Session B: Fluid Sulfurs
Soil Amendments

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## Western Fertilizer Handbook

Commonly Used Materials and Their Equivalent Amendment Values (Table 10-4)

<table>
<thead>
<tr>
<th>Material 100% Basis</th>
<th>Chemical Formula</th>
<th>Tons of Amendment Equivalent to:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 Ton of Pure Gypsum</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO(_4)\cdot2H_2O</td>
<td>1.00</td>
</tr>
<tr>
<td>Soil Sulfur</td>
<td>S</td>
<td>0.19</td>
</tr>
<tr>
<td>Sulfuric acid (conc.)</td>
<td>H(_2)SO(_4)</td>
<td>0.61</td>
</tr>
<tr>
<td>Ferric sulfate</td>
<td>Fe(_2)(SO(_4))(_3)\cdot9H_2O</td>
<td>1.09</td>
</tr>
<tr>
<td>Lime sulfur 22% S</td>
<td>CaS(_x)</td>
<td>0.68</td>
</tr>
<tr>
<td>Aluminum sulfate</td>
<td>AL(_2)(SO(_4))(_3)\cdot18H_2O</td>
<td>1.29</td>
</tr>
<tr>
<td>Ammonium polysulfide</td>
<td>(NH(_4))(_2)S(_x)</td>
<td>0.37</td>
</tr>
</tbody>
</table>

NH\(_4\) in APS is assumed to neutralize 1.8 lbs of CaCO\(_3\) when a crop is present.
From “Water Penetration Problems in California Soils”

**Soil Amendments**

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Trade Name/ composition</th>
<th>Tons equal to one ton sulfur</th>
<th>Lbs required per acre to replace 1 meq/100g of Na in 6” of soil</th>
<th>Pounds required per acre foot of water to obtain 1 meq/L of calcium</th>
<th>Chemical reaction in calcareous soils</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental sulfur</td>
<td>100 % sulfur</td>
<td>1.00</td>
<td>321</td>
<td>43.6</td>
<td>2S + 3O₂ + 2 CaCO₃ + 4NaX = 2CaX₂ + 2NaSO₄ + 2 CO₂</td>
</tr>
<tr>
<td>Gypsum</td>
<td>100% CaSO₄·2H₂O</td>
<td>5.37</td>
<td>1720</td>
<td>234</td>
<td>CaSO₄ + 2NaX = CaX₂ + Na₂SO₄</td>
</tr>
<tr>
<td>N-Phuric</td>
<td>10% N 55% Sulfuric acid</td>
<td>3.40</td>
<td>1090</td>
<td>148</td>
<td>H₂NCONH₂H₂SO₄ + CaCO₃ + 2NaX = CaX₂ + H₂NCONH₂ + Na₂SO₄ + CO₂ + H₂O</td>
</tr>
<tr>
<td>Ammonium Thiosulfate</td>
<td>Thio-Sul 12-0-0-26S</td>
<td>2.52</td>
<td>807</td>
<td>110</td>
<td>(NH₄)₂S₂O₃ + 2O₂ + CaCO₃ + 2NaX = CaX₂ + (NH₄)₂SO₄ + Na₂SO₄ + CO₂</td>
</tr>
<tr>
<td>Ammonium polysulfide</td>
<td>Nitro-Sul 20-0-0-40S</td>
<td>1.59</td>
<td>510</td>
<td>69.1</td>
<td>(NH₄)₂S₅ + 8O₂ + 4CaCO₃ + 8NaX = 4CaX₂ + (NH₄)₂SO₄ + 4CO₂</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>100% H₂SO₄ᵃ</td>
<td>3.06</td>
<td>981</td>
<td>143</td>
<td>H₂SO₄ + CaCO₃ + 2NaX = CaX₂ + Na₂SO₄ + CO₂ + H₂O</td>
</tr>
</tbody>
</table>

**Modified from Table 4.1**
Purpose of Soil Amendments

- Reduce the amount of sodium in the soil
- Improve water infiltration
- Softens the soil
- Release other nutrients; P, Zn, etc.
- Indirectly provides S nutrition
  - Improves crop quality
  - Improves nitrogen utilization
  - Reduces plant stress
Comparison of Soil Amendments

Elemental Sulfur oxidation

\[ S + 1.5 \text{O}_2 + \text{H}_2\text{O} \xrightarrow{\text{Thiobacillus}} \text{H}_2\text{SO}_4 \]

1 lb of S will produce 3.06 lbs of sulfuric acid in the soil.
Comparison of Soil Amendments

- \( \text{H}_2\text{SO}_4 + \text{CaCO}_3 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2 \)
  
  - 1 lb of sulfuric acid will neutralize 1.02 lbs of \( \text{CaCO}_3 \)
  - 1 lb of elemental S will neutralize 3.125 lbs of \( \text{CaCO}_3 \)
  - \( 3.06 \times 1.02 = 3.125 \) lbs
Ammonium - $\text{NH}_4$

- $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4 + \text{OH}^-$
- $\text{NH}_4 + 3/2\text{O}_2 \rightarrow \text{NO}_2 + \text{H}_2\text{O} + 2\text{H}^+$
- $\text{NO}_2 + 1/2\text{O}_2 \rightarrow \text{NO}_3$
- $2\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{H}^+$

Net products: $\text{NO}_3^- + \text{H}^+ + 2\text{H}_2\text{O}$ or $1 \text{H}^+/1 \text{N}$

Ammonium will neutralize 3.6 lbs of CaCO$_3$ per lb of N

From: “Fluid Fertilizer Science and Technology” by Palgrave
Urea

- \((NH_2)_2CO + H_2O\) \(\xrightarrow{\text{urease}}\) \((NH_4)_2CO_3\)

- \((NH_4)_2CO_3 + 2H_2O\) \(\rightarrow\) \(2NH_4^+ + 2OH^- + CO_2 + H_2O\)

- \(2NH_4^+ + 3O_2\) \(\rightarrow\) \(2NO_2^- + 2H_2O + 4H^+\)

- \(2NO_2^- + O_2\) \(\rightarrow\) \(2NO_3^-\)

- \(2OH^- + 4H^+\) \(\rightarrow\) \(2H_2O + 2H^+\)

Net products: \(2NO_3^- + 2H^+ + 5H_2O\) or \(1 H^+/ 1N\)

Urea will neutralize 3.6 lbs of CaCO\(_3\) per lb of N

From: “Fluid Fertilizer Science and Technology” by Palgrave
Comparison of Soil Amendments

- 1 lb of N as Ammonium (NH4) will neutralize 3.6 lbs of CaCO₃
- 1 lb of N as Urea will neutralize 3.6 lbs of CaCO₃
- 1 lb of elemental sulfur will neutralize 3.12 lbs of CaCO₃
- 1 lb of sulfuric acid will neutralize 1.02 lbs of CaCO₃
Comparison of Soil Amendments

<table>
<thead>
<tr>
<th>Product</th>
<th>Lbs CaCO$_3$ Neutralized</th>
<th>Lbs of Sulfuric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 lb of N as NH$_4$</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>1 lb of N as urea</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>1 lb of elemental S</td>
<td>3.12</td>
<td></td>
</tr>
<tr>
<td>1 lb of sulfuric acid</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>1 lb of S will produce</td>
<td></td>
<td>3.06</td>
</tr>
</tbody>
</table>
Comparison of Soil Amendments
Sulfuric acid

- 1 ton of 93% sulfuric acid has 1860 lbs of acid
- \( 1860 \text{ lbs} \times 1.02 \text{ lbs of CaCO}_3 = 1897 \text{ lbs of CaCO}_3 \text{ neutralized} \)
Comparison of Soil Amendments
N-Phuric 15/49

- N-Phuric is 15% N as urea with 49% sulfuric acid
- 2000 lbs X .49 = 980 lbs of sulfuric acid
- 980 lbs of acid X 1.02 lbs CaCO₃ = 1000 lbs CaCO₃ neutralized
- 300 lbs N as urea X 3.6 lbs CaCO₃ = 1080 lbs of CaCO₃
- Total = 2080 lbs of CaCO₃ plus the value of the nitrogen
15/49 VS Sulfuric Acid

- 15/49 will neutralize 2080
- Sulfuric acid will neutralize 1897
- The difference is in the value of the nitrogen
Comparison of Soil Amendments

N-Phuric 10/55

- N-Phuric is 10% N as urea with 55% sulfuric acid
- 2000 lbs $\times$ 0.55 = 1100 lbs of sulfuric acid
- 1100 lbs of acid $\times$ 1.02 lbs CaCO$_3$ = 1122 lbs CaCO$_3$ neutralized
- 200 lbs N as urea $\times$ 3.6 lbs CaCO$_3$ = 720 lbs of CaCO$_3$
- Total = 1842 lbs of CaCO$_3$ plus the value of the nitrogen
Comparison of Soil Amendments
Lime Sulfur
6.0% Ca and 22% S

- 440 lbs S/ton X 3.12 lbs CaCO$_3$ = 1375 lbs of CaCO$_3$ neutralized per ton of product
- Contains 6.0% calcium equivalent to 300 lbs of calcium carbonate
- Total = 1675 lbs of CaCO$_3$
• 800 lbs S X 3.12 lbs = 2,500 lbs of CaCO$_3$ neutralized.

• One pound of N as ammonium will neutralize 3.6 lbs of CaCO$_3$ = 400 X 3.6 = 1440 lbs.

• 2,500 + 1440 = 3,940 pounds of CaCO$_3$ neutralized per ton of product.
APS vs Sulfuric acid

• One ton of APS will neutralize 3,940 pounds of CaCO₃ (lime).
• One ton of 93% sulfuric acid will neutralize 1,897 pounds of CaCO₃.
• 3,937 / 1,897 = 2.074 tons: It will take this much sulfuric acid to equal the acidity developed by APS.
# APS vs Sulfuric Acid

<table>
<thead>
<tr>
<th>Product</th>
<th>Sulfuric Acid 93%</th>
<th>APS 20-0-0-40S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lbs/gal</td>
<td>15.3</td>
<td>9.4</td>
</tr>
<tr>
<td>Gal/ton</td>
<td>130.7</td>
<td>212</td>
</tr>
<tr>
<td>Amount of calcium carbonate neutralized/ton</td>
<td>1,897 lbs</td>
<td>3,940 lbs*</td>
</tr>
<tr>
<td>Lbs of CaCO$_3$ neutralized/gal</td>
<td>14.5</td>
<td>18.5</td>
</tr>
<tr>
<td>Lbs nitrogen/gal</td>
<td>0</td>
<td>1.9</td>
</tr>
</tbody>
</table>

- One pound of ammonium is assumed to neutralize 3.6 lbs of CaCO$_3$ when no crop is present.
- One pound of elemental sulfur will produce 3.125 pounds of sulfuric acid.
APS vs Sulfuric acid

- One ton of APS is equal to the acidity of 2.074 tons of 93% acid.
- Sulfuric acid at $____ /ton X 2.074 = $______
- One ton of APS contains 400 pounds of ammonium nitrogen (NH4) at $____ /lb or $ _____ /ton.
- One ton of APS is equal to $ _____worth of sulfuric acid plus $ _____.00 of nitrogen.
## Comparison of Soil Amendments Potential Acidity

<table>
<thead>
<tr>
<th>Product</th>
<th>Lbs of CaCO₃ neutralized/ton</th>
<th>Lbs of CaCO₃ neutralized/gal</th>
<th>Lbs CaCO₃ neutralized/100 lbs of product</th>
<th>N</th>
<th>Lbs/ton N</th>
<th>Application</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.) Sulfuric acid 93%</td>
<td>1897</td>
<td>14.5</td>
<td>95</td>
<td>No</td>
<td>0</td>
<td>Drip, flood</td>
<td>Fast acting</td>
</tr>
<tr>
<td>2.) N-Phuric 15/49</td>
<td>2080</td>
<td>13.2</td>
<td>104</td>
<td>Yes</td>
<td>300</td>
<td>Drip, flood</td>
<td>Fast acting plus the value of the nitrogen</td>
</tr>
<tr>
<td>3.) N-Phuric 10/55</td>
<td>1842</td>
<td>11.8</td>
<td>92</td>
<td>Yes</td>
<td>200</td>
<td>Drip, flood</td>
<td>Relatively fast acting plus value of the nitrogen</td>
</tr>
<tr>
<td>4.) Lime Sulfur 22% S</td>
<td>1675*</td>
<td>8.9</td>
<td>84</td>
<td>No</td>
<td>0</td>
<td>Flood</td>
<td>Relatively fast acting within 2 to 3 weeks plus soluble calcium</td>
</tr>
<tr>
<td>5.) APS 20-0-0-40S</td>
<td>3940</td>
<td>19</td>
<td>197</td>
<td>Yes</td>
<td>400</td>
<td>Flood</td>
<td>Relatively fast acting within 2 to 3 weeks plus the value of the nitrogen</td>
</tr>
</tbody>
</table>

* Corrected for soluble calcium content
Soil Amendments

• Are good products for what they are intended

• They are not liquid jack hammers or liquid plows

• Restricted layer – should use mechanical method to first break up the layer then use a soil amendment

• Time the application to take advantage of any fertilizer value
Soil Amendments

• 1% CaCO$_3$ in the soil is equivalent to 20,000 lbs of lime in 6 inches of soil
• Soil amendments will help flush out sodium and/or free up other nutrients
• Phosphorus and zinc are often precipitated on calcium carbonate crystals in the soil.
Myths

• Gypsum lowers soil pH.
• Gypsum does not lower soil pH. All of the sulfur in gypsum is already oxidized to the sulfate form – $\text{SO}_4$.
Myths

• The sulfur in sulfuric acid is the element that lowers the soil pH.

• Sulfuric acid: All of the acidity in sulfuric acid is due to the hydrogen ions and not the sulfur – $\text{H}_2\text{SO}_4$. 
Acid Forming Fertilizers

Some Commonly used fertilizers

- UAN 32
- Ammonium sulfate
- Ammonium thiosulfate
- Potassium thiosulfate
- Calcium thiosulfate
- Ammonium nitrate
Ammonium sulfate

\[(\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow 2\text{NH}_4 + \text{SO}_4 + \text{H}_2\text{O}\]

\[2\text{NH}_4 + 3\text{O}_2 \rightarrow 2\text{NO}_2 + 2\text{H}_2\text{O} + 4\text{H}^+\]

\[2\text{NO}_2 + \text{O}_2 \rightarrow 2\text{NO}_3\]

Since there is no hydroxyl produced there is a net production of \(2\text{H}^+\) per unit of N.

So, one lb of N as ammonium sulfate will neutralize 7.2 lbs of \(\text{CaCO}_3\).
### Acid Forming Fertilizers Potential Acidity

<table>
<thead>
<tr>
<th>Fertilizer</th>
<th>Lbs CaCO$_3$ neutralized / ton</th>
<th>Lbs CaCO$_3$ neutralized / gal</th>
<th>Lbs CaCO$_3$ neutralized / 100 lbs product</th>
</tr>
</thead>
<tbody>
<tr>
<td>UAN 32$^1$</td>
<td>2304</td>
<td>12.7</td>
<td>115</td>
</tr>
<tr>
<td>NH$_4$NO$_3$ (dry) 34% N</td>
<td>2448</td>
<td></td>
<td>122</td>
</tr>
<tr>
<td>Ammonium sulfate (dry) 21-0-0-24S</td>
<td>3024$^4$</td>
<td></td>
<td>151</td>
</tr>
<tr>
<td>Ammonium thiosulfate 12-0-0-26S</td>
<td>1680$^2$</td>
<td>9.3</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>2480$^3$</td>
<td>13.7</td>
<td>124</td>
</tr>
<tr>
<td>Potassium thiosulfate 0-0-25-17S</td>
<td>531</td>
<td>3.2</td>
<td>27</td>
</tr>
<tr>
<td>Calcium thiosulfate 6% Ca, 10%S</td>
<td>313</td>
<td>1.6</td>
<td>16</td>
</tr>
</tbody>
</table>

1, 2. From “Fluid Fertilizer Science and Technology” pp:437-438  
3. From “Water Penetration Problems in California Soils”  
4. Ammonium sulfate does not form hydroxide (OH) so 1 lb of N will neutralize 7.2 lbs of CaCO$_3$. 
Sulfur Deficiency in California?
Sulfate Ion Wet Deposition
1985

Sulfate as $SO_4^{2-}$ (kg/ha)

- ≤ 3
- 3 - 6
- 6 - 9
- 9 - 12
- 12 - 15
- 15 - 18
- 18 - 21
- 21 - 24
- 24 - 27
- > 27

1984 1985 1986
• Sulfur emissions from industrial activities has been reduced considerably, the fact still remains that 70% of the total S compounds in the atmosphere are not man made.
### Estimate of Available Sulfur from Various Manures

<table>
<thead>
<tr>
<th>Manure</th>
<th>Solid</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total Lbs/ton</td>
<td>Available Lbs/ton</td>
</tr>
<tr>
<td>Beef</td>
<td>1.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Dairy</td>
<td>1.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Swine</td>
<td>2.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Poultry</td>
<td>3.3</td>
<td>1.8</td>
</tr>
</tbody>
</table>

From: Crop and Soils 4-1
Sulfur Requirement

- Sulfur is required by crops such as beans, corn, wheat and potatoes in amounts about the same as phosphorus

- Alfalfa, cabbage and turnips contain larger amounts of S than P in their tissue

- N/S ratio in plant tissue ranges from 10:1 to 15:1 for many crops
Sulfur Nutrition

• Is essential for chlorophyll synthesis (but not a part of it)

• Enters into the composition of vitamins (co-enzyme A, Biotin, Thiomin in Vit B1)

• Is required for some lipids in membranes
  – Important for storage onions

• Has a key role in stress resistance

• Aids in protein formation and seed production

• Promotes nodulation for N fixation by legumes

• All plant enzymes require S, including the one for fixing CO2
  – In one study, alfalfa leaves fixed CO$_2$ at a rate 25% greater than from S deficient plants
Sulfur in the Plant

- Sulfur deficiency decreases stem and root diameter
- Sulfur deficiency delays maturity of the plant
- Essential in Nitrogen Utilization in the plant
Effects of Sulfur Applied in Furrow Irrigation on Cotton Yield

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Rate/ac</th>
<th>Yield</th>
<th>Increase over check</th>
<th>Increase Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Check</td>
<td></td>
<td>1294</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2) S</td>
<td>10 lbs</td>
<td>1366</td>
<td>+72</td>
<td>$37.00</td>
</tr>
<tr>
<td>3) S</td>
<td>20 lbs</td>
<td>1394</td>
<td>+100</td>
<td>$52.00</td>
</tr>
<tr>
<td>4) S</td>
<td>30 lbs</td>
<td>1477</td>
<td>+183</td>
<td>$95.00</td>
</tr>
</tbody>
</table>

Cotton pricing: $0.52/lb
Application timing: Starting at second irrigation – May 28th, 2 weeks later, 2 weeks later.
Research: Dr. Bill Weir, U.C. Davis
Balanced nutrition

- Plants need a balanced ratio of nutrients.
- Rates depend on the type of plant, its specific nutrient needs, and the stage of growth the application is being made.
Would you ring this door bell?
Acid Soils in California

• Soil surface has become acidic in some areas
  – East side of the San Joaquin Valley
  – Under drippers and micro-sprinklers
  – Near drip tube emitters

• Basic type of fertilizers can be used when the problem is not severe

• Lime is the only cost effective method for correcting low pH soils
  – Must be incorporated to be effective
  – May have an effect on nitrogen fertilizer application

• Soil sampling:
  – 0-3 inch sample
  – 3-12 inch sample