UAN Fertilizer Corrosion Management

Fluid Technology Roundup

Dec 10th, 2013

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NALCO NITROGEN TEAM

Agenda

- Who Is Nalco?
- UAN corrosion mechanisms
- UAN corrosion….. *what you can do*
  - Cause & Prevention Strategy
- *Nalco's efforts to help* producers reduce UAN corrosivity & improve UAN quality

Who Is Nalco?

Nalco joined with Ecolab in 2011

- Global leader in water, hygiene and energy technologies and services
  - Foodservice, food processing, hospitality and healthcare
  - Petroleum & Gas Production and Refining
  - Paper Manufacturing & Finishing
  - Mining
- 44,000+ Employees
- $12 Billion Sales in 2012
  - UAN Corrosion Management Leader since 1994
    - Primarily with UAN producers

Our Experience in the UAN Industry

- Nalco has had a long, on-going commitment to the fertilizer industry to improve UAN corrosion management
  - 1994: introduced molybdate-based passivation technology
  - 2003: started extensive UAN CI research program
    - Developed the Nalco UAN Corrosion Simulator
  - 2004: introduced two new technology UAN corrosion inhibitors
    - NITROSolve 220 **filmer** technology that works
    - NITROSolve 330 **passivation** technology that works and is affordable
  - 2006: introduced products for post-inspection and pre-treatments programs for new rail cars and storage tanks
  - 2012: 3D Trasar® for UAN
  - 2013: 3D Trasar® for % Nitrogen
- Many long-term relationships in the fertilizer industry
  - Nalco provides inhibitor for about half of the UAN producer sites in North & South America and for about 35% of Global UAN production!

Okay, enough about Nalco, let's talk about your business…..

Fertilizer Producers, Dealers & Terminals Are In The News

You may have heard about the explosion in West, Texas in May 2013

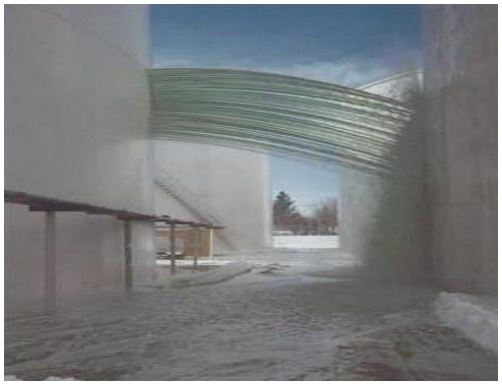
From the May 27th issue of Chemical & Engineering News:

The catastrophic explosion at a fertilizer depot in Texas last month is raising new questions about the effectiveness of *the federal government's program to ensure the* security of plants that handle large amounts of extremely dangerous industrial chemicals. Some Democratic lawmakers are suggesting that the disaster has **exposed major flaws** in the **Department of Homeland Security's** (DHS) **Chemical Facilities Anti-Terrorism Standards (CFATS) program**. The nearly six-year old initiative is designed to safeguard facilities that produce, store, or use hazardous chemicals that could be exploited by terrorists to inflict mass casualties in the U.S.

I'm sure I don't have to tell you that your "fertilizer" business is under increased scrutiny by local and state officials

Leaks from UAN and Other Liquid Fertilizer Assets Present A Real Business Risk

- For those attendees that have attended past **Technology Roundup Conferences** *you may have heard John Boyd's* presentation



In March 2000 in Ohio, USA a tank leak……

Quickly resulted in complete tank collapse……..

And a "river of fertilizer flowed through Main Street"

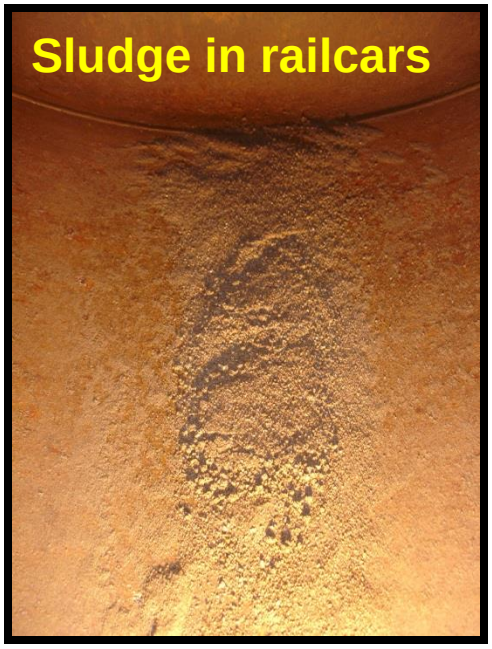
- **You could lose significant amounts of product and property**
- **Your business reputation may be put at risk**
- **The EPA and OHSA might become your new business partners**

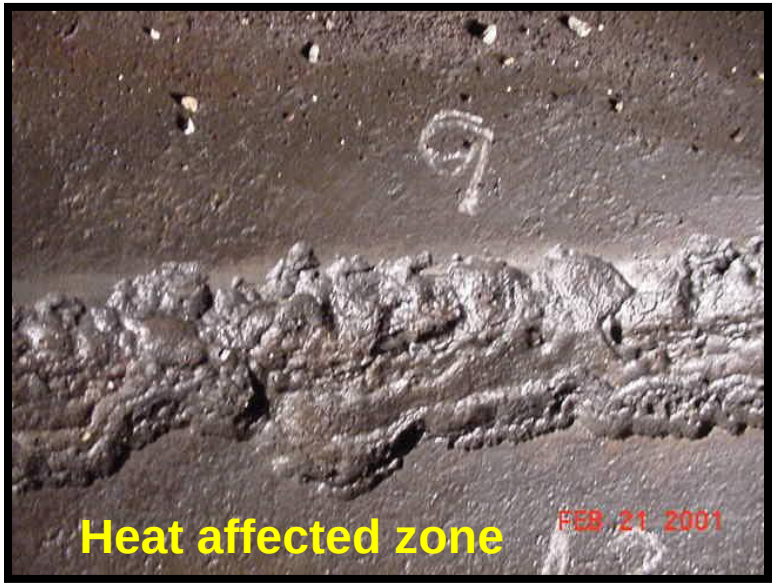
UAN Corrosion Management Should Be Taken Seriously by Every UAN Tank Owner

- All UAN producers strive to make quality material, that is clean, bright and only minimally corrosive
- However, you should not depend solely on the UAN producer to manage your corrosion concerns.
- Some producers have gone to lined tanks, or use epoxy coatings extensively. Their piping is all stainless.
- UAN corrosiveness can vary:
  - Producer to producer,
  - Plant to plant,
  - And even from day to day in the same plant

Let me share some examples of the severe corrosion that has occurred in producer storage tanks

UAN Corrosion Can Be Quite Serious!





Please allow me to tell you more about why UAN is so corrosive

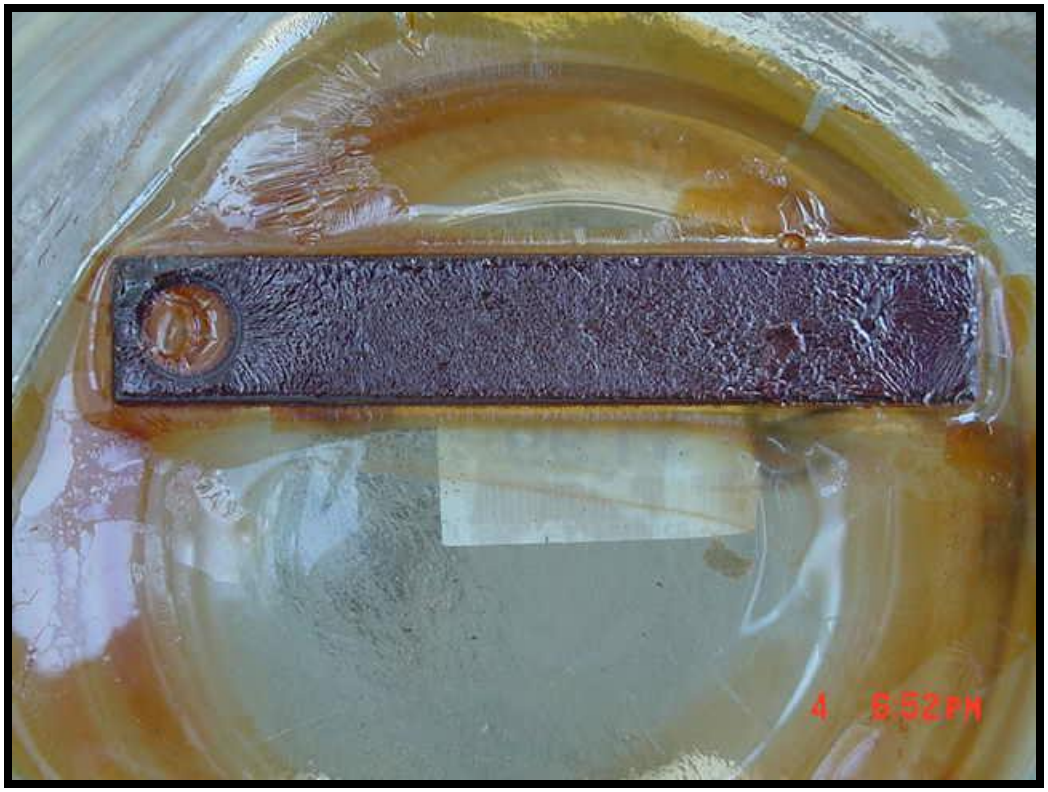
A Simple Example of A "Key UAN Corrosion Parameter"

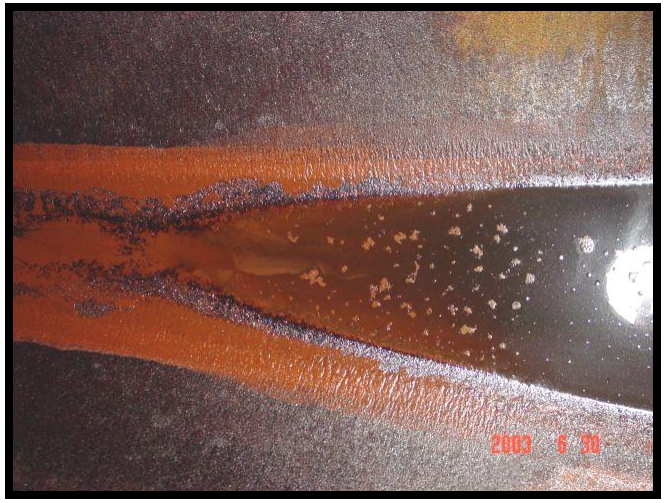
Ammonia Content

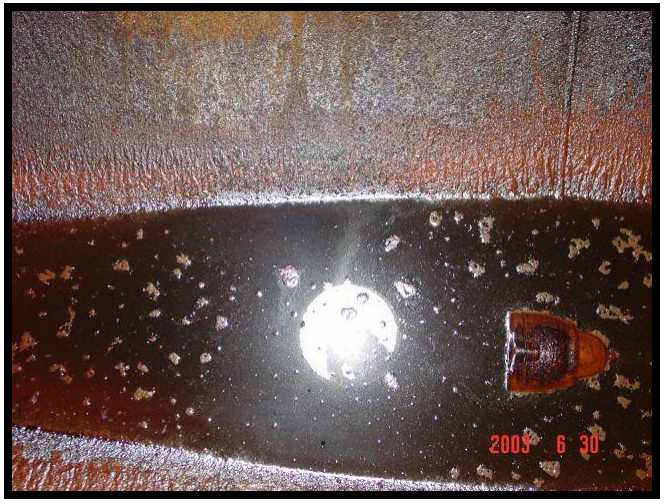
- A corrosion coupon with an existing corrosion spot, was placed in a sealed jar, ~ 20 mls of UAN was added –just enough to partially cover the surface
- The Jar was sealed and placed in the KS July sun for 7 days
- No new corrosion occurred while the jar was sealed
- This photo was taken just prior opening the jar for ~ 3 hours:
  - Allows for release of the ammonia that is dissolved in UAN
  - The jar was then resealed and allowed to bake in the sun for ~24 hours

Initial Investigation

- Photo taken after being resealed and 24 sun hour bake
- Note the similarity with rail car UAN heel discoloration & texture







Initial Investigation

Photo taken after paper towel wipe clean

Key Take Away

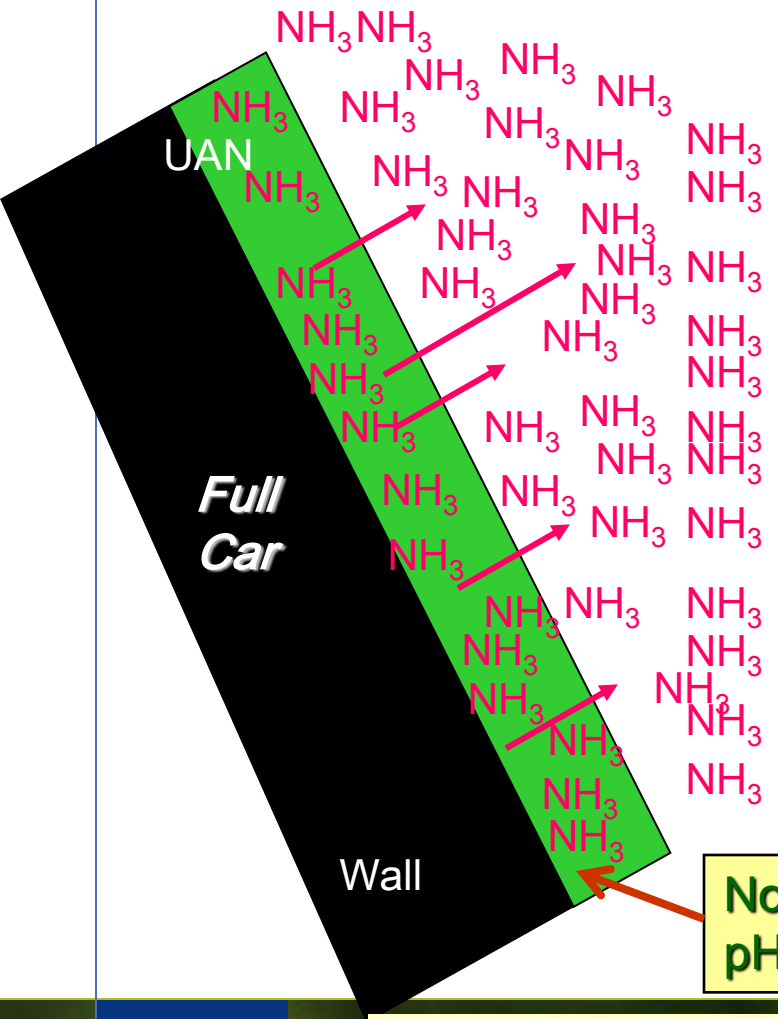
- **The pH and amount of excess ammonia in UAN is important**
- **“Thin UAN films” in tanks, pipelines and rail cars allow for rapid “surface corrosion” and produces lots of rust sludge!**

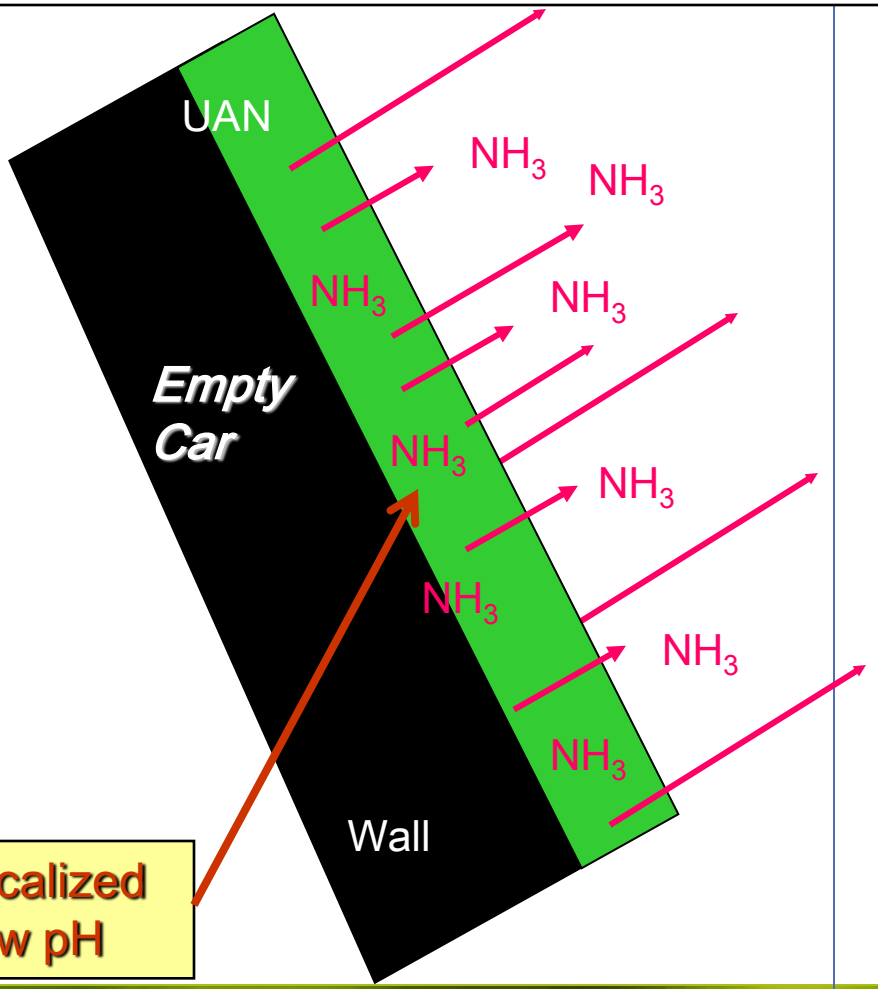
How might this be applicable to your business?

The "Thin UAN Film" Corrosion Mechanism in UAN Rail Cars

In a full rail car: The air in the car is saturated with NH3 vapor

In an empty rail car: The fresh air pulled into the car when emptied must re-establish equilibrium vapor pressure using NH3 available from the thin film on the tank wall

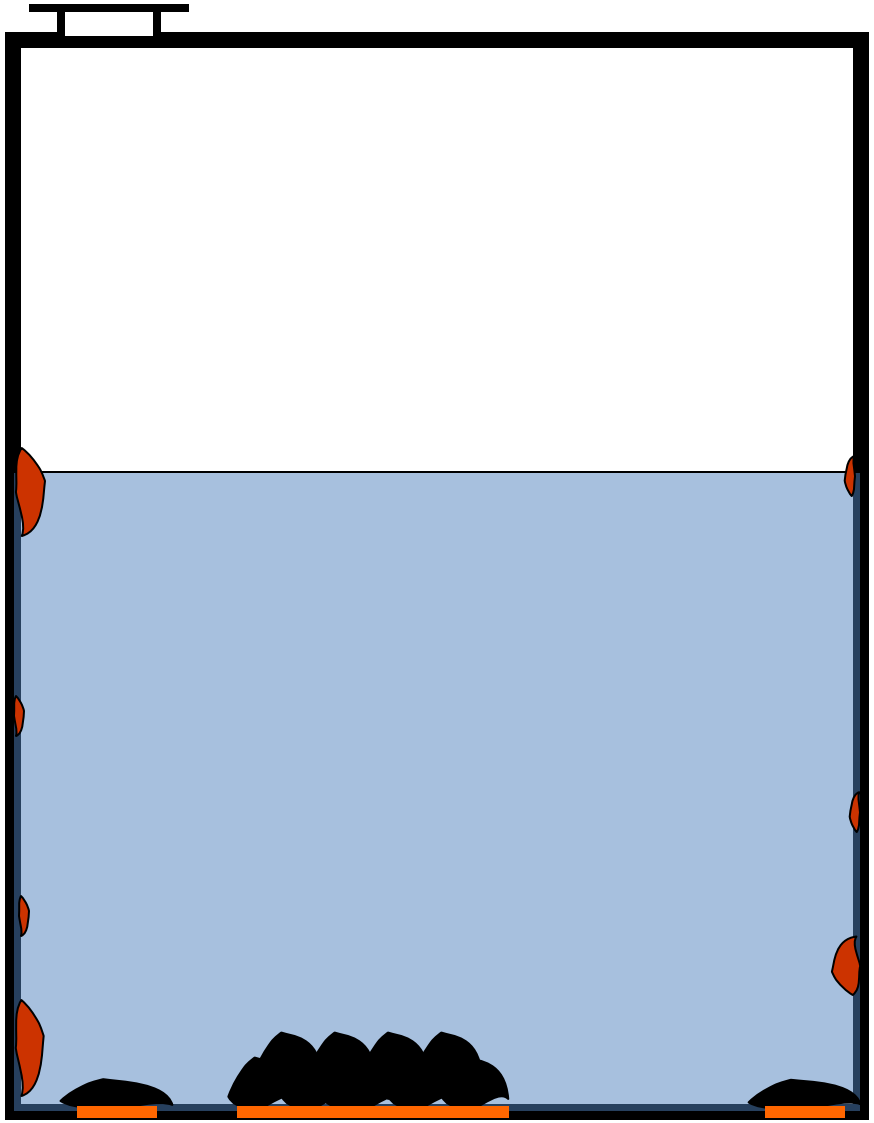




Normal pH	Localized Low pH

What about storage tanks?

“Thin UAN Film” Sludge Generation and Pitting Corrosion in UAN Tanks



UAN corrodes carbon steel by two different mechanisms:

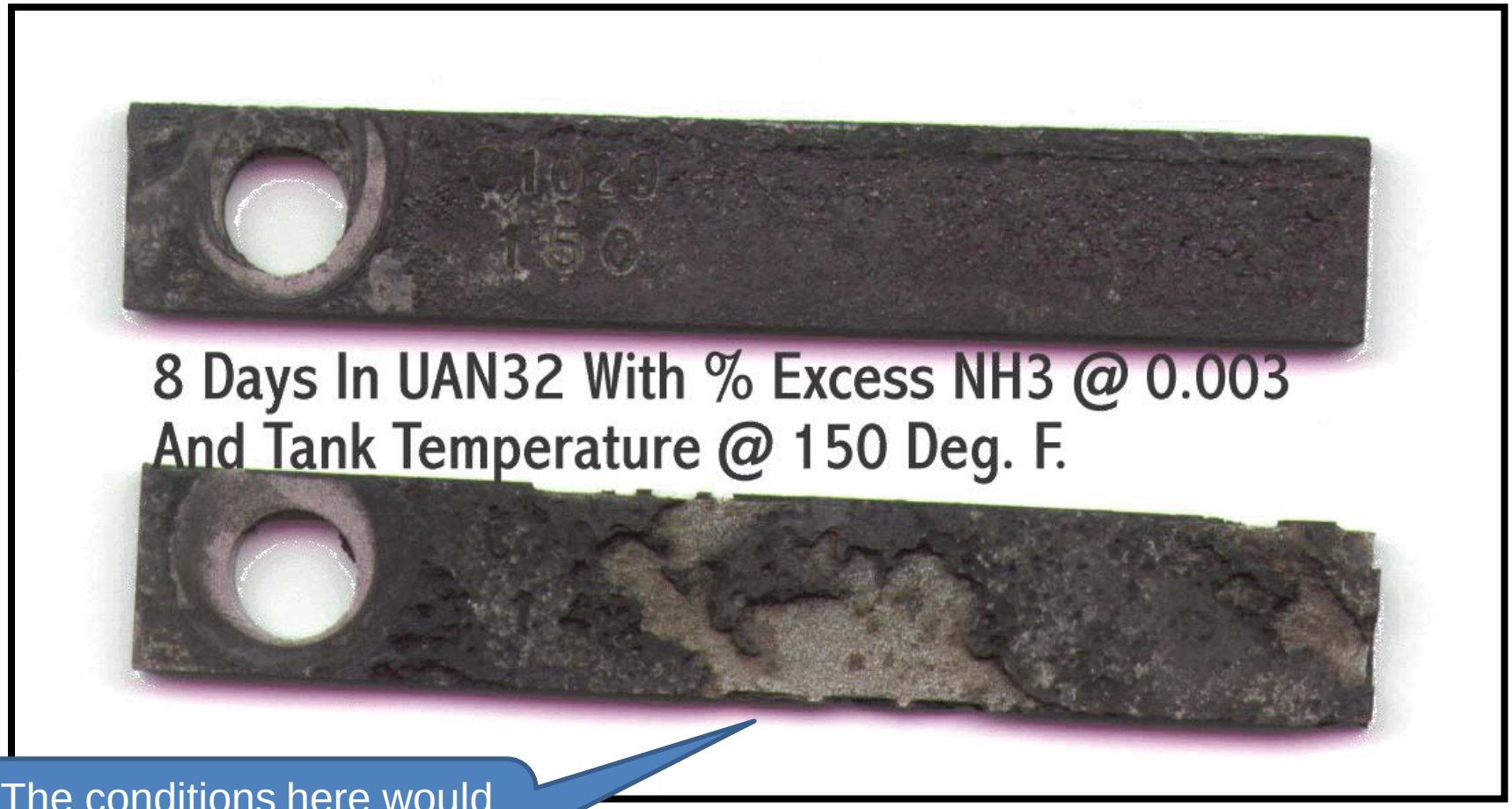
- **“Thin Film” or “Surface” Corrosion** occurs on the vertical tank walls and generates iron sludge that falls to the tank bottom
- **Under Deposit Corrosion** develops when iron sludge falls to the tank bottom and collects in low spots

This is why corrosion is usually minor on the vertical tank walls and is most severe on the tank bottom

What Makes UAN Corrosive?

CAUSE	Prevention
pH & excess NH3 are too low	Minimum pH: 7.0 Minimum NH_3: 0.05 % (500 ppm)
Temperatures that are too high or two low	Keep tank between 40-100^{o}F if possible

Example From Actual Conditions In A Real UAN Storage Tank



The conditions here would *"burn through" 2 inches of* steel in one year!

Let me show you more how temperature can affect pH & corrosivity

UAN pH Is A Function of Temperature

Non-Inhibited UAN 32 (actual pH will also vary as a function of excess NH3 content)

UAN Temp (F)	Med pH 7.0
68	7.00
77	6.84
86	6.69
104	6.40
122	6.13
140	5.88
158	5.64
138	5.82
120	6.30
100	6.50
82	6.80
73	6.90
70	6.95

- Note that the pH drops as Temperature increases
- However, the pH increases again as the UAN cools
- Why does this happen?

Because the ammonium nitrate "dissociates" to a strong acid and a weak base:

$NH_4NO_3 \rightleftarrows NH_4^+ + NO_3^-$

$NH_4^+ \rightleftarrows NH_3 + H^+$

$H^+ + NO_3^- \rightleftarrows HNO_3$ (Nitric Acid)

So why is this important to liquid fertilizer dealers?

Effect of Temperature on UAN Corrosivity

Actual pH *(will vary slightly as a function of the amount of excess NH3 and heating rate)*

UAN Temp (F)	Low pH 6.7	Med pH 7.0	Hi pH 7.5	Very High pH 8.0
68	6.70	7.00	7.50	8.00
77	6.54	6.84	7.34	7.84
86	6.39	6.69	7.19	7.69
104	6.10	6.40	6.90	7.40
122	5.83	6.13	6.63	7.13
140	5.58	5.88	6.38	6.88
158	5.34	5.64	6.14	6.64

Severe Corrosion Activation pH		
Metal Type	**UAN 32**	**UAN 28**
A36 Welds	6.60	6.95
A36 Plate	5.75	6.10

Storage Type	Typical Storage Temperature
Storage Tank	40-122 ^{o}F
Rail Car	Cold to 140 ^{o}F

What Can You Do?

- Consider the pH & Excess ammonia sales specification of your supplier
  - How good is their QC program?
  - How often do they test and what do they test?
  - Test incoming product yourself
- We recommend light colored storage tanks
- Prevent ammonia loss through proper tank venting

What else is important for managing UAN corrosion?

What Makes UAN Corrosive?

CAUSE	Prevention
pH & excess NH3 are too low	Minimum pH: 7.0 Minimum NH_3: 0.05 % (500 ppm)
Temperatures that are too high or two low	Keep tank between 40-100^{o}F if possible
UAN 28 and dilute UAN solutions	Where ever possible, avoid long term storage of UAN 28

16% Nitrogen UAN is MUCH more corrosive than 32% Nitrogen UAN

This is because the increased water content of UAN16 allows for increased ion formation:

$NH_4NO_3 \rightleftarrows NH_4^+ + NO_3^-$

$NH_4^+ \rightleftarrows NH_3 + H^+$

$H^+ + NO_3^- \rightleftarrows HNO_3$ (Nitric Acid)

Non Inhibited UAN 32		
32% Temp (°C)	32% Temp (°F)	UAN 32 Corr. Rate* (MPY)
23.1	73.6	0.1
23.5	74.3	0.1
57.8	136.0	1.6
73.5	164.3	5.5
93.8	200.8	7.1
102.8	217.0	7.3
90	194.0	6.2
68.8	155.8	5.5
50.7	**123.3**	**1.4**
46.4	115.5	1.3
39.5	103.1	1.0

*As measured per the Nalco Corrosion Monitor Probe

Note that at roughly the same temperature of 124 °F (51 °C) the corrosivity of UAN 16 is approx. 35-40 times more corrosive than UAN 32!

Non Inhibited UAN 16		
Temp (°C)	Temp (°F)	UAN 16 Corr. Rate* (MPY)
16.7	62.06	0.1
17.4	63.32	0.1
20	68	0.1
50.7	123.26	48.1
72.4	162.32	59.2
74.3	165.74	79.2
78.7	173.66	99.9
91.6	196.88	99.9
102.3	216.14	99.9
100.6	213.08	99.9
81.4	178.52	99.9
69.3	156.74	99.9
63	145.4	58.3
59.1	138.38	58.3
54	129.2	58.3
51	**123.8**	**58.3**
47.9	118.22	39.2
44.9	112.82	39.2
41.5	106.7	39.2
40	104	44.3
31	87.8	23.0

What Can You Do?

- Avoid storing dilute UAN solutions
- Be careful about leaving rinse water in tanks

What about UAN 28?

UAN 28 is about 20% more corrosive than UAN 32

This is because the increased water content of UAN 28 allows for increased ion formation:

$NH_4NO_3 \rightleftarrows NH_4^+ + NO_3^-$

$NH_4^+ \rightleftarrows NH_3 + H^+$

$H^+ + NO_3^- \rightleftarrows HNO_3$ (Nitric Acid)

Non Inhibited UAN 32		
32% Temp (°C)	32% Temp (°F)	UAN 32 Corr. Rate* (MPY)
23.1	73.6	0.1
23.5	74.3	0.1
57.8	136.0	1.6
73.5	164.3	5.5
93.8	200.8	7.1
102.8	217.0	7.3
90	194.0	6.2
68.8	155.8	5.5
50.7	**123.3**	**1.4**
46.4	115.5	1.3
39.5	103.1	1.0

*As measured per the Nalco Corrosion Monitor Probe

Non Inhibited UAN 28	
Temp (°F)	UAN 28 Corr. Rate* (MPY)
64	0.1
69	0.1
75	0.1
86	0.2
95	0.9
110	1.1
125	**1.7**
150	2.4
130	2.1
115	1.3
102	1.0
93	0.8
81	0.2
74	0.1
68	0.1

Note that at roughly the same temperature of 124 °F (51 °C) the corrosivity of UAN 28 is approx. 20% more corrosive than UAN 32!

What Can You Do?

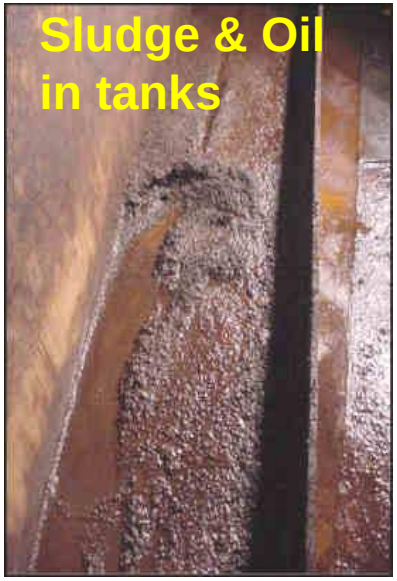
- **Where possible, avoid storage of UAN 28 and other dilute UAN solutions**

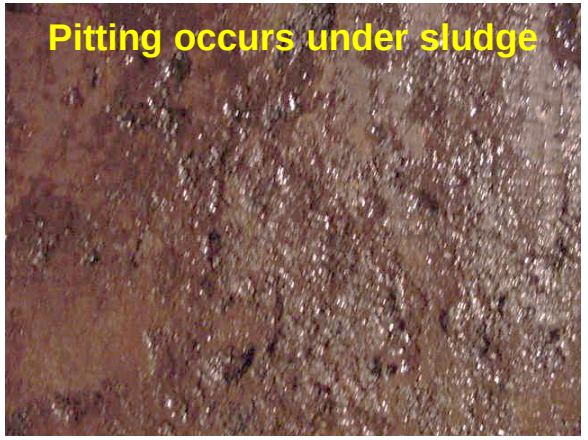
What Makes UAN Corrosive?

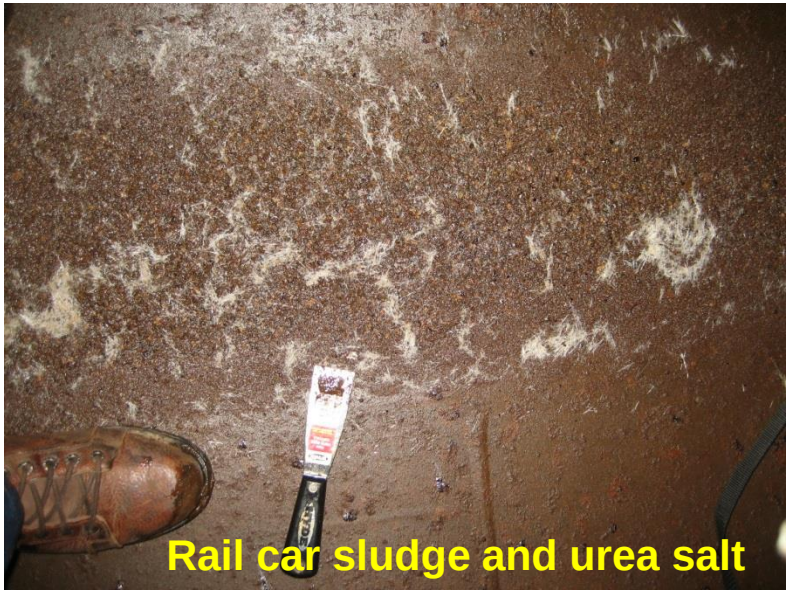
CAUSE	Prevention
pH & excess NH3 are too low	Minimum pH: 7.0 Minimum NH_3: 0.05 % (500 ppm)
Temperatures that are too high or two low	Keep tank between 40-100^{o}F if possible
UAN 28 and dilute UAN solutions	Where ever possible, avoid long term storage of UAN 28
Corrosion sludge	Clean tanks annually if possible

Corrosion Sludge Is What Leads To Serious Pitting Damage

Clean You Storage Tanks Annually







Electro-chemical Description of Pitting Corrosion in UAN

At Heat Affected Zone

$Fe^{+2} \rightarrow Fe^{+3}$ (occurs in crevices)

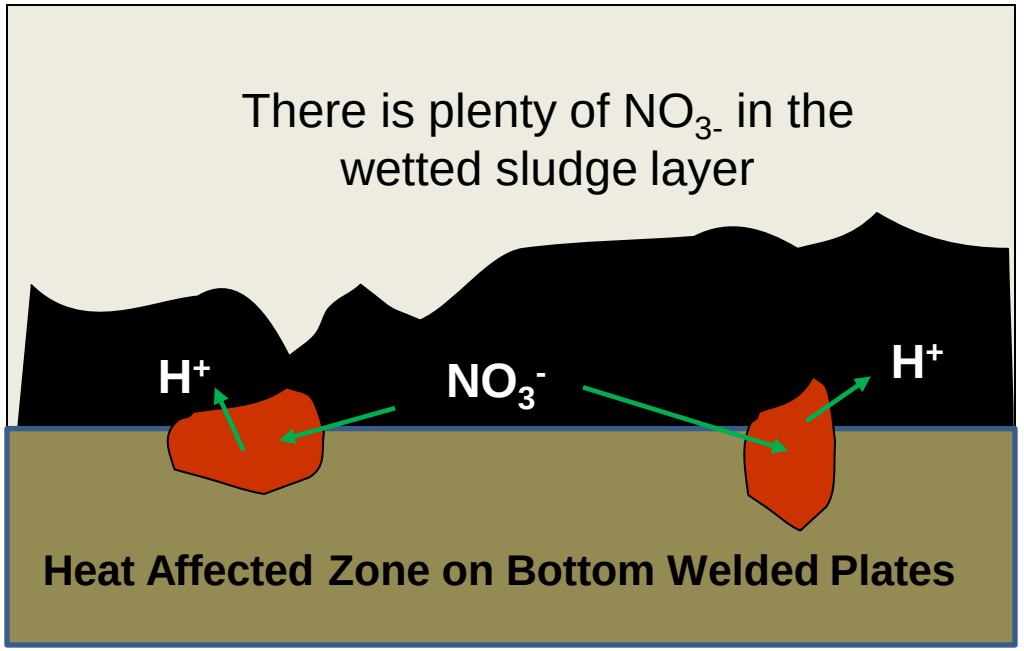
$Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

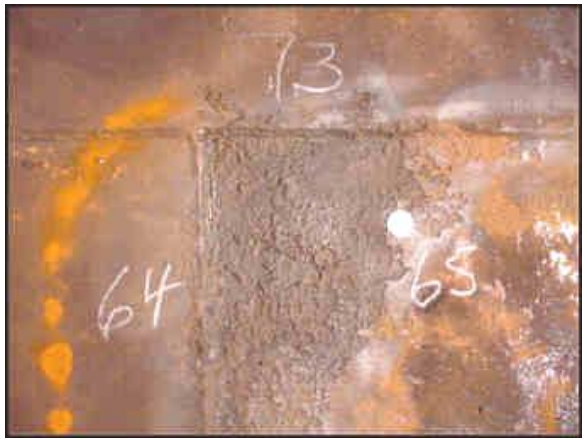
In Solution

$NH_4NO_3 \rightarrow NH4^+ + NO3^-$

$NO_3^- + H^+ \rightarrow HNO_3$

The H^+ can't diffuse out of the crevice fast enough. To remain electrically neutral, NO_3^- ions come in and in effect make Nitric Acid resulting in low pH inside the crevice, resulting in a pit



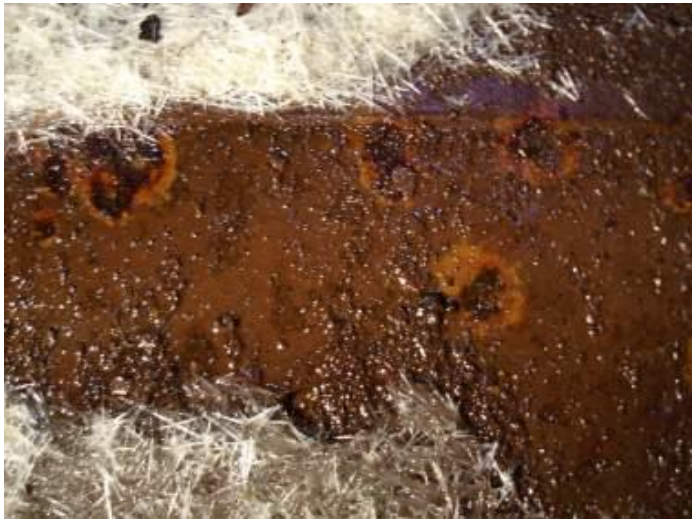


What Makes UAN Corrosive?

CAUSE	Prevention
pH & excess NH3 are too low	Minimum pH: 7.0 Minimum NH_3: 0.05 % (500 ppm)
Temperatures that are too high or two low	Keep tank between 40-100^{o}F if possible
UAN 28 and dilute UAN solutions	Where ever possible, avoid long term storage of UAN 28
Corrosion sludge	Clean tanks annually if possible
Empty spaces with UAN heels or residuals	Never leave a tank or pipe with a small heel of UAN especially in summer

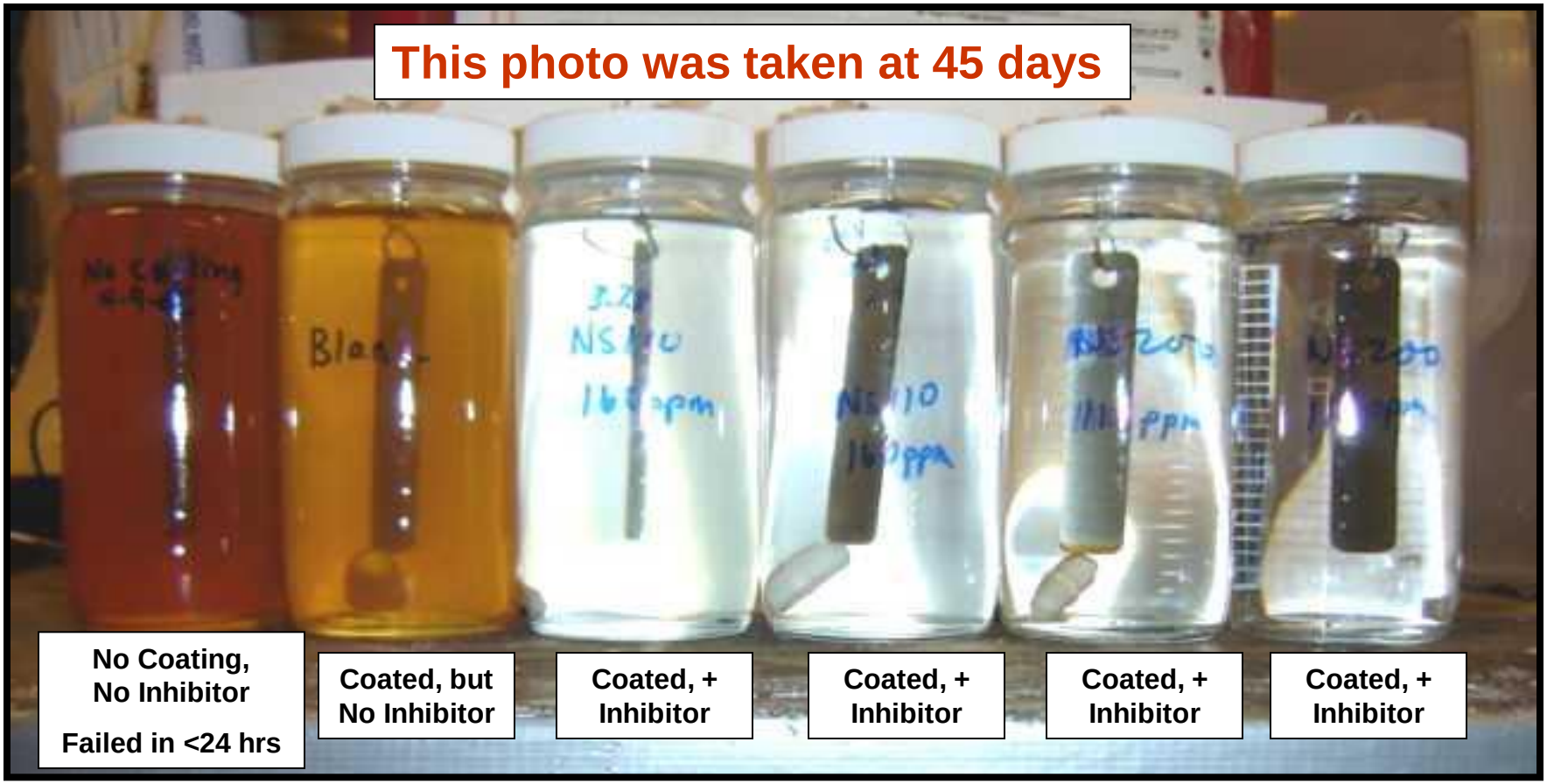
Dilute, Low Ammonia UAN Solutions Are Very Corrosive

- *Don't leave "a few inches"* of UAN in tanks
  - Especially in winter
- Never leave small puddles of UAN
  - Empty & water wash the floor thoroughly
- *Avoid "air blow" of carbon* steel UAN pipeline
  - Water flush pipes well then air blow
- Pre-treat idle or newly repaired tank bottoms with an appropriate passivator



Nalco UAN Pre-Treatments

for storage tanks, barges and rail cars helps prevent corrosion under severe conditions and maintain color and clarity



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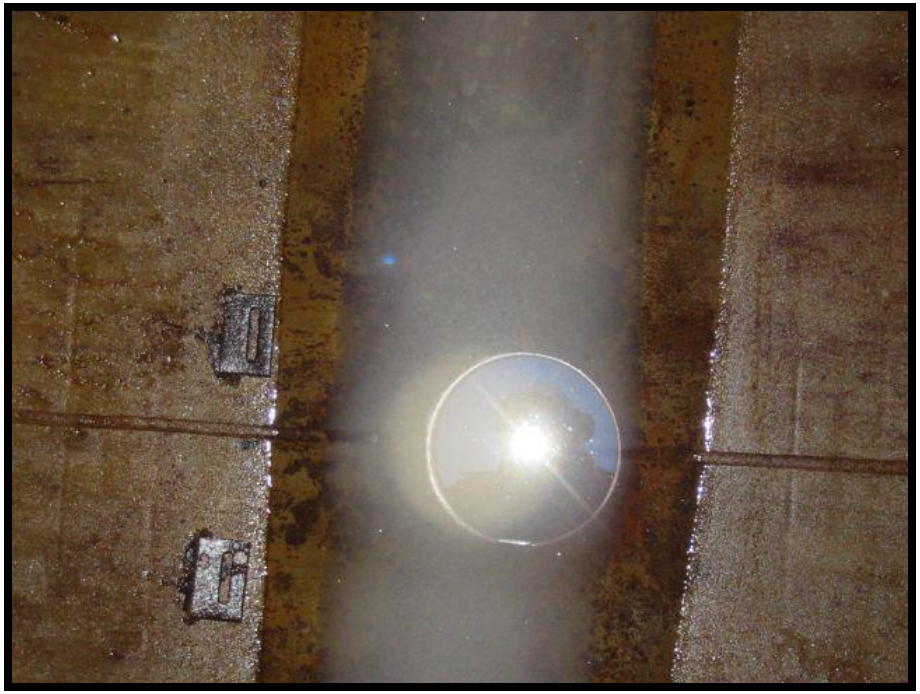
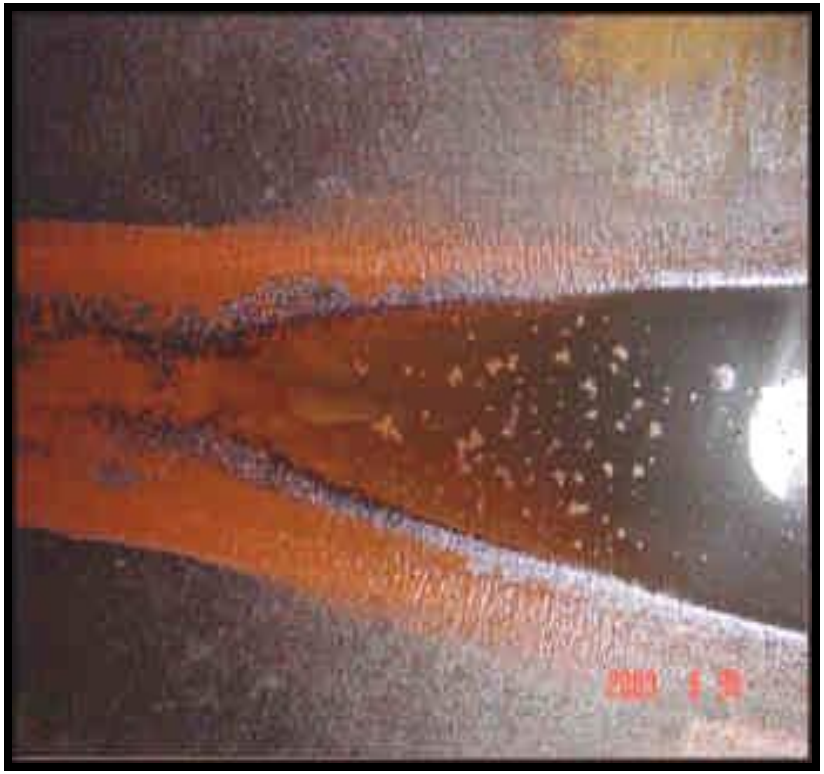


UAN heel in railcar pre- treated with a Nalco Pre-Treatment product

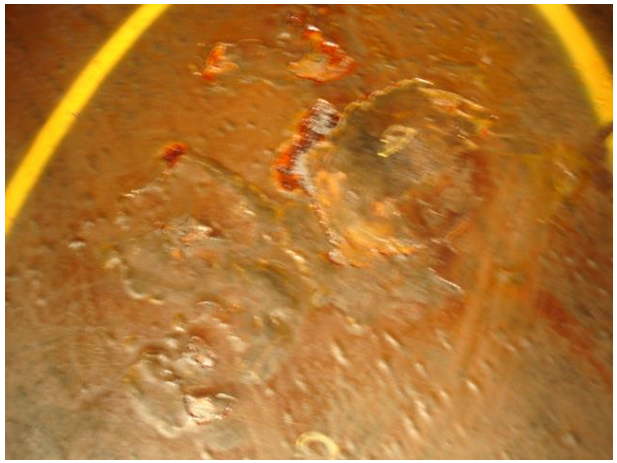
UAN heel in rail car NOT pre-treated



What about coatings?

A Word About Tank Coatings

- Various coatings have been applied to UAN tanks and even UAN rail cars for years
  - They can help minimize the impact of some major pH, temperature or poor corrosion inhibition events
  - They may also give a false sense of security
- Must be applied to clean surface floor & wetted side wall
- *Coatings almost always have "life" issues*
  - Any coating failure focuses the corrosivity of the entire tank on a small area



After sandblasting failed coatings often reveal <u>severe</u> corrosion

What about added chemical corrosion inhibitors?

UAN Corrosion Type and Dosage Matters!

- Purchasing UAN from multiple sites, may result in mixed inhibitors
  - The 3 dominant UAN corrosion inhibitor manufacturers in North & South America use very different chemistries
  - If mixed, these different inhibitors, (now each diluted), are not as effective together as they are by themselves when at full strength
- Purchasing quality UAN from one trusted source may be worth a little extra in price
  - Price is important but look closely at the quality of the UAN you are buying
  - Consider the value of the assets that will be exposed to that product

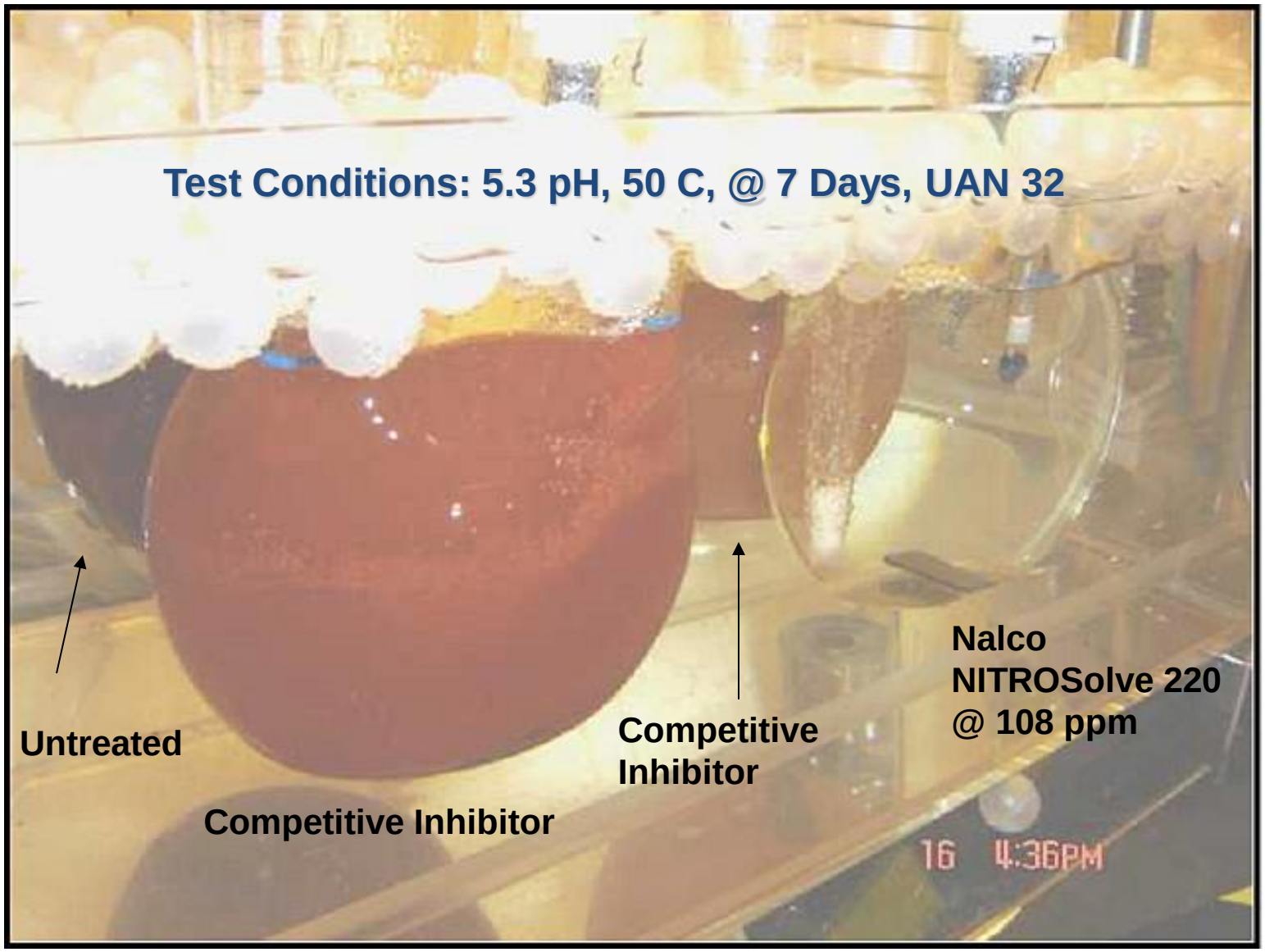
What Makes UAN Corrosive?

CAUSE	Prevention
pH & excess NH3 are too low	Minimum pH: 7.0 Minimum NH_3: 0.05 % (500 ppm)
Temperatures that are too high or two low	Keep tank between 40-100^{o}F if possible
UAN 28 and dilute UAN solutions	Where ever possible, avoid long term storage of UAN 28
Corrosion sludge	Clean tanks annually if possible
Empty spaces with UAN heels or residuals	Never leave a tank or pipe with a small heel of UAN especially in summer
Lack of a quality chemical inhibitor @ the proper dose	- Buy from trusted supplier(s) - Ask about inhibitor program ▪ *If you don't ask, they won't care*

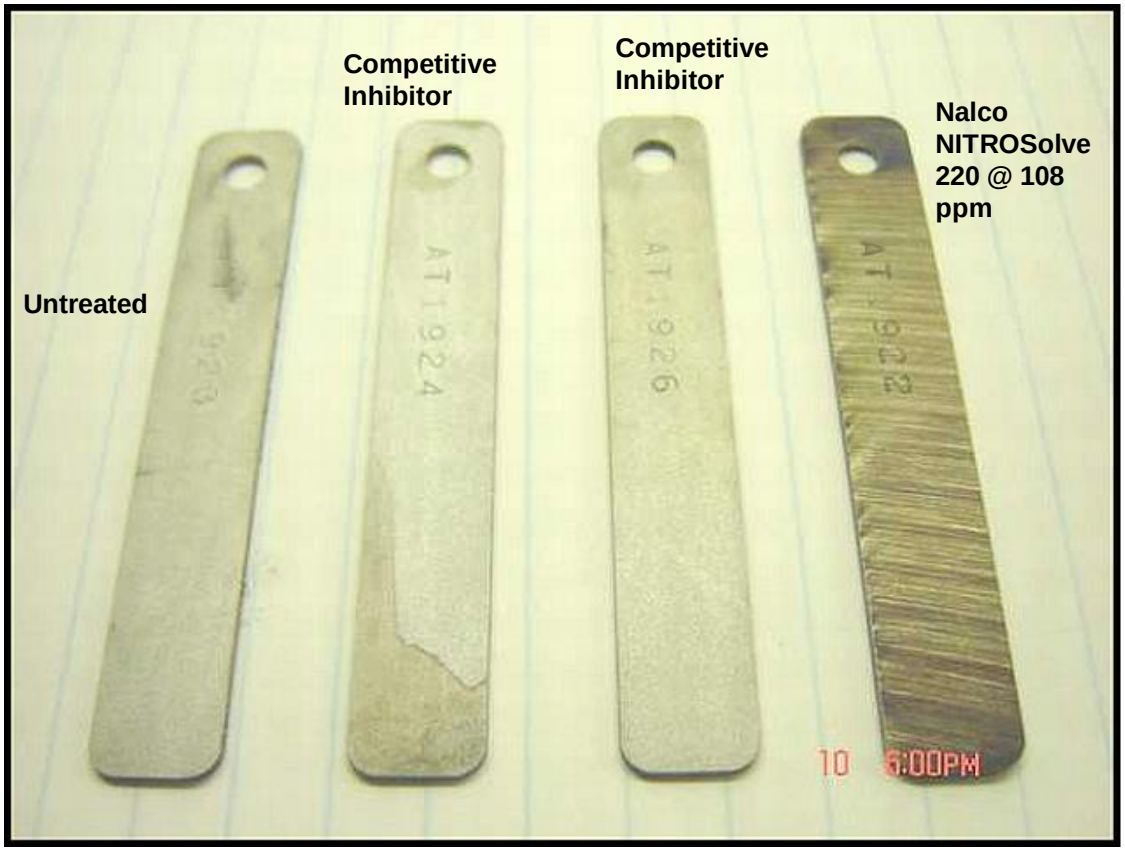
Or Consider Adding Your Own Corrosion Inhibitor

- UAN corrosion Inhibitors are relatively inexpensive and most are easy to handle and safe to work with
- Depending on your source of UAN and inhibitor package, treat costs will vary from $0.20 to $0.60 per ton of UAN treated
- Do not add petroleum oil to any UAN tank, car, truck, or pipe
- **UAN corrosion inhibitor choice matters**
  - If a producer has coated tanks and rail cars and stainless steel piping, corrosion inhibitor quality may not be a high priority

Nalco UAN Corrosion Simulator Test Rig



Test Conditions: 5.3 pH, 50 C, @ 7 Days, UAN 32



Treatment	MPY Corrosion Rate
Blank-Untreated	400
Competitive Inhibitor	330
Competitive Inhibitor	300
NITROSolve 220@ 108ppm	1.5

But added corrosion inhibitors **cannot** stop all UAN corrosion, manufacturer quality counts!

UAN manufacturing involves many complicated, problematic and <u>continuous</u> processes <u>and</u> <u>UAN is the last step</u>

Methane ➔ $H_2 + CO_2$

$H_2 + N_2$ ➔ NH_3

NH_3 ➔ NOx ➔ Nitric Acid + NH_3 ➔ AN

$CO_2 + NH_3$ ➔ Urea

AN + Urea + NH_3 ➔ UAN

Is on-line pH control accurate?

Is lab sample testing sufficient?

Issues w/ the NH3 Plant?

Trimming pH w excess nitric acid?

UAN Storage

How much excess NH3?
How much AN vs. Urea?
Temperature and pH?
Circulation?
Sludge buildup?
Shut downs & start ups

Is enough urea available? How much excess NH3?

How much NH3 recycle is coming back from the AN plant?

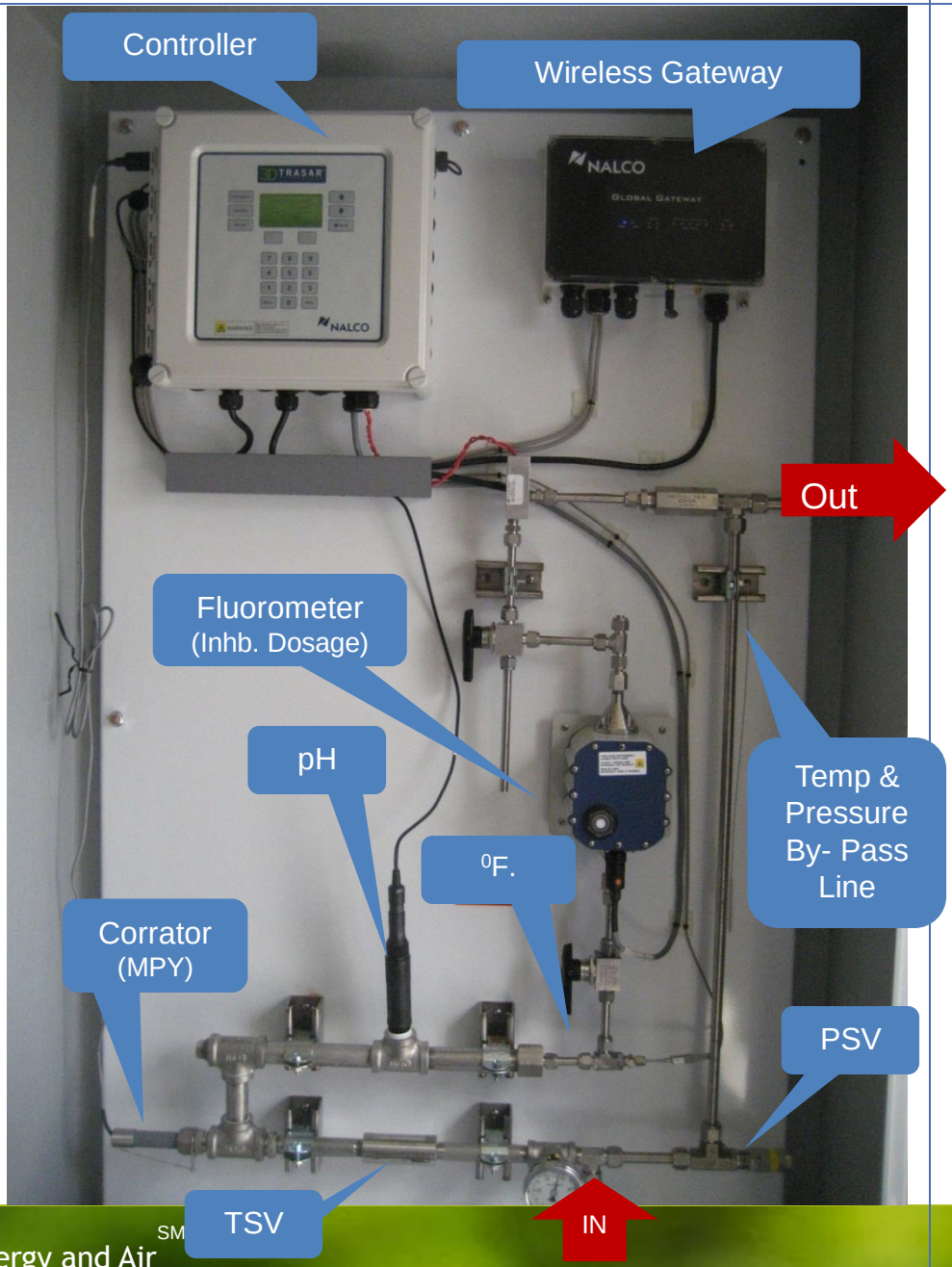
Grab Samples Vs On-line Monitoring

- Most UAN Producers sample newly produced UAN via grab samples taken every few hours
- Those samples are often taken only from the large final storage tanks
- Short term upsets can go undetected

- So we introduced a new way to monitor and manage UAN quality using On-line Technology
- **Nalco adapted our core 3DTRASAR Technology for use with manufacture of UAN**
  - TRASAR technology has been used in cooling water applications for more than 20 years

3D Trasar for UAN

- Controls or Monitors
  - Corrosion Inhibitor Dosage
- Monitors:
  - pH
  - Temperature
  - Corrosivity
- Logs, Alarms and Reports all data wirelessly to the producer
- Helps the plant identify root causes of operational problems **so they don't get to you**

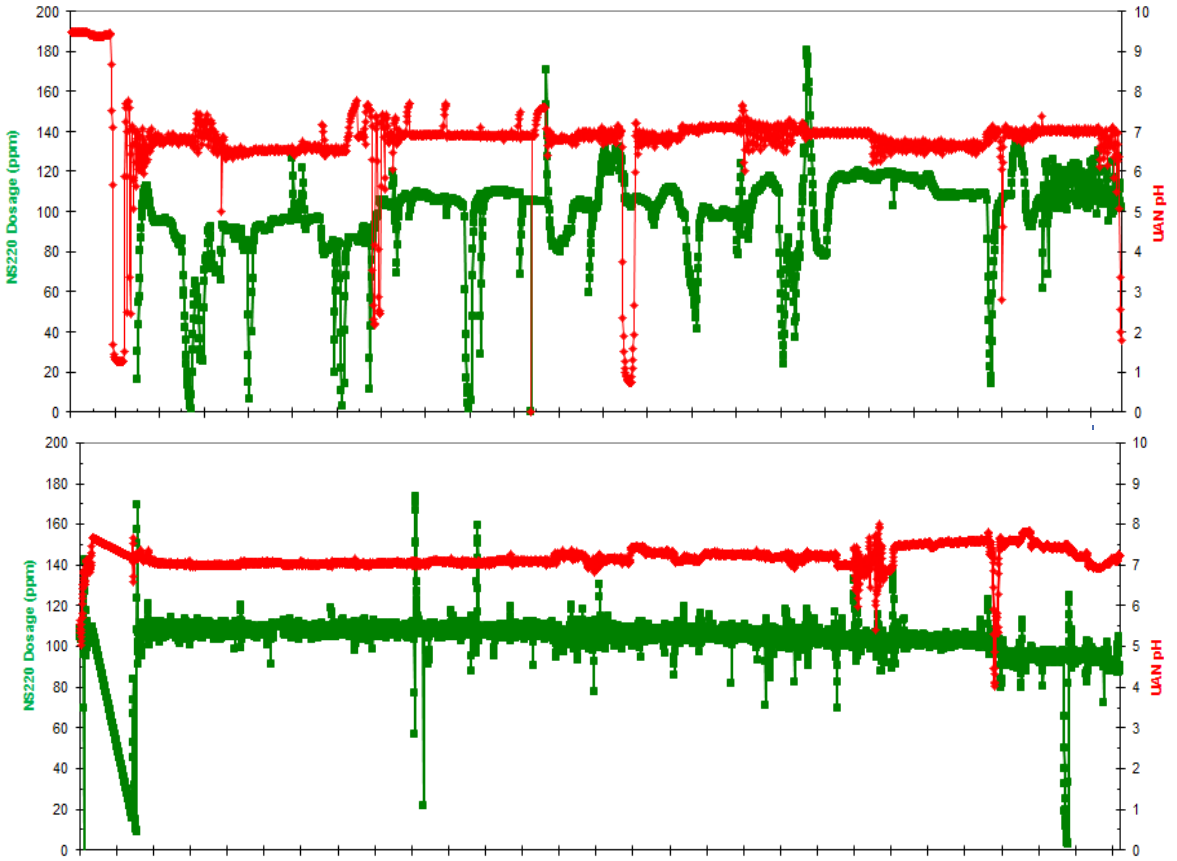


3DTfUAN Reduces Variability & Improves UAN Quality

- Continuous monitoring offers a step change over periodic laboratory spot checks or mass balance calculations in maintaining target inhibitor treatment dosage and good pH control

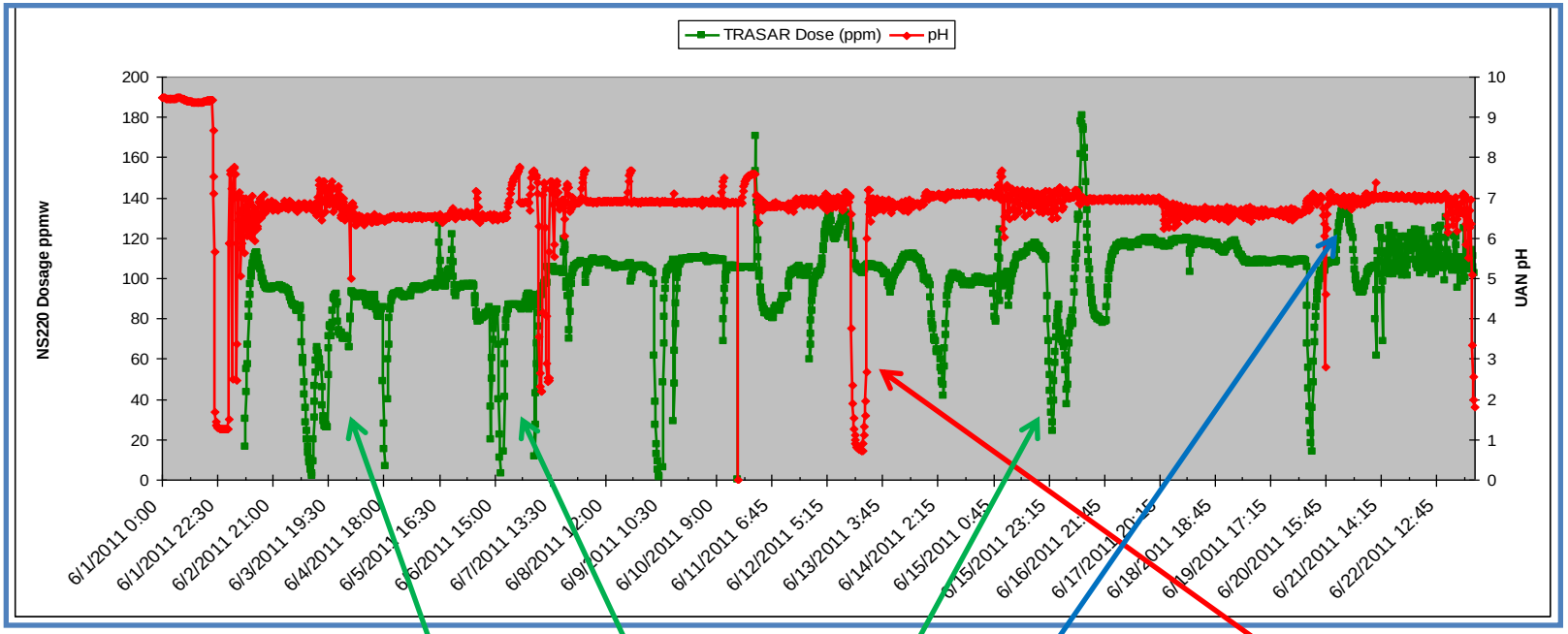
- **Before**
  - Erratic treatment control
  - pH fluctuations

- **After**
  - Consistent inhibitor dosage
  - Fewer, less severe acidic events



But these swings "equal out" in the storage tank…

Highs & Lows DON'T always "even out" in the storage tank"

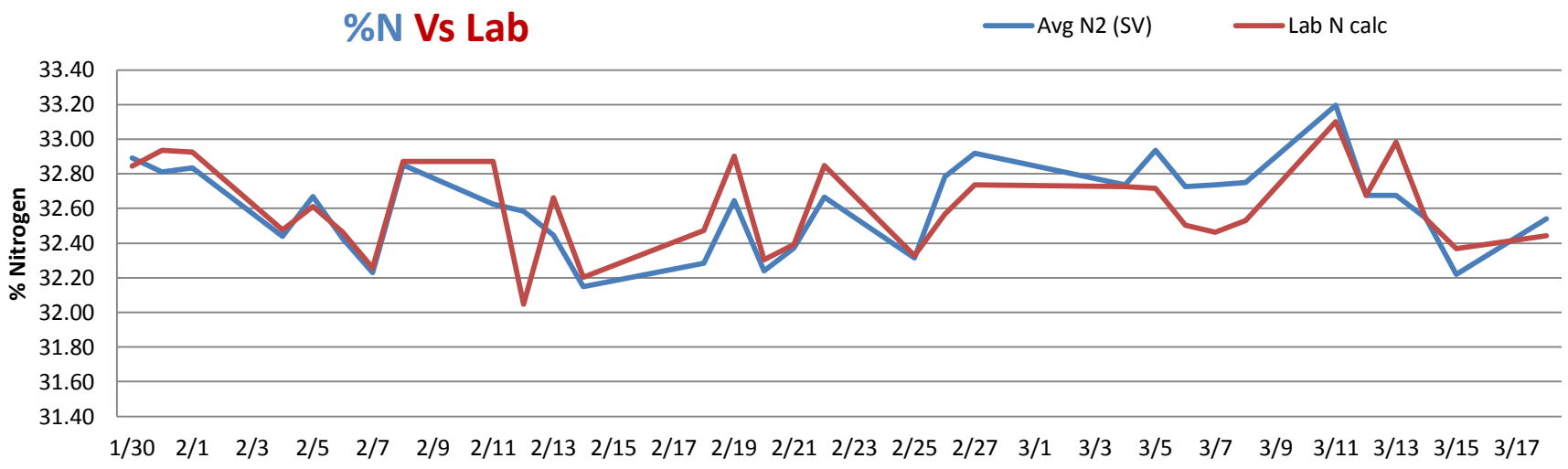


Tank #	Date	Time	ppm NS220
5 Tank	07-Jun-11	5:00:00 AM	85.00
5 Tank	08-Jun-11	5:00:00 AM	84.00
5 Tank	13-Jun-11	5:00:00 AM	83.00
2 Tank	03-Jun-11	6:00:00 AM	88.20
2 Tank	08-Jun-11	7:30:00 AM	83.00
2 Tank	09-Jun-11	6:00:00 PM	89.00
CF1	16-Jun-11	7:00:00 PM	81.00
CF1	16-Jun-11	10:00:00 PM	79.00
CF2	16-Jun-11	1:00:00 AM	28.00
CF2	16-Jun-11	7:00:00 AM	53.00
CF2	22-Jun-11	10:30:00 AM	134.00
CF2	24-Jun-11	3:00:00 PM	126.00
CF2	24-Jun-11	7:00:00 PM	125.00

Tank #	Date	Time	pH
2 Tank	13-Jun-11	6:00:00 AM	5.53
2 Tank	13-Jun-11	7:30:00 PM	6.48
2 Tank	12-Jun-11	7:00:00 PM	5.90
CF2	12-Jun-11	7:00:00 PM	4.00

In addition, we have also introduced on-line nitrogen content measurement

Nalco On-line Nitrogen Analyzer for UAN



Statistic	On-line Vs Lab Measurement (Abs Value of Diff.)	On-line Vs Lab Measurement (Actual Diff.)
Average Difference	**0.14**	**0.00**
Std Deviation (68%)	**0.12**	**0.18**

This same technology may be applied to the addition of water to UAN 32 to create UAN 28

UAN Corrosion Management Summary

- **UAN Corrosion creates real risk to your company, your employees and your community**
- **Liquid fertilizer dealers must manage this risk**
- **Don't assume that all the liability will be your supplier's problem**
- **You can take effective steps to minimize this risk!**

Thank You For Your Time!

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