Chemistry of N Fertilizer Additives

Dave Franzen, PhD
Professor Soil Science
Extension Soil Specialist
North Dakota State University
Focus on two processes-

Ammonia volatilization from urea caused by the action of urease enzyme

Nitrification- bacterial oxidation of ammonium to nitrate
Urea is subject to ammonia volatilization if placed on or near the surface.

\[
\text{NH}_2\text{-CO-NH}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 \uparrow + 2 \text{NH}_3 \uparrow
\]  
(Urea)
Yield for side-dressed no-till corn in Hardin County, KY.  
(From Schwab and Murdock, 2009)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Yield, bushels per acre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Check (50 lb N/acre preplant N only)</td>
<td>117 d*</td>
</tr>
<tr>
<td>Urea</td>
<td>158 c</td>
</tr>
<tr>
<td>Urea + Agrotain</td>
<td>201 b</td>
</tr>
<tr>
<td>SuperU</td>
<td>201 b</td>
</tr>
<tr>
<td>UAN</td>
<td>150 c</td>
</tr>
<tr>
<td>UAN + Agrotain</td>
<td>179 bc</td>
</tr>
<tr>
<td>UAN + Agrotain Plus</td>
<td>175 bc</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>239 a</td>
</tr>
</tbody>
</table>
Ammonia volatilization from surface and incorporated urea at various depths-
Rochette et al., 2014, J. Env. Q.

<table>
<thead>
<tr>
<th>Period-hours</th>
<th>Surface (% loss)</th>
<th>1 inch (% loss)</th>
<th>2 inch (% loss)</th>
<th>3 inch (% loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-166</td>
<td>2.2</td>
<td>18.4</td>
<td>2.6</td>
<td>0.0</td>
</tr>
<tr>
<td>167-334</td>
<td>29.5</td>
<td>15.2</td>
<td>3.2</td>
<td>0.1</td>
</tr>
<tr>
<td>335-502</td>
<td>15.2</td>
<td>3.8</td>
<td>1.8</td>
<td>0.5</td>
</tr>
<tr>
<td>503-598</td>
<td>3.4</td>
<td>1.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Total</td>
<td>50.3</td>
<td>38.4</td>
<td>8.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Slightly acid silt loam soil
Urease is produced by plants, bacteria, fungi, invertebrates and is one of the last compounds to degrade after the organism dies.

‘The Zombie Enzyme’
Gardner

- Urea
- Agrotain
- LIMUS
- NBPT
- Check

Valley City

- Urea
- Agrotain
- LIMUS
- NBPT
- Check
- ESN (100 lb N)
- BASF Coating (100 lb N)
Ammonia volatility from surface/near surface application increases with Residue Soil pH
Urea is acted on in the ‘keyhole’ structure of the urease enzyme.
N-(N-Butyl)thiophosphoric triamide

Has same tri-atom configuration as urea

NPPT has same tri-atom structure, but tail has an additional C group.
NBPT (Agrotain and siblings) and NPPT (Limus) are the only chemistries known to inhibit urease activity for days (usually about 10)

Ammonium thiosulfate has measurable short-term activity, but NBPT is much better.
ATS does not directly affect the urease enzyme and is only indirectly inhibiting after interacting with soil-

Thiosulfate reacts rapidly and abiotically with soil, forming tetrathionate and liberating Fe$^{2+}$ and Mn$^{2+}$

\[
2 \text{Fe(OH)}_3 + 2 \text{S}_2\text{O}_3^{-2} + 6 \text{H}^+ \quad \text{2Fe}^{+2} + \text{S}_4\text{O}_6^{-2} + 6 \text{H}_2\text{O}
\]

\[
\text{MnO}_2 + 2 \text{S}_2\text{O}_3^{-2} + 4\text{H}^+ \quad \text{Mn}^{+2} + \text{S}_4\text{O}_6^{-2} + 2 \text{H}_2\text{O}
\]

Adapted from Goos, 1987, NC Ext. Ind. Soil Fertility Conf.
Nitrification-
Factors influencing rate of transformation:

- Moisture (moist, not saturated)
- Temperature: max ~ 80F, min 32F
- pH: favored by pH > 7, slowed by pH < 6
Nitrapyrin-
2-Chloro-6-(trichloromethyl)pyridine (N-Serve®/Instinct®)

From PubChem
Nitrapyrin mode of action is a bacteriocide

Active at concentrations as low as 1 ppm
Fall N, Touchton et al., 1978
N-Serve 24, Illinois

Spring N, Touchton et al., 1978
N-Serve 24, Illinois
Some studies showed a yield increase with N-Serve, while others showed no yield increase. Yield increases were more a result of weather between application and N uptake rather than performance of the product.

Yield increases over the seven years in Minnesota were 15 bushels per acre more for fall anhydrous ammonia + N-Serve over fall anhydrous ammonia alone, and 27 bushels per acre more for spring anhydrous ammonia compared to fall anhydrous ammonia (Randall et al., 2008).
Inherent issues with N-Serve for ammonia

Corrosive-

Replace aluminum float-gauges with stainless steel
Replace normal acme gaskets with BunaN gaskets/Teflon
First time use, be prepared to clean out screens frequently on first tank fill of each tank

Volatility- 2-3 times more than the most volatile incorporated herbicides
Direct injection system (not an endorsement)
Instinct® is a new formulation of Nitrapyrin that can be mixed with ammonium fertilizers and can stay on the soil surface without incorporation.

The formulation is microencapsulated nitrapyrin. That means that nitrapyrin release is slow compared to nitrapyrin for ammonia.
Release rates of Instinct indicated a slow release through the encapsulation, with only 14% released in a 70 day incubation study. (Menelas, 2014, PhD thesis, Purdue).

Speculated that use in the field might be better if soil pH/soil biology acted on the microencapsulation.
Three soils with rapid nitrification (Glyndon, Ulysses, Bearden), 4 week incubation. Initial N level 200 ppm as urea.

NP-nitrapyrin
ENP- Instinct
DCD
ATS
MIP
Ammonium thiosulfate
Instinct performance in other studies-

Purdue, 2012 (Ferrel, MS Thesis with Camberado)
Instinct had no effect on nitrification, either ammonia left in the system or nitrate produced by the N application w/o inhibitor. DCD effectively inhibited nitrification in the same study.
Field study, Purdue
(Omonode and Vyn, 2013, AJ)

Instinct treated UAN had higher ammonium and lower nitrate than untreated UAN.

Nitrification was significantly reduced. Nitrous oxide emissions were reduced 44%.
Wisconsin 2008-2012
Laboski and Andraski, 2013 Wis Fert and Lime

Soil ammonium levels were higher and soil nitrate levels lower with Instinct than without.

Yield increases documented, as well as sites with no yield differences.
DCD- Dicyandiamide

First developed as a fertilizer (66.7-0-0)

Found that DCD was toxic to plants when DCD was used at rates equivalent to use as a fertilizer

Image from PubChem
DCD is bacteriostatic-
It interferes with bacteria metabolism, preventing replication.
Mode of action proposed is inhibition of ammonia monooxygenase, a key enzyme in nitrification.

Ammonia monooxygenase

DCD- a nitrification inhibitor

Found in
  AgrotainPlus (Agrotain, Int.)
  SuperU (Agrotain, Int.)
  Guardian DF (Conklin)
  Guardian DL (Conklin)
  Others.....

Needs to be added at >1% of total N content of fertilizer needing protection.
Best commercial product is about 1.2%
DCD is about 67% N

Rates used in successful nitrification inhibition range from 1 to 5 % of N in mix as DCD.

It is hard to find DCD content on labels.
<table>
<thead>
<tr>
<th>Timing</th>
<th>No. of comparisons</th>
<th>DCD</th>
<th>With significant advantage</th>
<th>Average response %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fall</td>
<td>4</td>
<td>+1</td>
<td>+1.6</td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>15</td>
<td>+3</td>
<td>+3.4</td>
<td></td>
</tr>
<tr>
<td>Sidedress</td>
<td>3</td>
<td>+1</td>
<td>+1.4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>N Source</th>
<th>Total</th>
<th>With significant advantage</th>
<th>Average response %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulfate</td>
<td>2</td>
<td>0</td>
<td>-1.0</td>
</tr>
<tr>
<td>Anhydrous ammonia</td>
<td>6</td>
<td>1</td>
<td>+3.6</td>
</tr>
<tr>
<td>Urea</td>
<td>4</td>
<td>4</td>
<td>+2.2</td>
</tr>
</tbody>
</table>

From Malzer et al., 1989
Illinois-

4 locations over 12 years, ESN was similar in corn yield to urea + Agrotain, and 3 bu/a higher in yield than urea alone.

In 4 years of no-till, ESN was 21 bu/a better than urea surface-applied.

(Ebelhar et al., 2010)
Minnesota-

3 different ESN application methods-

deep band (4 inches), broadcast incorporated
fall and spring resulted in similar corn yield
to urea using the same methods over a
4-year period.

(Randall and Vetsch, 2009)
Kansas-

At drier locations, ESN not beneficial to corn or grain sorghum.

At wetter locations, some studies showed a benefit to its use.

(Weber et al., 2009a and 2009b)
In Michigan in winter wheat, fall ESN at the 60 lb N/acre rate produced higher yield than urea. Not at the 90 lb N/acre rate.

(Warncke, MSU)
50/50 blends of urea/ENS?

KS studies (Weber and Mengel, 2009) compared to straight ESN or Urea. Results showed that in some years, the blend was superior, and in some years it was not.
Best fit for ESN-

Spring wheat/Durum- in soil

Corn as a blend in preplant to keep plant healthy until side-dress

Maybe a 4 part urea/1 part ESN blend

Enough ESN to carry N into late grain fill season for higher protein.
Start with odd products-
‘Biologicals’
Expensive starter fertilizers
Humic substances
Foliar enhancers

There is little scientific evidence that any of these are either more effective than their conventional counterparts (starters) or that they have any positive effect on yield under field conditions.
http://extension.agron.iastate.edu/compendium/index.aspx

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<Dave Franzen NDSU>

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