Corrosion in Systems Storing and Dispensing Ultra Low Sulfur Diesel (ULSD)

Lorri Grainawi
Director of Technical Services
STI/SPFA
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Corrosion Related to ULSD

- Severe & Rapid Corrosion
- Systems Storing & Dispensing Ultra Low Sulfur Diesel
- Observed sporadically since 2007
- ASTM D02 Committee
- PEI, Petroleum Equipment Institute
- Clean Diesel Fuel Alliance (CDFA)
  - Battelle Report

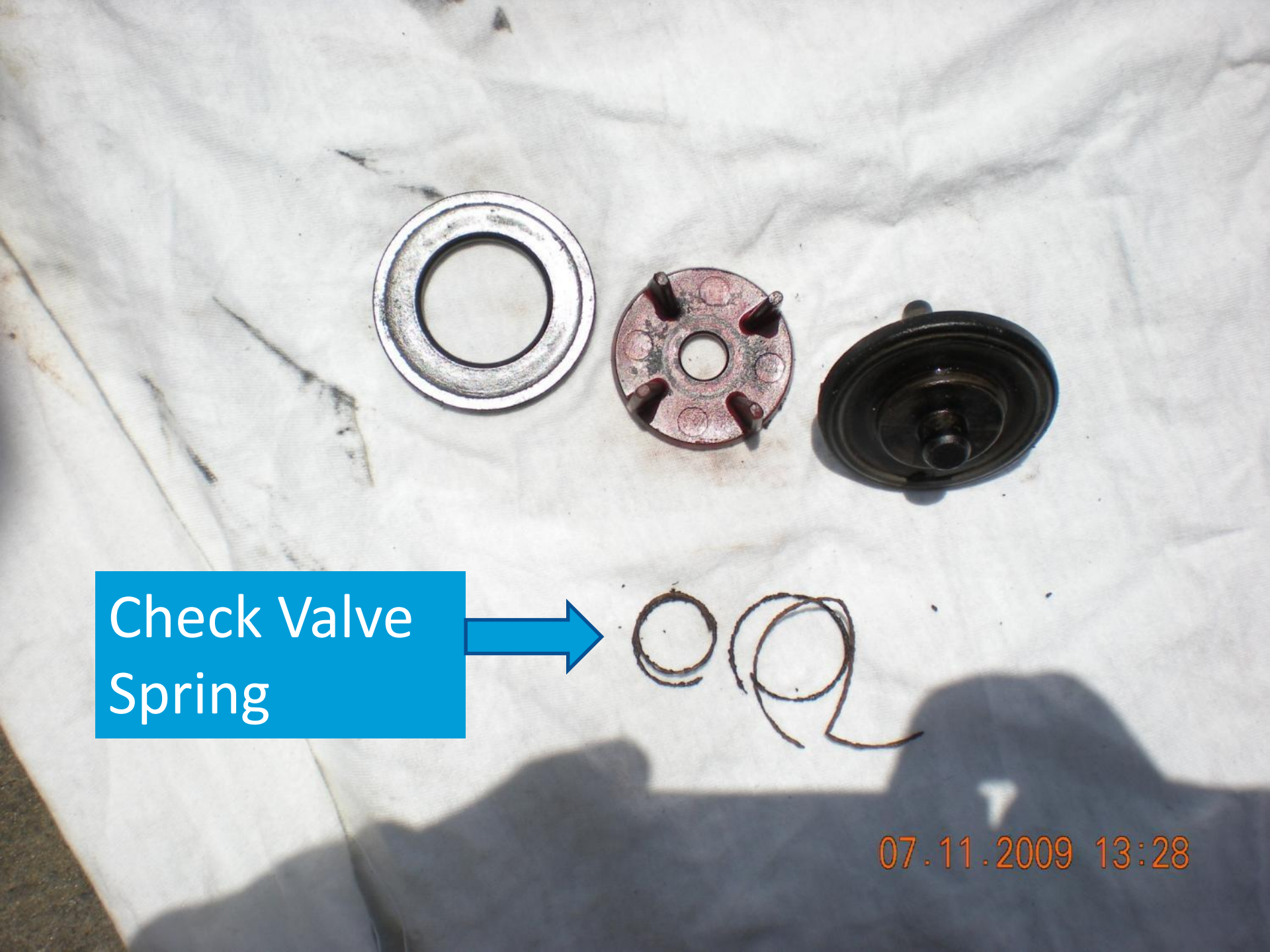
STP column pipe inside FRP tank

Upper section of STP – vapor only

Pump connection corroded thru

Strainer – in Liquid

Trash Inside Strainer


Check Valve Spring
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Filter Threads


In service less than one year
STP Column Pipe


Had to be pried out – Check Valve

History of Investigation

- 2006 ULSD became law, 80% switch
- 2008-2009: STI report problem to industry
- April 2010: PEI posts 5 question survey
- May, 2010: CDFA task group formed to investigate
- August, 2010: Battelle/Tanknology team chosen
- Nov 30, 2010: First CDFA meeting with Battelle
- Jan 24, 2012: Test plan finalized
- Feb 8-23, 2012: Inspected sites
- Sep 12. 2012: Report of Hypothesis of Failure Complete
- Current: Planning Phase 2 of investigation

CDFA Interested Parties

Contract No. CON00008697
Study No 10001550
Final Report

Corrosion in Systems Storing and Dispensing Ultra Low Sulfur Diesel (ULSD), Hypotheses Investigation

Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201

To
Clean Diesel Fuel Alliance
C/O Mr. Prentiss Searles
American Petroleum Institute
1220 L Street, NW
Washington, DC 20005-4070

September 5, 2012

- First study report of published Sept 2012
- CDFA interested parties meet in Chicago Oct 3, 2013
- Agreed to several goals and projects

Even before we began the Battelle study, we knew:

- Problems reported from all regions of the country
  - That means it's not one refinery
  - And it's not one pipeline
  - And it's not one brand of fuel
- Not related to age of equipment
- Corrosion occurs both in liquid and vapor areas

Not sure about:

- Not enough data to know if there is relationship between:
  - Tank volume
  - Throughput of the system
  - Tank maintenance

Resultant Problems

- Flow rate reduced below level needed for nozzles to automatically shut off
  - Product spilled from vehicle overfill
- Threads corroded, seal not maintained
  - Product Release

Clean Diesel Fuel Alliance,CDFA

- AAA
- Alliance of Automobile Manufacturers
- **American Petroleum Institute**
- American Trucking Associations
- **American Association of Railroads**
- Association of International Automobile Manufacturers
- Association of Oil Pipe Lines
- Diesel Technology Forum
- **Ford Motor Co.**
- Engine Manufacturers Association
- Independent Liquid Terminals Association
- **National Association of Convenience Stores**
- **NATSO, Inc., representing Truck Stops & Travel Plazas**
- National Petrochemical & Refiners Association
- National Tank Truck Carriers, Inc.
- **Petroleum Equipment Institute**
- **Petroleum Marketers Association of America**
- Society of Independent Gasoline Marketers of America
- **Steel Tank Institute**
- U.S. Environmental Protection Agency
- U.S. Department of Energy
- U.S. Energy Information Administration
- * **Bolded** groups on R&D committee

Why Sites Chosen

- Five sites that exhibited severe corrosion symptoms.
- One intended “clean site” as a control.
  - The site, however, was found to have corrosion symptoms;
- The five sites with severe symptoms all had FRP tanks.
- Therefore, the sixth “clean” site was chosen specifically because it had an FRP tank.

Steel Tanks – Different issues

Steel Tank Top
Vapor Space is Clean

Steel Coupon in Tank Bottom

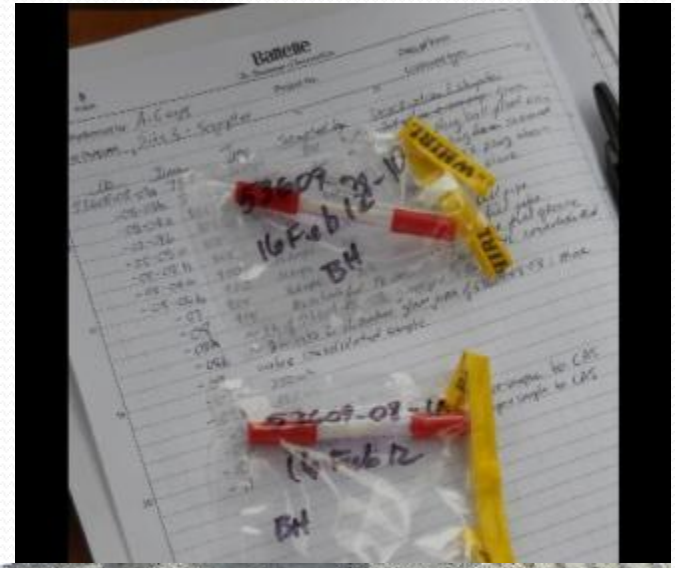
Some sludge is evident, but no corrosion pits.

Site Characteristics

Site ID	***NC-1***	***NY-1 "Clean Site"***	***NY-2***	***CA-1***	***CA-2***	***CA-3***
Inspection Date	8-Feb-12	15-Feb-12	16-Feb-12	21-Feb-12	22-Feb-12	23-Feb-12
Tank Year of Installation	1998	2008	1988	1990	1991	1991
Tank Capacity (gallons)	17,265	12,000	6,000	10,000	12,000	6,000
Tank Material	FRP- Double	FRP-Double	FRP-Single	FRP-Double	FRP-Double XERXES	FRP-Double OC
Tank Diameter (inches):	120	120	92	92	120	92
Monthly Throughput (gallons/month)	29,000	18,000	6,500	26,000	20,000	25,000
Product Level (inches)	27.5	48	35	15	49	28
Filter Replaced Date	24-Jan-12	No Date	Filter not identified	2-Feb-12	13-Jan-12	9-Jan-12
Biocide Treatment History	December 2011	unknown	2 times in past year	unknown	none	unknown

Inspection Process
Vapor Sampling: SKC Tubes

- 2 SKC tubes/site
- 100 minute collection at 1L/min
- Carboxylic acids and formic acid analysis by GC-MS (CAS Method 102)



Water Bottom Sampling

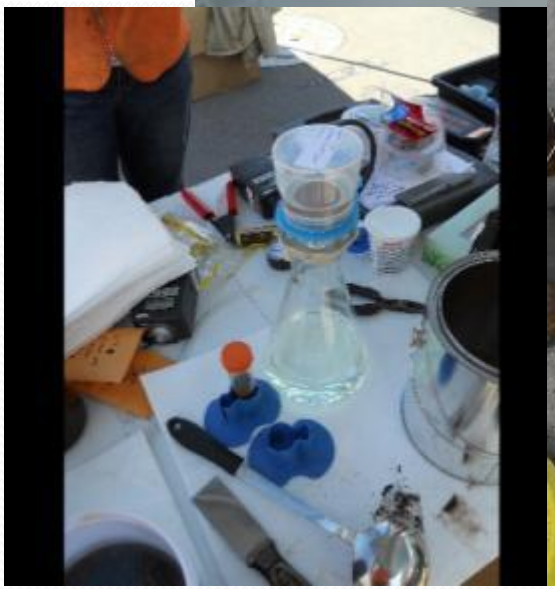
- ~1-2 Liters of water bottom sample/site
- Bottom sediment
- Consolidated from multiple risers
- Bacon Bomb triggered by bottom of tank
- Filtered ~50-150mL for biological analysis

Inspection Process Disassembled System

- Collected scrape, wipe, o-rings, and other samples
- Used metal ladle or scraper to loosen the corrosion into a conical tube
- Used filters as wipes
- Documented state of system on checklist and with pictures
- Fouling investigation process by 2 labs

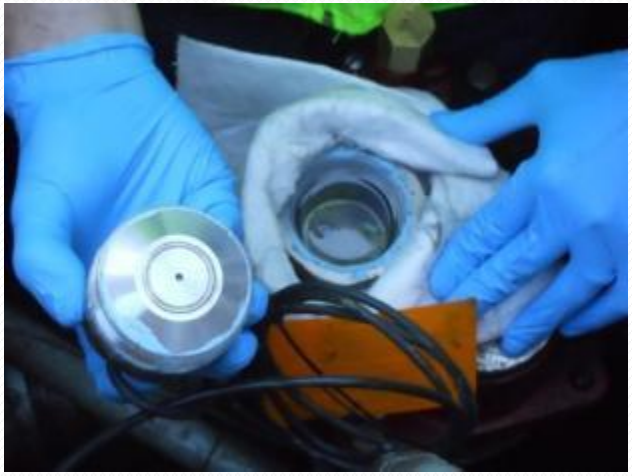
Inspection Process Fuel Sampling

- ~1 gallon of diesel sample/site
- Consolidated from multiple risers
- Bacon Bomb with string to trigger collection within fuel column
- Split for chemical analysis
- Filtered ~700-900mL for biological analysis



Site NY-2 (Feb 18)

Site CA-3 (Feb 23)



Liquids and Vapor Summary

- Low biodiesel levels
- 3 fuels have failing NACE ratings
- Sulfur content ranged from 5.9 – 7.7 ppm
- pH ranged from 3.5 to 5.3
  - 3 NACE failures had pH of 3.5 – 3.8
- Trace amounts of ethanol at 4 sites
- Acetate (dominant acid) and formic acid detected in all water and vapor samples
- Acetobacter dominant organism found at 3 sites

Other elements found

- Significant levels of sodium and chlorides (4 of 6)
- Significant level of potassium (3 of 6)
- Significant level of magnesium (4 of 6)
- Others:
  - Methyl vinyl ketone, phthalate, glycol and dioxane

Microorganisms

- Not all samples yielded DNA above limits of detection
  - By direct measurement of DNA or by PCR reaction (16s)
- Samples analyzed by sequencing (NY-1, NY-2, CA-2) showed the following:
  - Dominant microorganisms are *Acetobacteraceae*
    - Bacteria
    - Need oxygen to grow
    - Prefer 20-30ºC temperatures and low pH
  - NY-1 and NY-2 contains more organisms than CA-2
  - NY-2 had high levels of Lactobacillus sp.
    - Grow at low oxygen levels
  - NY-1 had high levels of fungus
    - Grows well with ethanol, acetic acid and low pH

Conclusions of Batelle Report

- Among other contaminants, acetic acid was found in all samples taken (fuel, water bottoms, vapor and corrosion scrapings).
- Acetobacter microorganisms and traces of ethanol were found in the majority of water bottom samples.
- Combined, the two are known to create acetic acid.
- Battelle has identified this as the most likely mechanism for the cause of the corrosion.
- Conclusions are still in hypothesis stage

Oct 14th, CRC meeting
Coordinated Research Council

- CDFA participants would like to continue the work but want additional expertise
- Phase 2 will be conducted under the umbrella of the CRC Diesel Performance Group

STI conducted own study

- Study included both fiberglass and steel tanks
- USTs from five regions of the countries tested
- One fiberglass and one steel tank in each region
- Tanks were chosen randomly with no previous investigation of any corrosion issues
- Both fuel and water bottom sample obtained

Testing

- Testing was based on Battelle study
- Analysis based on what appeared to be causing corrosion in tanks
  - Ethanol
  - Acetate
  - Other acids
  - pH level of fuel

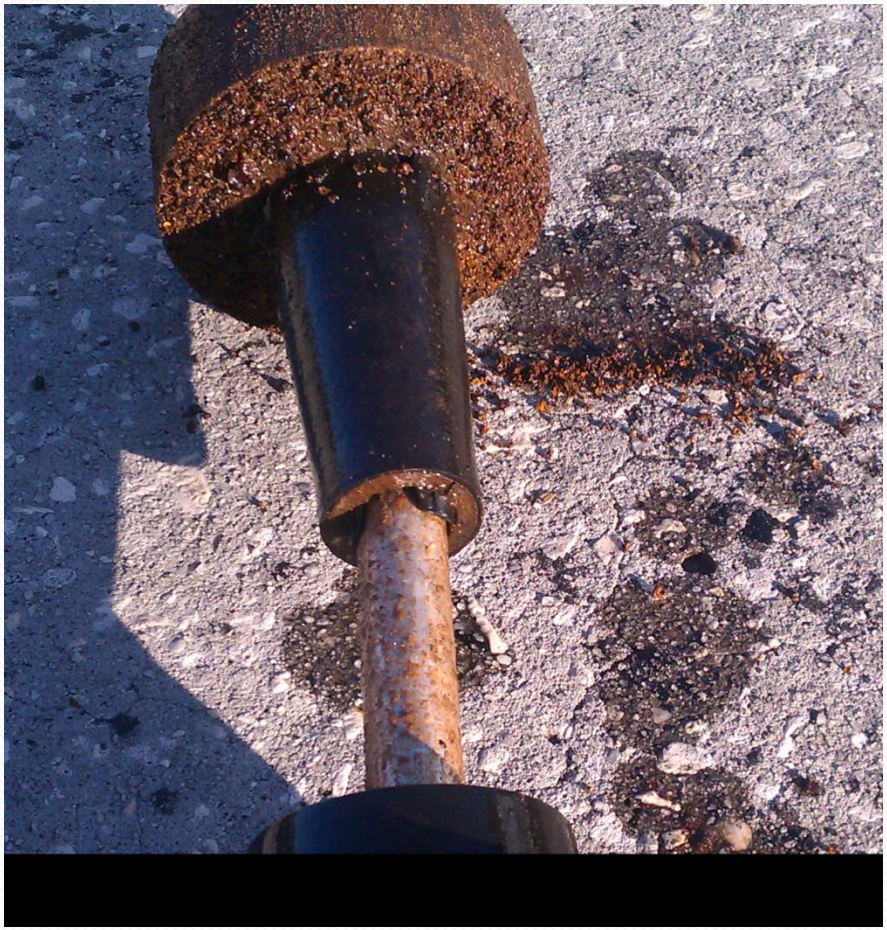
STI conducted own study

- Acetic acid and ethanol found in 5 regions
- Highest levels of acetic acid found in fiberglass tanks
- However data inconclusive to answer big questions
  - Is same type of corrosion happening in steel tanks?
  - Is acetic acid/ethanol responsible for corrosion?

Results

- Ethanol found in all but one region of the country
  - How is ethanol getting in diesel fuel
  - Transporting trucks is one possibility
  - Also possible for ethanol to be formed inside the tank
- Acetic acid found in all but one region of the country

Equipment from Southeast Region in fiberglass tank



FRP tank riser NW area Acetate 462 ppm

Steel Tank riser, NW area Acetate 108 ppm

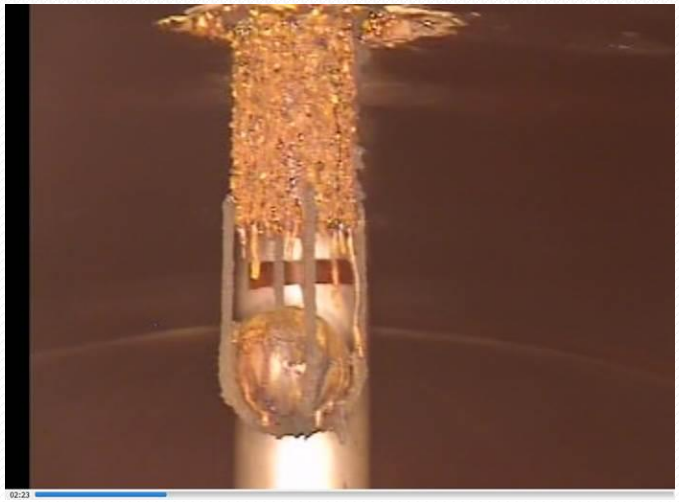
FRP riser, MA area
Acetate 25,600 ppm

Mixed Results

- Hypothesis that high acetate would indicate high corrosion
- Photos of risers don’t indicate this
- Next step cameras inspected inside tanks at 3 locations

STI Research

- Las Vegas service stations tanks under same owner
- FRP tank vapor control fitting – top right photo
- Steel tank vapor control fitting – bottom right photo



Future Research

- CRC, Coordinated Research Council
- US EPA

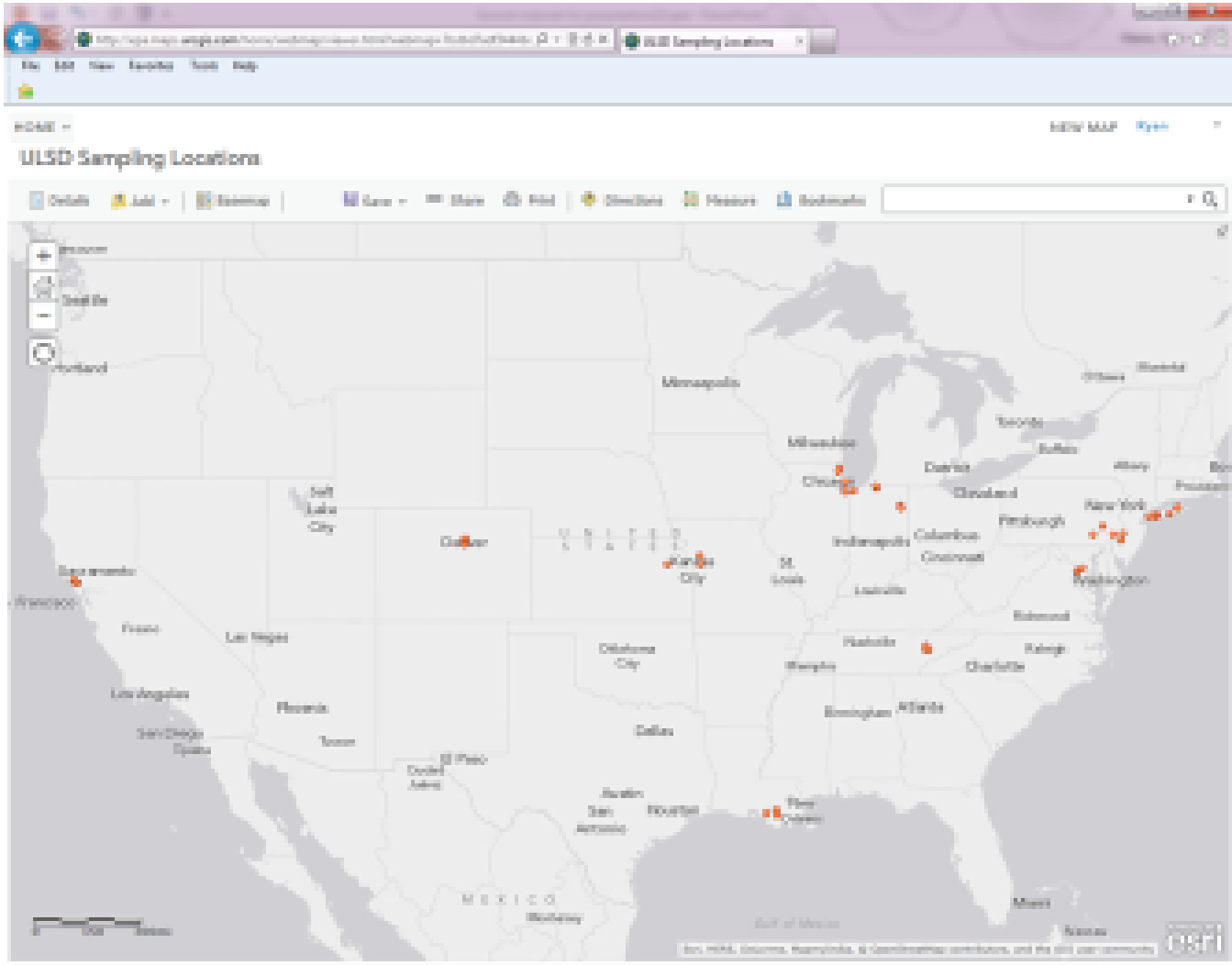
2014 Study of Conditions Correlating with Severe Corrosion in USTs Storing ULSD

-Severe and rapid corrosion being seen nationwide in USTs storing ULSD

-Severe corrosion with rapid onset on metal components inside of the tanks; previous study of 6 tanks suggested microbes feeding on contaminants in ULSD could be causing corrosive environment

-Study will document extent of corrosion inside of 42 tanks (21 steel, 21 FRP) from multiple owners nationwide, focusing on the STP shaft

-Fuel, vapor, and water bottom samples will be analyzed to attempt to determine what conditions correlate with varying levels of corrosion; results will be used to help determine possible solutions

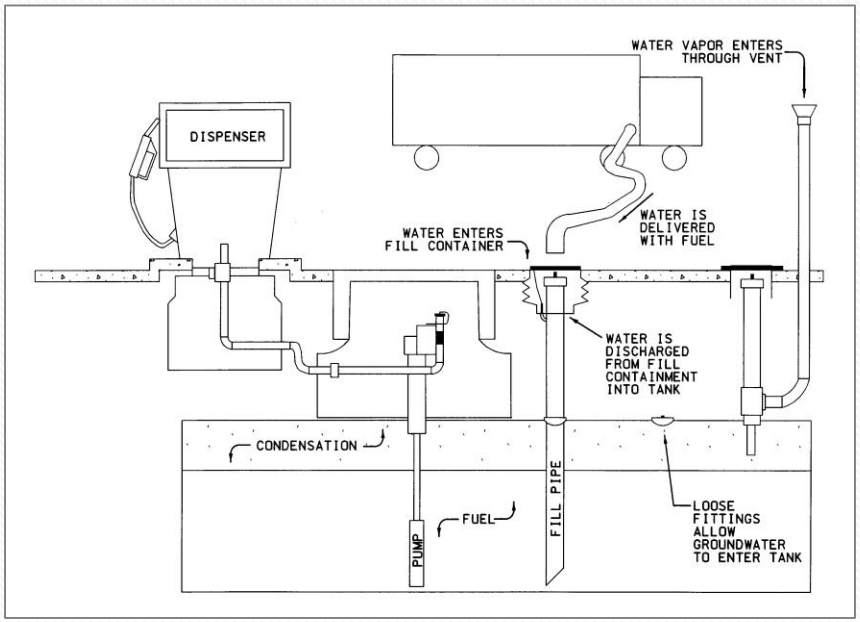


Best Management Practice

Improve Storage Tank Maintenance

Inspection and Maintenance

STI R111
Storage Tank Maintenance



Check Your Fuel - ASTM

Inspection and Maintenance of the Tank System

STI Webinar

December 18, 2013

www.steeeltank.com

Thank you!

Lorri Grainawi

STI/SPFA

944 Donata Court

Lake Zurich, IL 60047

Web: www.steeltank.com

Phone: 847/438-8265 x244

E-Mail: lgrainawi@steeltank.com