SOIL CHEMICAL RESPONSES TO FGD GYPSUM AND THEIR IMPACT ON CROP YIELDS

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CHEMICAL REACTIONS OF GYPSUM IN SOILS

- Aqueous phase
  - Ion pair formation
  - Ion activities in solution
- Solid phase
  - Cation and anion exchange reactions
  - Mineral dissolution/precipitation reactions
- Chemical effects in dispersion/flocculation
Ions in Soil Solution

Precipitation from Solution

Plant Roots

Cation Exchange

Microorganisms
AQUEOUS PHASE REACTIONS

- Ion pair formation

\[ \text{Al}^{3+} + 3\text{Cl}^- + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{Cl}^- + \text{AlSO}_4^+ + \text{Cl}^- \]

Toxic aluminum

Gypsum

Much less toxic

![Graph showing the relationship between Al\(^{3+}\) activity and soybean tap root length.](image)

![Graph showing the relationship between gypsum concentration and Al\(^{3+}\) activity.](image)

![Graph showing the relationship between gypsum concentration and AlSO\(_4^+\) activity.](image)
Evidence for Ion Pair Detoxification

50 μM Ca 200 μM Al

1250 μM Ca 200 μM Al
SOLID PHASE REACTIONS

• “Self-liming Effect” (Ligand exchange OH $\rightleftharpoons$ 2 SO$_4$)

\[
[\text{Fe,Al}](\text{OH})_2 + \text{CaSO}_4\cdot2\text{H}_2\text{O} \rightarrow [\text{Fe,Al}]\text{OHSO}_4^{-} \cdot \frac{1}{2}\text{Ca}^{2+} + \frac{1}{2}\text{Ca(OH)}_2
\]
Iron/aluminum hydroxide Gypsum New negative charge On surface Hydrated lime

\[
2\text{Al}^{3+} + 3\text{Ca(OH)}_2 \rightarrow 2\text{Al(OH)}_3 + 3\text{Ca}^{2+}
\]
Toxic aluminum Hydrated lime Gibbsite insoluble

• pH increases
• Negative charge increases

(Reeve & Sumner, 1972)
EFFECT OF GYPSUM ON EXCHANGEABLE AI & Ca

Exchangeable Al+H (cmolc/kg)

Exch Ca (cmolc/kg)

- Control
- 4.5 T Gypsum/ac
### Evidence for Self-Liming Effect
(Sumner, 1990)

<table>
<thead>
<tr>
<th>I (mol/L)</th>
<th>CaSO₄</th>
<th>pH</th>
<th>CaCl₂</th>
<th>ΔpH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0300</td>
<td>4.54</td>
<td>4.20</td>
<td></td>
<td>+0.34</td>
</tr>
<tr>
<td>0.0140</td>
<td>4.72</td>
<td>4.44</td>
<td></td>
<td>+0.28</td>
</tr>
<tr>
<td>0.0028</td>
<td>4.95</td>
<td>4.74</td>
<td></td>
<td>+0.21</td>
</tr>
<tr>
<td>0.0014</td>
<td>5.08</td>
<td>4.91</td>
<td></td>
<td>+0.17</td>
</tr>
<tr>
<td>0.0007</td>
<td>5.19</td>
<td>5.06</td>
<td></td>
<td>+0.13</td>
</tr>
</tbody>
</table>
Gypsum Increases Negative Charge
(Sousa et al., 1986)

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Negative charge (cmol_c/kg)</th>
<th>Control</th>
<th>Gypsum (6t/ha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-15</td>
<td>2.87</td>
<td></td>
<td>3.65</td>
</tr>
<tr>
<td>15-30</td>
<td>1.11</td>
<td></td>
<td>1.42</td>
</tr>
<tr>
<td>30-45</td>
<td>1.04</td>
<td></td>
<td>1.15</td>
</tr>
<tr>
<td>45-60</td>
<td>0.74</td>
<td></td>
<td>1.13</td>
</tr>
<tr>
<td>60-75</td>
<td>0.83</td>
<td></td>
<td>1.13</td>
</tr>
<tr>
<td>75-90</td>
<td>0.58</td>
<td></td>
<td>0.91</td>
</tr>
<tr>
<td>90-105</td>
<td>0.40</td>
<td></td>
<td>0.65</td>
</tr>
</tbody>
</table>
Responsive Soils Exhibit “Salt Sorption”

<table>
<thead>
<tr>
<th>Treatment</th>
<th>EC</th>
<th>( \Sigma \text{Cat}_{\text{sol}} )</th>
<th>( \Sigma \text{Cat}_{\text{displ}} )</th>
<th>( \Sigma \text{An}_{\text{sol}} )</th>
<th>( \Sigma \text{An}_{\text{displ}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CaSO}_4 \text{ soln} )</td>
<td>1830</td>
<td>23</td>
<td></td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>( \text{CaSO}_4 + \text{ soil} )</td>
<td>35</td>
<td>2.7</td>
<td>1.2</td>
<td>3.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Test for Gypsum Responsive Soils (Sumner, 1994)

- Measure pH in 0.005 M CaSO$_4$ and 0.005 M CaCl$_2$.
- Calculate $\Delta$ pH (CaSO$_4$ – CaCl$_2$).
- Measure EC of 0.005 M CaSO$_4$ before and after addition of soil.
- Calculate amount of gypsum adsorbed.
- Plot $\Delta$ pH vs gypsum adsorbed.
• Enhanced Ca levels in soil solution
  • Peanuts
  • Tomatoes
  • Cantalopes

– Reduced levels of toxic Al
  • Alfalfa & Alfalfa/Bermuda
  • Cotton
  • Soybeans

– Improved clay flocculation
  • Increased available water
  • Better drainage
  • Reduced subsoil hardpan strength
CROP RESPONSES TO GYPSUM

Enhanced Soluble Ca Levels in Soils
PEANUTS
## PEANUTS

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Yield</th>
<th>SMK*</th>
<th>Value</th>
<th>Seed Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>2.1a</td>
<td>71a</td>
<td>375.12</td>
<td>0.049</td>
</tr>
<tr>
<td>0.5 T FGD gypsum/ac</td>
<td>2.6b</td>
<td>75b</td>
<td>481.96</td>
<td>0.059</td>
</tr>
</tbody>
</table>

*SMK = Sound mature kernels*
Summary of Peanut Responses to Gypsum

Total sites = 85
Positive responses = 70
Predicted by NaNO₃ method = 53
Predicted by Mehlich I method = 11
# Gypsum and Tomatoes

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Yield (T/ac)</th>
<th>Skin Ca (% T/FGD)</th>
<th>Fruit Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>26.5a</td>
<td>0.21a</td>
<td>95</td>
</tr>
<tr>
<td>5 T FGD gypsum/ha</td>
<td>37.5b</td>
<td>0.34b</td>
<td>15</td>
</tr>
</tbody>
</table>

*After storage for 4 weeks @ 4 °C
Effect of Storage at Room Temperature for 4 Weeks - 2006
## GYPSUM AND CANTALOUPES

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Yield</th>
<th>Wt/fruit</th>
<th>Skin Ca</th>
<th>Fruit rejection*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>6.71a</td>
<td>2.12a</td>
<td>1.07a</td>
<td>89</td>
</tr>
<tr>
<td>1.25 T FGD gypsum/ha</td>
<td>10.17b</td>
<td>2.14a</td>
<td>1.24b</td>
<td>15</td>
</tr>
</tbody>
</table>

* After storage for 4 weeks @ 4 °C
Fruit Quality after 4 Weeks of Storage @ 40°F

No Gypsum

0.5 T Gypsum/ac
CROP RESPONSES TO GYPSUM

High Al and Low Ca Cause Root Pruning
CROP RESPONSES TO GYPSUM

Reduced Levels of Toxic Al
Increased levels of soluble Ca
Root Development

Control

Gypsum

Alfalfa
<table>
<thead>
<tr>
<th>Treatment</th>
<th>Hay yield (lb/ac)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cut 1</td>
<td>Cut 2</td>
<td>Cut 3</td>
<td>Cut 4</td>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>1.31</td>
<td>1.00</td>
<td>1.29</td>
<td>0.88</td>
<td>4.48</td>
<td></td>
</tr>
<tr>
<td>4.5 T Gypsum/ac</td>
<td>1.53</td>
<td>1.06</td>
<td>1.38</td>
<td>1.01</td>
<td>4.98</td>
<td></td>
</tr>
</tbody>
</table>
ALFALFA-BERMUDA

Root weight (lb/ac)

Depth (in)

Control
4 T Gypsum/ac
## COTTON RESPONSE TO GYPSUM

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Cotton lint yield (lb/ac)</th>
<th>Value ($)</th>
<th>Cumul. Income ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2000</td>
<td>2001</td>
<td>2002</td>
</tr>
<tr>
<td>Control</td>
<td>309</td>
<td>767</td>
<td>889</td>
</tr>
<tr>
<td>Gypsum</td>
<td>308</td>
<td>985</td>
<td>1113</td>
</tr>
<tr>
<td>Difference</td>
<td>0</td>
<td>218</td>
<td>224</td>
</tr>
<tr>
<td>Value ($)</td>
<td>0</td>
<td>269.50</td>
<td>276.10</td>
</tr>
<tr>
<td>Cumul. Income ($)</td>
<td>-125.00</td>
<td>144.50</td>
<td>420.60</td>
</tr>
</tbody>
</table>
Gypsum Improves Tap Root Penetration
SOYBEANS

4.5 T/acre Gypsum

No Gypsum
CROP RESPONSES TO GYPSUM

Improved Clay Flocculation
GYPSUM IMPROVES PERCOLATION

No gypsum

Gypsum
GYPSUM INCREASES INFILTRATION & PERCOLATION RATES IN CLAY SOIL

Rainfall intensity = 2 in/hr

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Water infiltrated in 20 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>in</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0.42</td>
</tr>
<tr>
<td>Increased available water for crop</td>
<td>0.17 (68%)</td>
</tr>
</tbody>
</table>

Time to ponding

Water infiltrated in 20 min

Control

2 T Gypsum/ac

Steady state Percolation rate

Infiltration rate (mm/hr)

Time (min)
ROOTS & HARDPAN
GYPSUM SOFTENS SUBSOIL HARDPANS & IMPROVES AGGREGATION

![Graph showing cone index (MPa) vs. depth (in) for 4.5 T Gypsum/acre and Control samples.](image)

![Graph showing stable aggregates (%) vs. mesh size (mm) for Depth 18-24 in, with Control and Gypsum samples.](image)
CONCLUSIONS

• Gypsum
  – Supplies essential elements (Ca & S) to crops
  – Reduces levels of toxic Al in subsoils
  – Promotes clay flocculation
  – Softens subsoil hardpans
  – Improves aggregation

• Result
  – Crop yields and quality improved
Thank you for your attention
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