What is Gypsum and What is Its Value for Agriculture?

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What is gypsum?

- Calcium sulfate mineral
- Flat crystals with lozenge-shaped facets
- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum)
- $\text{CaSO}_4$ (anhydrite)
- Specific gravity
  - Gypsum - 2.3
  - Anhydrite - 2.9
Gypsum is a soft mineral

- 1 talc (soft)
- 2 gypsum
- 3 calcite
- 4 fluorspar
- 5 apatite
- 6 feldspar
- 7 quartz
- 8 topaz
- 9 corundum
- 10 diamond (hard)
Origin of Gypsum Beds

- Evaporation of seawater in basins or on salt flats
- 1000 ft column of seawater
- 0.4 ft column of calcium sulfate
- Thick beds possibly produced by leaching thin beds and redeposition in deeper basin
Evaporate 1000 ft. of seawater

Produce 0.4 ft. of gypsum
CaSO$_4$ in Seawater

- Seawater contains 3.5% salts by weight
- Salts in seawater
  - NaCl 77.76% by weight
  - MgCl$_2$ 10.88%
  - MgSO$_4$ 4.74%
  - CaSO$_4$ 3.60%
  - K$_2$SO$_4$ 2.46%
  - MgBr$_2$ 0.22%
  - CaCO$_3$ 0.34%
## World Mined Production

- 90 countries produce 110 million tons/yr

<table>
<thead>
<tr>
<th>Country</th>
<th>Tons (million)</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>17.5</td>
</tr>
<tr>
<td>Iran</td>
<td>11</td>
</tr>
<tr>
<td>Canada</td>
<td>9.5</td>
</tr>
<tr>
<td>Thailand</td>
<td>8</td>
</tr>
<tr>
<td>Spain</td>
<td>7.5</td>
</tr>
<tr>
<td>China</td>
<td>7.5</td>
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</table>
U. S. Crude Gypsum Production

- 46 mines in 20 states
- Leading states
  - Oklahoma
  - Texas
  - Nevada
  - Iowa
  - California
  - Arkansas
  - Indiana
Synthetic Gypsum

- 24% of total U.S. gypsum in 2005
- Increased production will reduce need for mining
- FGD gypsum
- Phosphogypsum – phosphoric acid production
  - 4.5 tons gypsum for each ton of phosphoric acid produced
- Titanogypsum – TiO₂ production
- Citrogypsum – citric acid production
History of Gypsum in Agriculture

- Early Greek and Roman times
- Fertilizer value discovered in Europe in last half of 18th century
  - Germany (1768) – Reverend A. Meyer
  - France (date?) – Men working with alabaster (plaster of paris) noted better grass growth in areas they shook dust from clothing
- Extensive use in Europe in 18th century
History of Gypsum in Agriculture

- Widespread use in America (Pennsylvania region) in late 1700’s
  - Benjamin Franklin demonstration – “This land has been plastered”
  - Richard Peters book – gypsum came from Nova Scotia
Gypsum Use in America – 1780’s

“Agricultural Inquiries on Plaister of Paris”
Richard Peters- Philadelphia (1797)
Collected info from farmers in Pennsylvania
Rates – 2-5 bushels/acre (approx. 210-525 kg/ha)
Best soils – light, sandy, well-drained
Great increase in yield of legumes (double yield of red clover)
Increased drought tolerance of plants (better rooting into subsoil?)
Response when applied wet to oats seed
Gypsum Benefits in Agriculture

Arthur Wallace (1994)

“Use of gypsum on soil where needed can make agriculture more sustainable”

Lists 30 benefits from use of gypsum

Some overlap of functions:

Reclaim sodic soils

Decreases pH of sodic soils
Summary of Gypsum Benefits in Agriculture

- Ca and S source for plant nutrition
- Source of exchangeable Ca
  - Ameliorate subsoil acidity and Al$^{3+}$ toxicity
  - Reclaim sodic soils
- Flocculate clays to improve soil structure
Properties of Gypsum Important in Soil Effects

- Solubility
  - 2.5 g/L or 15 mM
  - Contributes to ionic strength of soil solution

  $\text{Ca}^{++}$ for clay flocculation

  $\text{SO}_4^{--}$ for complex ion formation
### Relative Numbers of Atoms Required by Plants

<table>
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<tr>
<th>Element</th>
<th>Number</th>
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<tr>
<td>Mo</td>
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<tr>
<td>Cu</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>300</td>
</tr>
<tr>
<td>Mn</td>
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<td>B</td>
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<tr>
<td>Cl</td>
<td>3,000</td>
</tr>
<tr>
<td>S</td>
<td>30,000</td>
</tr>
<tr>
<td>P</td>
<td>60,000</td>
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<tr>
<td>Mg</td>
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<tr>
<td>Ca</td>
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<tr>
<td>K</td>
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<tr>
<td>N</td>
<td>1,000,000</td>
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<tr>
<td>O</td>
<td>30,000,000</td>
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<tr>
<td>C</td>
<td>35,000,000</td>
</tr>
<tr>
<td>H</td>
<td>60,000,000</td>
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Source of Ca and S

- Gypsum supplies Ca and S for plant nutrition
- Plants require relatively large amounts of Ca and S
  - Ca – 0.5% shoot dry weight
  - S – 0.1% to 0.5% dry weight for optimal growth
Sulfur in Plant Physiology

- Amino acids methionine and cysteine
  - Proteins
  - Precursors of other sulfur-containing compounds
- Sulfolipids (fatty compounds) in membranes, especially chloroplast membranes
- Nitrogen-fixing enzyme (nitrogenase)
  - 28 S atoms in active site
Causes of Sulfur Deficiencies in Crops

- Shift from low-analysis to high-analysis fertilizers
- High-yielding crop varieties use more S
- Reduced atmospheric S deposition
- Decreased use of S in pesticides
- Declining S reserves in soil due to loss of organic matter (erosion and tillage), leaching, and crop removal
Shift in Phosphorus Fertilizer Use Has Affected Crop S Nutrition

- Main cause of worldwide S deficiencies (based on reviews in 1980’s)
- Ordinary superphosphate
  - 7 – 9.5% P
  - 8 – 10% S as CaSO₄
- Concentrated or triple superphosphate
  - 19 – 23% P
  - <3% S often 0 – 1% S
Reduction in Atmospheric S Deposition

- Increasing in importance as cause for crop S deficiencies
- Annual S deposition at Wooster, OH
  - 34 kg/ha in 1971
  - 19 kg/ha in 2002
S Mineralization in Ohio Soils

- Organic S $\rightarrow$ Plant available S (SO$_4$)
- Assumptions
  - Bulk density $= 1325$ kg/m$^3$
  - 1 kg S per 60 kg C in organic matter
  - 2% of organic S is mineralized each year

- Predict
  - 8.8 kg S/ha are mineralized each year
  (for each 1% of organic C in the top 20 cm layer)
Loss of Organic Matter Decreases Plant Available S

- Loss may be caused by:
  - Tillage – the remaining organic matter may be more resistant to decomposition
  - Erosion

- A decrease from 2% to 1% organic C:
  - Rate of S mineralization decreases
  - 8.8 kg S/ha per year decrease
### Annual Balance of S Available for Crop Growth (kg S per ha per year)

<table>
<thead>
<tr>
<th>Year</th>
<th>S (deposited) + S (mineralized)</th>
<th>S (leached)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>19</td>
<td>8.8</td>
</tr>
<tr>
<td>19</td>
<td>19</td>
<td>17.6</td>
</tr>
</tbody>
</table>

**Crop requirements**
- corn (15)
- alfalfa (30)
Calcium in Plant Physiology

- Required for proper functioning of cell membranes and cell walls
- Needed in large amounts at tips of growing roots and shoots and in developing fruits
- Relatively little Ca is transported in phloem
  - Ca needed by shoot tips is transported in the transpiration stream of xylem
  - Ca needed by root tips comes from soil solution
Gypsum as a Ca Source in Plant Nutrition – Peanut

- Peanuts require supplemental Ca in flowering stage
- Gypsum superior to limestone (known since 1945)
- Common practice uses fine-ground (anhydrite) mined gypsum
Gypsum as a Ca Source in Plant Nutrition – Sugar Cane

- Gypsum was as effective as limestone and ordinary superphosphate on Ca-deficient soils in Hawaii
Gypsum as a Ca Source to Improve Fruit Quality

- Ca supplied by gypsum prevents:
  - blossom end rot of watermelons and tomatoes
  - bitter pit in apples
Ca and Root Growth in Acid Subsoils

- Roots must have adequate Ca for good growth
- Ca is phloem immobile
  - Is not translocated in roots down to subsoil even if topsoil is adequately limed
  - Roots in the subsoil must get Ca from external soil solution
- Ca from surface applied gypsum leaches to subsoil and is absorbed by growing roots
Ca from lime will not reach the subsoil
Amelioration of Subsoil Acidity and Al$^{3+}$ Toxicity

- Surface-applied gypsum leaches down to subsoil
- Ca$^{2+}$ exchanges with Al$^{3+}$
- SO$_4^{2-}$ forms complex ion AlSO$_4^+$ with Al$^{3+}$
- AlSO$_4^+$ is not toxic to plant roots
- Results in increased root growth in the subsoil
Gypsum applied to surface of soil with acidic subsoil

| SO4 | Ca$^{2+}$ | Ca$^{2+}$ | Ca$^{2+}$ | SO4 | Ca$^{2+}$ |

Clay platelet in subsoil
Increased Root Growth into Subsoil

- Increased water absorption
- Increased recovery of N from subsoil
  - Demonstrated in Brazilian soils
  - Improved N-use efficiency
Gypsum and Clay Flocculation

- Reduces soil crusting
- Improves water infiltration
- Improves water transmission (conductivity)
Gypsum Has Two Functions in Reclamation of Sodic Soils

- Properties of sodic soils are dominated by excessive exchangeable Na
- Ca to replace exchangeable Na
- Salt to maintain electrolyte concentration at soil surface
  - Prevents (reduces) clay dispersion and swelling
  - Maintains good surface infiltration rate
Gypsum applied to surface of sodic soil

Clay platelet in sodic soil
Flocculation and Dispersion

Flocculated clay

Clay particle

Ca$^{2+}$

Dispersed clay

HOH

Na+

HOH
Summary of Gypsum Effects

- Specific provision of Ca and S
- Provision of soluble salts