   | Mine production |      | USGS, 2010    | IFDC est.                          | IFDC est.              |
|---|-----------------|------|---------------|------------------------------------|------------------------|
|   | 2008            | 2009 | est. reserves | reserves <sup>1</sup><br>(product) | resources <sup>2</sup> |
|   |                 |      | mmt           |                                    |                        |
| Morocco   | 25.0            | 24.0 | 5,700         | 51,000                             | 170,000                |
| China   | 50.7            | 55.0 | 3,700         | 3,700                              | 16,800                 |
| United States   | 30.2            | 27.2 | 1,100         | 1,800                              | 49,000                 |
| Jordan  | 6.3             | 6.0  | 1,500         | 900                                | 1,800                  |
| Russia  | 10.4            | 9.0  | 200           | 500                                | 4,300                  |
| Other countries   | 38.5            | 35.8 | 3,427         | 2,007                              | 45,580                 |
| World total (rounded)   | 161             | 158  | 16,000        | 60,000                             | 290,000                |
| Estimated longevity in years based<br>on 2008-09 average production level |                 |      | 100           | 376                                |                        |

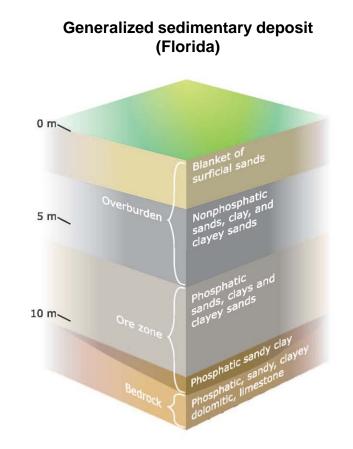
<sup>1</sup>Reserves as usable or marketable product.

<sup>2</sup>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<sub>2</sub>O<sub>5</sub> (may be as low as ~23%)
- Low free carbonate content to avoid excess consumption of acid in phosphoric acid production
- Low Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and MgO contents (below ~5%) to avoid formation of intermediate products
- Low Cl<sup>-</sup> 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 though 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

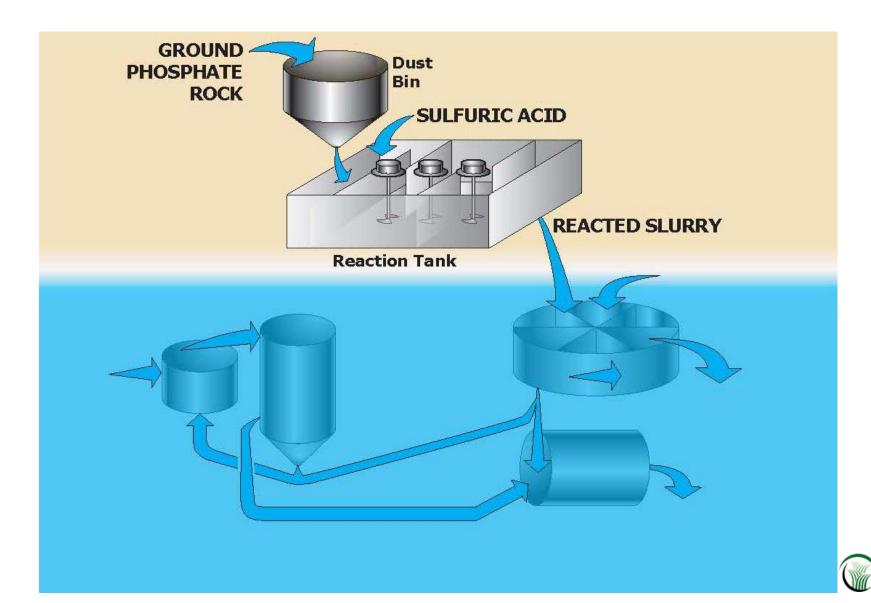




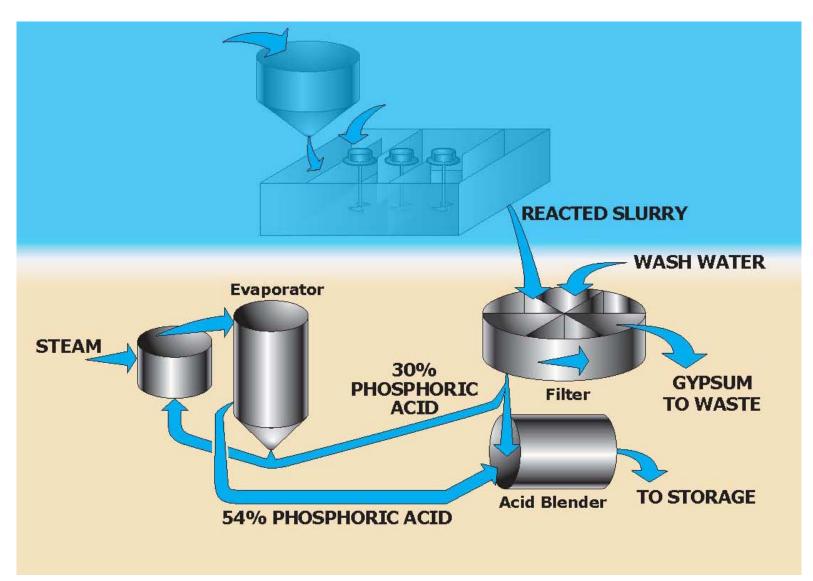




#### **Wet Process Phosphoric Acid Production**



#### (Cont.) Wet Process Phosphoric Acid Production





## **Tailing Disposal**

- Two major tailings produced in P fertilizer manufacture
  - <u>Slime</u>
  - <u>Phosphogypsum</u>
- 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 (H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>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

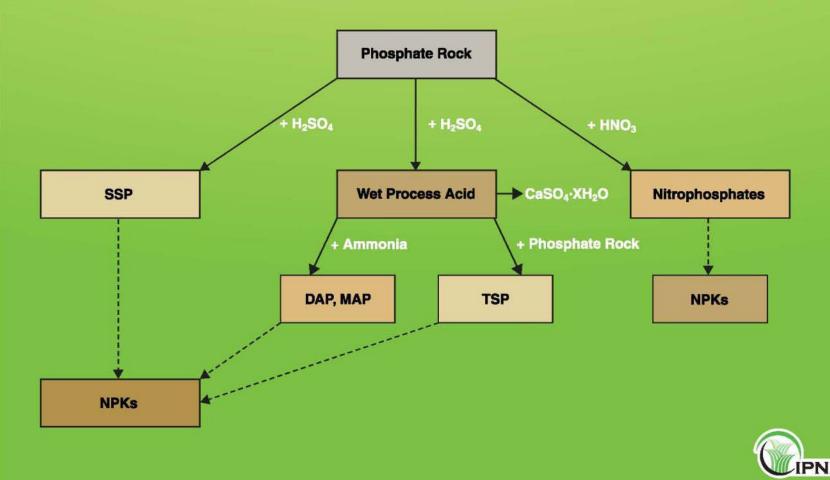






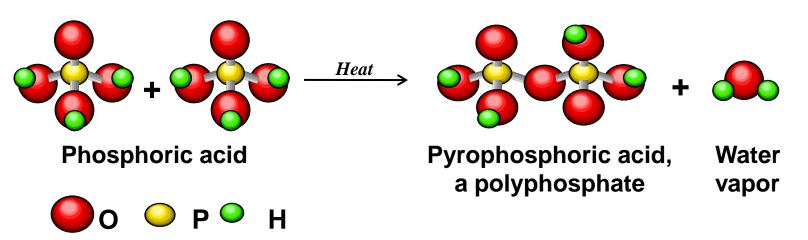
#### **P Fertilizer Sources – Dry Granular**

Simplified flowchart of granular P production



#### **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

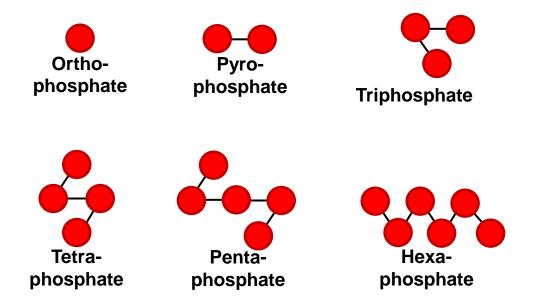




#### P Fertilizer Sources – Fluid (Cont.)

#### 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





#### P Fertilizer Sources – Fluid (Cont.)

#### Suspensions

- 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 (KCI)
- 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**

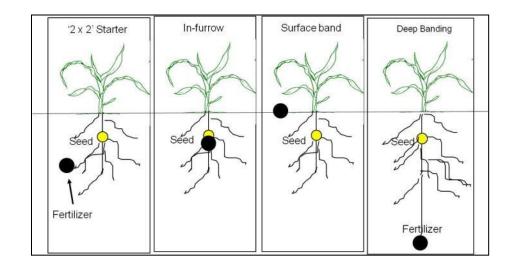
- Common commercial P fertilizers are highly (≥90%) water soluble
- Once dissolved in soils, orthophosphate is available for plant uptake
- Polyphosphates in APP must be converted to orthophosphate for plant uptake.
- Conversion or hydrolysis of poly to ortho in soils happens readily and does not affect 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

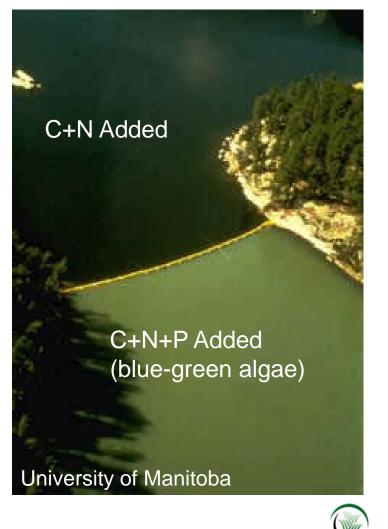


| Сгор    | Yield/A | Nutrient<br>removal,<br>Ib P <sub>2</sub> O <sub>5</sub> /A | Yield,<br>mt/ha | Nutrient<br>removal,<br>kg P <sub>2</sub> O <sub>5</sub> /ha |
|---------|---------|---|-----------------|--|
| Maize   | 180 bu  | 80  | 11              | 90   |
| Wheat   | 60 bu   | 30  | 4               | 34   |
| Rice    | 70 cwt  | 45  | 7.8             | 50   |
| Cotton  | 3 bales | 35  | 1.6             | 39   |
| Alfalfa | 8 tons  | 120   | 18              | 134  |
| Potato  | 500 cwt | 75  | 56              | 84   |



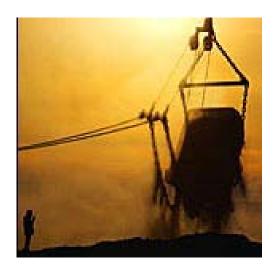
### **Phosphorus and the Environment**

- 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



## 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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