Chapter 8: Acid Soils

I. Development of soil acidity

A. Release of $H^+$ from nitrification, $S$ oxidation, Al hydrolysis, organic matter.

Soil acidity can arise from several processes, some processes are biologically mediated, others are purely chemical.

1.) Nitrification

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

In this process, $\text{NH}_4^+$ is converted to $\text{NO}_3^-$ by nitrifying bacteria, and $\text{H}^+$ is produced as a by-product.

2.) Oxidation of pyrite ($\text{Fe}_2\text{S}$) and elemental $S$

$$\text{S} + 3/2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+$$

$$2\text{FeS}_2 + 7\text{H}_2\text{O} + 7\frac{1}{2}\text{O}_2 \rightarrow \text{SO}_4^{2-} + 8\text{H}^+ + 2\text{Fe(OH)}_3$$

These reactions often occur in strip mine soils where pyrite is abundant or in acid sulfate soils, sometimes called cat clays. When these soils are drained and exposed to oxidation, pH values as low as 2 have been observed.

3.) Hydrolysis of Al

Trivalent $\text{Al}^{3+}$ hydrolyzes easily to form monomeric and polymeric hydroxyaluminum complexes and produces $\text{H}^+$.

$$\text{Al}^{3+} + 6\text{H}_2\text{O} \rightarrow \text{Al(H}_2\text{O)}_6^{3+} \leftrightarrow \text{Al(OH)}(\text{H}_2\text{O})_5^{2+} + \text{H}^+$$

4.) Oxidation of organic matter

Similarly, the oxidation of organic matter to form humus also produces $\text{H}^+$. This reaction is important, especially in forest soils.

$$\text{R-COOH} \leftrightarrow \text{R-COO}^- + \text{H}^+.$$

B. Leaching of bases ($\text{Ca}^{2+}$, $\text{K}^+$, $\text{Mg}^{2+}$) from soil profile.

Such cations as $\text{Ca}^{2+}$, $\text{K}^+$, $\text{Mg}^{2+}$ would gradually move down the soil profile where rainfall is greater than evapo-transpiration. Since the electrical neutrality must be maintained at all times, $\text{H}^+$ and $\text{Al}^{3+}$ will replace these basic cations. Therefore, acidity of
soils will increase. The acidity caused by leaching is most severe where the rainfall is high and soils are sandy such as in the southeast region of the US.

II. Titration of clays

A. Instability of H-saturated clays

Hydrogen-saturated soils and clays prepared by strong acid leaching or dialysis decompose rapidly to Al and iron saturated materials.

Ex: If you look at table 8.1, it took less than 1 day for half of exchangeable H of a H saturated montmorillonite to decompose or convert to Al (at 30°C), at higher temp. (ex: 80°C) this reaction took only 30 minutes. For kaolinite, the time is a little bit longer but eventually, H-saturated kaolinite is also decomposed.

$$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \rightleftharpoons 2\text{Al}^{3+} + 2\text{Si(OH)}_4 + \text{H}_2\text{O}$$

\[\text{TABLE 8.1}\]
Rates of Decomposition of Hydrogen-Saturated Layer Silicates, Showing the Time for One Half of the Exchangeable Hydrogen to the Loss at Various Temperatures*

<table>
<thead>
<tr>
<th>LAYER SILICATE</th>
<th>RATES OF DECOMPOSITION (HALF-TIME)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
</tr>
<tr>
<td>Montmorillonite (Utah bentonite)</td>
<td>1080</td>
</tr>
<tr>
<td>Montmorillonite (Volclay bentonite)</td>
<td>—</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>—</td>
</tr>
</tbody>
</table>


B. Nature of acid soils. Al-saturated clays.

Research in the early 1950’s by Russians and Americans has shown that most H-saturated soils are in reality saturated with aluminum. For example, if you look at figure 8.1, you see that curve 1, which is a freshly prepared H-saturated montmorillonite, looks very much like a titration curve of a strong acid. Ex: the titration curve of HCl by NaOH. Meanwhile if the H-saturated montmorillonite was allowed to dry before being titrated with a strong base, then the titration curve looks like curve (2) or (3) that is typical of a weak acid titration curve (such as H$_3$PO$_4$ titration curve).
III. Aluminum Hydrolysis

A. Monomeric hydroxyaluminum species: Al(OH)$^{2+}$, Al(OH)$_2^+$, Al(OH)$_3$, Al(OH)$_4^-$

The chemical behavior of acid soils is closely related to the solution chemistry of aluminum. Trivalent aluminum hydrolyses to monomeric and polymeric hydroxyaluminum complexes. For example:

\[
\begin{align*}
\text{Al}^{3+} + 1 \text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}^{2+} + \text{H}^+ & \text{low pH} \\
\text{Al}^{3+} + 2 \text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}_2^+ + 2\text{H}^+ \\
\text{Al}^{3+} + 3 \text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}_3 + 3\text{H}^+ \\
\text{Al}^{3+} + 4\text{H}_2\text{O} & \rightleftharpoons \text{Al(OH)}_4^- + 4\text{H}^+ & \text{high pH}
\end{align*}
\]

All the above products: Al(OH)$^{2+}$, Al(OH)$_2^+$, Al(OH)$_3$, and Al(OH)$_4^-$ are called monomeric hydroxyaluminum species because only one Al atom is involved in those complexes. When you measure Al in soil solution, for example, by AA method or by some colorimetric methods, you are measuring total solution Al or the sum of all Al species in solution. However, if we know total solution Al and equilibrium constant of all the above reactions then we can partition Al into various species as presented in the...
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text book. If you’re interested in how it is done, please contact me or try to take the advanced soil chemistry course. I’ll show you how to partition these Al species.

B. Hydroxy-Al polymers \([\text{Al(OH)}_x(\text{H}_2\text{O})_{6-x}(3-x)^+)_n]\)

The hydrolysis products of trivalent Al rapidly polymerize to form large, multi-charged unit. For example: the gibbsite like structure

In the polymerization process, hydroxyl groups are shared by adjacent Al ions to produce polymers of the general formula: \([\text{Al(OH)}_x(\text{H}_2\text{O})_{6-x}(3-x)^+)_n\], where \(n\) is a large number. The polymers are strongly retained by soil surfaces and behave as if they are virtually nonexchangeable.

C. Effects of Al hydrolysis on soils

Exchangeable Al to a large extent controls soil acidity.

1.) \(\text{Al-soil} + \text{KCl} \rightarrow \text{K-soil} + \text{Al}^{3+}\)

2.) \(\text{Al}^{3+} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_2^+ + \text{H}^+\)

On the other hand, hydroxyl-Al polymers have positive charge and are held tightly by negatively charged soil surface. Consequently, this formation decreases the net negative charge in soil surface and lowers the CEC of soil colloids. Raising the pH decreases the positive charge on the polymers and increases the CEC of the mixture. This is an important source of pH dependent charge for inorganic soil colloids.
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Polymers of hydroxyl-Al and hydroxyl-Fe can also be held between the lattices of expanding soil minerals and consequently stabilize soil minerals against shrinking and swelling. The resultant minerals are termed *intergrades*: chlorite-vermiculite intergrades or chlorite-montmorillonite intergrades.

IV. Types of soil acidity.

Soil acidity can be divided into at least 3 components.

A. *Active acidity*

Which is represented by $H^+$ concentration, or actually, $H^+$ activity in soil solution and is often measured with a pH meter equipped with a glass electrode.

B. *Exchangeable acidity*

This type of acidity is obtained by extracting soil with a neutral salt such as KCl. Neutral salt does not react with water, so it does not affect soil pH. Exchangeable $Al^{3+}$ and $H^+$ are replaced by cations of the neutral salt and then they are titrated with a base.

\[
\begin{align*}
Al^{3+} + OH^- &\rightarrow Al(OH)_3 \text{ solid} \\
H^+ + OH^- &\rightarrow H_2O \text{ water}
\end{align*}
\]

acid-base neutralization reaction.

C. *Titratable acidity*

Or total acidity is measured by the quantity of a strong base (such as NaOH or Ca(OH)$_2$) that is required to raise the soil pH to a predetermined value. Titratable acidity is dependent on the initial and final pH values of the soil and on the operational conditions such as stirring time, waiting time between each increment of base. Titratable or total acidity includes exchangeable acidity as well as non-exchangeable acidity.

Non-exchangeable acidity arises from such OH$^-$ consuming reactions as:

\[
X-Al(OH)^{2+} + OH^- \rightarrow Al(OH)_2^+
\]

(Hydroxyl-Al polymers on soil surface)

and

\[
R-COOH + OH^- \leftrightarrow R-COO^- + H_2O
\]

weakly acidic functional group of soil organic matter.
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V. Factors affecting soil pH measurements

A. Soil: solution ratio

Increasing soil to solution ratio usually lowers the measured soil pH. This is not surprising if we recall that \( \text{pH} = -\log(\text{H}^+) \). Increasing soil/solution ratio, we increase \((\text{H}^+)\) activity, therefore lower soil pH. This effect, however, is minor, because we are dealing with the log scale here. For example, in order to lower the soil pH one unit we have to increase soil/solution ratio by a factor of 10.

B. Drying soil (field-moist pH > dried soil pH)

For most soils, the pH measured at field-moist condition is higher than the one measured after the soil has been dried.

C. Salt concentration

High salt concentration, such as from newly added fertilizers, normally decreases soil-water pH. This is explainable if we consider these reactions:

\[
\begin{align*}
\text{Al}^3+ + \text{H}_2\text{O} & \rightarrow \text{Al(OH)}^{2+} + \text{H}^+ & \text{hydrolysis} \\
\text{H-X} + \text{KCl} & \rightarrow \text{K}^+ + \text{Al}^{3+} \text{ or H}^+ & \text{Exchangeable reaction}
\end{align*}
\]

Salt effect can drop soil pH as much as 1 unit. However, sometimes the reverse case also happens. That is, high salt concentration increases soil pH. This is the case when soils have net positive charge on the surface. Anion exchange reaction between OH\(^-\) of the soil and anions of the added salt occurs in this case.

We can reduce the salt effect in soil by

1.) leaching soil with a large volume of water to reduce the salt concentration before taking pH measurement.
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2.) Measuring soil pH in 1M KCl or 0.01M CaCl₂ solution.

**Measuring soil pH**

When you use a pH meter with a pair of electrodes (usually a glass and a calomel electrodes) to measure the soil pH, you should keep in mind that there are several factors affecting the reading. Therefore, you should be careful in interpreting the pH value.

When you immerse the electrodes into a soil suspension at low salt concentrations, besides the potential caused by H⁺ activity in the solution, some extraneous potentials are also developed. One of them is the junction potential, which is caused by the differential velocity of K⁺ and Cl⁻ ion from the calomel electrode in a negatively charged soil suspension. In such a medium, K⁺ ions diffuse more rapidly from the KCl bridge of the calomel reference electrode, and Cl⁻ ions less rapidly. The effect is such that:

The greater the soil CEC (or more clay) the greater the junction potential; or the lower the concentration of the electrolyte in which the soil is suspended, the great the junction potential.

In order to reduce the junction potential, you should measure soil pH in 0.01M CaCl₂ or 1M KCl solutions and/or place the calomel electrode in the relatively clear supernatant solution, and the glass electrode in the settled clay suspension.

**VI. Base saturation**

By definition:  

\[ \% \text{ B.S.} = \frac{\Sigma \text{ (exch. Ca, Mg, Na, K)}}{\text{CEC at pH 7 or pH 8.2}} \]

If you report % B.S., then the pH at which CEC was determined must be reported, because the CEC is usually lower at lower pH, but exchange bases remain nearly constant, therefore % B.S. will increases when based on CEC at lower pH.

Strictly speaking, % B.S. is as much a measure of the pH dependent charge of soils as it is of the actual percentage of cation exchange sites occupied by exchangeable bases because exchange Al or H is negligible at pH > 5.5. Although imprecise, % B.S. is still useful for soil genesis and classification and for empirical liming recommendations because the increase in % B.S. is usually proportional to the increase in pH of a soil.
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VII. Lime requirement

One of the most important things in managing acid soils is liming. Liming is a process in which lime such as CaCO\(_3\) (calcite), or CaCO\(_3\) + MgCO\(_3\) (dolomitic lime) or silicate salts are added to a soil to raise soil pH to a certain level.

The main function of liming materials is to produce OH\(^{-}\) ions which neutralize soil acidity (exch. Al and H\(^{+}\))

\[
\text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \\
\text{CaSiO}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{H}_2\text{SiO}_3 + 2\text{OH}^- 
\]

(Indirectly organic matter can also raise pH and precipitate Al. Thus, organic matter can serve as a short term liming material).

The reference method for estimating lime requirement of an acid soil is to titrate the soil with a standard base, then to calculate the quantity of base required to raise soil pH to a specified level. In this method, time must be allowed for neutralizing reactions to complete. Soil pH drops quite a bit between 30 minutes and 48 hours waiting after a base is added. The waiting time can be as long as 2 weeks or a month.

The titration method is accurate but very time consuming, and therefore impractical. For soil testing purpose, the usual procedure is to add a pH buffer solution to the soil, measure the amount of buffer consumed or the resultant pH of the soil-buffer suspension, and calibrate results with field lime requirements for similar soils.

For example (Adam-Evans method): a soil with a soil-water pH = 5.10

- pH buffer solution used (without soil) = 8.00
- add 20cc soil/ 20cc buffer solution = 7.65

From field calibration, we know that each 0.10 drop in buffer pH from 8.00 (\(\Delta\)pH = 0.10) is equivalent to 1 metric ton of CaCO\(_3\)/ha to bring soil pH to 6.5.

Therefore: the lime requirement for this soil is:

\[(8.00 \times 7.65) \times 1 = 3.5 \text{ metric tons of CaCO}_3/\text{ha}\]

Proper mixing and finely ground particles are important in liming.

In the fields, CaCO\(_3\) or ground limestone is often used as liming material. CaCO\(_3\) is sparingly soluble in H\(_2\)O therefore the mixing of CaCO\(_3\) with soil and the size of CaCO\(_3\)
particles are essential for liming. The reason is that the diffusion rate of OH- from CaCO$_3$ to soil particles is very slow. The neutralizing reaction would be much faster if all CaCO$_3$ particles are in contact with soil particles and the smaller the size of CaCO$_3$ particles the faster they will dissolve.

VIII. Factors that cause acid soils to be infertile

A. Al and Mn toxicities to plants

Many plants grow poorly in acid soils, the most important cause is probably Al and Mn toxicities. Al in soil solution becomes appreciable when soil pH < 5.5, and Al can restrict or stop root growth at a solution concentration as low as 0.50ppm. Mn also becomes more soluble under acid conditions.

$$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$$

$$\text{Al(OH)}_3 + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O}$$

The toxic level of Mn in soil solution is about 0.5-5ppm and Mn toxicity often affects the above-ground portion of plants such as developing buds and leaf edges more than the roots.

Hydrogen ion, itself, is not very important in mineral soils as far as its phytotoxicity is concerned because H$^+$ does not become phytotoxic until the pH drops below 4.0 but mineral soils seldom become that acid.

B. P and Mo deficiencies

The availability of soil phosphate (largely H$_2$PO$_4^-$ and HPO$_4^{2-}$) decreases significantly under acid conditions because of the formation of Al and iron phosphate insoluble compounds.

$$\text{H}_2\text{PO}_4^- + \text{Al(OH)}_3 + \text{H}^+ \leftrightarrow \text{Al(OH)}_2\text{H}_2\text{PO}_4 + \text{H}_2\text{O}$$

variscite

$$\text{Fe(OH)}_2\text{H}_3\text{PO}_4: \text{strognite}$$

The greatest phosphate availability is about at pH 5.8 - 6.5.
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Molybdenum is also less available at low pH. Occasionally the harmful effect of soil acidity on leguminous plants seems to be caused by Mo deficiency rather than by Al toxicity. Mo is required by the rhizobium in the N\textsubscript{2} fixation process of legumes.

On the other hand, liming an acid soil usually reduces the availability of plant micronutrients such as Zn, Fe, B. On the other hand, liming also reduces the concentration of toxic metals such as Cd, Ni and Cr.

Ca and Mg deficiencies are also often associated with acid soils. However, low levels of Ca or Mg availability are not the direct result of soil acidity because Ca is still the major exchangeable cation in most soils (of pH 4.0 - 4.5) of the mainland USA. However, Ca and Zn deficiencies are often a problem in acid soils of Hawaii.