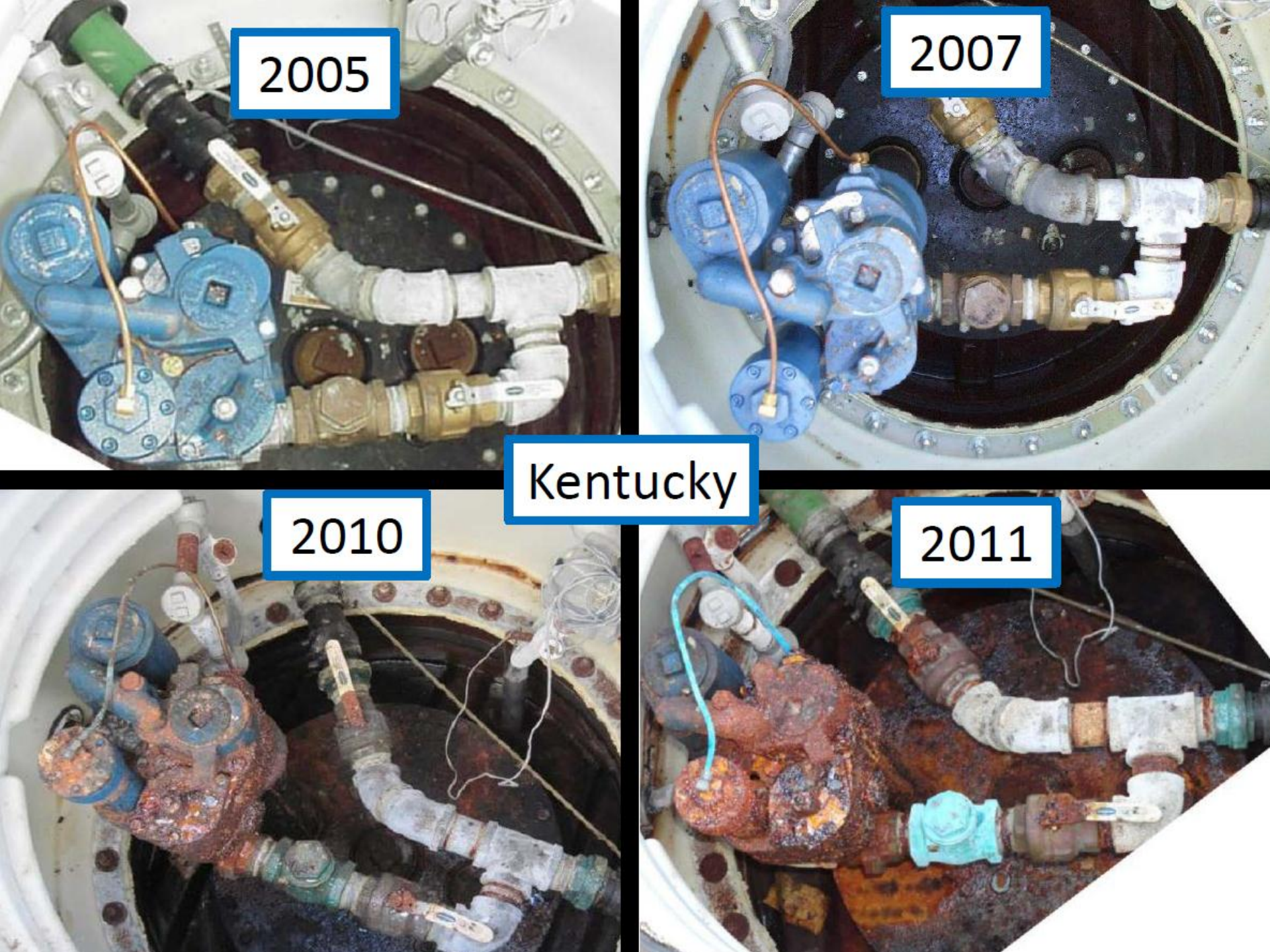
ULSD, Ethanol, Gas, Water and your UST- Do they mix?

Christian Quijano
Rounds and Associates

John Albert
Department of Agriculture

Heather Peters
Department of Natural Resources


2005
2007
Kentucky
2010
2011

E10 STP, unknown grade (Florida) – Feb. 2011

91 octane STP (California) – August 2010

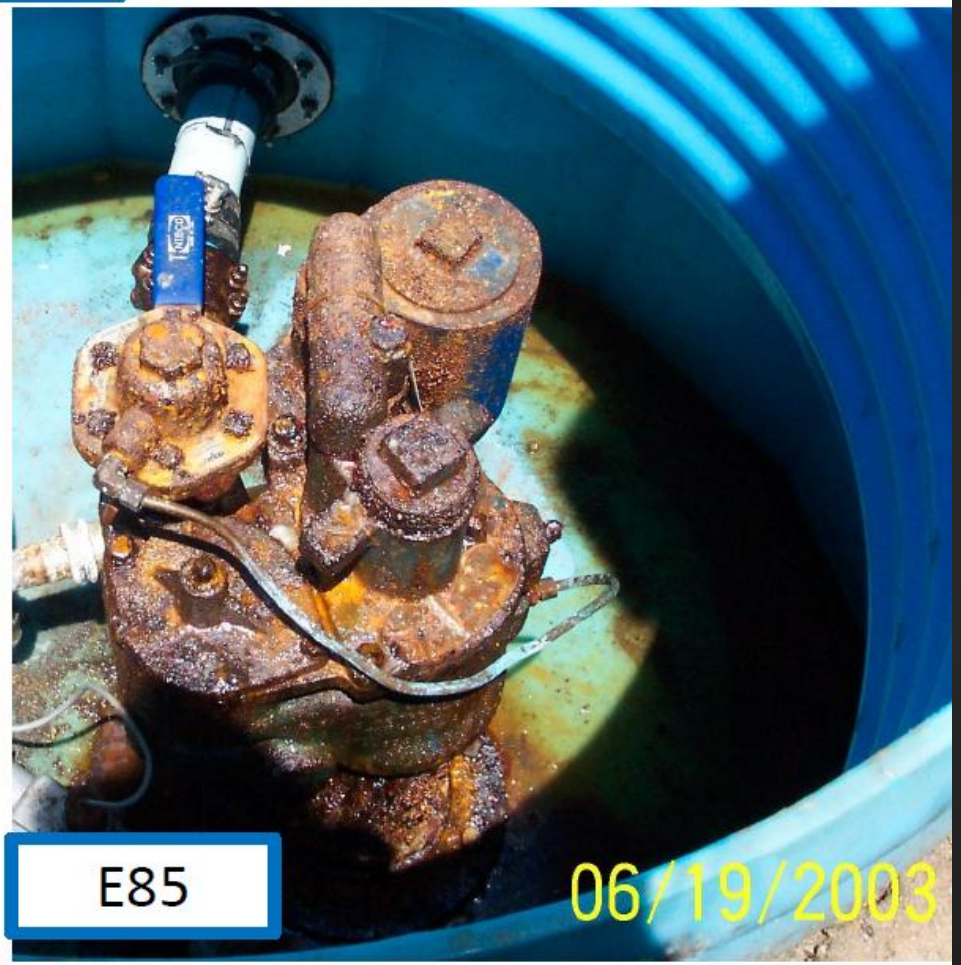
Premium/E10 STP (Tennessee) – March 2010

Same sump!

Premium/E10 STP (Tennessee) – August 2010

Why Do Some Sumps Get It and Some Don't?

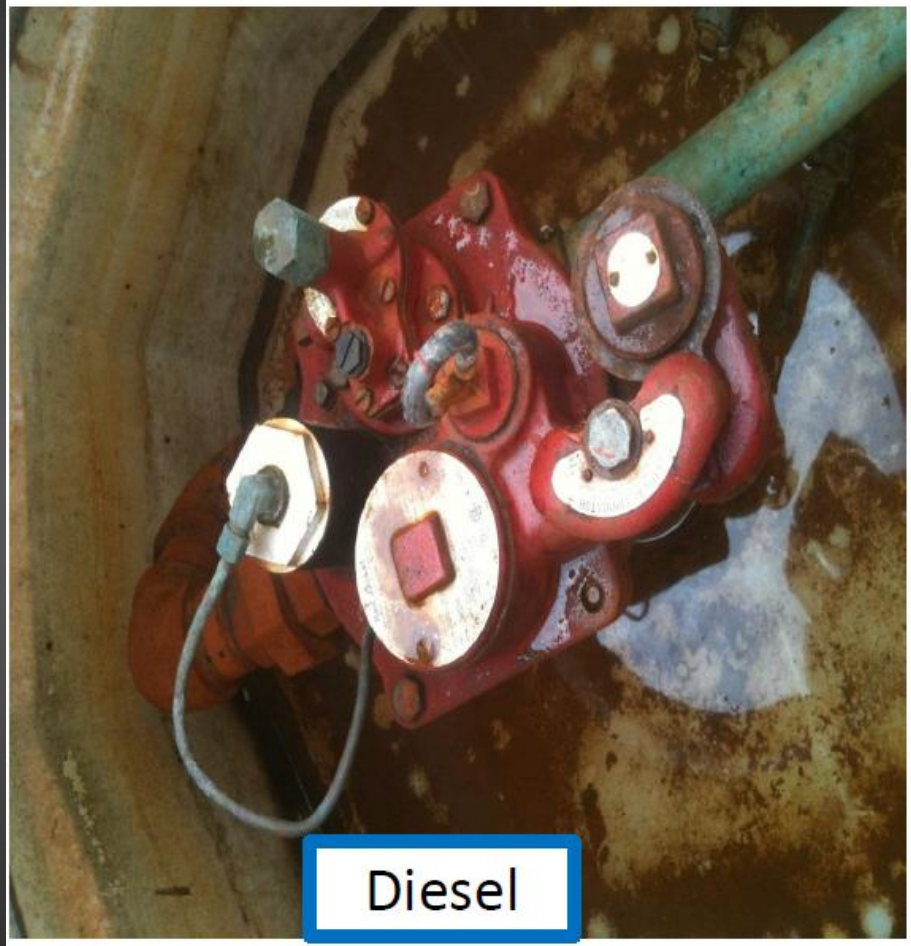
Iowa



Same Facility - Same Equipment – Same Day- Different Sumps

Why Do Some Sumps Get It and Some Don't?

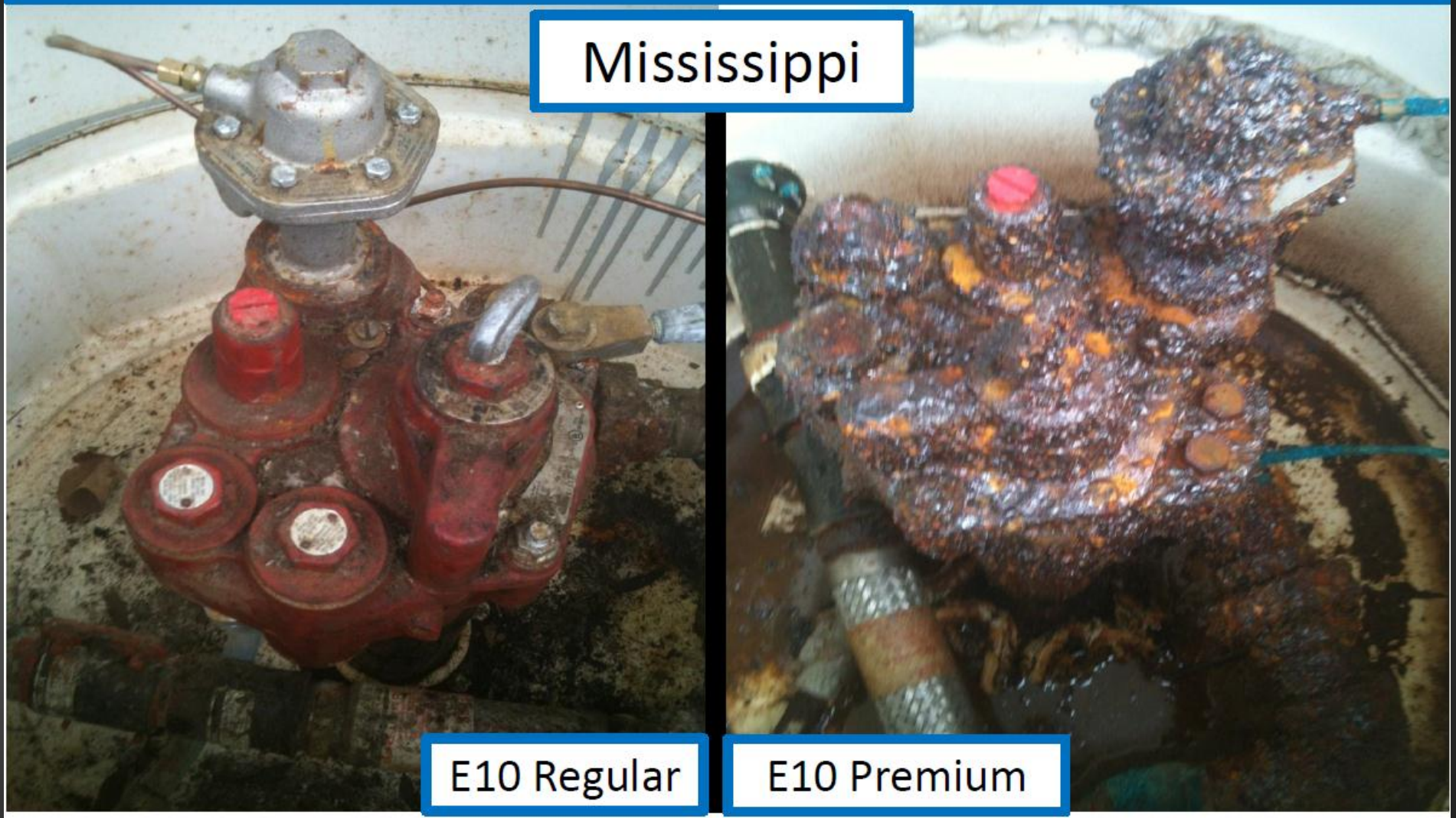
Mississippi



Installed 8-07 - Photos 3-12

Same Facility - Same Equipment – Same Day- Different Sumps

Why Do Some Sumps Get It and Some Don't?



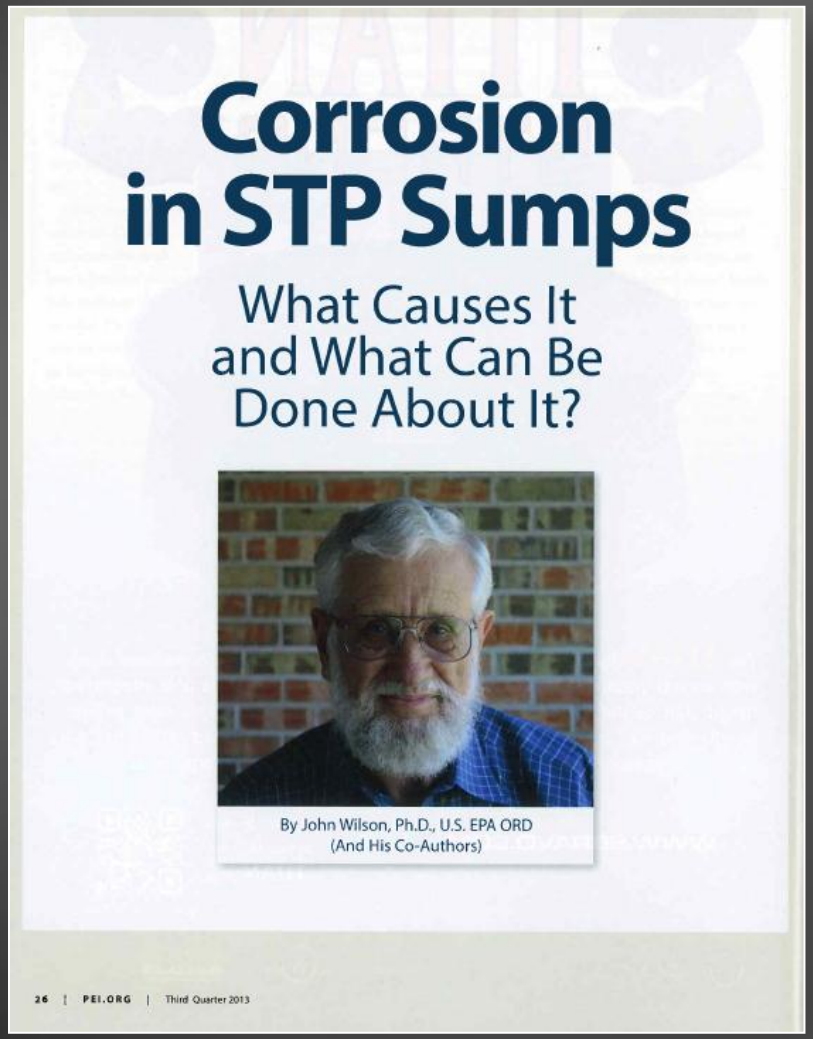
Installed 7-08 - Photos 3-12

Same Facility - Same Equipment – Same Day- Different Sumps

Alternative and New Fuels

- Compressed Natural Gas
- Liquefied Propane (LP)
- Electric/Solar (battery)
- Hydrogen
- Ethanol blends (i.e. E85)
- Biofuels
- Ultra-Low-Sulfur Diesel

Ethanol Related Corrosion



Corrosion in STP Sumps

What Causes It and What Can Be Done About It?

By John Wilson, Ph.D., U.S. EPA ORD
(And His Co-Authors)

26 | PEI.ORG | Third Quarter 2013

- PEI Journal – Vol. 7 Issue 3 – 2013
- Discusses corrosion related to ethanol
- Study conducted in FL, TN, IL, WI, CA, and IA
- Focused on ethanol vapors and acetic acid

Corrosion in STP Sumps by John Wilson

- Focused on extensive corrosion in STP sumps
- Cause? Acetic acid produced by biodegradation of ethanol vapors
- EPA evaluated association by sampling sump liquid and vapors at locations across USA
- Sampled sumps over Unleaded, Midgrade, Premium, E-85, and Diesel
- Photographed corrosion condition in sumps

Corrosion in STP Sumps by John Wilson

- Found no significant difference in ethanol vapors and acetic acid between tanks containing Premium, E-85, and Unleaded
- Many of the sumps contained high levels of both
- 81% of the photographed sumps showed signs up corrosion
- Corrosion associated with higher concentrations of ethanol and acetic acid

Corrosion in STP Sumps by John Wilson

- Similar findings in 2012 Battelle study
  - Identified corrosion in tanks containing ULDS
- Both studies, Ethanol was available in the fuel
- Necessary components = CORROSION
  - ✓Ethanol (liquid or vapor)
  - ✓Bacteria (degrades ethanol to acetic acid)
  - ✓Water (intrusion or condensation)
- Theory: prevent corrosion by eliminating any of the 3 components

Corrosion in STP Sumps by John Wilson

- Stop fuel/vapor leaks
  - Vent tube on MLLD
  - Manway gasket
  - STP packer o-rings
  - ATG probe caps/cord grips
  - Other risers and fittings in the sumps

Corrosion in STP Sumps by John Wilson

- Manage water in sumps
  - Difficult to keep all water out and control condensation
  - Constant inspection and maintenance
  - Vent piping sumps????

Corrosion in STP Sumps by John Wilson

- Eliminate Bacteria
  - Biocides have limited effect in sumps
  - Will not control bacteria in condensation
- Controlling bacteria in tanks
  - Test fuels routinely for bacteria
  - Use Biocides/Inhibitors
  - Some added benefits: fuel efficiency, lower emissions, removes water from fuel

Corrosion in STP Sumps by John Wilson

Comparison of corrosion in sumps with low and high measureable concentrations of acetate in the passive diffusion samplers.

Sump 9, 0.33 mg/L

Sump 48, 4530 mg/L

Corrosion in STP Sumps

Other examples of corrosion dissimilarity at the same facility.

E-85 Sub after one year of operation (Installed 11/3/05)

Photo taken 11/3/05

Fast forward 8 years...

Corrosion in ethanol STP sump after 2 years of operation!

Current Issues in Ultra-Low-Sulfur Diesel

Fuels and *Fueling*

Current Issues in Ultra-Low-Sulfur Diesel

Petroleum Marketers Can Handle Them

by Jean Feingold

Government environmental regulations have changed to favor ultra-low-sulfur diesel (ULSD), changing the product mix offered by petroleum marketers. Several problems with this product compared to higher-sulfur diesel have been encountered by petroleum marketers. They are microbes, corrosion, lower lubricity and gelling at low temperatures.

ULSD tanks sometimes become contaminated with microbes and are subject to corrosion. "In higher concentrations, sulfur served as a natural biocide in diesel fuel, killing off bacteria that were present due to contamination," explained Phil Hamilton, national fuel additive sales manager for Schaeffer Manufacturing Company. ULSD's lower sulfur levels let bacteria survive and breed. He said ULSD also retains more moisture as a result of the refining process used to remove the sulfur, giving bacteria an even greater chance to thrive. However, he said bacteria don't grow at temperatures below 60 degrees Fahrenheit.

"The Clean Diesel Fuel Alliance commissioned a study to identify possible reasons for corrosion in ULSD storage and dispensing equipment," said Michael C. Trunzo, president and CEO of the New England Fuel Institute. "Preliminary findings point to ethanol contamination as one possible cause, though it is too early to say with certainty where the ethanol contamination is occurring and if it is the only factor involved with microbial growth." While research continues, petroleum marketers should be aware that the problem occurs only in underground storage tanks and not in the aboveground tanks where the majority of the heating-oil supply is kept.

While ULSD itself does not degrade dispensing equipment or shorten its operational life, water accumulation and microbes inside ULSD tanks may contribute to this. "Good tank management practices that address water contamination are important to maintain the operational life of dispensing equipment," Trunzo said. Facility owners and operators can implement simple, routine management and housekeeping practices to monitor and minimize fuel-quality and fuel-system issues. This management can be coordinated with the help of fuel-testing and fuel-quality companies.

"In general, it is recommended that facilities install a nominal five-micron filter on the dispenser to ensure that fuel being dispensed to a vehicle is free of suspended particulate matter," Trunzo noted. "If a fuel storage tank has chronic water-accumulation problems, then a five-micron water-absorbing filter may be advisable." While occasional tests for sulfur content on deliveries are desirable, he said additional testing is not needed unless the filters show abnormal signs of corrosion or the fuel smells like rotten eggs. Tests can cost from $100 to $400, depending on the parameters set. Many labs offering such tests are available throughout the United States. The price of testing is modest compared to the expense of replacing corroded auto fuel and delivery truck nozzles and hoses, which can range from $150 to $600 each, depending on nozzle type and features and hose length.

ULSD also has lower lubricity, which can damage engines and is subject to gelling in freezing temperatures. The temperature at which ULSD gels varies based on refinery processes and the type of crude used, but fuel filters will begin plugging at about 0 degrees Fahrenheit. Once ULSD gels, it won't pump, Hamilton said. This is a potential problem

TREATED FUEL

Winterized ULSD fuel additives contain a nonalcohol jet fuel deicer/water dispersant. This eliminates the problems associated with dissolved water present in the fuel by dispersing the water into tiny droplets. These tiny droplets are suspended in the fuel so they can be carried with the fuel in controlled amounts through the fuel filters and fuel lines and into the combustion chamber to be burned with the fuel. By having any remaining water dispersed and suspended in the fuel, the winterized fuel additive eliminates the formation of ice crystals that can block fuel lines and plug fuel filters and prevents the formation of stable fuel-water emulsions.

NONTREATED FUEL

ULSD fuel contains a small amount of dissolved water that, under normal operating conditions, does not appear in droplet form. In extreme cold-weather conditions, when temperatures drop to below freezing, the fuel's capacity to hold water is diminished, allowing the dissolved water to separate from the fuel and form ice crystals. These crystals can become a serious problem if they congeal in fuel lines or filters. This phenomenon, called "icing," blocks the flow of fuel and causes the engine to shut down.

10 PMAA Journal

- PMAA Journal - Fall 2013 Publication (Jean Feingold)
- Noted several problems with ULSD compared to higher-sulfur diesel
  - Microbe survival
  - Corrosion
  - Lower lubricity
  - Gelling at low temperature

Current Issues in Ultra-Low-Sulfur Diesel

- Lower sulfur levels allow bacteria to survive and reproduce (acidic bi-product)
- ULSD also retains more moisture supporting the bacteria survival
- Clean Diesel Fuel Alliance commissioned a study (i.e. Battelle Study) to ID possible reasons for corrosion in ULSD tanks and dispensers.

Current Issues in Ultra-Low-Sulfur Diesel

- Preliminary findings indicate ethanol contamination, i.e. acetic acid production
- Seems to occur in USTs, not ASTs
- Although ULSD seems harmless to the UST system, water accumulation and microbes inside the system contribute to problem
- Advise use of 5-micron filter, or 5-micron water absorbing filter if chronic water bottom

Current Issues in Ultra-Low-Sulfur Diesel

- ULSD has lower lubricity; accelerates wear/tear on end user
- Also begins gelling in freezing temps, clogs filters at 0°F
- Fuel additives combat all of these issues:
  - Biocide to kill bacteria
  - Season anti-gelling additive
  - Improve fuel efficiency, horsepower, lower emissions, etc.

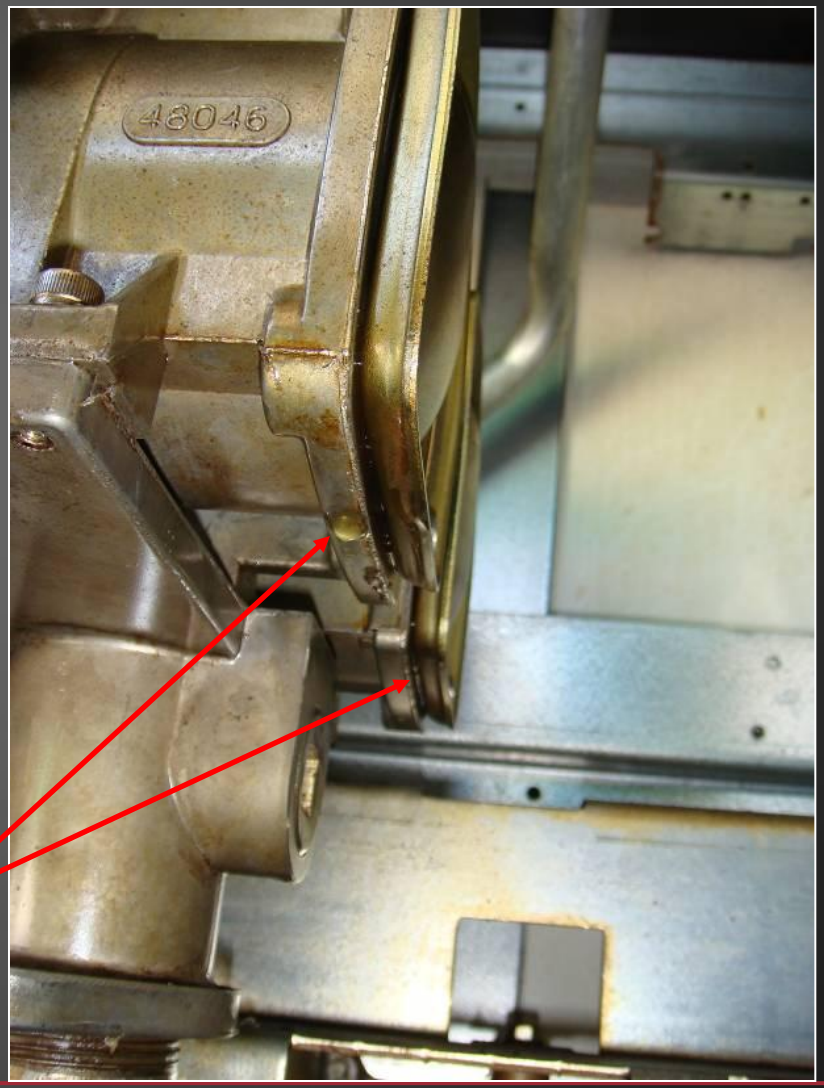
Current Issues in Ultra-Low-Sulfur Diesel

- Do not rely on constant biocide treatment
- Proper cleaning and management practices
- Encourage marketers to advertise additives
- Some already using pump toppers to advertise

- Most likely future plans to continue studying storage and usage effects of ULSD

Emergence of Leaking Meters

- Leaks found most at diesel meters
- Appeared to become more common with introduction of ultra low sulfur diesel
- Repair kits available!

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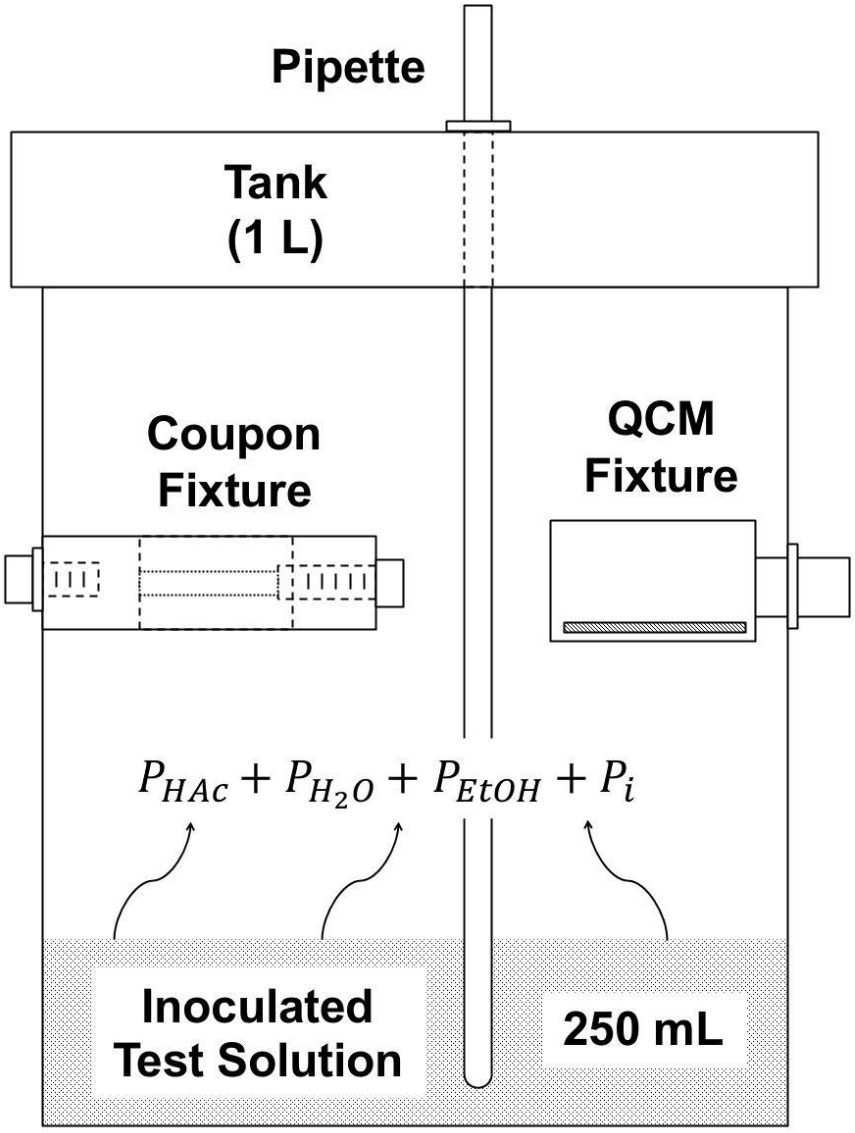
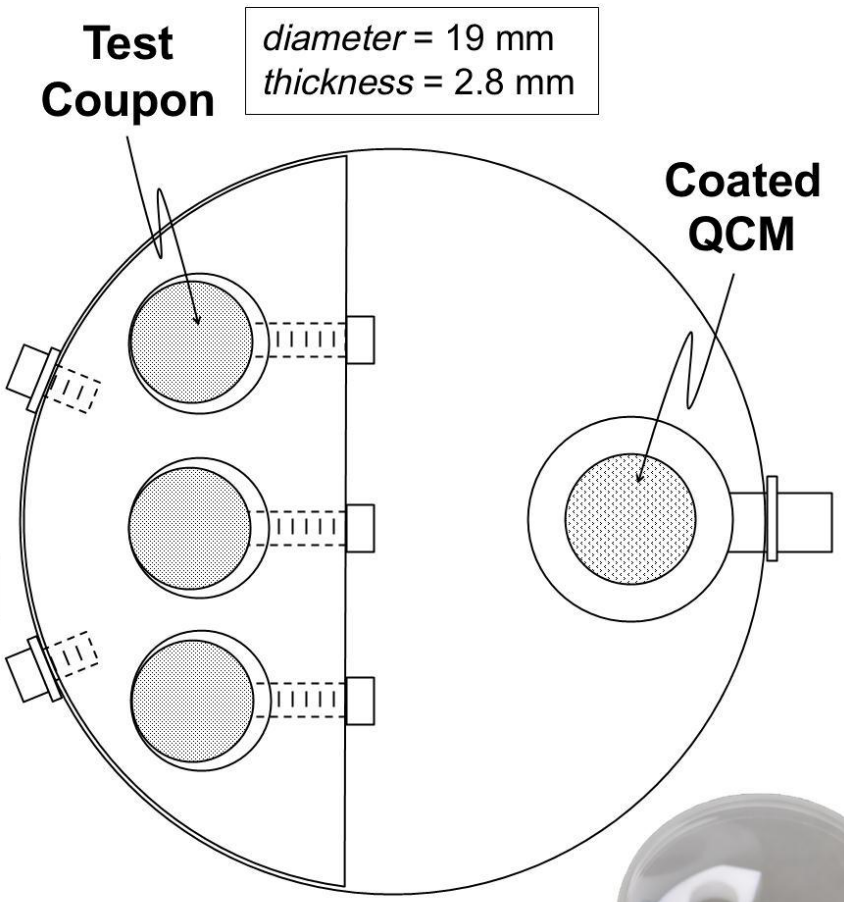
Headspace Corrosion Test Setup

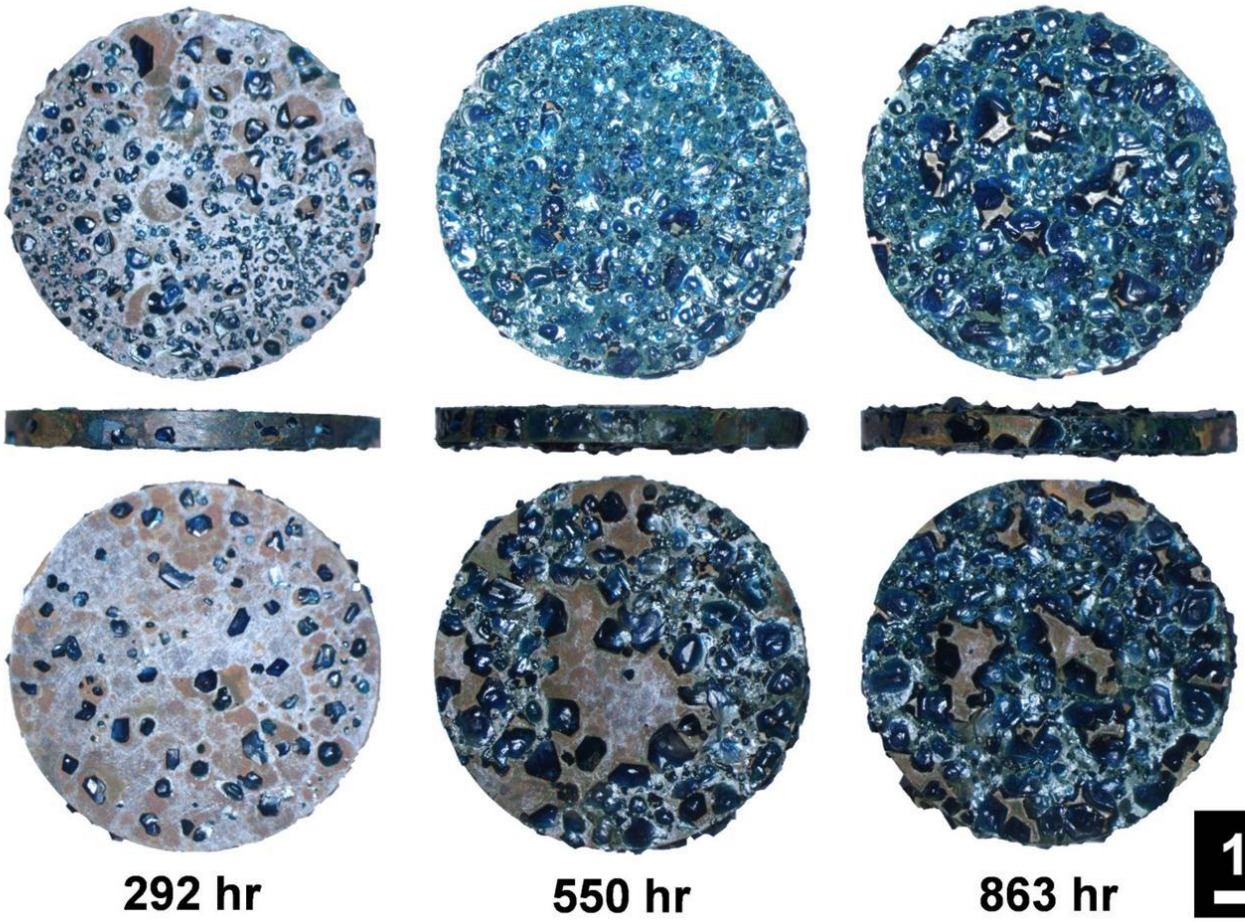
NIST





View looking UP
from Tank Bottom

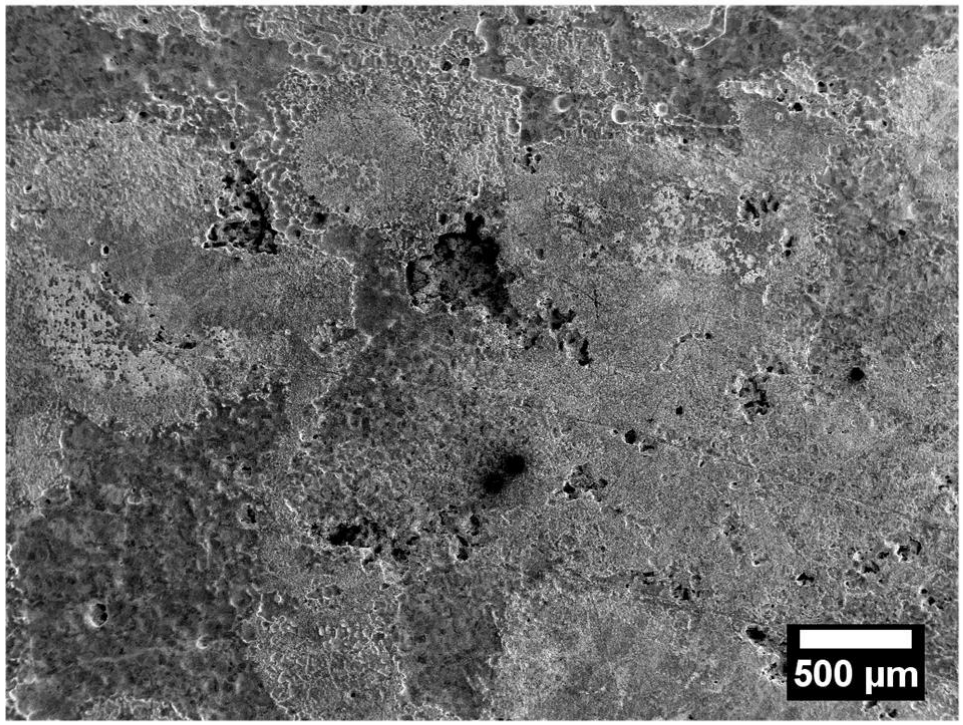
Copper Corrosion After Headspace Exposure



X-Ray Diffraction (XRD) was used to identify corrosion products:

- Copper acetate dihydrate
- Copper hydroxide acetate
- Cuprite

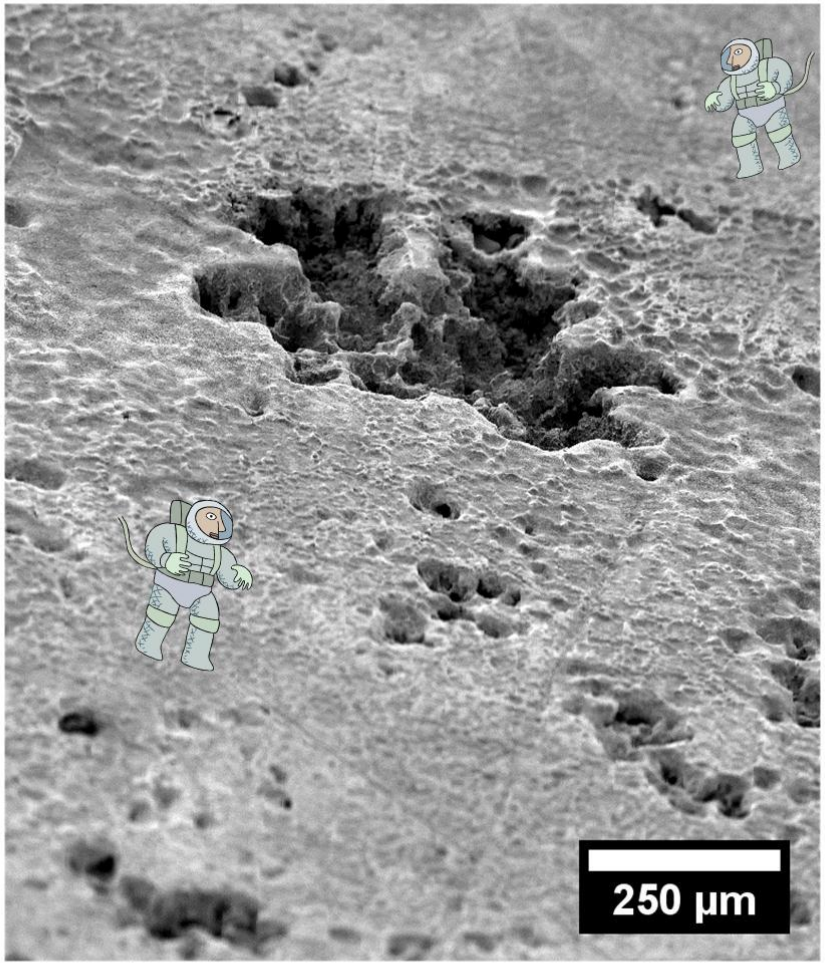
Headspace Corrosion Morphology



Removal of copper acetate revealed that general corrosion and pitting corrosion occurred under the crystals.

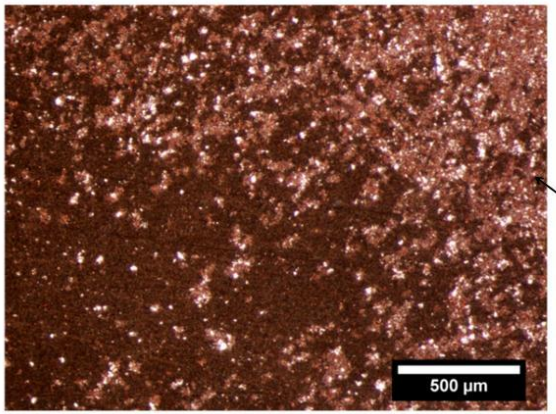
Small pits coalesced into larger pits with a wide, shallow appearance.

Pit Depth: Pit Width ≈ 1:2



Copper Corrosion After Immersion

TANK 4

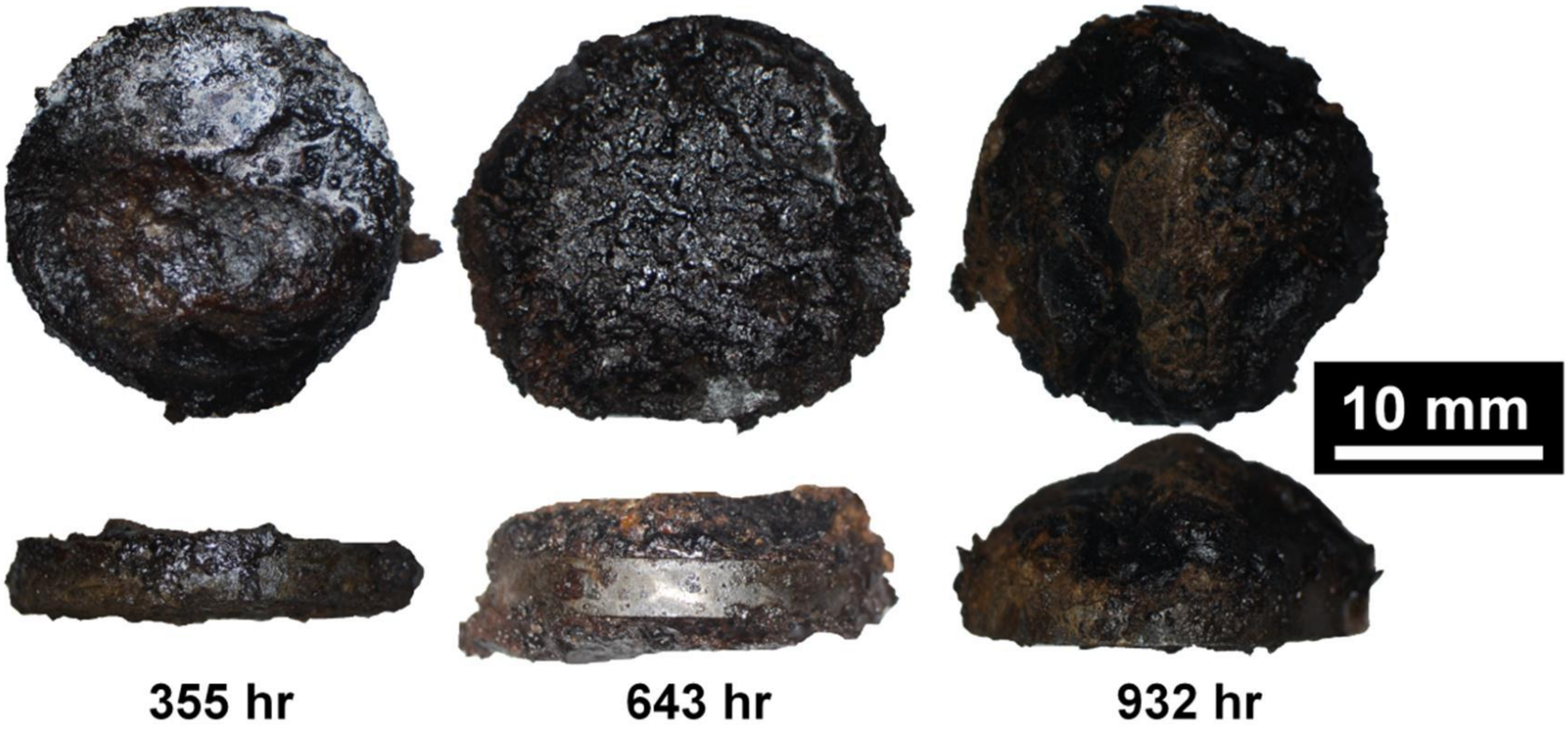


Surface Pitting

10 mm

Corrosion was not as extensive on the immersion coupons as compared to the headspace coupons. Pit morphology exhibited a shallow and coalesced appearance. The test solution notably turned a blue color during testing, indicating the presence of dissolved copper acetate.

Steel Corrosion After Headspace Exposure

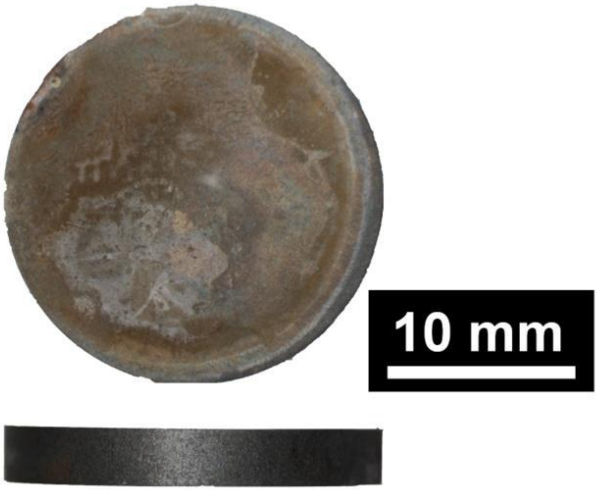


Corrosion product on the steel grew in thickness with longer exposure periods, and flaked easily from the coupons.

XRD was used to identify corrosion products:

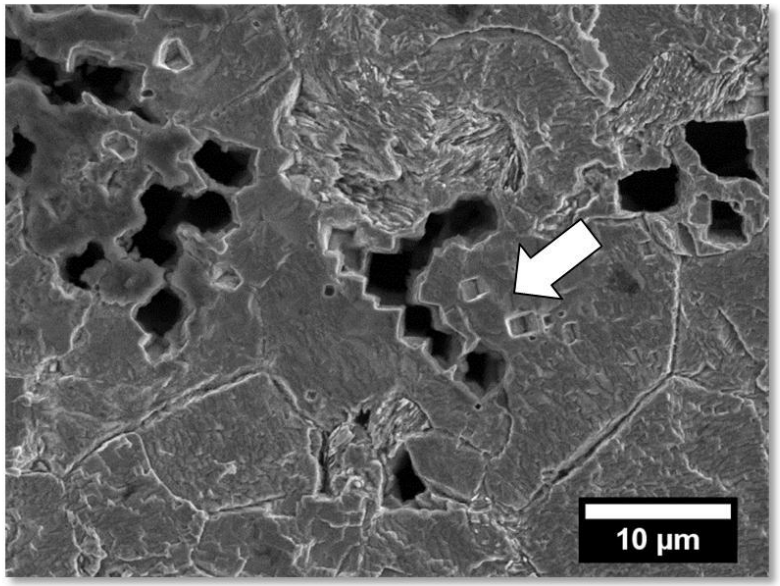
- Iron oxides
- Iron hydroxides

Steel Coupon Appearance After Immersion

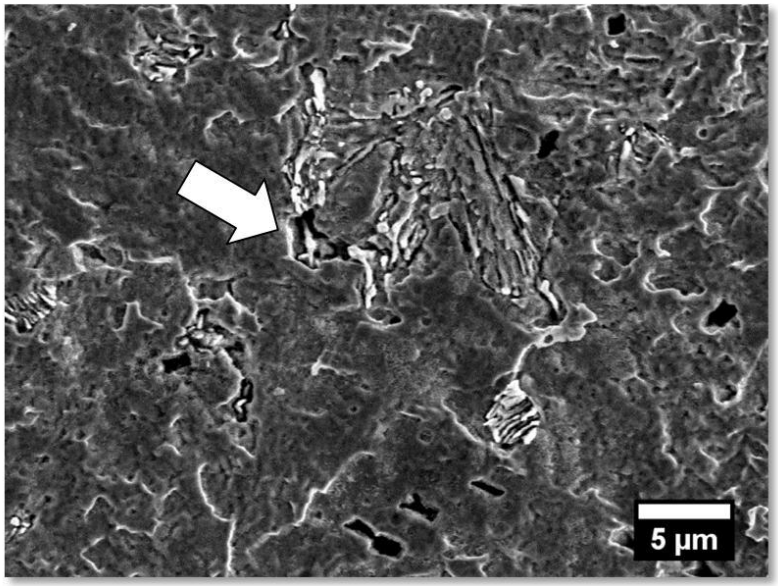


Corrosion rate was comparable to the copper headspace coupons and copper immersion coupons. This low rate may be related to bacterial attachment to the steel surface, which could protect the steel by a passivation mechanism. However, the surface was still covered with a deep pitting attack. Pits were predominantly found within ferrite grains, although some attack at ferrite-pearlite boundaries was noted.

Dislocation Etch Pits



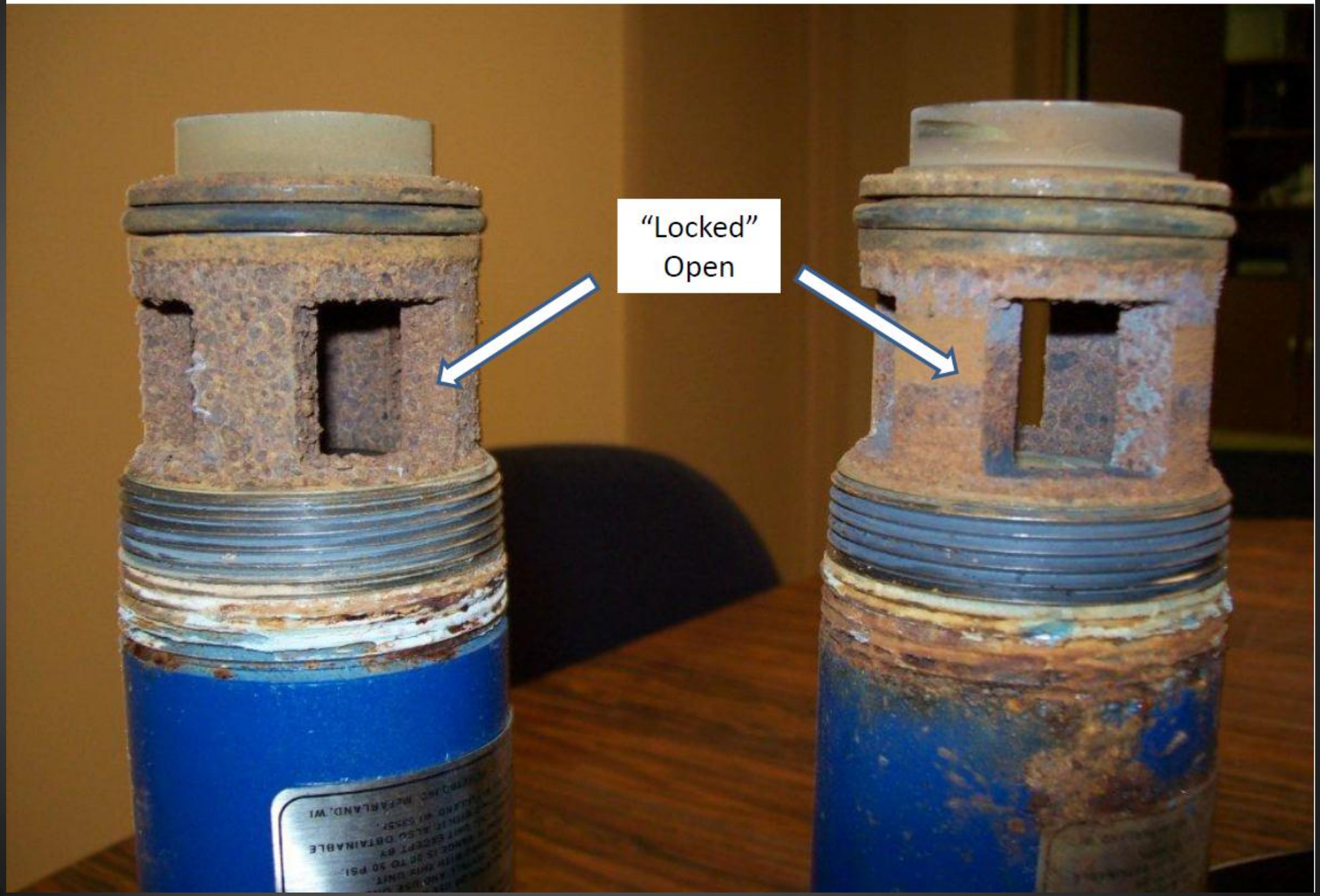
Pearlite Boundary Attack



API Study Findings

- Acetic acid was determined to be a likely cause of corrosion
- A plausible source of the acetic acid is *Acetobacter* (by-product)
- The components for *Acetobacter* to thrive were in the tested USTs (oxygen, water, low pH, ethanol)
- Acetic acid repeatedly "doses" the equipment when the UST contents are disturbed
- It is feasible for enough acetic acid to be produced in the timeframes being reported
- It is possible that there are other mechanisms in play

COMPATIBILITY – METALS (E10)



Ethanol Math

- 1+1=2, Easy right?
- 1 gallon Water + 1 gallon ethanol =
- Did you guess 2 gallons of liquid??
- If so, you would be **wrong**!

- I know! You *all* got it right…

Gasoline, Ethanol and Water

- Water is heavier/denser than gasoline and diesel
- 1st grade science- oil and water don't mix

BUT

- Ethanol is miscible in water
- Ethanol will absorb water

Compatibility ≠ Functionality

- Compatibility- Does the product stored/tested affect or react with the equipment?
  - In other words, will it last in the product?

- Functionality- Does the equipment work as designed? Does it meet the standard, protocol and threshold?
  - In other words, does it test correctly?

"Since long term material compatibility with the product stored is not addressed in the test procedures and evaluations, the NWGLDE makes no representations as to the compatibility of leak detection equipment with the product stored."

Water / Product Float Sensors

- Product float= floats on top of the product layer
- Water float= floats on top of the water layer

- If the ethanol/gasoline and water are mixing,
  - Is there a layer?
  - Is some of the water ingress absorbed into the "product" layer?
  - Where will that float go?

Some manufacturers now have better water detection floats.

Conductivity Float Sensors

- Gasoline: $1x10^{-14}$ mho/cm
- Ethanol: (95%): 10^{-9} mho/cm
- Water: approximately $5x10^{-6}$ mho/cm
- They work because each of the separate layers have distinct conductivity- the current passes through at a specific rate
- Blending/mixing of these products leaves transition areas = no distinct layer

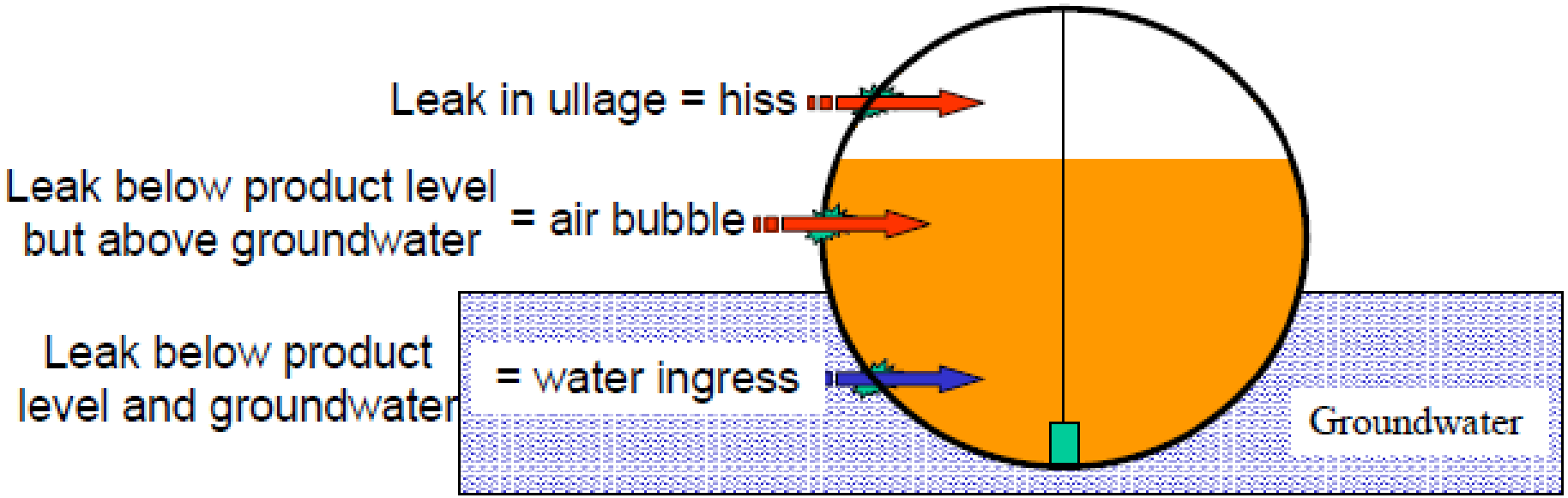
- At least one test that uses this method "calibrates" to start by intentionally adding water to a gas tank to create that layer

E-10 QUESTIONS & CONCERNS

"Vacuum" Precision Tank Tightness Testing

Several different scenarios possible depending on relationship between product level in tank and the groundwater conditions

Tank is Partially Submerged by Groundwater

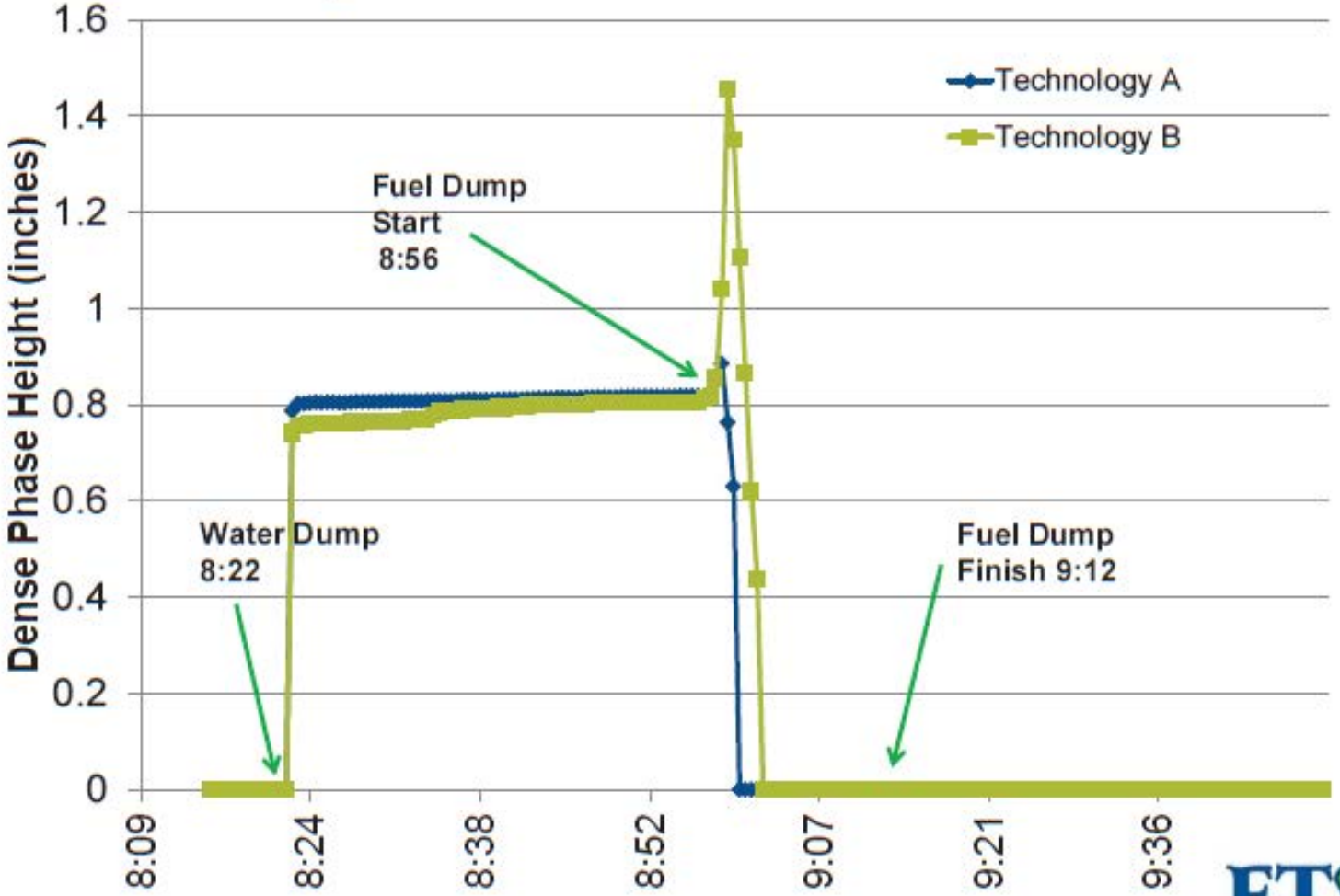


Battelle Research Study

- Ethanol, gas and water
- Release detection equipment functionality
- Started with automatic tank gauges
- Now studying properties of gas, ethanol and water blends
- Anticipate changes to release detection evaluation protocols

- Anne Marie Gregg
- (614) 424- 7419
- Gregga@battelle.org

Testing Observations
E15 Dump Test



Removing Water From Your Storage System

MISSOURI DEPARTMENT OF AGRICULTURE

- *Weights, Measures and Consumer Protection*


Water detecting paste

Examples of Water Finding Paste

- Missouri inspectors use a variety of pastes.
- If found, water is confirmed with a 2nd product.
- If results conflict, tank is sampled with tank thief.

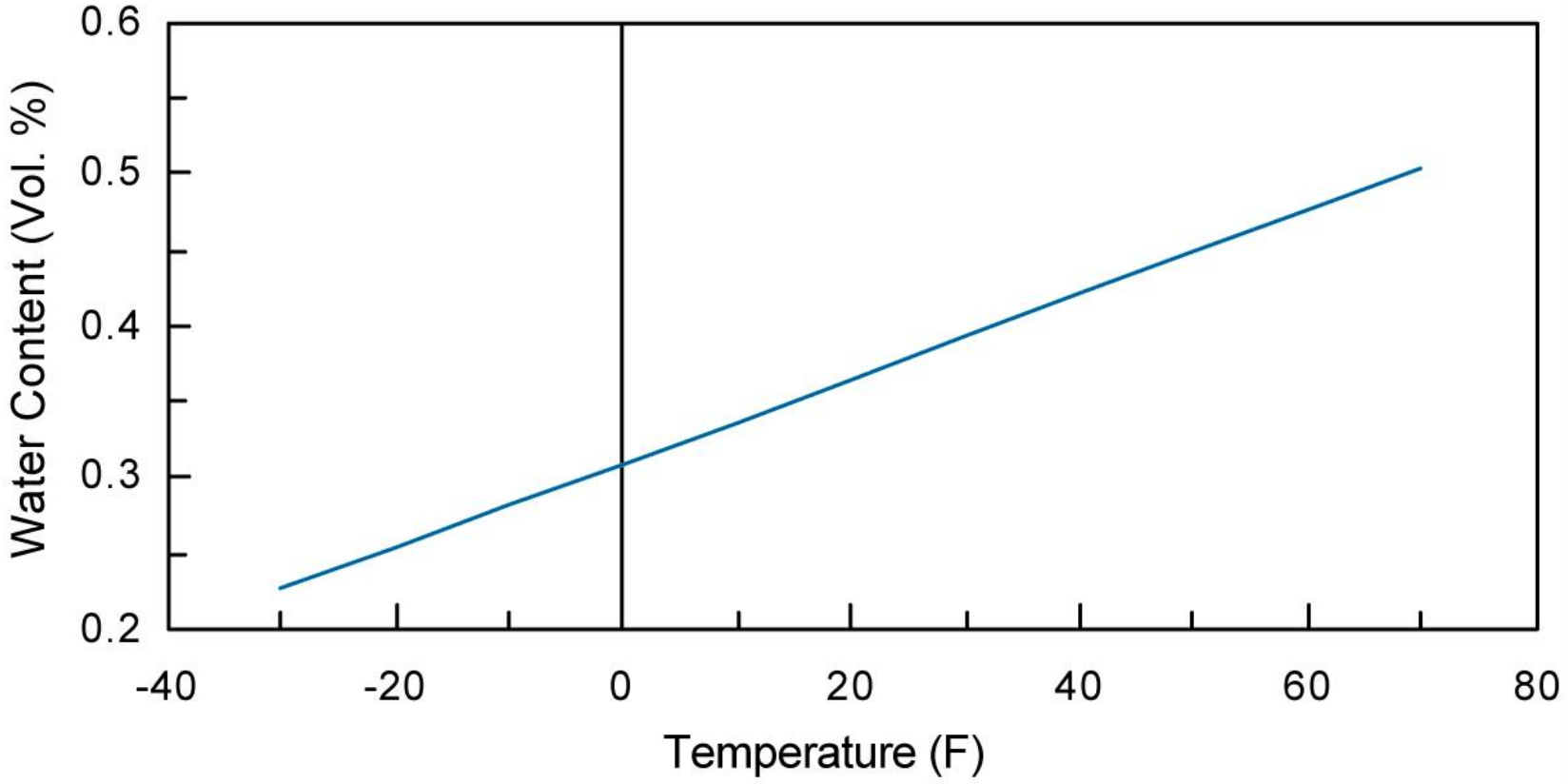

Water detecting paste should be used frequently and confirmed by visual inspection

Water in gasoline


A thief can also be used to visually inspect product

- Missouri Law prohibits water from exceeding 1 inch in any fuel storage tank
- Fuel must be “clear and bright” and free of water and sediment
- Many stop sales occur on ethanol blends when water is <1 inch in tank.
- Maximum phase separation temperature varies year round.

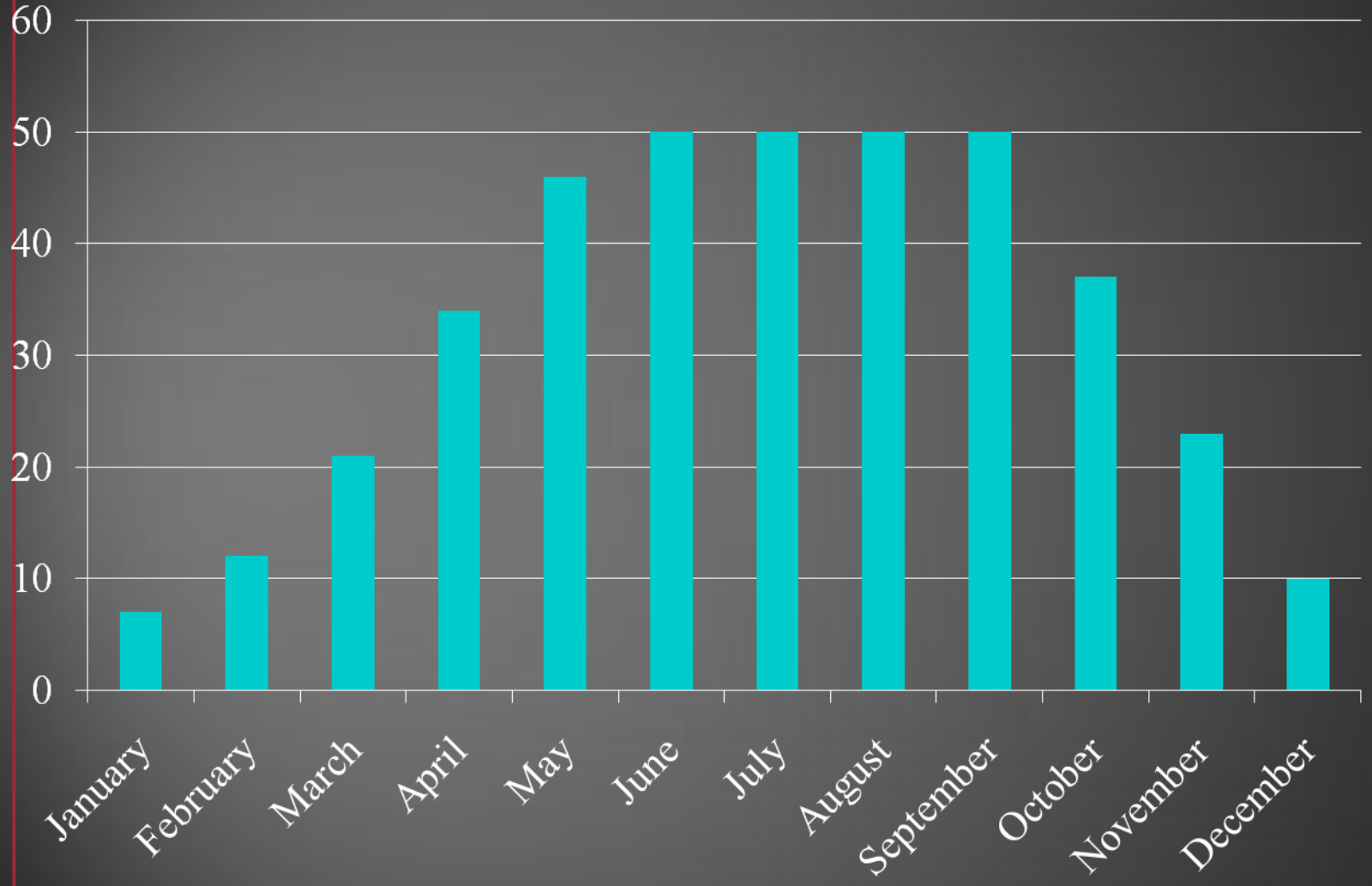
Water Tolerance of
90% Gasoline/10% Ethanol Blends



Water Contamination Effects in Ethanol Blended Gasoline

- Maximum phase separation temperature varies year round. Samples are chilled to temperatures in the following chart to ensure no water/alcohol phase separation occurs as the product drops in temperature.

Missouri Maximum Phase Separation Temperatures
Degrees Fahrenheit




Common sources of water contamination
In underground storage tanks.

Common sources of water contamination in aboveground tanks

Methods of water removal for aboveground tanks

Methods for removing water and maintaining storage tanks including (Diesel and non-ethanol)

- Pumping out water bottoms from the fill openings.
- Difficult to entirely remove all water and especially difficult with vertical aboveground tanks without water draws.
- Water absorbing materials can be a great tool to completely remove water and maintain zero water bottoms.

Water Contamination Effects in Ethanol Blended Gasoline

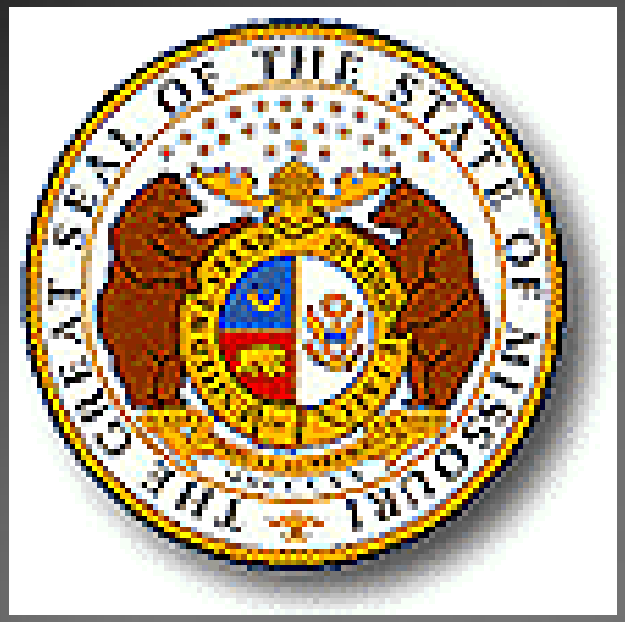
- When ethanol blended gasoline is exposed to water, the water will combine with the ethanol and cause it to separate into an alcohol-poor upper phase, and an alcohol rich lower phase.
- The upper phase will remain unstable causing ethanol and water to continue separating from the mixture.

Water Contamination Effects in Ethanol Blended Gasoline

- Virtually all regular unleaded gasoline sold in Missouri is sub-grade (~83 octane) blended with 10% ethanol.
- When ethanol is removed from this gasoline the octane of the gasoline is lowered below minimum requirements.
- Contaminated gasoline must be analyzed to determine the ethanol concentration if blending this product with fresh fuel to correct.

Corrective Measures for Water in Ethanol Blended Gasoline

- Identify the source of water in tank and repair
- Remove the water/alcohol phase separation from storage tank and place in approved containers.
- Remove all contaminated ethanol blended gasoline and replace with fresh product.
- Purge all dispensers into separate containers until product flows clear.
- Install new dispenser filters (10micron or less)
- Contact regulatory authority for release of stop sale and follow-up inspection.



Thank you

MISSOURI DEPARTMENT OF AGRICULTURE

- ***WEIGHTS, MEASURES, and Consumer Protection***

Conclusions