SOILS AND FERTILIZERS
MODULE 9
LIMING
REACTIONS OF CALCIUM, MAGNESIUM, AND SULFUR WITH SOILS

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1. Calcium
   a. Role in plants - A part of all plant structures (cell walls, etc.); a deficiency is manifested as a weakening of cell structure, e.g. petiole collapse.
   b. Amount of Ca required varies with plant species; range in plant tissue of 0.6 to 4%; legumes require more than average because Rhizobia need Ca for nodule formation.
   c. Calcium is relatively immobile in plants; it does not move from old to new leaves; plants require a continuous supply of Ca from soil and/or water for optimum growth.
   d. If a calcium deficiency occurs, it is difficult to identify until it becomes critical. Deficiency symptoms occur in the young leaves and growing points because Ca is immobile in plant tissues.
   e. Soil calcium
      i. Calcium is relatively abundant in soils and rarely limits crop production.
      ii. Calcium can exist:
         (1) as soil solution Ca^{2+}
         (2) on the cation exchange complex as Ca^{2+}
         (3) in the solid form as
            (a) carbonates - $CaCO_3$
            (b) sulfates - $CaSO_4$ (gypsum)
            (c) phosphates - $Ca(H_2PO_4)_2$, $CaHPO_4$, $Ca_3(PO_4)_2$
      iii. In soils not containing calcium carbonate, dolomite, or gypsum, the amount of Ca in the soil solution depends on the amount of exchangeable Ca present.
      iv. Factors affecting availability of Ca to plants:
         (1) Total calcium supply.
         (2) Soil pH.
         (3) Cation exchange capacity.
         (4) Percent calcium saturation of soil colloids.
         (5) Type of soil colloid.
         (6) Ratio of calcium to other cations in solution.
      v. Soil levels of Ca required for plant growth are difficult to pinpoint; there is no definitive soil analysis for Ca.
      vi. Mehlich 1 extractant (also known as the double-acid extractant) has the ability to dissolve dicalcium phosphate, which may or may not be plant-available; this reserve form of P can build up in the soil.
      vii. If a Mehlich 1 soil extraction shows 300 to 400 ppm Ca in the soil, this is usually sufficient for optimum plant growth.

f. Calcium sources

Source	Chemical formula	Calcium carbonate equiv. (pure form)
Burned lime (Quicklime)	CaO	179
Hydrated lime (Builder's lime)	$Ca(OH)_2$	135
Dolomitic lime	$CaCO_3 \bullet MgCO_3$	109
Calcitic lime	$CaCO_3$	100
Basic slag (by-product)	$CaSiO_3$	80
Marl (soft carbonates)	$CaCO_3$	70 to 90
Gypsum	$CaSO_4$	0
Calcium nitrate	$Ca(NO_3)_2$	---
Ordinary superphosphate	$Ca(H_2PO_4)_2$ + $CaSO_4$	---
Concentrated superphosphate	$Ca(H_2PO_4)_2$	---

i. Burned and hydrated lime are very caustic; they should be used if an immediate soil pH change is needed; must be very careful with their use because they burn both people and plants if not quickly rinsed off; effect of these sources does not last very long due to their high water solubility.
ii. The definition of **lime** is a material that **supplies calcium** and **neutralizes acidity**; thus, gypsum is not a liming material.
iii. Twice as much dolomitic lime is used in Florida compared with calcitic lime.

2. Benefits of Liming Acid Soils
   a. Increase soil pH to increase availability of some nutrients, especially P.
   b. Increase exchangeable Ca^{2+} and Mg^{2+}.
   c. Increase root growth and development.
   d. Provide more favorable environment for soil microorganisms.
   e. Reduce toxic concentrations of Al, Fe, and Mn.
   f. Improve performance of some herbicides.

3. Soil Reactions with Lime
   a. Calcium carbonate is usually supplied as a liming material to neutralize soil acidity; in water, calcium carbonate behaves as follows:

Dissolution: $CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^-$

Neutralization: H^+ (soil solution) + $OH^- \rightarrow H_2O$
H^+ (soil solution) + $HCO_3^- \rightarrow H_2O + CO_2$ (gas)

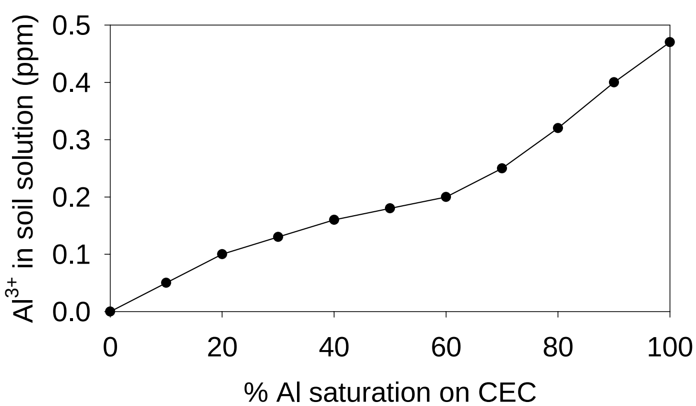
Source of H^+ in soils containing aluminum: $Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$

b. H^+ in an organic soil does not originate from aluminum because the aluminum is not chemically active (organic matter ties it up) or not present.
c. Other sources of acidity in soils:
    i. Plant root exudation of H^+.
    ii. Crop removal or leaching of Ca^{2+}, Mg^{2+}, or K^+.
    iii. Application of acid-forming fertilizers.
    iv. Acid rain.
d. The soil pH increases because of the neutralization of the H^+ ions by OH^- (hydroxyl) ions, **not** because of the addition of Ca.
e. The origin of acidity in mineral soils is primarily due to Al^{3+}, and some H^+; alumino-silicate clays weather to produce $Al(OH)_3$, which is gibbsite; this is the end product of soil weathering.
f. By adding lime, Ca^{2+} replaces Al^{3+} on the exchange sites by mass action; the Al is taken out of solution, water is formed, and CO_2 is evolved.
g. If $CaCO_3$ is added to water, the pH will rise to 8.3 but no higher; thus, in soils where $CaCO_3$ dominates, the pH should never be higher than 8.3 unless sodium (Na) is present; if Na is present, the pH can go higher.
h. If $Ca(OH)_2$ is used as the liming material, the pH can go up to 10.5; if CaO is used, the pH can go to 11 to 12; thus, the amount applied must be monitored very carefully if these materials are used.

4. Effects of aluminum
    a. Aluminum saturation as a percentage of CEC:

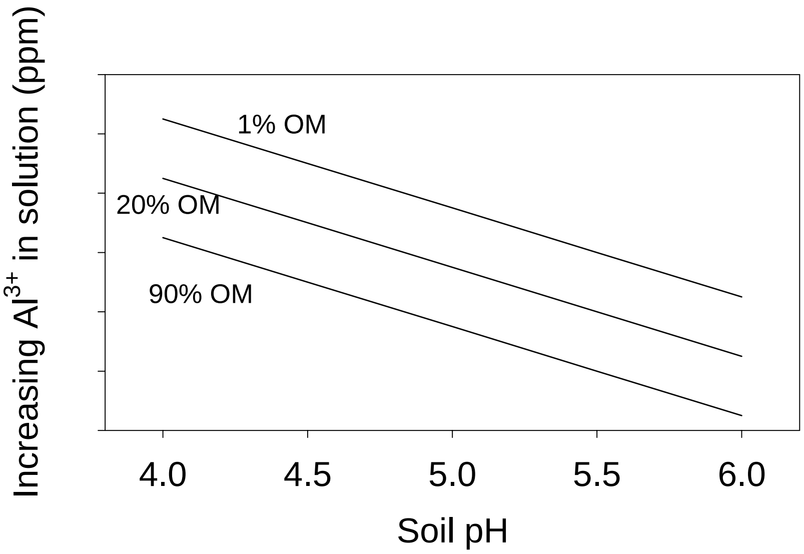
       % Al saturation = (Al) ÷ (Al+Ca+Mg) on the cation exchange complex.

       The cations can be extracted off of the CEC by mixing the soil with a KCl solution; the Al, Ca, and Mg are then analyzed for their concentration in the extracting solution. An example: If the extracted amounts were 2.0 meq Al, 1.0 meq Ca, and 0.5 meq Mg per 100 g soil, an estimate of the soil's cation exchange capacity (CEC) would be 3.5 meq of positive charge per 100 g of soil. The %Al saturation is 2 ÷ 3.5 = 57%. This soil may have a problem with Al in solution.
    b. Soil solution Al as related to % Al saturation:



   i. Al in solution is highly toxic to root growth; if 0.2 ppm Al exists in the soil solution, root growth will be limited and the root system will be ineffective for absorption of water and nutrients.
   ii. When the %Al on the exchange complex reaches about 50%, plants cannot be grown successfully.

c. Lime response in organic soils

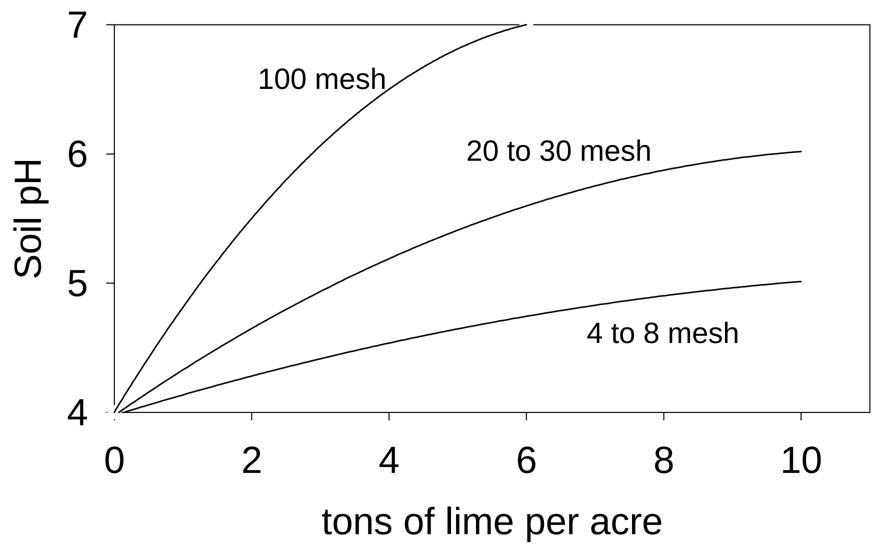


   i. Organic matter complexes Al, thus have less in solution at any given pH as the OM content of the soil increases.
   ii. In organic soils, there is little Al in solution even at very low pH.
   iii. Clay is a source of Al, and there is very little clay in organic soils.
   iv. There is no yield response in organic soils when they are limed above pH 4.5 because there is no Al to cause problems.

5. Determination of Lime Requirement
   a. The most scientific way is to run a lime incubation experiment, where increments of lime are added to soil samples. The samples are incubated for several months, and the new pH is measured; this takes too long to be of practical use.
   b. Chemical methods can be used in a soils lab which are much faster, but somewhat less accurate than incubation experiments.
      i. First, the soil pH in water is measured.
      ii. Next, a buffer solution with a known pH is added to a second soil sample (in Florida, the Adams-Evans buffer is used, which has a pH of 7.2).
      iii. The lime requirement is indicated by how much the soil is able to lower the pH of the buffer.
      iv. The lime recommended using the Adams-Evans test is that amount required to raise the soil pH to 6.5.
   c. A drawback to using the Adams-Evans buffer is that it was designed for soils with CEC > 5 meq/100 g; most mineral soils in Florida have CEC values less than 2 meq/100 g.

d. The use of lime in Florida has dropped due to the use of high-pH irrigation water (contains dissolved calcium carbonate).

6. Effect of Lime Rate and Particle Size on Soil pH



In Florida, if lime has a particle size of larger than about 60 mesh, the overall effectiveness is poor for an immediate growing season

7. Applying Lime
   a. Liming recommendations are based on $CaCO_3$ as the liming material.
   b. Dolomitic lime has a slightly higher neutralization equivalent due to the presence of Mg (atomic weight of Mg is lower than Ca).
   c. Neutralization equivalent indicates the amount of the material that would have to be applied to get the same neutralization that a given amount of $CaCO_3$ would apply.
   d. Example: Want to use hydrated lime in place of calcitic lime:

      100 lbs $CaCO_3$ ÷ 135 (neutralizing equivalent for hydrated lime) = 74 lbs

      Thus, 74 lbs of hydrated lime will provide the same amount of neutralization provided by 100 lbs $CaCO_3$.

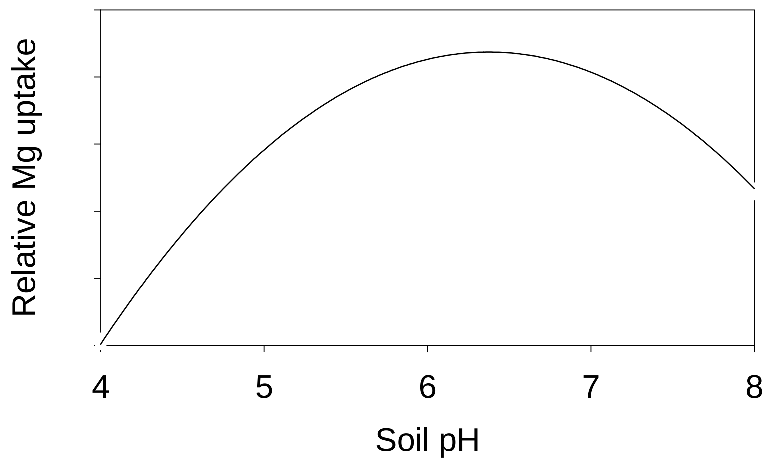
   e. Gypsum is **not** a liming material because it does **not** neutralize any soil acidity.

8. Regulations Governing Liming Material in Florida
   a. Particle size - Calcitic and dolomitic limestones shall be ground so that:
      i. Not less than 90% passes an 8-mesh sieve.
      ii. Not less than 80% passes a 20-mesh sieve.
      iii. Not less than 50% passes a 50-mesh sieve.
      Particle size is related to speed of reaction in the soil.

b. Moisture content - Limestone shall contain a maximum of 10% moisture.
c. Chemical specifications:
   i. Standard **agricultural liming material** shall have a minimum neutralizing value of 90% calcium carbonate equivalence (CCE):
      (1) Standard calcitic liming material - minimum of 86% Ca expressed as $CaCO_3$.
      (2) Standard dolomitic liming material - minimum of 36% Mg expressed as $MgCO_3$.
   ii. Non**-standard materials** (must have 70% CCE):
      (1) Calcitic limestone - minimum of 70% Ca expressed as $CaCO_3$; example would be marl.
      (2) Dolomitic limestone - minimum of 30% Mg expressed as $MgCO_3$.
      (3) Calcium-magnesium limestone: any Ca-Mg blend that has at least 75% CCE.
   iii. "**Liming** Materials" are higher grade than "Limestones."
   iv. **Lime** sources in Florida are soft pebble lime that provides a fast response; lime from areas such as Virginia is hard rock and reacts slower.
d. Labeling of limestone - what is required:
   i. **Calcium** carbonate equivalence.
   ii. **Calcium** as $CaCO_3$.
   iii. **Magnesium** as $MgCO_3$ (if limestone is dolomitic).
   iv. **Passing** 8 mesh sieve, not less than _____.
   v. **Passing** 20 mesh sieve, not less than _____.
   vi. **Passing** 50 mesh sieve, not less than _____.
   vii. **Moisture**, not more than _____.
   viii. This product requires _____ lbs to be equal to 1 ton of standard liming material.

9. Magnesium
   a. Role - Magnesium is a component of chlorophyll, thus a deficiency results in a yellowing of plant foliage.
   b. Plant needs
      i. Legumes require more Mg than non-legumes; the Mg is needed by the Rhizobia for the fixation of atmospheric N; the nitrogenase enzyme (needed to convert NO_3 to NH_4) is activated by Mg.
      ii. Plant content of Mg is species-dependent; usually leaf tissue is 0.1 to 0.2% Mg (spinach can have up to 4%); need 4:1 to 5:1 ratio of Ca:Mg in the soil for adequate plant growth; if the ratio exceeds 10:1, Mg deficiency is possible.
   c. Primary sources in soil:
      i. Primary and secondary minerals.
      ii. Decomposition of plant residues.
      iii. Dolomite if soil has been limed with this material.
   d. Magnesium deficiencies
      i. Deficiency is usually associated with sandy soils with pH 5 or less, which are highly saturated with Al.

ii. Can also see Mg deficiency in calcareous soils with inherently low Mg levels, or soils receiving high rates of lime which is low in Mg.
iii. Mg deficiency may be induced by high potassium fertilizer rates.
iv. Soil pH influences Mg status:



If clover that has been over-fertilized with K is fed to cattle, grass tetany may occur in the animals (a Mg deficiency).

e. Sources of magnesium
   i. Potassium-magnesium sulfate: K_2SO_4 + $MgSO_4$ (22% K, 20% S, 18% Mg).
   ii. Dolomite: 9 to 12% Mg. This is the primary source of Mg when it is applied as a soil amendment to raise soil pH.
   iii. Epsom salts: $MgSO_4$ Common name is "Emjeo."

10. Sulfur
   a. Background
      i. Role: primary building block for three amino acids in plants.
      ii. S concentration in plants is similar to P concentration: the critical minimum leaf tissue concentration is about 0.10%.
      iii. S is supplied "naturally" from a number of different sources, including the environment (atmosphere) via air and rain (S is responsible for some acid rain), soil organic matter, and as a component of other fertilizers like ordinary superphosphate (which contains $CaSO_4$).
      iv. If an agricultural area is downwind of an industrial area, it may not need to be supplied with fertilizer S (gets into air from burning of S-containing coal).
      v. Increased use of diammonium phosphate (DAP) or concentrated superphosphate (CSP), which contain no S, as phosphorus fertilizer over ordinary superphosphate (OSP, which contains gypsum) has led to sulfur deficiencies in some areas.
      vi. S deficiency looks like N deficiency; difficult to tell the difference except by leaf analysis.

b. Forms of sulfur in soils
   i. Most of the sulfur in surface soils is in the organic form; sulfur transformations between organic and inorganic forms are similar to those that occur with N.
   ii. Organic S: The ratio of N to S in soil organic matter is about 10:1.2. Roughly have about 1/30 as much S as N in plant tissue. Organic S is oxidized to the available SO_4^{2-} form in warm, well-aerated soils (very similar to the ammonification reaction that changes organic N to plant-available NH_4^+).
   iii. Inorganic S: Water-soluble S is present in the soil solution as sulfate (SO_4^{2-}) at concentrations of 3 to 5 ppm; sulfate reaches plant roots via mass flow and diffusion. Most soils contain less than 25% of their total S content in the inorganic form.
   iv. Adsorbed S: This is an important fraction in highly-weathered soils of the southeast USA, and contributes significantly to the S needs of plants growing in these soils because the adsorbed S is usually readily available.
   v. Sulfides (S^{2-}): Under anaerobic conditions in waterlogged soils, there may be accumulations of H_2S formed by the decay of organic matter; sulfides are present in most spodic horizons in flatwoods areas; can tell of their presence by a rotten-egg odor.

c. Location of S in the soil
   i. Difficult to relate plant response to soil S level in the surface only; need to look at both topsoil and subsoil to determine need.
   ii. Few soil testing laboratories will test soils for S because it is not easy to do.
   iii. S is found within the organic hardpan of Spodosols (flatwoods soils); the spodic may occur at different depths. For example, the hardpan is found 24" deep in a Myakka soil, but is more than 30" deep in an Immokalee soil. Depending on hardpan depth, may or may not have a sulfur deficiency.

d. Sources of sulfur
   i. Weathering of rocks: Elemental S in rocks oxidizes to SO_4.
   ii. Atmospheric deposition due to air pollution: In rural areas, might receive only 1 lb of S per acre per year; in metropolitan areas, might receive 100 lbs of S per acre per year.
   iii. Fertilizer sources:
      (1) Ammonium sulfate $(NH_4)_2SO_4$ (24% S)
      (2) Potassium sulfate K_2SO_4 (18% S)
      (3) Ammonium thiosulfate $(NH_4)_2S_2O_3$ (26% S)
      (4) Potassium thiosulfate $K_2S_2O_3$ (17% S)
      (5) Magnesium sulfate $MgSO_4$ (13% S)
      (6) Potassium-magnesium sulfate (22% S)
      (7) Ordinary superphosphate (14% S) (not as common anymore)
      (8) Gypsum $CaSO_4$ (18% S)
      (9) Elemental sulfur
   iv. Organic matter

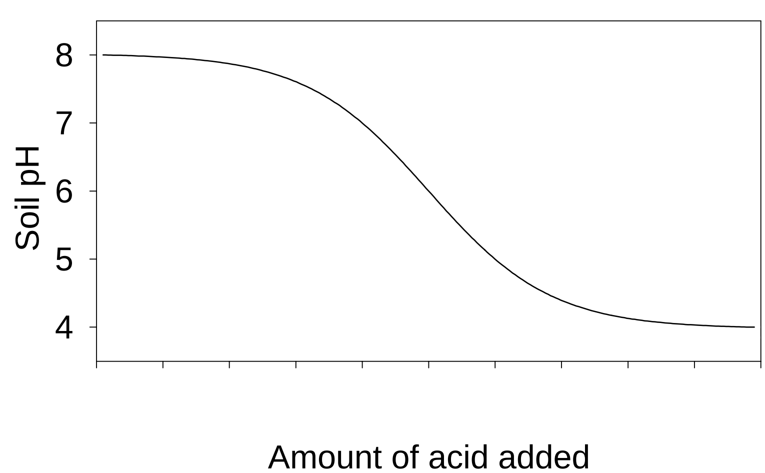
e. Acidification of soil using sulfur

   i. Reaction is caused by soil microflora, e.g. Thiobacilli; these bacteria will oxidize elemental S to form sulfuric acid, gaining energy for themselves in the process:

$$\underset{\text{elemental sulfur}}{\underset{\uparrow}{S}} + CO_2 + O_2 + H_2O \rightarrow \underset{\text{carbohydrate}}{\underset{\uparrow}{[CH_2O]}} + 2\ \underset{\text{sulfuric acid}}{\underset{\uparrow}{\underline{H^{\pm} + SO_4^{2-}}}}$$

   ii. Get increased oxidation of S with increasing temperature, increasing soil moisture (up to field capacity), and increasing aeration; get increased oxidation with decreasing particle size of sulfur material.

   iii. It is sometimes necessary to acidulate the soil to grow certain plant species or counteract high carbonate levels in soil; pound for pound, elemental S is the most effective of the soil acidulents; other acidulents include sulfuric acid, aluminum or iron sulfate, ammonium thiosulfate, potassium thiosulfate, and high-ammonium N fertilizers; theoretically, 1000 lbs of limestone ($CaCO_3$) could be neutralized by 320 lbs of elemental sulfur if it were completely transformed to sulfuric acid by soil microorganisms; the only way to tell how much S to add to decrease the soil pH a given amount is by measuring the soil buffer curve:



Some soils contain too much $CaCO_3$ to economically neutralize; an alternative to solving this problem might be banded applications of acidulating material.