

# **REINHOLD ENVIRONMENTAL Ltd.**



## **2011 NO<sub>x</sub>-Combustion Round Table & Expo Presentation**

February 7-8, 2011, in Birmingham, AL / Hosted by Southern Company

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**WAHLCO, Inc.**

**Urea to Ammonia Systems  
Safety and Economics**

2011 NOx Roundtable  
February 8, 2010

# NOx Reduction Requirements

- SCRs Required all New Fossil Units
- Increasing regulations for Industrial Applications
- Many SCR's Required in 2011 to 2012



# NOx Reduction Technology

- Low NOx Burner
- SNCR's
  - Urea Based
  - Aqueous Ammonia
  - Anhydrous Ammonia
- SCR's
  - Anhydrous Ammonia
  - Aqueous Ammonia
  - Urea to Ammonia

# DeNOx Reagents

- Somewhat Depends upon System Type
- SNCR's boiler temperatures influence selection
  - Direct Urea Injection Most Common
  - Some systems use aqueous or anhydrous ammonia
  - Urea to Ammonia can replace anhydrous ammonia
- SCR Technology
  - Temperatures usually not conducive for direct urea injection
  - Anhydrous Ammonia
  - Aqueous Ammonia
  - Urea to Ammonia

# Feed Stock Issues

- Equipment Capital Costs
- Operating Costs
  - Feedstock
  - Energy
  - Manpower Requirements
- Permitting and Safety Related Issues



# Ammonia Feed Stocks

- Urea
  - Supplied Dry
  - 70% Solution
  - 40% Solution
- Aqueous Ammonia
  - Concentrations from 19 to 29%
  - Above 19% requires pressure vessel

# Anhydrous Ammonia

- Anhydrous = Very little water (0.2-0.5%)
- Pungent, colorless gas
- Stored as liquid under pressure (or refrigerated)
- Flammable compressed gas
- Pressure varies greatly with temperature
  - e.g. 50° F ≈ 72 psig ; 90° F ≈ 160 psig



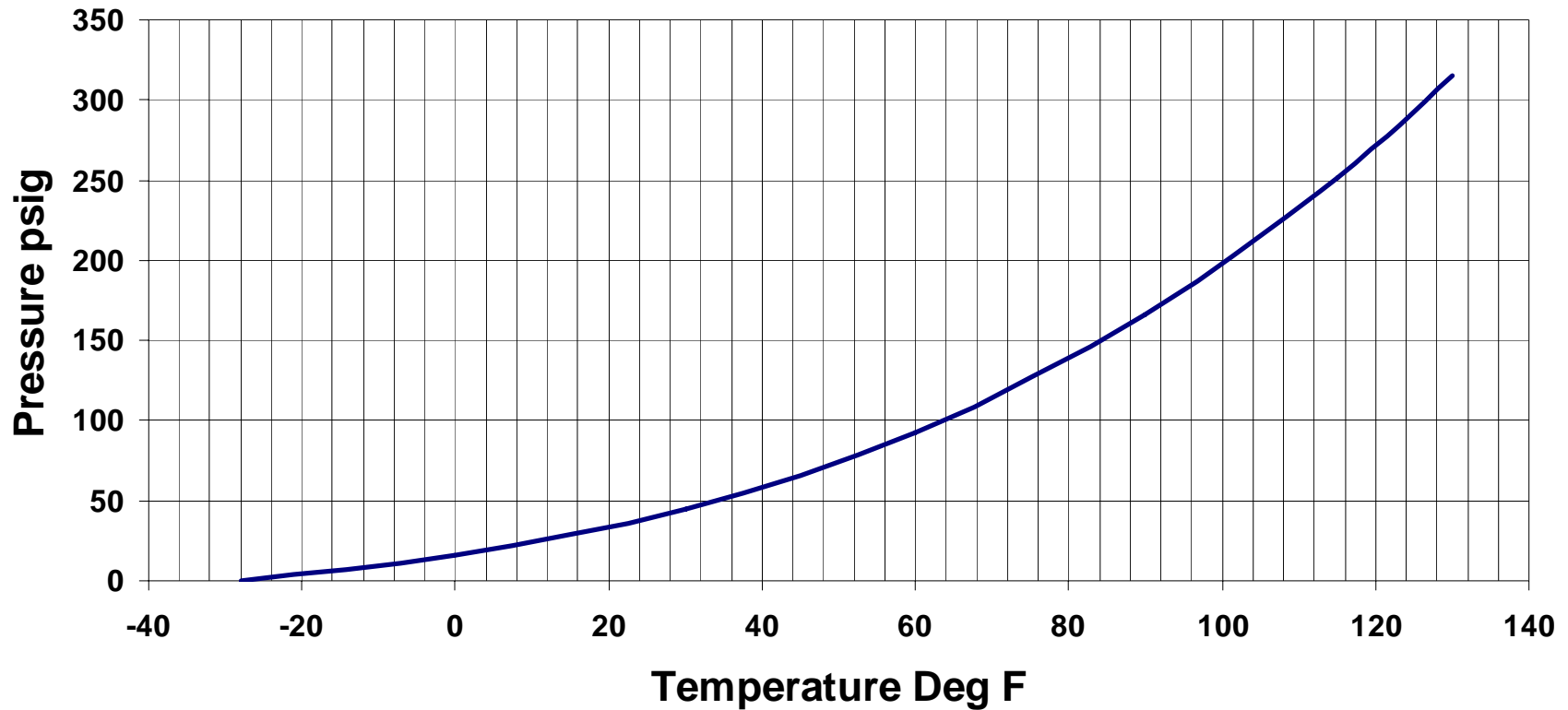
# Anhydrous Properties

- Density @ 60 deg F ~ 38.5 lbs/ ft<sup>3</sup>
- Explosive Limits 16 to 25% in air
- Boiling point -28 deg F
- Energy to Vaporize ~ 540 btu/ lb
- National Response Center Notification with 100 lb release
- Lethal Limit 5 minutes at 5000 ppm



# Anhydrous Ammonia

## Vapor Pressure vs. Temperature



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# Anhydrous NH3 Safety Issues

- Anhydrous Ammonia highly toxic lethal chemical
- Almost 10,000 accidental releases in ten years
- Storage entails high liability
- Regulated by Homeland Security
- Requires Coded Pressure Vessels
- Transportation costs rapidly increasing due to Liability issues – can not be trucked in many areas

# AQUEOUS AMMONIA SYSTEMS



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# Aqueous Ammonia

- Ammonium Hydroxide ( $\text{NH}_4\text{OH}$ )
- Various Concentrations
  - 29.4%, 25%, 19.5%, 11% others
  - At 29% Pressure Vessel Required
- Liquid
- Low pressure
  - at  $100^\circ\text{F} = 10\text{ psig}$  (29.4%)
- 7.3 lb/gal (29.4% solution)



# Aqueous Ammonia 19%

- National Response Center Notification with 1000 lb release (190 lbs of ammonia)
- Required EPA risk management plan for >20% and 20,000 lbs
- Freezing point ~ -30 deg F
- Heat of Vaporization ~ 981 btu's/lb (5163 btu's / 1 lb NH<sub>3</sub>)
- Must keep vaporized mixture above dewpoint to point of use

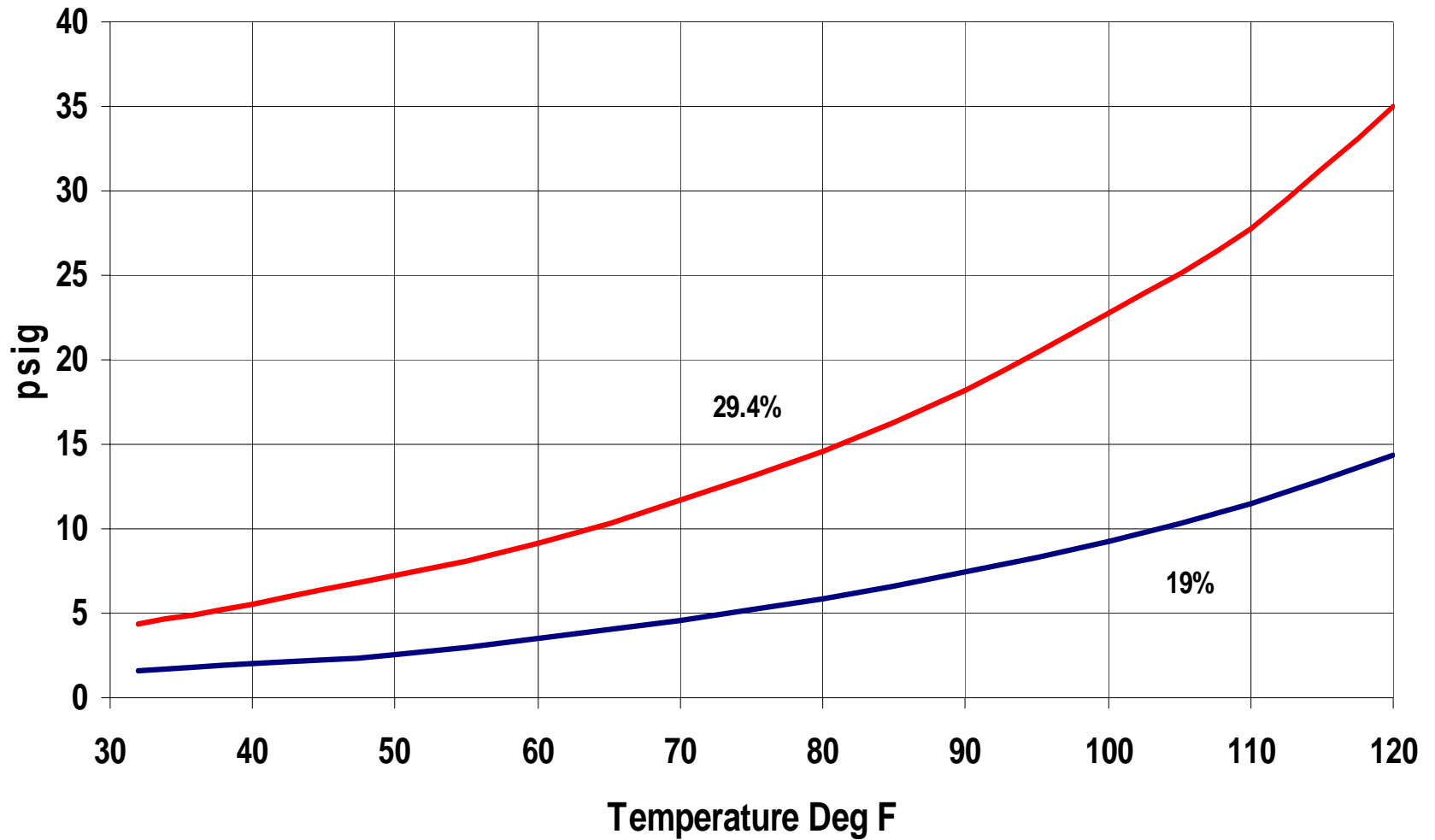


# Aqueous Ammonia 29.4%

- Requires coded pressure vessel
- Freezing point ~ -110 deg F
- Heat of Vaporization ~ 929 btu's/lb (3160 btu's / 1 lb NH<sub>3</sub>)
- Must keep vaporized mixture above dewpoint to point of use



# Aqueous Ammonia



# Aqueous Ammonia Safety Issues

- Regulated toxic chemical
- EPA RMP toxic release distances 1/3 to 1/2 of Anhydrous Ammonia
- Large Storage Volumes
- Increased Transportation Handling Risk



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# Safety Considerations of Ammonia



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# Ammonia Effects

Effect	Ammonia ppm
Least perceptible odor	5 ppm
Readily detectable odor	20-50 ppm
No discomfort or impairment of health for prolonged exposure	50-100 ppm
General discomfort and eye-tearing; No lasting effect on short exposure	150-200 ppm
Severe irritation of eyes, ears, nose and throat; No lasting effect on short exposure	400-700 ppm
Coughing, bronchial spasms	1,700 ppm
Dangerous, less than ½ hour exposure may be fatal	2000-3000 ppm
Serious edema, strangulation, asphyxia, rapidly fatal	5000-10,000 ppm
Immediately fatal	>10,000 ppm



# The reality of disaster . . .



## From NTSB – Pipeline Accident Brief

Accident No.: DCA05-MP001

Date: October 27, 2004

Material Released: Anhydrous Ammonia

Location: 6 miles west of Kingman, Kansas

- Ammonia pipeline accident near Kingman, Kansas (population 3,387 as of 2000)
- 204,000 gallons released
- Ammonia aerosol cloud formed that traveled close to the ground
- **Severe Hazard** – one breath of aerosol cloud vapor would have been **immediately fatal**



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# EPA RMP Comp

14 Day Storage for 4 units each 612 lb/hr

RMP\*Comp

Summary of Scenario

Chemical: Ammonia (anhydrous)  
CAS #: 7664-41-7  
Category: Toxic Gas  
Scenario: Worst-case  
Liquefied under pressure  
Quantity Released: 825216 pounds

**Estimated Distance to Toxic Endpoint:**  
.....15 miles  
.....24 kilometers

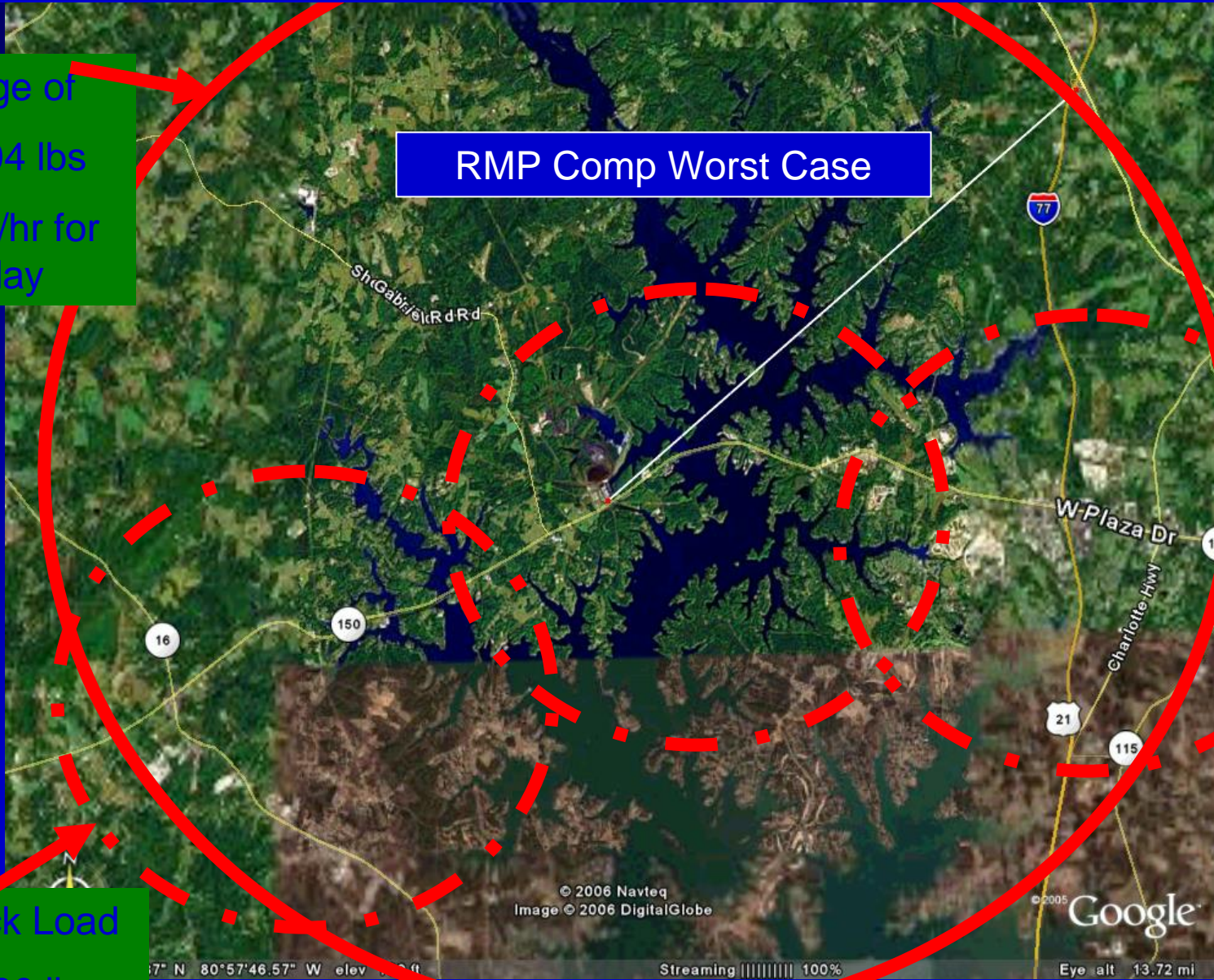
This is the downwind distance to the toxic endpoint specified for this regulated substance under the RMP Rule. Report all distances shorter than 0.1 mile as 0.1 mile, and all distances longer than 25 miles as 25 miles.

Start Over      Tips      < Back      Next >

# Toxic End Pts for NH3 Spills

Storage of  
204,304 lbs  
612 lbs/hr for  
14 day

RMP Comp Worst Case



1 Truck Load  
50,000 lbs

# U<sub>2</sub>A<sup>®</sup> Technology

- Process Converts Urea to Ammonia on Site
- U<sub>2</sub>A<sup>®</sup> (urea to ammonia): Reduces risks associated with ammonia handling:
- (U.S. patents 6,077,491, 6,322,762, 6,436,359 and 6,506,350; European and Asian patents issued or pending)



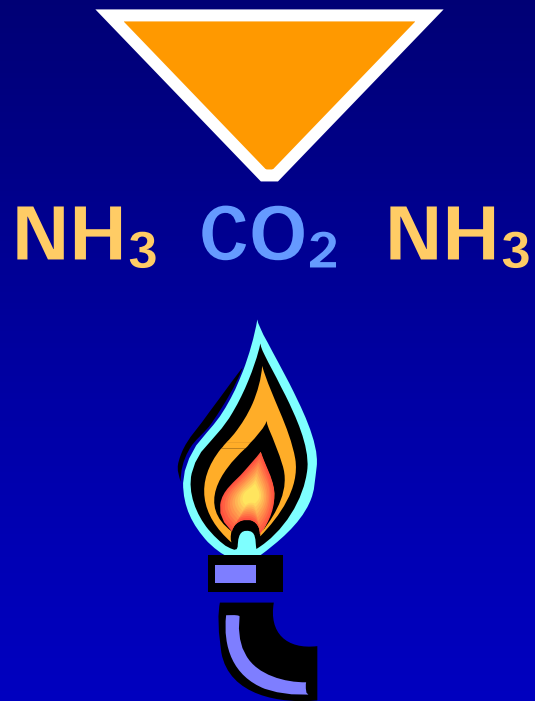
# Why U<sub>2</sub>A®

- U<sub>2</sub>A® (urea to ammonia): Reduces risks associated with ammonia handling:
- Eliminates the hazards from: shipping, handling, transfer or storage of ammonia
- Easier and less expensive to permit
- New Railroad Regulations will make Ammonia much more Expensive
  - Armor front of Rail Cars
  - Reduce max speed to 35 mph

# Urea

- Urea ( $\text{NH}_2\text{CONH}_2$ )
  - Essentially harmless to the environment
  - Safely transported, stored and handled
- Readily available bulk commodity chemical
  - Used as fertilizer, in plastics, in adhesives and in pharmaceuticals
  - Available in solid form or as commercial solution
- Economical alternative to aqueous ammonia
  - Significantly less expensive to operate than 19% aqueous

# Urea Production



# Urea Production



Ammonium Carbamate



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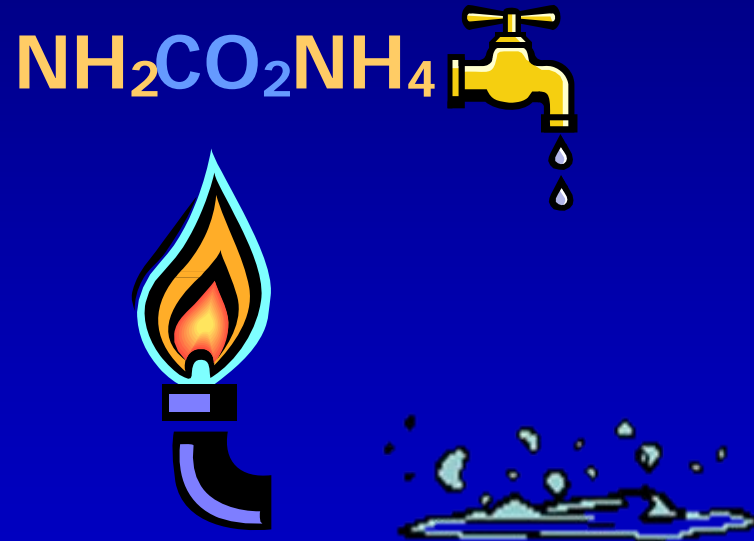
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# Urea Production



Ammonium Carbamate

# Urea Production



**UREA**



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# Urea back to Ammonia



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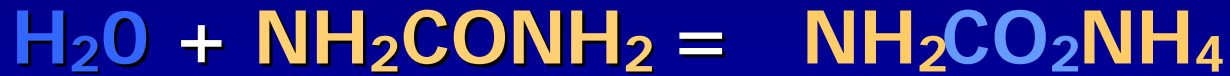
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# Urea back to Ammonia



Ammonium Carbamate



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# Urea back to Ammonia



Ammonia, Carbon Dioxide &  
Water Vapor



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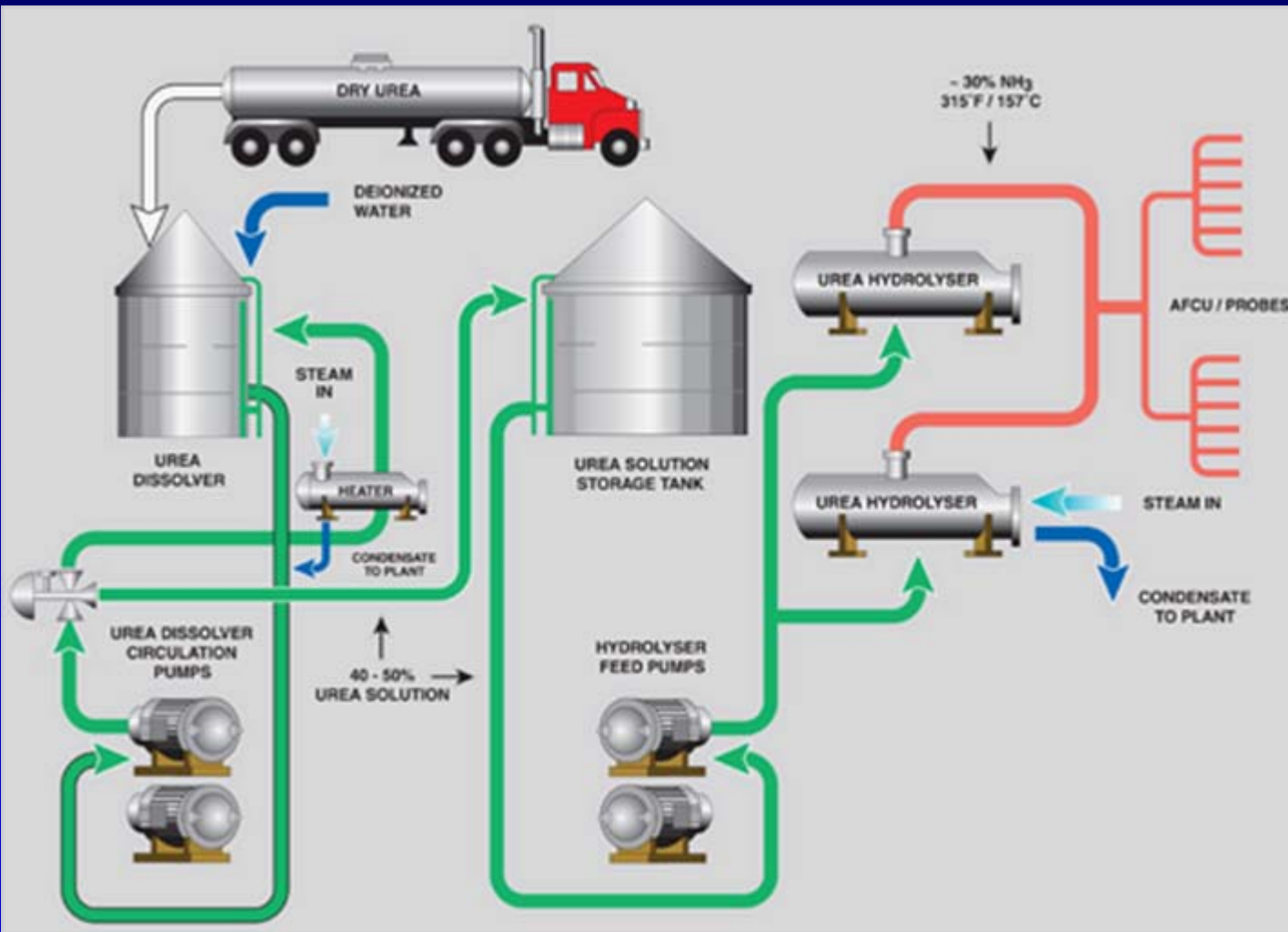
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# How does U<sub>2</sub>A<sup>®</sup> work?



**Dissolve Urea**  
(Urea + Water)



**Hydrolyze**  
Urea Solution



**Deliver**  
**Product Gas**  
(on-demand)



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# Process Description

- Urea Hydrolysis
  - 40 to 50% Urea Pumped to Reactor
  - Heated to about 300°F
  - Pressure of 40 to 120 psig
  - 40% Decomposes to:
    - 28.5%Vol. Ammonia Vapor
    - 14.3%Vol. Carbon Dioxide
    - 57.2%Vol. Water Vapor



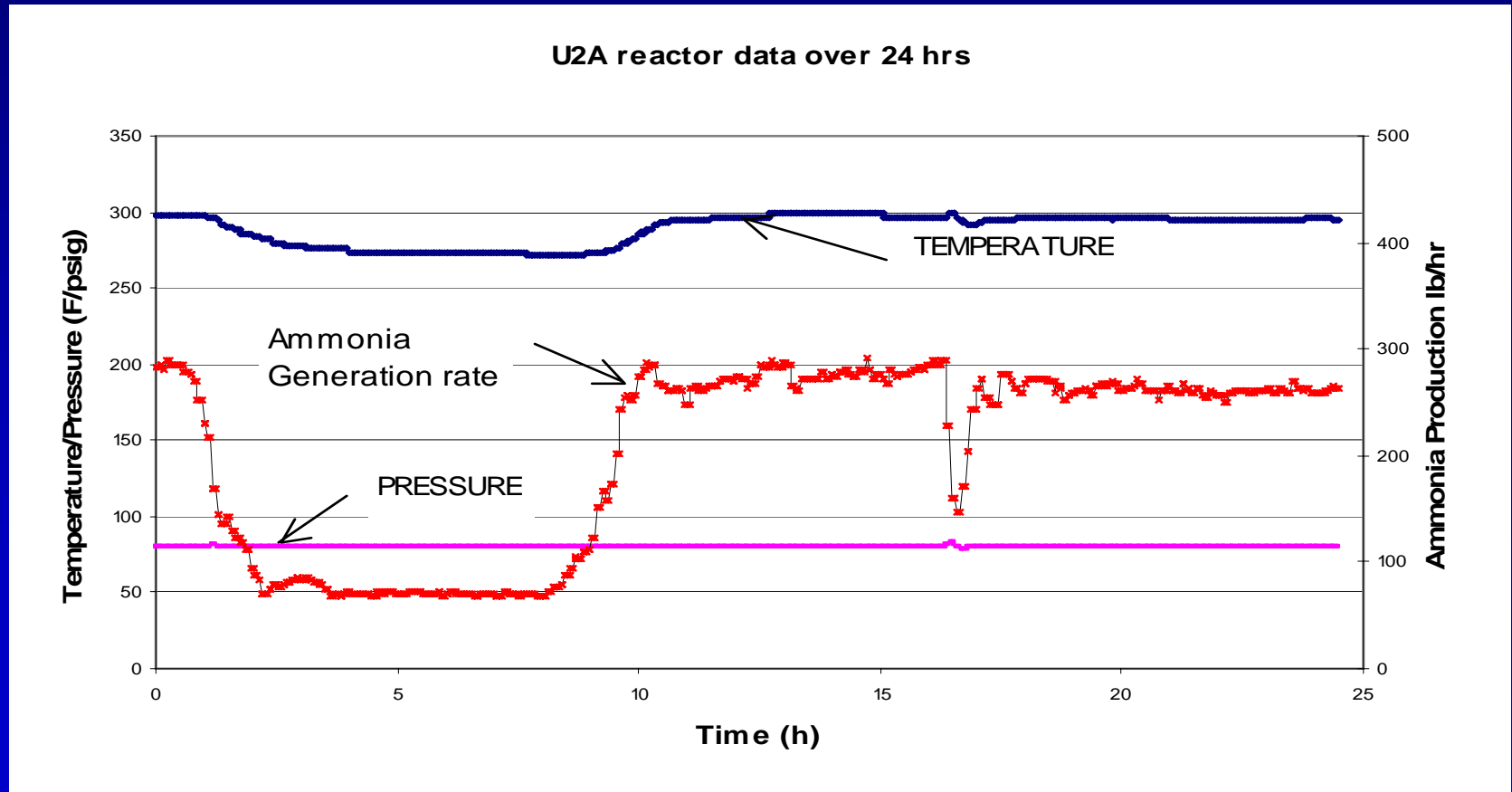
# Process Requirements

- Urea Hydrolysis
  - 1 lb NH<sub>3</sub> per 1.74 lb of Urea
  - For 40% Solution
    - Steam ~ 6 lb/ lb NH<sub>3</sub>
    - 20% less Steam for 50%
- Urea Solution
  - 40% Requires 2.65 lb Water per lb NH<sub>3</sub>
  - 50% Requires 1.76 lb Water per lb NH<sub>3</sub>



# Load Following Data

- Process easily follows boiler load variations



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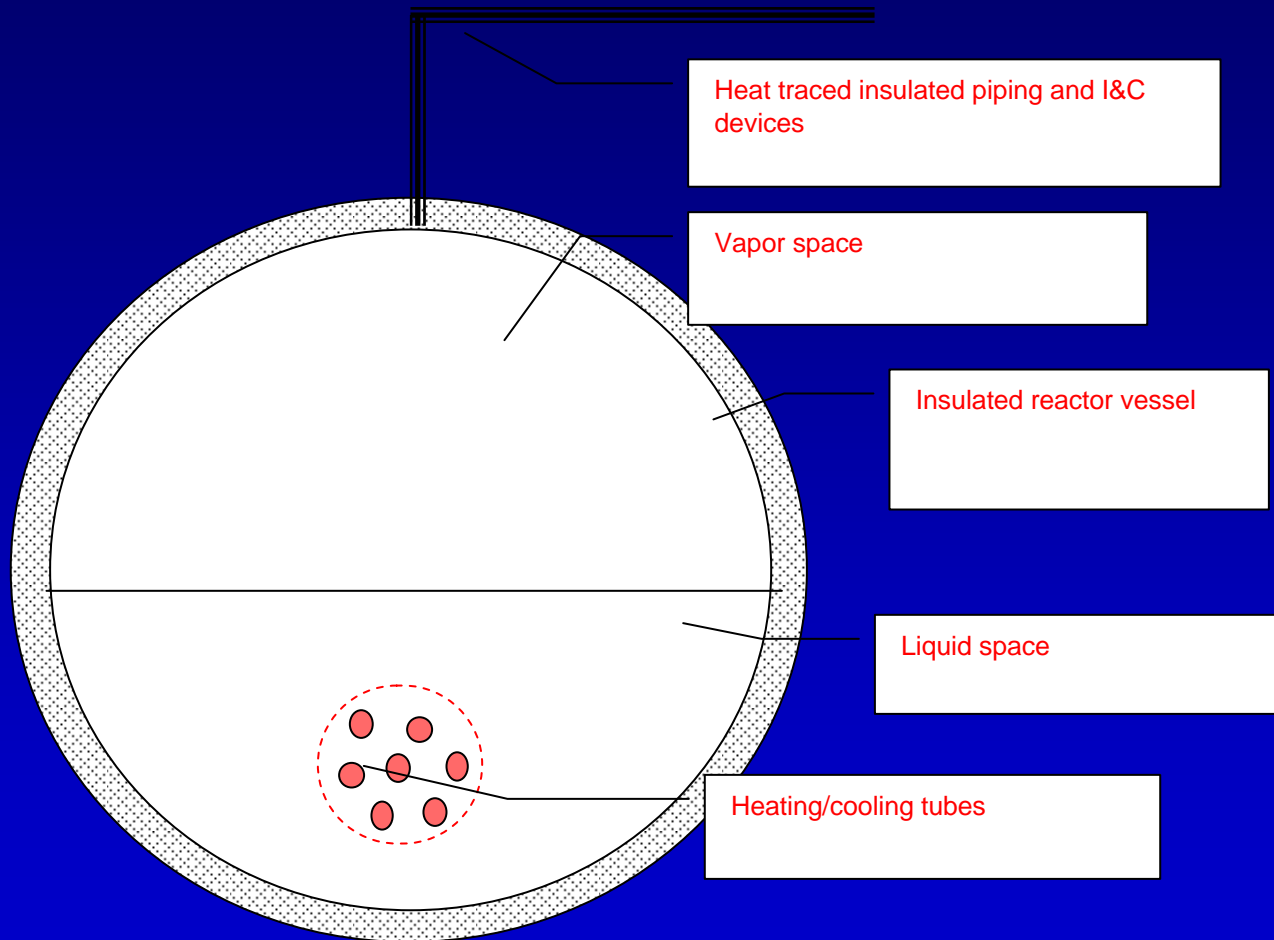
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# Operating Principles

- Heat modulated to achieve set pressure
- Hydrolyzer temperature increases with production rate
- Steam flow increases with production rate
- Pressure required to maintain correct water balance



# Reactor Cross Section



# 3500 lb/hr Hydrolyzer



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# System Configurations

- About Half of Systems have Single Hydrolyzer feed one or Multiple Boilers
- Most Large Coal Fired Applications have 2 X 100% Hydrolyzers
  - Generally we recommend operating both hydrolyzers at reduced rates
  - Instead of one standby and other operating
- Some Large Systems Have 3 X 50% Hydrolyzers

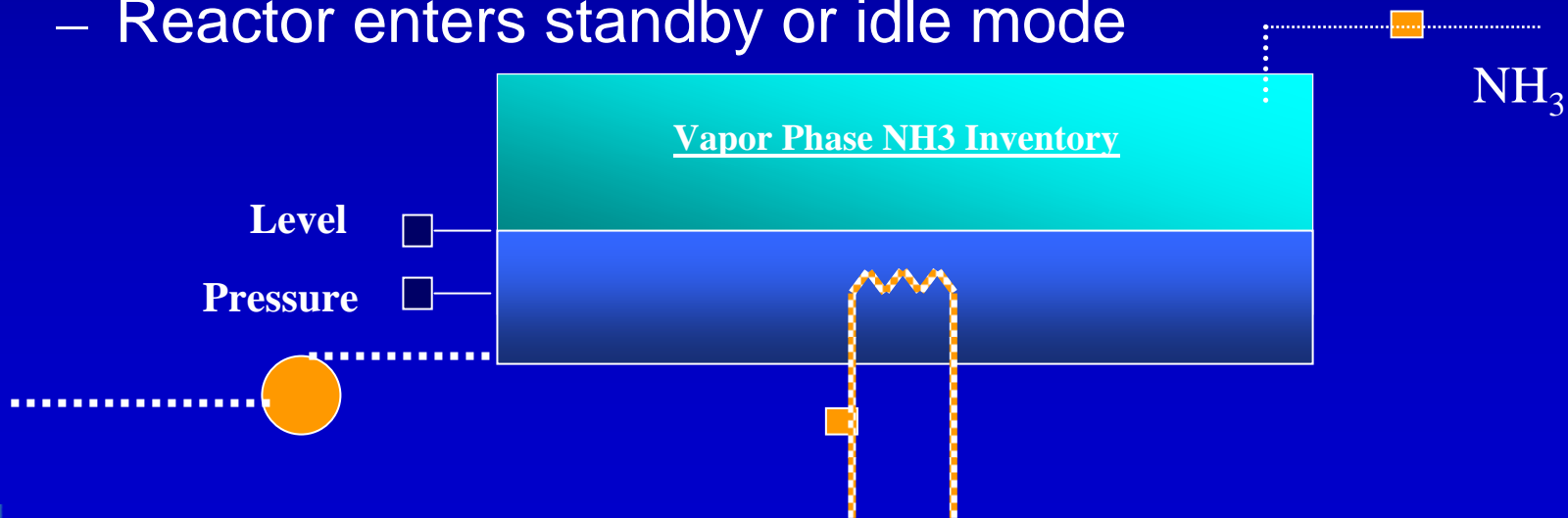


# Reliability

- With Redundant Hydrolyzers 99+% Reliability Generally Guaranteed
- Each Hydrolyzer has Redundant Critical Instrumentation
  - Two or Three Radar Level Devices
  - Two to Three Pressure Transmitters
- One Line Blow Down Enables Many Systems to Operate Continuously from Outage to Outage

# $U_2A^{TM}$ Process Shutdown

- Normal shutdown
  - $NH_3$  to process continues
  - Shut off Steam control valve
  - Shut off Feed pump
  - Hold  $NH_3$  control valve minimum open to bleed pressure
  - Reactor enters standby or idle mode



# Immediate Shutdown Capability

- Cooling Water (patented feature)
- Automated Blow Back
  - Relief to Urea Feed Tank – interlocked low level
  - Minimal Ammonia Relief
- Manual Relief Valve
  - To Urea Feed Tank
  - Very fast
  - Minimizes ammonia release

# System Improvements

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- Accurate Radar Level Sensing
- Blow down capability to remove contaminants
- Simplified Control System



# Blow Down

- Urea Impurities Concentrate in Hydrolyzer
  - Metals in urea feed
  - Impurities from DI water
  - Handling / transportation contaminants
- Frequency of Removal
  - Urea Quality
  - Operating Rate
- Periodic Draining of Hydrolyzer

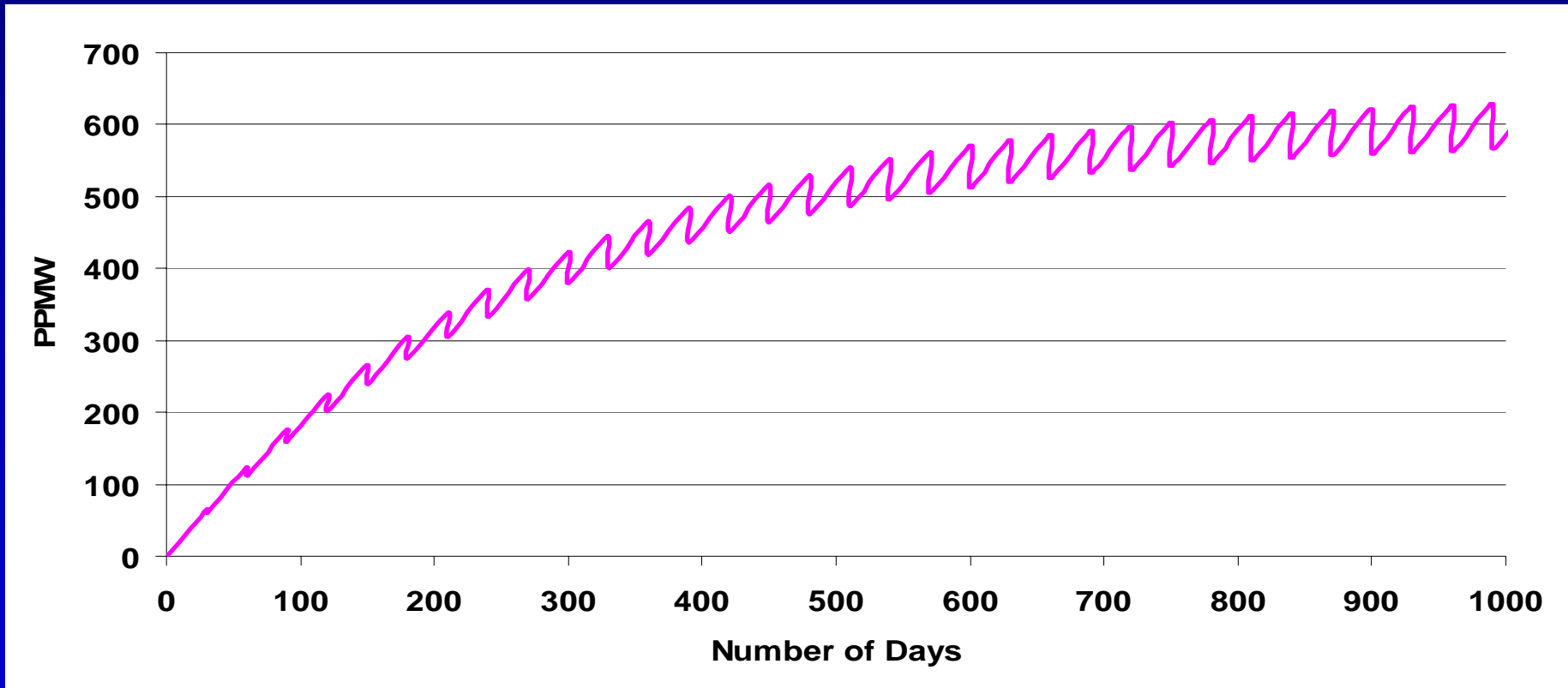


# Typical Urea Analysis

- < 0.1 ppm Chlorides
  - Hydrolyzer should be less than 800 ppm
- <0.05 ppm Chrome
  - Generally can be discharged to drain < 5 ppm
- 0.3% Formaldehyde
  - Most escapes hydrolyzer as vapor and destructed in SCR

# Blow Down

- Urea Feed of 1.0 ppm Chlorides
- 10% Blow Down Once Per Month



# Differences in U2A

- Simpler Process
- Only two Control Loops – Pressure and Urea Level
- No feed forward signal required for urea flow rate
- No recycle
- No steam stripping
- No economizer
- Lower energy consumption
- No scrubber needed (cooling water & blow back)
- Contaminants controlled with blow down

# U<sub>2</sub>A<sup>®</sup> Projects (partial list)

– Crystal River	5,892 lb/hr
– AEP Mitchell Station Units 1 & 2	3,500 lb/hr
– Moneypoint Power Station	2,860 lb/hr
– Mirant Morgantown	2,650 lb/hr
– Constellation Brandon Shores Station	2,350 lb/hr
– Hitachi Seminole	2,176 lb/hr
– Allegheny Energy Pleasants Station	1,850 lb/hr
– AEP Conesville Station Unit 4	1,700 lb/hr
– Progress Energy Asheville	820 lb/hr
– Duke Marshall 3	610 lb/hr
– Mid American Council Bluffs	410 lb/hr



# U<sub>2</sub>A<sup>®</sup> Projects (continued)

– Constellation Wagner Station	460 lb/hr
– AES Huntington Beach Station	380 lb/hr
– City of Spokane	300 lb/hr
– S & W Astoria	250 lb/hr
– AES Alamitos Station	240 lb/hr
– Namjeju Korea	160 lb/hr
– Termokimik AMSA	138 lb/hr
– White Mountain Energy	90 lb/hr
– Termokimik AMSA	33 lb/hr
– IST/(Dominion)/Kauai	28 lb/hr
– Protecma – Reggio Emilia	22 lb/hr
– UCLA	21 lb/hr
– Sinclair Oil	6 lb/hr



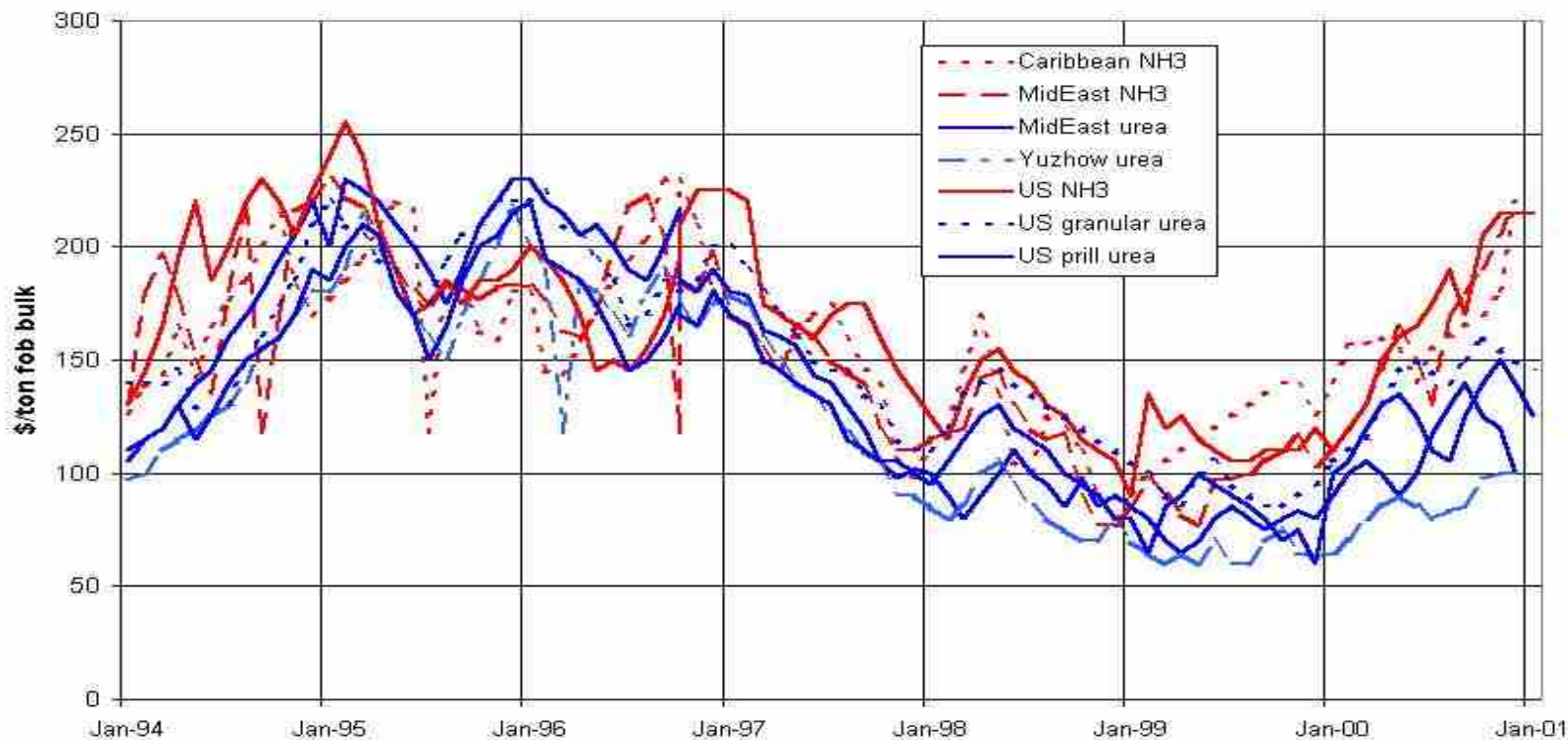
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# AMMONIA REAGENT COST COMPARISONS

# Urea vs. Ammonia - chemical cost

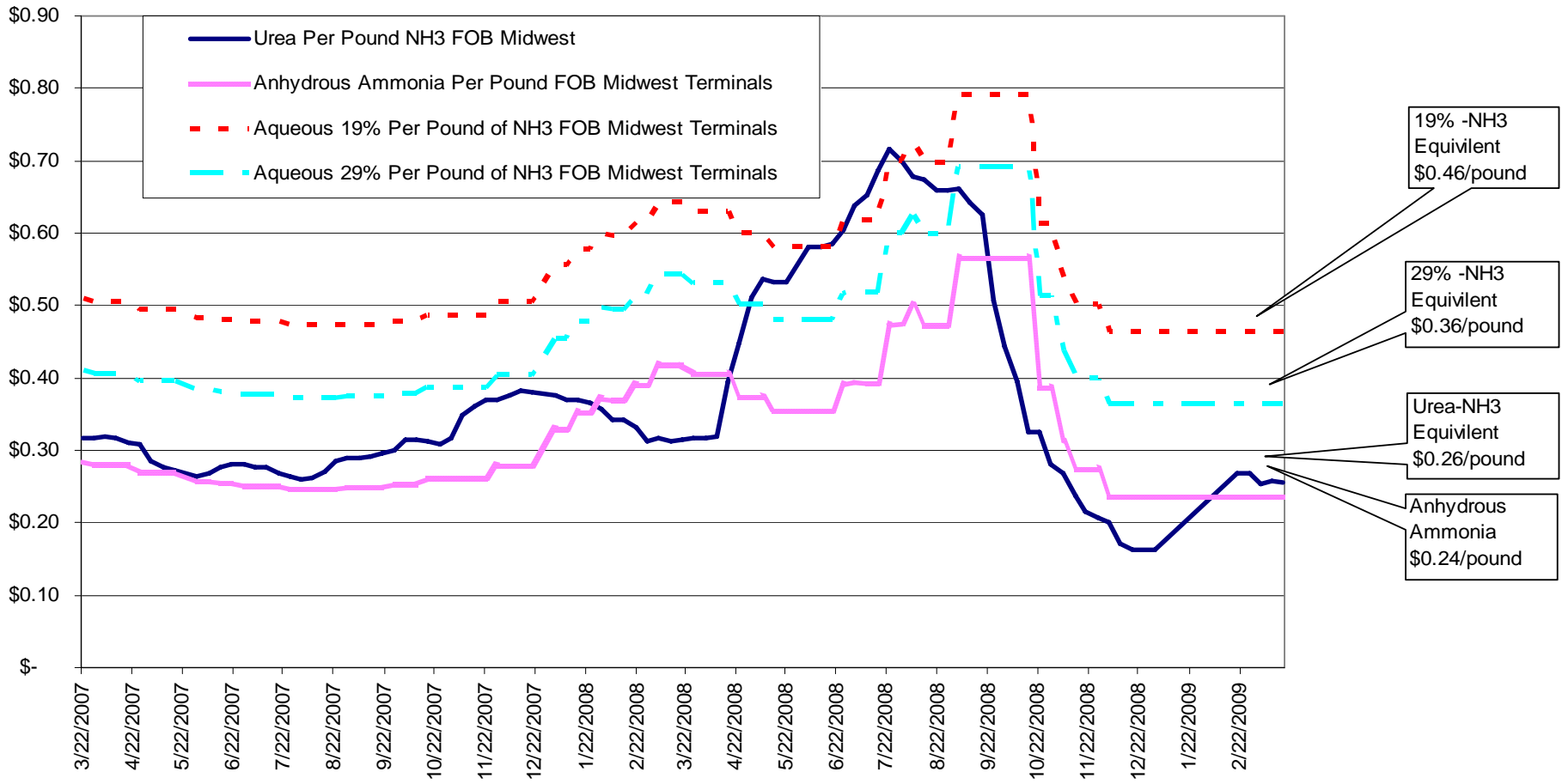
– Ammonia and urea track with natural gas prices

Urea vs ammonia  
Bulk Chemical Costs  
Fertecon data



# Urea to Ammonia Price Trends

Urea - Ammonia Price Trends



# Recent Ammonia Prices

- Delivered Central Illinois
- Quoted 2/1/10
- NH<sub>3</sub> ~ \$500 ton (\$375 ton Tampa)
- Urea ~ \$370 ton (\$650 ton NH<sub>3</sub>)
- 29% Aqueous ~ \$230 ton ( \$788 ton NH<sub>3</sub>)
- 19% Aqueous ~ \$190 ton ( \$1000 ton NH<sub>3</sub>)
- Transportation Costs much more for Anhydrous

# Reagent System Cost Comparison

- Budgetary Costs for Capital Equipment
  - Nominal 3,500 lb per hour ammonia
  - 15 day chemical storage capacity
  - 100% equipment redundancy
    - \_ 2 x 100% Hydrolyzers serving 2 boilers
- Anhydrous Ammonia: \$2.5-\$2.8 million
- Aqueous Ammonia: \$3.2-\$3.5 million
- U2A \$4.5-\$5.5 million



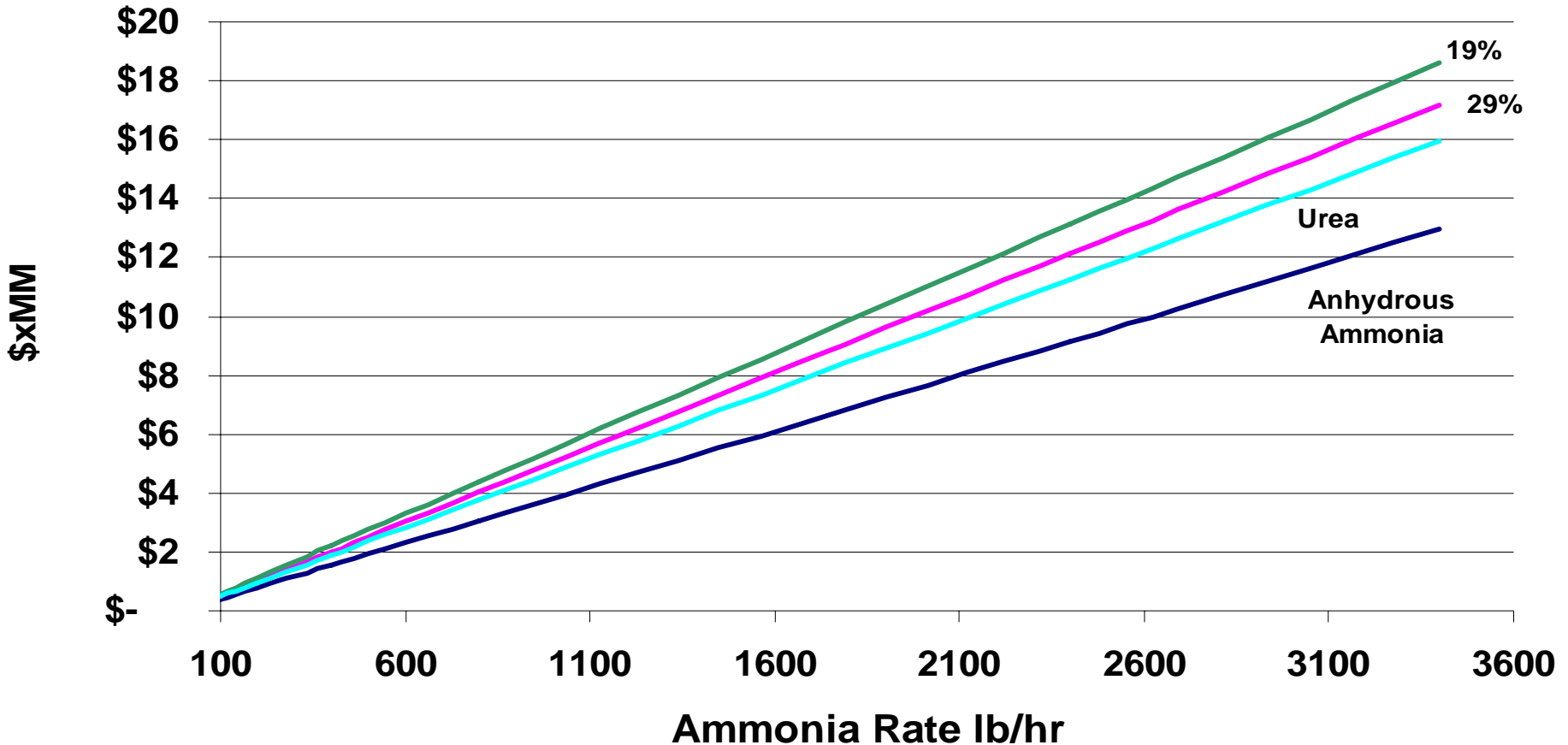
# Utility Consumption for SCR Applications

- Anhydrous Ammonia Vaporization
  - 540 btu's per lb of ammonia (0.16 kW)
  - AFCU ~ .32 kW lb NH<sub>3</sub>
- Aqueous Ammonia (19%) Vaporization
  - 7750 btu's/lb of ammonia (2.3 kW)
  - AFCU ~ .70 kW lb NH<sub>3</sub>
  - (5.26 lb water / lb ammonia)
- Urea to Ammonia -50% Urea
  - 3354 btu's/lb ammonia (0.98 kW)
  - AFCU ~ .28 kW lb NH<sub>3</sub>
  - (1.76 lb water / lb ammonia)



# Yearly Operating Cost

Feed stock costs based on average of first 9 months of 2008



# Feed Stock Comparisons

- Anhydrous
  - Highest Risk
  - Presently the Lowest Capital and Operating Costs
  - Greatest Permitting Issues
  - On Going Safety Training Costs
  - Greatest Uncertainty with Future Regulatory Issues
  - Increasing Transportation Costs

# Feed Stock Comparisons

- Aqueous
  - Much Higher Capital and Operating Costs
  - Slightly Less Risk than Anhydrous
  - Huge Storage Volumes and Handling Costs
  - Regulated Toxic Chemical
  - Permitting Issues
  - On Going Safety Training Costs
  - Some Uncertainty with Future Regulatory Issues
  - Increasing Transportation Costs

# Feed Stock Comparisons

- Urea
  - Lower Operating Costs than Aqueous Ammonia
  - Lowest Risk
  - No Permitting Issues
  - No Uncertainty with Future Regulatory Issues



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# Summary

- Urea to Ammonia Systems
  - Safe Alternative to Anhydrous or Aqueous Ammonia
  - Similar Operating Costs to Aqueous Ammonia
  - Non Regulated Feed Stock
  - Less Uncertainty of Future Regulations

# Questions



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