

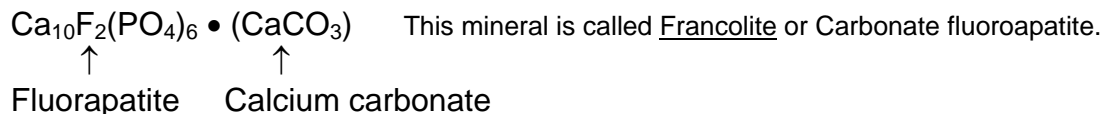
SOILS AND FERTILIZERS
MODULE 7
PHOSPHORUS FERTILIZER – MANUFACTURE, MATERIALS, AND USES

1. Phosphorus production and consumption
 - a. More than 50 countries produce phosphorus fertilizer. The top five P fertilizer-producing countries in 1996 were: United States, China, Russia, India, and Brazil.
 - b. The top five phosphorus fertilizer-consuming states in 1997 were: Illinois (444,162 tons), Iowa (319,919 tons), Minnesota (294,393 tons), Texas (241,619 tons) and Nebraska (211,990 tons).
 - c. Florida consumed 95,585 tons of P fertilizer in 1997 (ranked 18th among states).
2. Role of phosphorus in plants
 - a. Energy storage and transfer: P compounds act as energy storage and transport “currency” in plants, including adenosine diphosphate and triphosphate (ADP and ATP). Phosphorus is also involved in the photosynthetic capture of light energy.
 - b. Structural component of a wide variety of biochemicals, including nucleic acids such as DNA and RNA.
 - c. Reproduction: Large concentrations of P are found in seeds and fruit; P is considered essential for seed formation.
 - d. A good supply of P has historically been associated with increased root growth.
 - e. P deficiency is seldom exhibited as a foliar symptom on citrus.
3. Phosphate rock: The starting point for phosphorus fertilizer manufacture
 - a. Phosphorus fertilizer production primarily involves the mining, upgrading, and conversion of phosphate rock to more water-soluble P compounds.
 - b. Rock deposits were laid down in beds under the ocean, which became part of the landmass after the sea level declined.
 - c. Phosphate is usually in the form of small pellets cemented together by calcium carbonate (CaCO_3); in some places, the cementing agent has been leached away, leaving more or less loose pebbles; in other places, the whole mass has been compressed into hard rock.
 - d. There are many different locations of phosphate deposits worldwide, with varying quality of phosphate, thus the location of the deposit is important. The P rock supplies in Florida, North Carolina, and Tennessee are soft-pebble P and can be strip mined; those in Utah, Wyoming, Montana, and Idaho are the largest U.S. reserves, but are hard rock P (have to mine underground or blast to get it out).
 - e. Florida has a large, high-grade phosphate deposit; much has been already mined; the center of the mining has been Polk Co., but is now migrating south to Hardee Co.
 - f. Florida phosphate deposits have 10 to 20 ft of sand overburden over 5 to 20 ft of phosphate matrix; the matrix is 25% clay, 50% sand, and 25% phosphate rock; it takes 2 tons of rock phosphate to produce 1 ton of concentrated superphosphate (CSP), or 8 tons of matrix to produce 1 ton of CSP.

- g. Florida P must be **beneficiated** to make it suitable for processing into fertilizers; this is a complex process that involves wet screening, hydroseparation, and concentration by floatation; the result is several different size fractions of P rock.
- h. During the course of beneficiation, the impurities removed (iron, aluminum, magnesium) are discarded as slimes and tailings; these contain a lot of unrecoverable small-particle P; they usually end up settling out in slime ponds.
- i. Slime pond areas are not really solid (can contain 30 to 40% moisture after 40 yrs); they are high in clay content. Can bring in sand to allow these areas to grow crops sooner; must be careful in selection of crop because of Cd levels in phosphatic clays; some mined-out areas have been converted to residential developments; environmental concerns with gypsum disposal and uranium; a 1975 law mandated the reclamation of mined land within 5 years of the closing of the mine.
- j. Of the total USA phosphate rock reserves, 75% exists in Florida deposits; the USA is the no. 1 P rock producer, but is exporting much less now than in years past to extend its reserves; Morocco is the no. 1 phosphate rock exporter - the majority of their economy is based on these sales, but quality is poorer. Substantial phosphate reserves also exist in Russia and China.
- k. The phosphate reserves in Florida may only last slightly into the 21st century; the remaining ore has a lower grade and lies deeper underground, so it will be more expensive to mine.
- l. The world P market rate determines the amount of P available; there are huge deposits left in Morocco (50 to 100 yr supply); the largest reserves are in the Former Soviet Union, but are in remote locations; do not have technology yet for removal; the world estimate of P reserves is a 400-yr supply.

4. Obtaining the phosphate rock

- a. Mining of phosphate material - what is actually mined:



- b. Solubility of sources: North Carolina is the highest, Florida is intermediate, western reserves are the least. P from other sources is usually inferior to Florida phosphate. North Carolina rock does carry lime potential (increases soil pH).

5. Manufacture of phosphate fertilizer

- a. Production of sulfuric acid (H₂SO₄)

- i. Sulfuric acid is the workhorse of the fertilizer industry; more than 60% of the total consumption of this industrial acid is accounted for by the fertilizer industry.
- ii. Easily produced from elemental sulfur (a relatively inexpensive raw material in abundant supply).

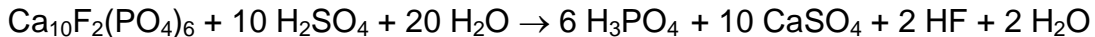
iii. Sources of sulfur:

- (1) Elemental S, from "dome sulfur" deposits primarily in Louisiana located several hundred feet down.
- (2) Pyrites - sulfides of heavy metals, such as FeS_2 ; S is driven off by burning the ore (not used much).
- (3) Sour gas - H_2S is a component of some natural gas sources; must be removed before gas can be used; S can be recovered from H_2S .
- (4) Volcanic S - largest deposit is in Sicily.

b. Phosphoric acid (H_3PO_4) ("Green acid" or "Wet process acid")

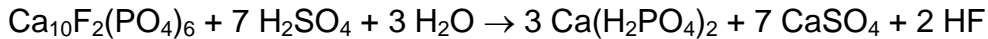
Wet process acid at production is 28% P_2O_5 ; through dehydration it is brought up to 54% (commonly used) or 64% (a more concentrated form for use in making N-P solutions)

Apatite + Sulfuric Acid + Water \rightarrow
Phosphoric acid + Gypsum + Hydrofluoric acid + Water



c. Ordinary Superphosphate (OSP)

Apatite + Sulfuric Acid + Water \rightarrow
Monocalcium phosphate + Gypsum + Hydrofluoric acid

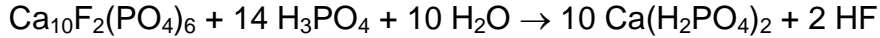


This process was patented in 1842. Previous to that time, phosphate was obtained from ground-up bones or animal manure.

- i. Ordinary superphosphate is referred to as OSP, normal super, single super, or superphosphate.
- ii. OSP contains 20% P_2O_5 .
- iii. Gypsum (CaSO_4) is an integral part of monocalcium phosphate; it cannot be separated out, thus **if OSP is applied as fertilizer, gypsum is applied along with it**; gypsum is a source of sulfur in the soil; OSP is 12% S and 20% Ca.
- iv. The hydrofluoric acid (HF) produced can be trapped and sold.
- v. Will get uranium cake (about 3 lb/ton) from OSP production.
- vi. Problems with forming monocalcium phosphate: impurities such as Al, Fe, and Mg (most deleterious); these are picked up especially in lower grade ores; their presence will precipitate out P and will not let manufacturing reaction proceed.
- vii. Monocalcium phosphate as OSP is 80% water- and citric-acid soluble; large amounts are sold in Florida.

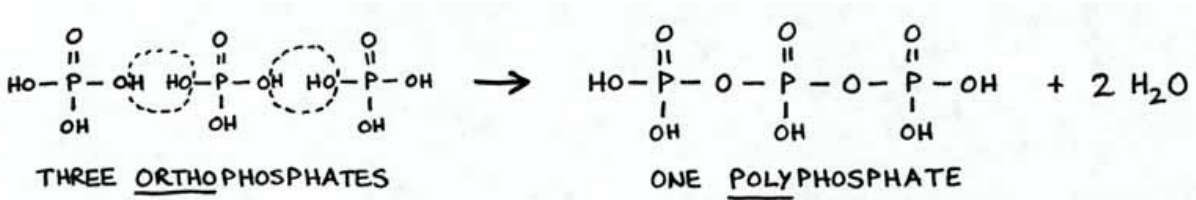
d. Concentrated Superphosphate (CSP)

Apatite + Phosphoric Acid + Water →
Monocalcium phosphate + Hydrofluoric acid



- i. This reaction produces **no gypsum** because no S is added as sulfuric acid.
- ii. This material is referred to as triple superphosphate (TSP), or triple super.
- iii. TSP contains 46% P_2O_5 .
- iv. TSP is 90 to 95% water- and citric-acid soluble.

e. Manufacture of superphosphoric acid (**polyphosphate**)



- i. Removes two H_2O molecules from 3 molecules of wet process acid to form **polyphosphoric acid** (106 to 115% H_3PO_4 , or 76 to 85% P_2O_5); reaction requires high temperature and centrifugation.
- ii. Principally used in production of **liquid polyphosphate** fertilizers.

f. Monoammonium phosphate (MAP) $\text{NH}_4(\text{H}_2\text{PO}_4)$ 11-48-0

Ammonia (NH_3) + phosphoric acid (H_3PO_4) → $\text{NH}_4(\text{H}_2\text{PO}_4)$ (MAP)

g. Diammonium phosphate (DAP) $(\text{NH}_4)_2\text{HPO}_4$ 18-46-0

Ammonia (NH_3) + phosphoric acid (H_3PO_4) → $(\text{NH}_4)_2\text{HPO}_4$ (DAP)

- i. **DAP is the single most popular fertilizer in the world.**
- ii. Both MAP and DAP are 100% water- and citric-acid soluble.

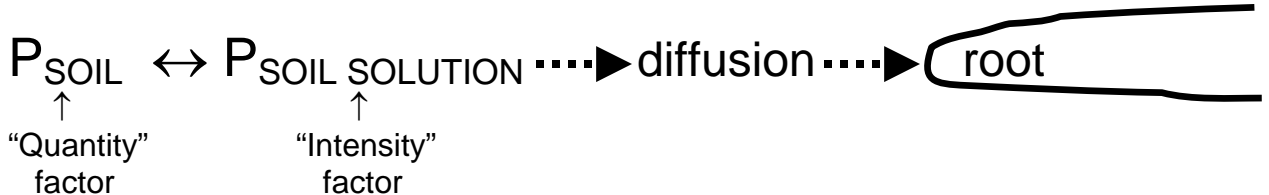
6. Summary of properties of common phosphate fertilizers

Material	Water solubility	pH of solution from dissolving granule
OSP	80 to 85%	1.48
TSP	90 to 95%	1.48
MAP	100%	3.47
DAP	100%	7.98

- a. OSP contains gypsum, more residual contamination.
- b. It is OK to apply MAP to calcareous (high Ca, high pH) soil.
- c. **Do not apply DAP to calcareous soil**; high soil Ca will tie up the HPO_4^{2-} , forming CaHPO_4 , which is relatively unavailable to plants.

7. Soil Phosphorus Reactions

- a. General considerations: Phosphorus reactions and availability in soil:



Phosphorus is generally very **insoluble** in soil; there is only a small concentration of soluble P in the soil solution; there is a whole array of possible soil reactions that take fertilizer P out of solution, making it less available to plants.

- b. Quantity and intensity factors

- i. Quantity factor can be small or large, and can include all forms of P in the soil (including apatite, which is very insoluble).
- ii. Monocalcium phosphate (that form of P in OSP and TSP) is the only calcium-phosphate compound that is water-soluble. Plants absorb either H_2PO_4^- or HPO_4^{2-} .
- iii. The first reaction of monocalcium phosphate (MCP) in the soil is to form dicalcium phosphate, CaHPO_4 , which is somewhat soluble; weak acids do dissolve this material, so it may or may not be available depending on soil conditions.
- iv. The quantity factor is directly related to soil solution P; soil solution P may range from 0.03 to 0.5 ppm; 0.5 ppm is very high; 0.2 ppm is considered adequate or sufficient.
- v. Example: if the soil solution P concentration was 0.25 ppm and citrus needs to take up 80 lbs P_2O_5 per acre, how many times would the quantity factor equilibrium need to turn over to make that amount of P available?

$$(0.25 \text{ ppm P}) * 2.29 = 0.6 \text{ ppm } \text{P}_2\text{O}_5 \text{ or } 1.2 \text{ lb } \text{P}_2\text{O}_5/\text{acre}$$

$$80 \text{ lbs } \text{P}_2\text{O}_5 \text{ required/acre} \div 1.2 \text{ lbs } \text{P}_2\text{O}_5/\text{acre in solution} = 67$$

Thus, the soil solution has to be renewed 67 times by the quantity factor.

- vi. Soil solution P moves by **diffusion** to the root; the distance over which this occurs is 1/8 to 1/4 inch; the P must be this close or it will become tied up before it gets to root; roots must "grow" towards the soil P.
- vii. The temperature influences the release of soil P into solution P because it affects the solubility of the various forms of soil P; thus, P is more available during the warmer seasons.

c. Forms of phosphorus in soil

i. Acid soils (pH less than 5):

(1) If soluble phosphorus is added, it ends up as aluminum or iron phosphate

(AlPO_4 or FePO_4):

(a) $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ Variscite (insoluble)

(b) $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ Strengite (insoluble)

(2) Can have many different combinations of Al, NH_4 , K, Ca, Fe with phosphate.

ii. Calcareous soils (pH greater than 7)

(1) Get transformations of phosphate over time; each transformation results in a compound that is less water soluble than the one before:

(a) $\text{Ca}(\text{H}_2\text{PO}_4)$ Monocalcium phosphate (sol. 15 lbs/100 gal)

(b) CaHPO_4 Dicalcium phosphate (sol. 0.25 lbs/100 gal)

(c) $\text{Ca}_3(\text{PO}_4)_2$ Tricalcium phosphate (sol. 0.02 lbs/100 gal)

(d) $[\text{Ca}_3(\text{PO}_4)_2]_3 \cdot \text{Ca}(\text{OH})_2$ Hydroxy apatite

(e) $[\text{Ca}_3(\text{PO}_4)_2]_3 \cdot \text{CaF}$ Apatite

(2) Time affects P availability to plants; calcium phosphate is converted to less and less available forms of P; if excess Ca is available in the soil, it will react with P.

iii. **Best pH** for soil phosphorus availability is **5.5 to 7.0** (same as the best pH range for agronomic crops).

d. Factors influencing phosphorus retention in soils

i. Nature and amount of soil components

(1) Iron and aluminum compounds (in acid soils) and calcium (in alkaline soils) will precipitate P (phosphorus **fixation**).

(2) Phosphorus retention increases as soil clay concentration increases.

(3) The activity of phosphorus will be lower in soils with a large concentration of highly-reactive calcium carbonate.

ii. Cation effects: Soils containing large amounts of Ca^{2+} can retain greater amounts of phosphorus than if other ions like K^+ or Na^+ are present.

iii. Organic matter: Phosphorus bound to organic matter or in organic compounds can move to greater depths in the soil than can dissolved inorganic phosphorus.

iv. Coated vs. uncoated sands

(1) Some sands are **coated** with iron and aluminum oxides, so they are able to trap and fix phosphorus through formation of Fe/Al phosphates.

(2) **Uncoated** sandy layers (usually white in color) have no mechanism to fix phosphorus, so P is able to leach until encountering a soil layer that can trap it (a clay or spodic layer).