Ammonia Volatilization

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

$NH_4^+ \leftrightarrow NH_3 + H^+$

If pH and temperature can be kept low, little potential exists for NH_3 volatilization. At pH 7.5, less than 7% of the ammoniacal N is actually in the form of 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%

Share of world N consumption by product group

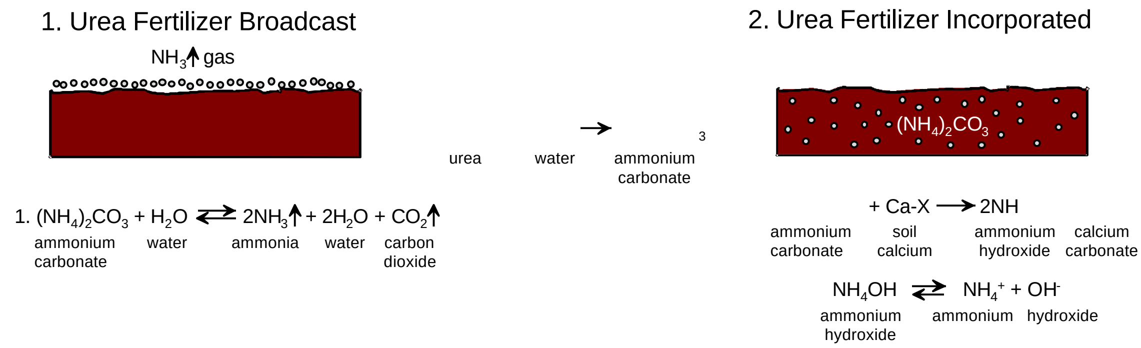
	1970	1986
Ammonium sulfate	8	5
Ammonium nitrate	27	15
Urea	**9**	**37**
Ammonium phosphates	1	5
Other N products (NH_3)	36	29
Other complex N products	16	8

Urea Hydrolysis

increase pH (less H^+ ions in soil solution)

$CO(NH_2)_2 + H^+ + 2H_2O$ --------> $2NH_4^+ + HCO_3^-$
pH 6.5 to 8
$HCO_3^- + H^+$ ---> $CO_2 + H_2O$ (added H lost from soil solution)

$CO(NH_2)_2 + 2H^+ + 2H_2O$ --------> $2NH_4^+ + H_2CO_3$ (carbonic acid)
pH <6.3



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^+.

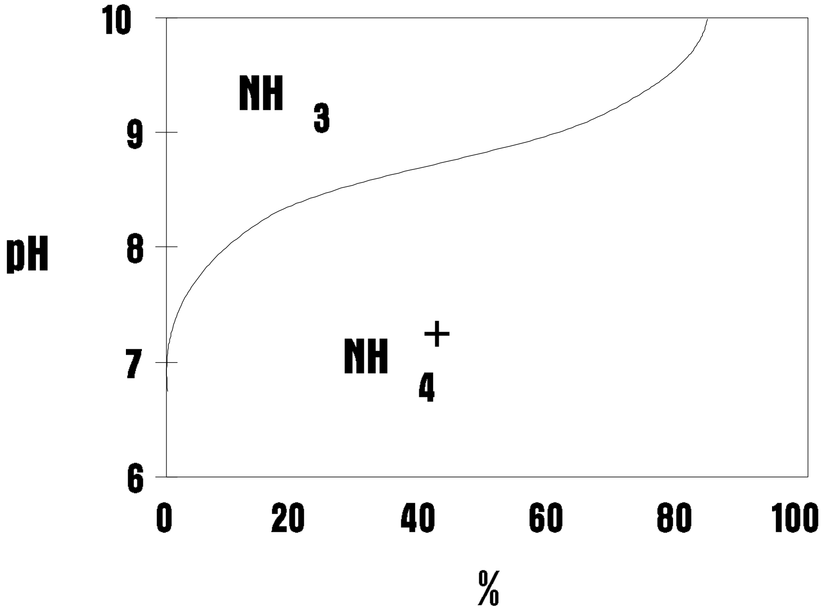
In an alkaline soil, removing more H^+(from a soil solution already low in H^+), can increase pH even higher

$NH_4^+ + OH^-$ ---> NH_4OH ---->$NH_3 + H_2O$

pH = pKa + log [(base)/(acid)]

At a pH of 9.3 (pKa 9.3) 50% NH_4 and 50% NH_3

pH	Base (NH_3)	Acid (NH_4)
7.3	1	99
8.3	10	90
9.3	50	50
10.3	90	10
11.3	99	1



Equilibrium relationship for ammoniacal N and resultant amount of NH_3 and NH_4 as affected by pH for a dilute solution.

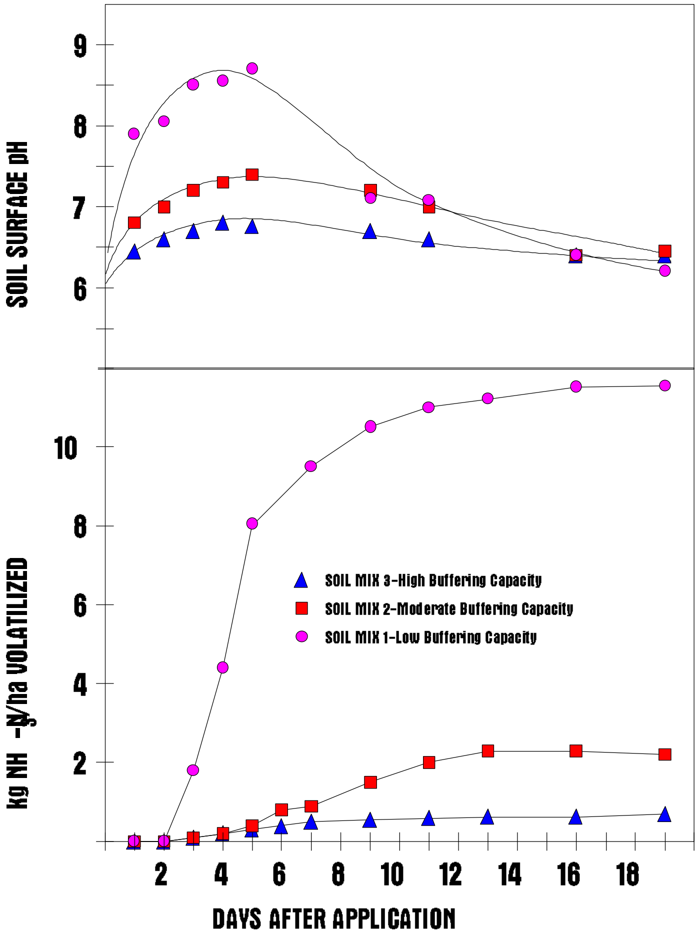
As the pH increases from urea hydrolysis, negative charges become available for NH_4^+ adsorption because of the release of H^+ (Koelliker and Kissel)

Decrease NH_3 loss with increasing CEC (Fenn and Kissel, 1976)
assuming increase pH = increase CEC, what is happening?

In acid soils, the exchange of NH_4^+ 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, NH_4 exchanges for Ca, precipitation of $CaCO_3$ ($CO_3^=$ from HCO_3^- above) and one H^+ released which helps resist the increase in pH

However, pH was already high,



Soil surface pH and cumulative NH_3 loss as influenced by pH buffering capacity (from Ferguson et al., 1984).

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
(soils 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_3PO_4)

References:

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