Ammonia Volatilization

- Urease activity
- Temperature
- CEC (less when high)
- Air Exchange
- N Source and Rate
- Application method

\[
\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+
\]

If pH and temperature can be kept low, little potential exists for \(\text{NH}_3\) volatilization. At pH 7.5, less than 7% of the ammoniacal N is actually in the form of \(\text{NH}_3\) over the range of temperatures likely for field conditions.

Urea

- Urea is the most important solid fertilizer in the world today.
- In the early 1960's, ammonium sulfate was the primary N product in world trade (Bock and Kissel, 1988).
- The majority of all urea production in the U.S. takes place in Louisiana, Alaska and Oklahoma.
- Since 1968, direct application of anhydrous ammonia has ranged from 37 to 40% of total N use (Bock and Kissel, 1988)
- Urea: high analysis, safety, economy of production, transport and distribution make it a leader in world N trade.
- In 1978, developed countries accounted for 44% of the world N market (Bock and Kissel, 1988).
- By 1987, developed countries accounted for less than 33%

<table>
<thead>
<tr>
<th>Share of world N consumption by product group</th>
<th>1970</th>
<th>1986</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulfate</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>27</td>
<td>15</td>
</tr>
<tr>
<td><strong>Urea</strong></td>
<td><strong>9</strong></td>
<td><strong>37</strong></td>
</tr>
<tr>
<td>Ammonium phosphates</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Other N products (NH₃)</td>
<td>36</td>
<td>29</td>
</tr>
<tr>
<td>Other complex N products</td>
<td>16</td>
<td>8</td>
</tr>
</tbody>
</table>
Urea Hydrolysis

increase pH (less H⁺ ions in soil solution)

\[
\text{CO(NH}_2\text{)}_2 + \text{H}^+ + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{HCO}_3^- \\
pH 6.5 \text{ to } 8 \\
\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O} \text{ (added H lost from soil solution)}
\]

\[
\text{CO(NH}_2\text{)}_2 + 2\text{H}^+ + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{H}_2\text{CO}_3 \text{ (carbonic acid)} \\
pH <6.3
\]

1. Urea Fertilizer Broadcast

2. Urea Fertilizer Incorporated

Potential for gaseous loss from applied urea, both broadcast and incorporated.

During hydrolysis, soil pH can increase to >7 because the reaction requires H⁺ from the soil system.

(How many moles of H⁺ are consumed for each mole of urea hydrolyzed?) 2

In alkaline soils less H⁺ is initially needed to drive urea hydrolysis on a soil already having low H⁺.

In an alkaline soil, removing more H⁺ (from a soil solution already low in H⁺), can increase pH even higher

\[
\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_4\text{OH} \rightarrow \text{NH}_3 + \text{H}_2\text{O} \\
pH = \text{pKa} + \log [(\text{base})/(\text{acid})]
\]
At a pH of 9.3 (pKa 9.3) 50% NH₄ and 50% NH₃

<table>
<thead>
<tr>
<th>pH</th>
<th>Base (NH₃)</th>
<th>Acid (NH₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3</td>
<td>1</td>
<td>99</td>
</tr>
<tr>
<td>8.3</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>9.3</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>10.3</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>11.3</td>
<td>99</td>
<td>1</td>
</tr>
</tbody>
</table>

Equilibrium relationship for ammoniacal N and resultant amount of NH₃ and NH₄ as affected by pH for a dilute solution.

As the pH increases from urea hydrolysis, negative charges become available for NH₄⁺ adsorption because of the release of H⁺ (Koelliker and Kissel)

Decrease NH₃ loss with increasing CEC (Fenn and Kissel, 1976) assuming increase pH = increase CEC, what is happening?

In acid soils, the exchange of NH₄⁺ is for H⁺ on the exchange complex (release of H here, resists change in pH, e.g. going up)

In alkaline soils with high CEC, NH₄ exchanges for Ca, precipitation of CaCO₃ (CO₃⁻ from HCO₃⁻ above) and one H⁺ released which helps resist the increase in pH
However, pH was already high,

Ernst and Massey (1960) found increased NH$_3$ volatilization when liming a silt loam soil. The effective CEC would have been increased by liming but the rise in soil pH decreased the soils ability to supply H$^+$

Rapid urea hydrolysis: greater potential for NH$_3$ loss. Why? management: dry soil surface, incorporate, localized placement- slows urea hydrolysis
H ion buffering capacity of the soil:

Ferguson et al., 1984
(socios total acidity, comprised of exchangeable acidity + nonexchangeable titratable acidity)

A large component of a soils total acidity is that associated with the layer silicate sesquioxide complex (Al and Fe hydrous oxides). These sesquioxides carry a net positive charge and can hydrolyze to form H\(^+\) which resist an increase in pH upon an addition of a base.

H\(^+\) ion supply comes from:
1. OM
2. hydrolysis of water
3. Al and Fe hydrous oxides
4. high clay content

A soil with an increased H\(^+\) buffering capacity will also show less NH\(_3\) loss when urea is applied without incorporation.

1. hydroxy Al-polymers added (carrying a net positive charge) to increase H\(^+\) buffering capacity.
2. strong acid cation exchange resins added (buffering capacity changed without affecting CEC, e.g. resin was saturated with H\(^+\)).

resin: amorphous organic substances (plant secretions), soluble in organic solvents but not in water (used in plastics, inks)

Consider the following
1. H\(^+\) is required for urea hydrolysis
2. Ability of a soil to supply H\(^+\) is related to amount of NH\(_3\) loss
3. H\(^+\) is produced via nitrification (after urea is applied): acidity generated is not beneficial
4. What could we apply with the urea to reduce NH\(_3\) loss?

an acid; strong electrolyte; dissociates to produce H\(^+\);increased H\(^+\) buffering; decrease pH

reduce NH\(_3\) loss by maintaining a low pH in the vicinity of the fertilizer granule (e.g. H\(_3\)PO\(_4\))
References:


