State of Tennessee

Division of Underground Storage Tanks

2011 ASTSWMO Meeting

Ethanol Related Corrosion in Submersible Turbine Pump Sumps (STPs)

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Office of Research & Development

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DEPARTMENT OF ENVIRONMENT & CONSERVATION

Ethanol Vapor Study

Staff of the Tennessee Department of Environment & Conservation, Division of Underground Storage Tanks, with support of staff in the U.S. EPA Office of Underground Storage Tanks and staff of the U.S. EPA Office of Research and Development, examined selected USTs in Tennessee for evidence of an association between ethanol in vapors or water in sumps and corrosion of metal fixtures.

Ethanol related corrosion article, written by Ellen Frye, in June 2010 LustLine Bulletin.

NOT FOR THE SQUEAMISH!

Those Alcohol-Loving Acetobacters at Work...or What?

by Ellen Frye

SENT: Wednesday, December 17, 2008, 4:30 PM
SUBJECT: Some odd corrosion and reactions
FROM: Steve Pollock

I ran across this mess in a sump today. I've seen similar messes, but this was just a little different. The environmental consultant I was with had never seen anything like it either. Kind of mounded, with recently active-looking bubbles (hydrogen gas?) on top. Sort of like the sulfur-reducing bacteria crud we sometimes find, but somehow a little more pillowy. The consultant knocked it around a little (with his neatly designed lid lifter which he described as the best tool they've ever purchased), and I was waiting for the whoosh of rotten-egg smell. Instead, it was a vinegar smell-acetic acid. Maybe in the presence of E10, our native soil/water bacteria now prefer to chomp on the ethanol first as Acetobacters or just as opportunistic bacteria loving an easier chain (the alcohol) to digest, creating acetic acid--you know, like wine going bad. Or perhaps, in the presence of E10, these are the first bacteria to feast at the buffet, then the vultures, and then the oil metabolizers

Anyway, the acetic acid, bacteria, and some funky mold (or yeast?) is tearing up the steel, too. Also note that the line leak detector was supposedly replaced this past February with a Red Jacket FX-1V series part. Maybe...though it sort of looked like the older, bigger XL's. But if it's new as of Feb '08, it has had a hurting put on it. Oddly, the next-door STP sump was also full of water, but not this mess. And it was clear that the LLD had been replaced.

Ethanol Blended Gasoline Use in Tennessee

- **E-10 gasoline blend use in Tennessee:**

  Driven by the Energy Independence and Security Act of 2007, as of January 2008, E-10 fuel sold at more than half of gasoline retailers; today 85-90% of gasoline dispensed is E-10.

- **E-85 gasoline blend use in Tennessee: Approximately 40 retail facilities are dispensing E-85 across the state.**

STP Sump Corrosion Information

- **EPA Region 4 in Feb. 2007 Meeting Note: External UST equip. corrosion noted from ethanol blend fuels, not sure cause of corrosion.**
- **March 2010, TDEC, notices significant STP sump corrosion at UST facility, two years old.**

A typical Non-E-10 gasoline STP sump, 11 years old. (vapors noted in sump).

800128 Regular E-10 “all in one sump”

June 2008

Nov. 2010

Stagecoach 800023 Prem. Sump

Mar. 2010

Aug. 2010

Ethanol Vapor Sampling Procedure

a. Vapor samplers were left in selected sumps for two months.

b. The vapor samplers are simply 40 ml screw cap VOA vials, where the septum has been replaced with a porous nylon filter. Vapors pass through the filter and dissolve in the water. The water contains trisodium phosphate to preserve the samples from biodegradation.

c. When the samplers are recovered, the filter is replaced with a conventional Teflon faced septum, and the VOA vial and its contents are shipped the lab for analysis by Method 8260.

Ample ethanol in vapors

Water condensing on fixtures

Ample production of acetic acid

Extensive corrosion

800023 Premium	Sump Water	Vapor Samplers
	mg/L	mg/L
Ethanol	No Sample	14850
Acetic acid	No Sample	125
Benzene	No Sample	1
Total BTEX	No Sample	21
no standing water, STP 2 years old, pH condensate 5.3		

Analysis of corrosion product

As expected, the corrosion product of the steel fitting is iron(III) oxyhydroxide.

	Acetate	Copper (Cu)	Iron (Fe)	Zinc (Zn)
	mass fraction	mass fraction	mass fraction	mass fraction
8000023	0.00475	0.0000125	**0.512**	0.000237
$Fe(OH)_3$			0.523	

Ample ethanol in vapors

Water condensing on fixtures

Ample production of acetic acid

Corrosion

800128 Premium	Sump Water	Vapor Samplers
	mg/L	mg/L
Ethanol	No Sample	24000
Acetic acid	No Sample	778
Benzene	No Sample	2
Total BTEX	No Sample	10
no standing water, STP 2 years old, pH condensate <4		

Analysis of corrosion product

The corrosion product of the steel fitting is iron(III) oxyhydroxide.

A major component of the corrosion on the brass fitting was copper(II) acetate.

	Acetate	Copper (Cu)	Iron (Fe)	Zinc (Zn)
	mass fraction	mass fraction	mass fraction	mass fraction
800128 Steel	0.0229	0.0015	**0.483**	0.00233
$Fe(OH)_3$			0.523	
800128 Brass	**0.257**	**0.306**	0.000816	0.0261
$Cu(C_2H_3O_2)_2*2H_2O$	0.542	0.292		

Ample ethanol in vapors

Water condensing on fixtures

Ample production of acetic acid

Corrosion

800128 Regular	Sump Water	Vapor Samplers
	mg/L	mg/L
Ethanol	No Sample	13700
Acetic acid	No Sample	667
Benzene	No Sample	2
Total BTEX	No Sample	5
no standing water, STP 2 years old, pH condensate <4		

Ample ethanol in vapors

No water

Little acetic acid

No corrosion

18 DOT E85 Gasoline	Sump Water	Vapor Samplers
	mg/L	mg/L
Ethanol	No Sample	1340
Acetic acid	No Sample	0.332
Benzene	No Sample	0.002
Total BTEX	No Sample	0.030

Minimal ethanol in vapors

No water

No acetic acid

No corrosion

560100 Premium	Sump Water	Vapor Samplers
	mg/L	mg/L
Ethanol	No Sample	24.3
Acetic acid	No Sample	<0.005
Benzene	No Sample	0.13
Total BTEX	No Sample	1.41
no water, STP 4.5 years old		

Minimal ethanol in vapors

Adequate water

Little acetic acid

Normal amount of corrosion

800023 7 Regular	Sump Water	Vapor Samplers
	mg/L	mg/L
Ethanol	1.87	12.21
Acetate or Acetic acid	1.34	2.07
Benzene	0.22	0.72
Total BTEX	2.59	6.36
7" water, STP 2 years old, pH 5.8		

Minimal ethanol in vapors

Adequate water

Conc. acetic acid not above trip blank (0.77 mg/L)

No evidence of corrosion

4-560089 Regular	Sump Water	Vapor Samplers
	mg/L	mg/L
Ethanol	ND	8.49
Acetate or Acetic acid	0.35	0.99
Benzene	0.09	0.04
Total BTEX	0.98	0.69
19" water, STP 5+ years old, pH 5.3		

Ample ethanol in sump water

Ample acetic acid in sump water

Corrosion

4-930055	Sump Water	Vapor Samplers
	mg/L	mg/L
Ethanol	126	No Sample
Acetate	1790	No Sample
Benzene	1.6	No Sample
Total BTEX	21.4	No Sample
2" water in sump, STP 4 years old, pH 5		

Analysis of corrosion product

The corrosion product of the steel fitting is iron(III) oxyhydroxide.

	Acetate	Copper (Cu)	Iron (Fe)	Zinc (Zn)
	mass fraction	mass fraction	mass fraction	mass fraction
4-930055	0.00419	0.000199	0.453	0.00147
$Fe(OH)_3$			0.523	

A link exists between ethanol in motor fuels and the corrosion of metals in the sumps of an underground storage tank.

In the summer, the contents of a UST tend to be cool with respect to the atmosphere. There is a tendency for water to condense from the air onto cool metal fixtures in a sump. The sump can also collect precipitation.

The vapors in the ullage of the UST contain high concentrations of ethanol.

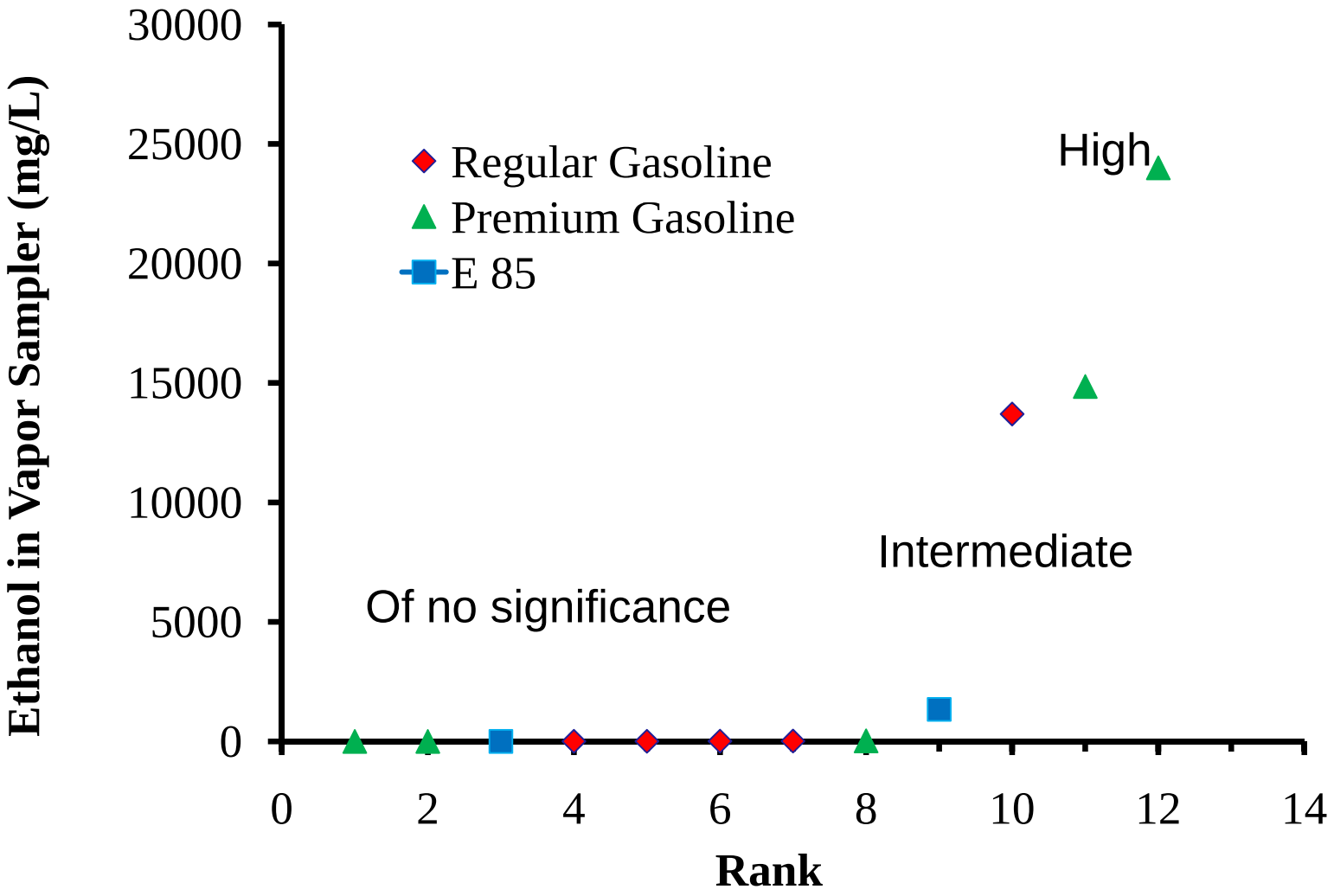
If the vapors escape the UST, they can dissolve in standing water in the sump or in water that has condensed on metal fittings.

Acetic acid bacteria can use oxygen from the atmosphere to rapidly transform the ethanol to acetic acid.

$$2\ CH_3CH_2OH + O_2 \longrightarrow 2\ CH_3COOH + 2\ H_2O$$

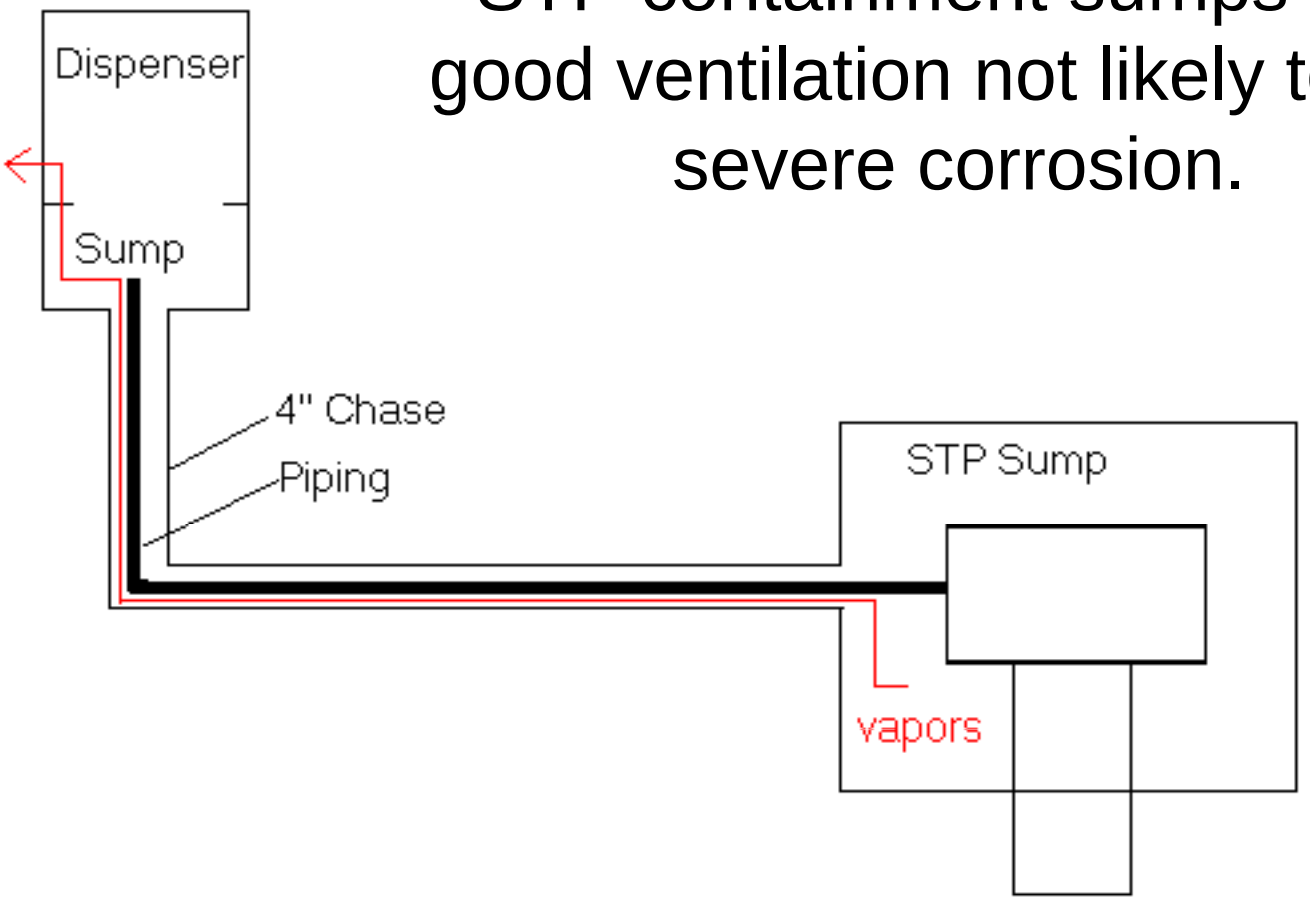
The acetic acid produced by biological degradation of ethanol can facilitate the corrosion metals.

Ethanol Vapor Concentration Vs. Types of Ethanol Blends



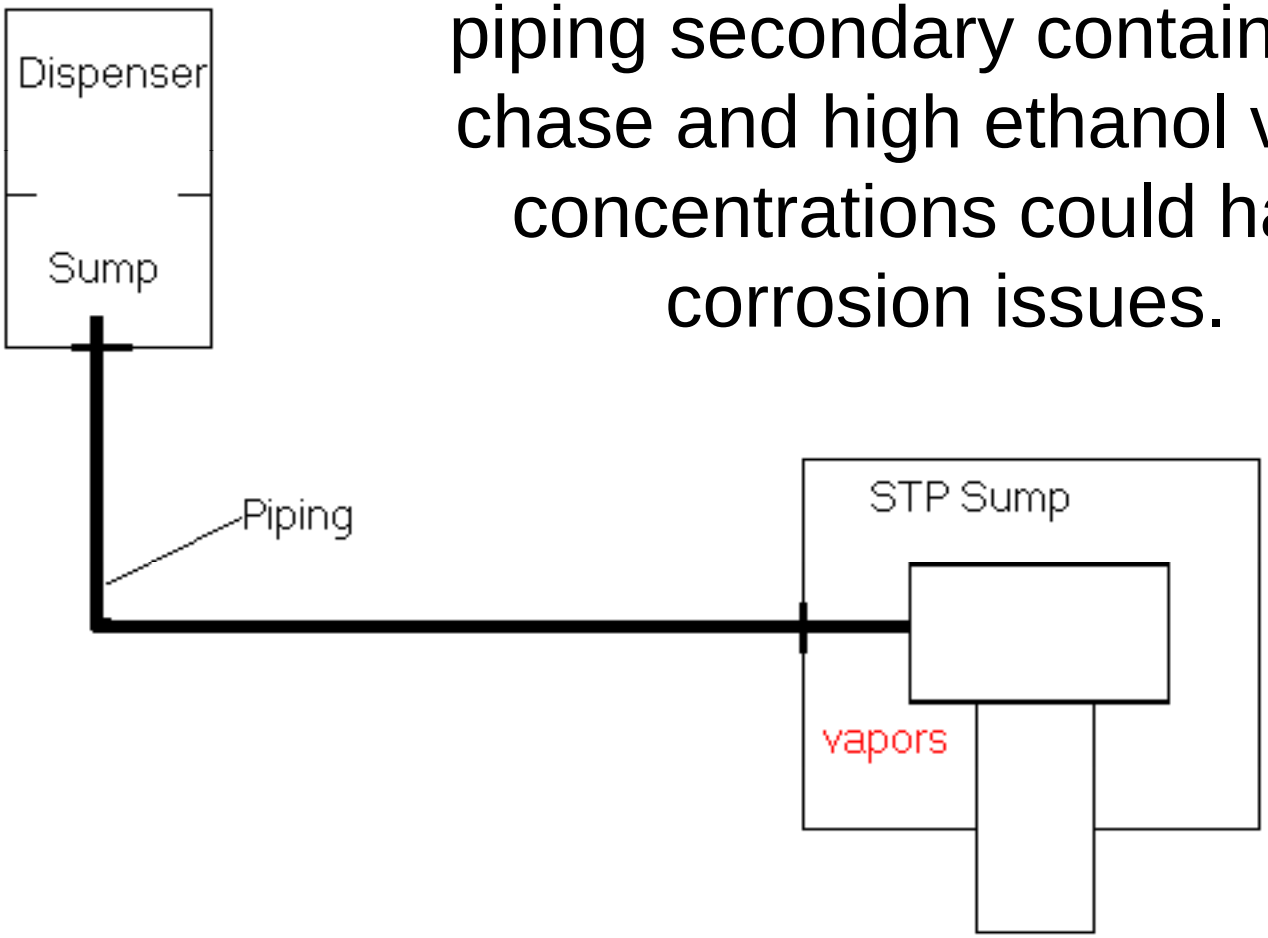
Ventilated sump through 4” piping secondary containment chase

STP containment sumps with good ventilation not likely to see severe corrosion.



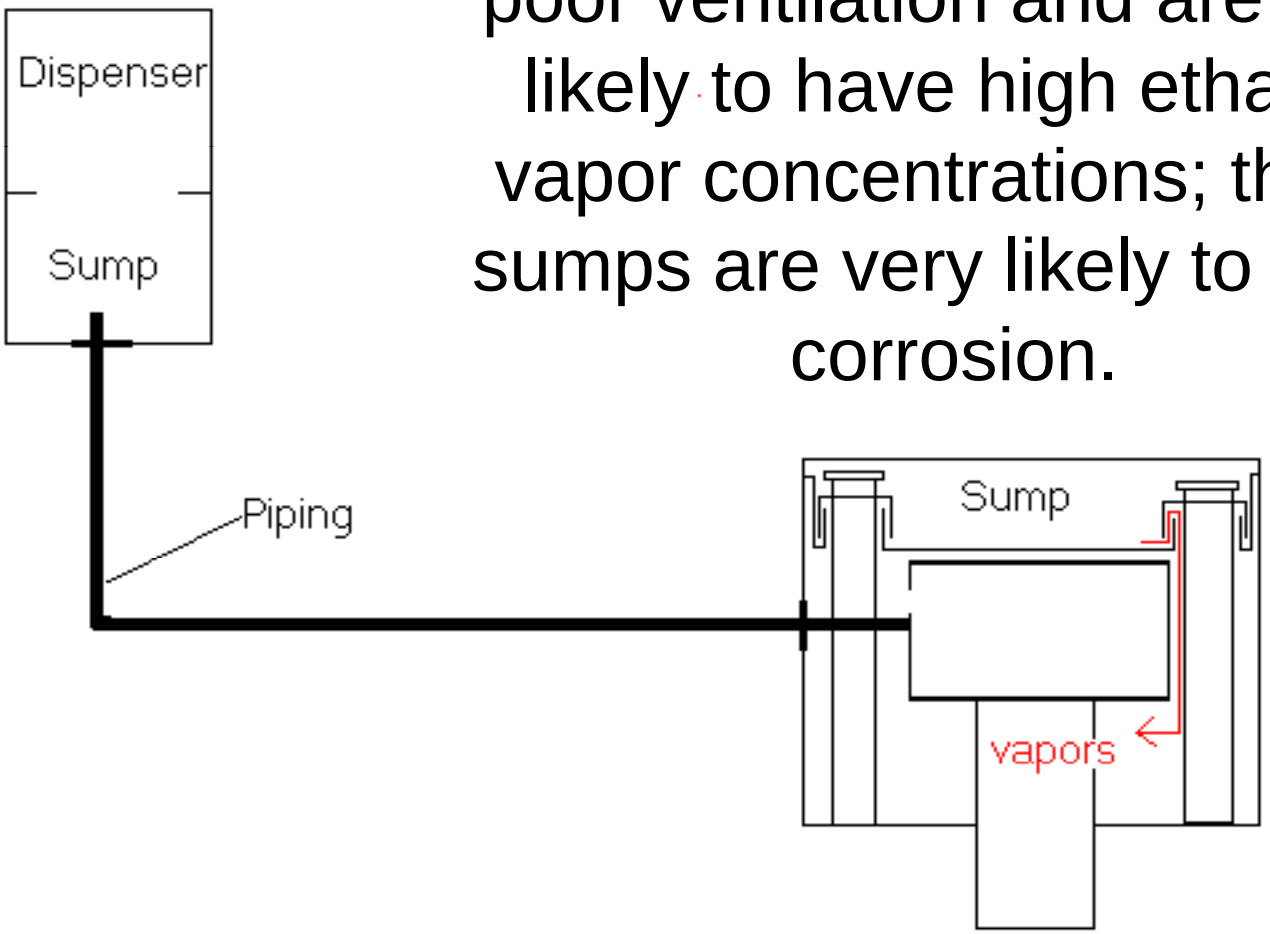
STP sump no ventilation

STP sumps without the 4” piping secondary containment chase and high ethanol vapor concentrations could have corrosion issues.



All in one sump, poor ventilation

The “all in one sump” have poor ventilation and are very likely to have high ethanol vapor concentrations; these sumps are very likely to have corrosion.

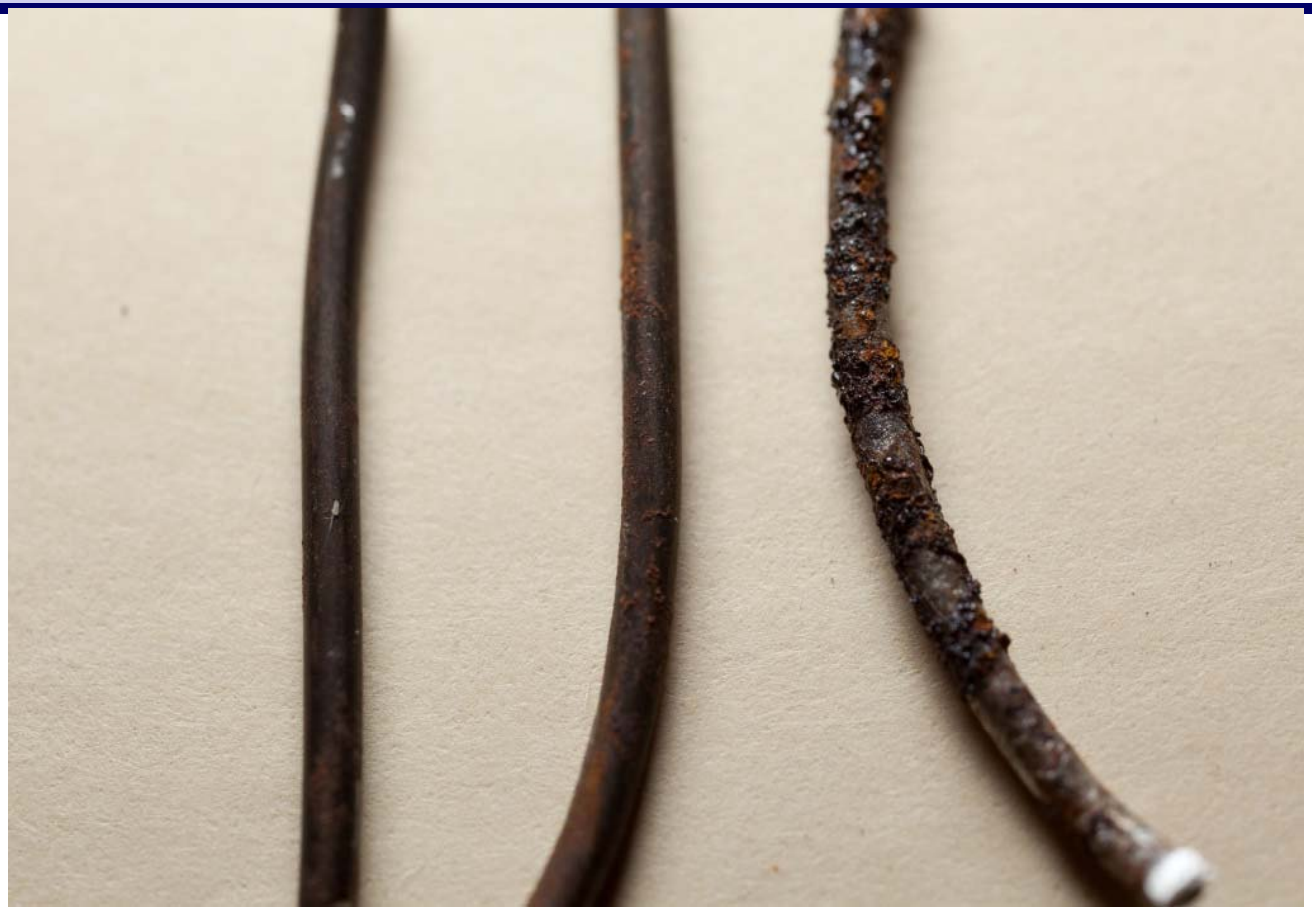


All in one sump with spill pan in place over STP sump

Corrosion Characteristics

- Severe STP sump corrosion occurs in sumps with limited ventilation.
- Corrosion deposits have globular shape (tubercles) which could be indicative of MIC.
- Corrosion rate seems related to sump temperature.

Corrosion Rate Related to Temperature

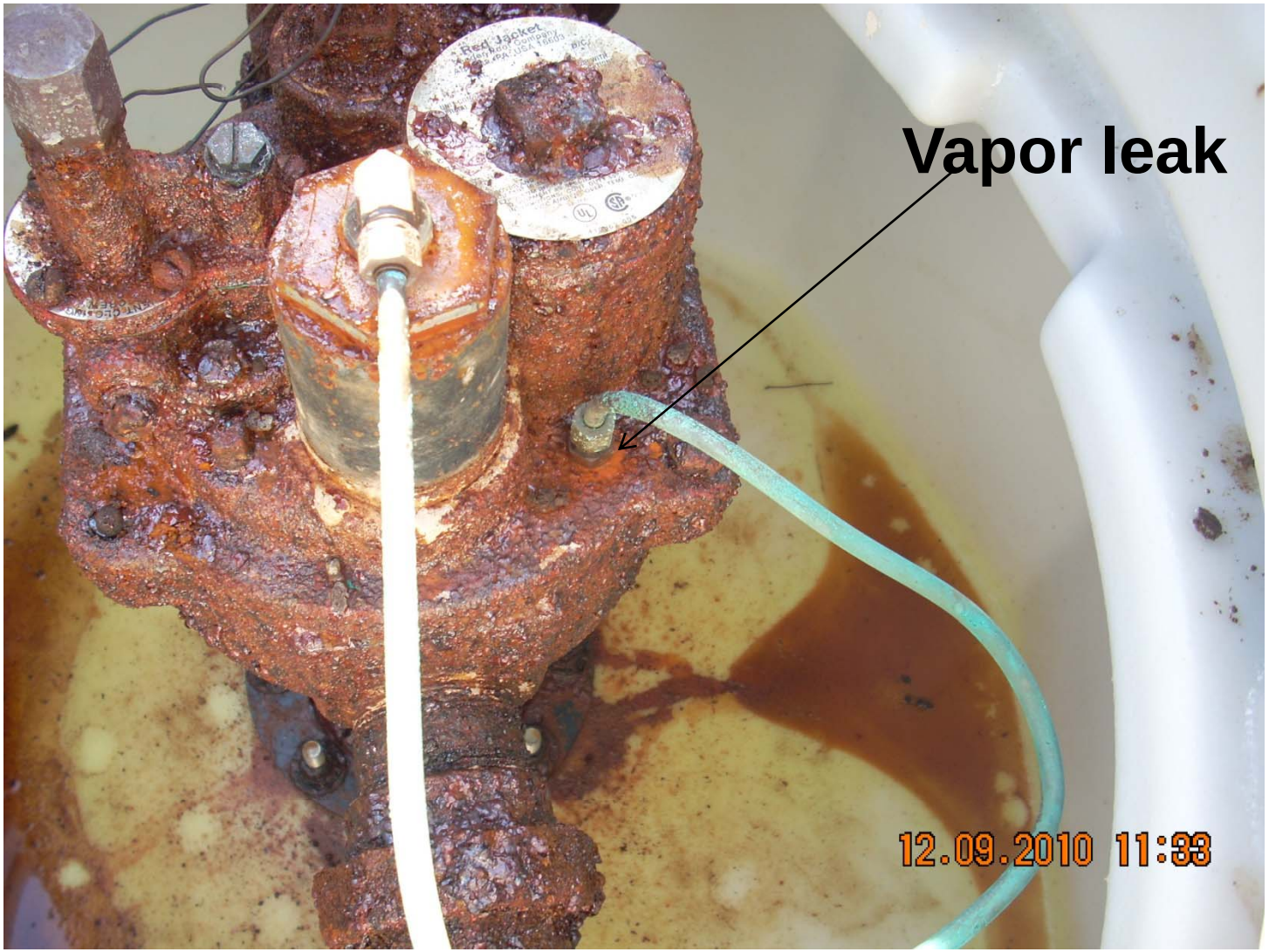


Left to Right: Control, Wire in Sump Oct.-Dec., Wire in Sump 2 weeks in Aug.

Controlling STP Sump Corrosion

- Detecting & Reducing vapor leaks
- Use more corrosion resistant stp components
- Improve STP sump ventilation
- Corrosion resistant coatings examples: Tape Coat TC-7100 or 3M 323
- Biocides
- Fuel additive: corrosion inhibitor

Finding Vapor Leaks

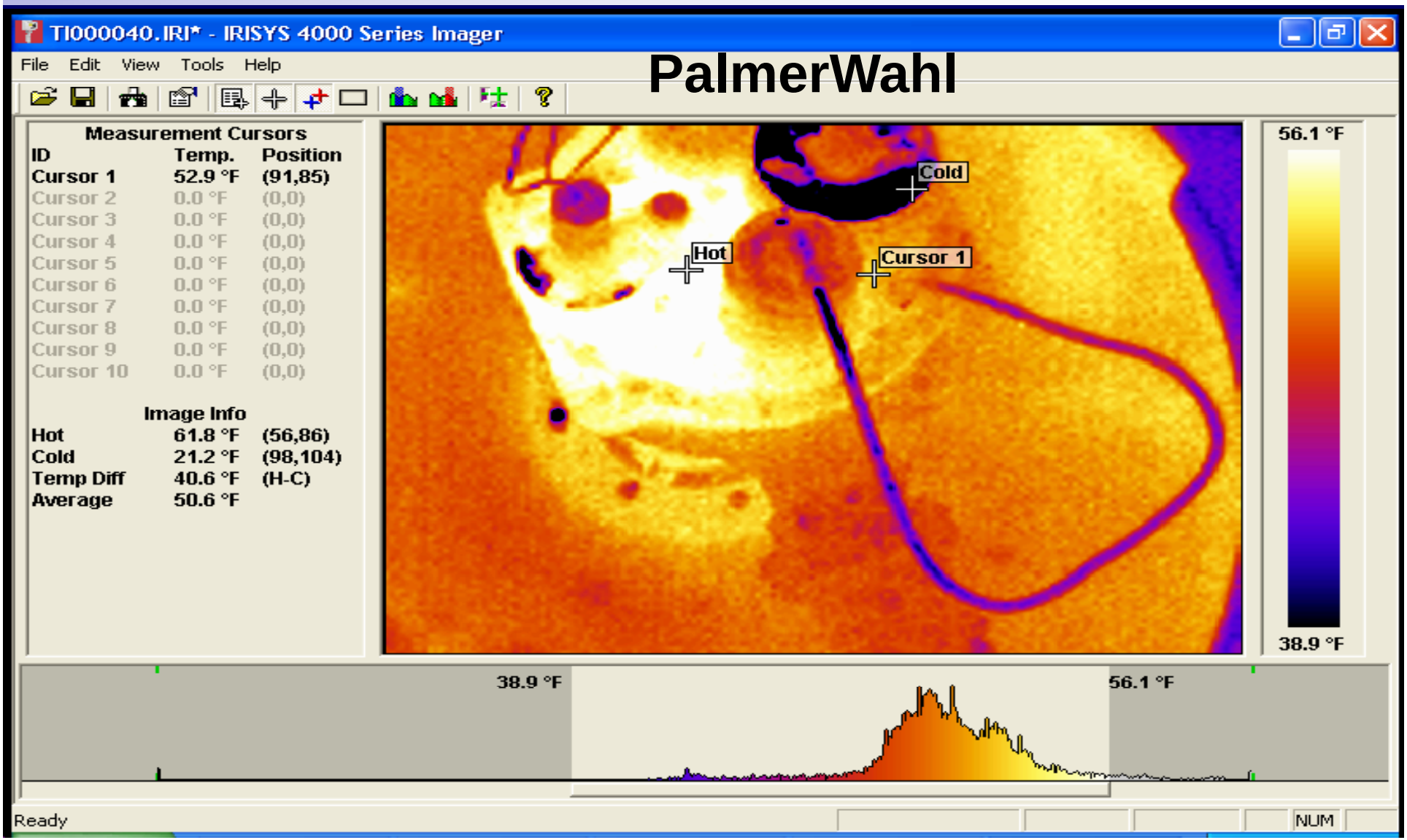


Vapor Leak Detection

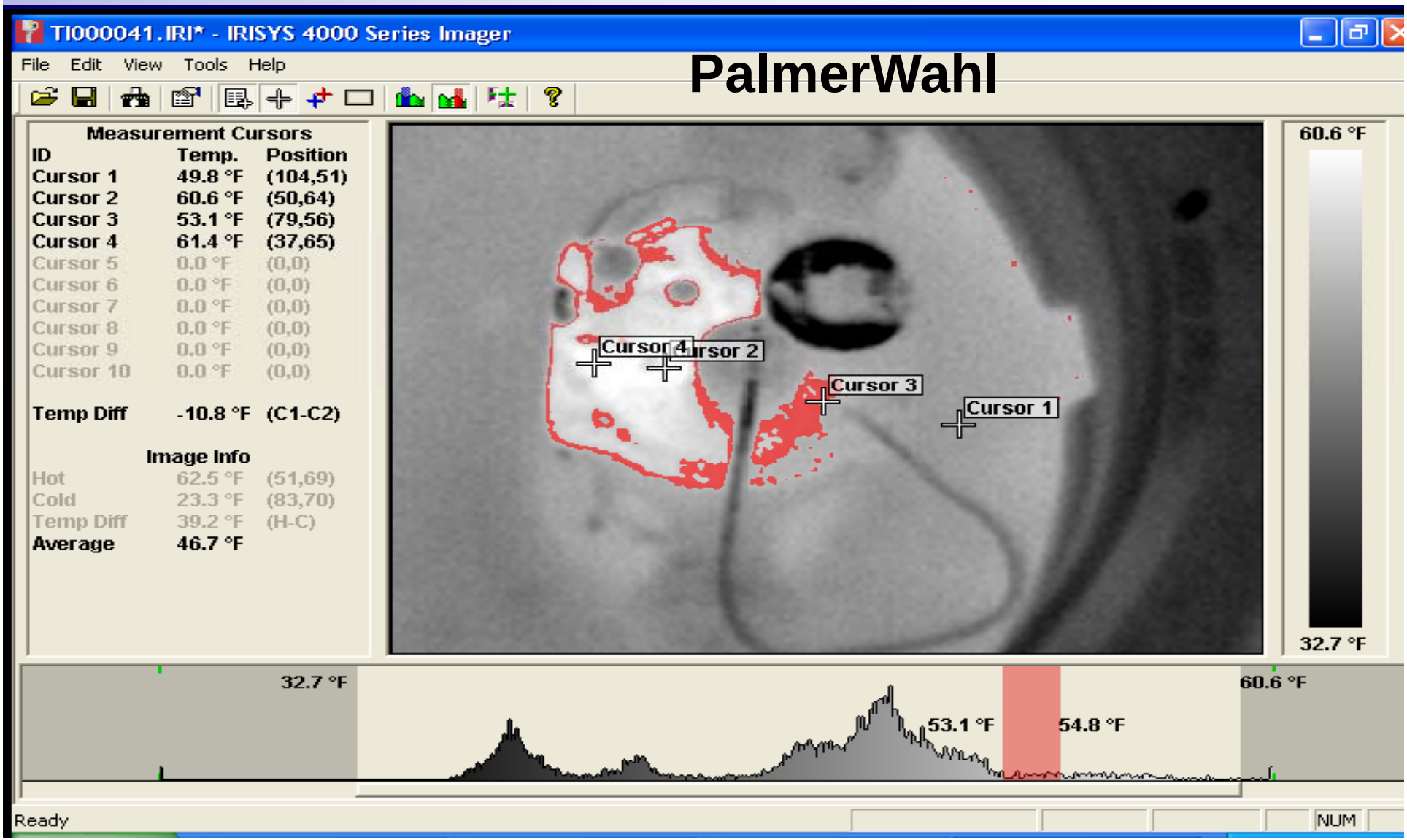
Palmer Wahl Infrared Detector

Sensit Gold CGI Explosivity Meter

Stagecoach premium sump vapor leak at cursor 1 (yellow color at marker).

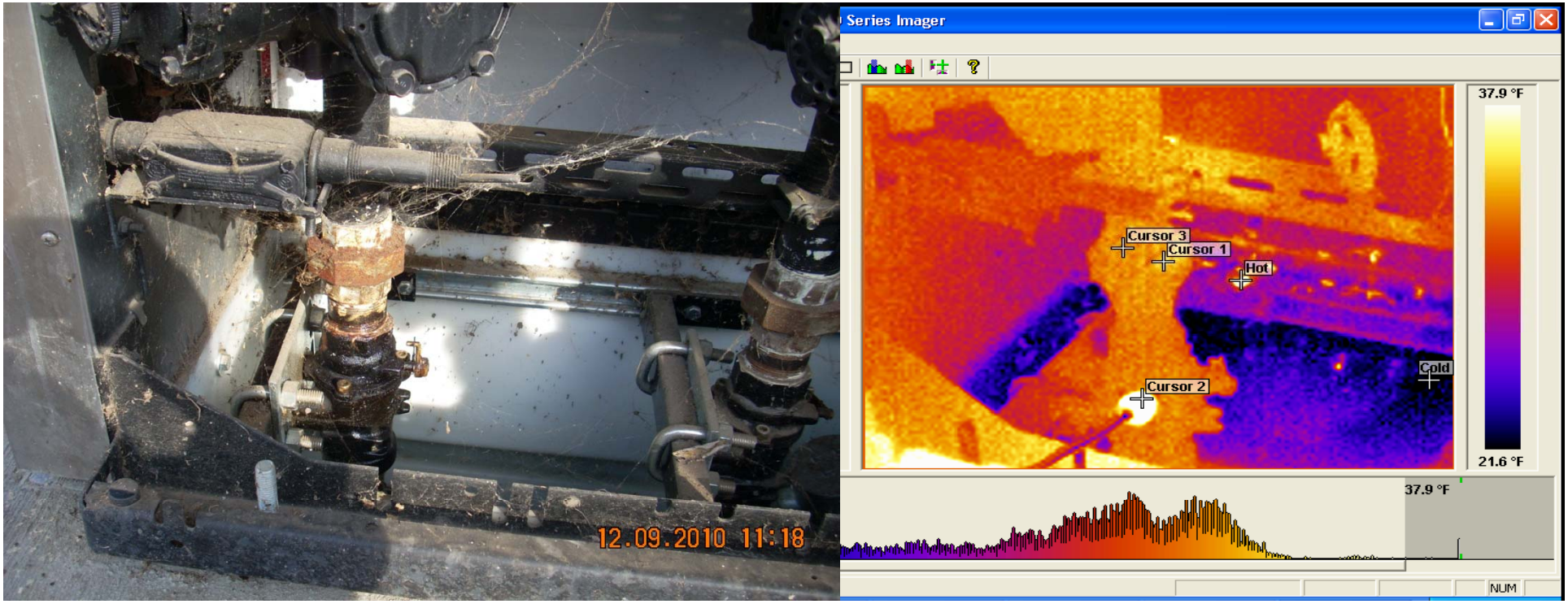


Stagecoach premium sump, vapor leak at cursor 3 (pink area).



Dispenser piping leak at cursor 1 (yellow color is vapor leak).

Palmer Wahl



Petroleum residual on shear valve body below the actual leak at coupler

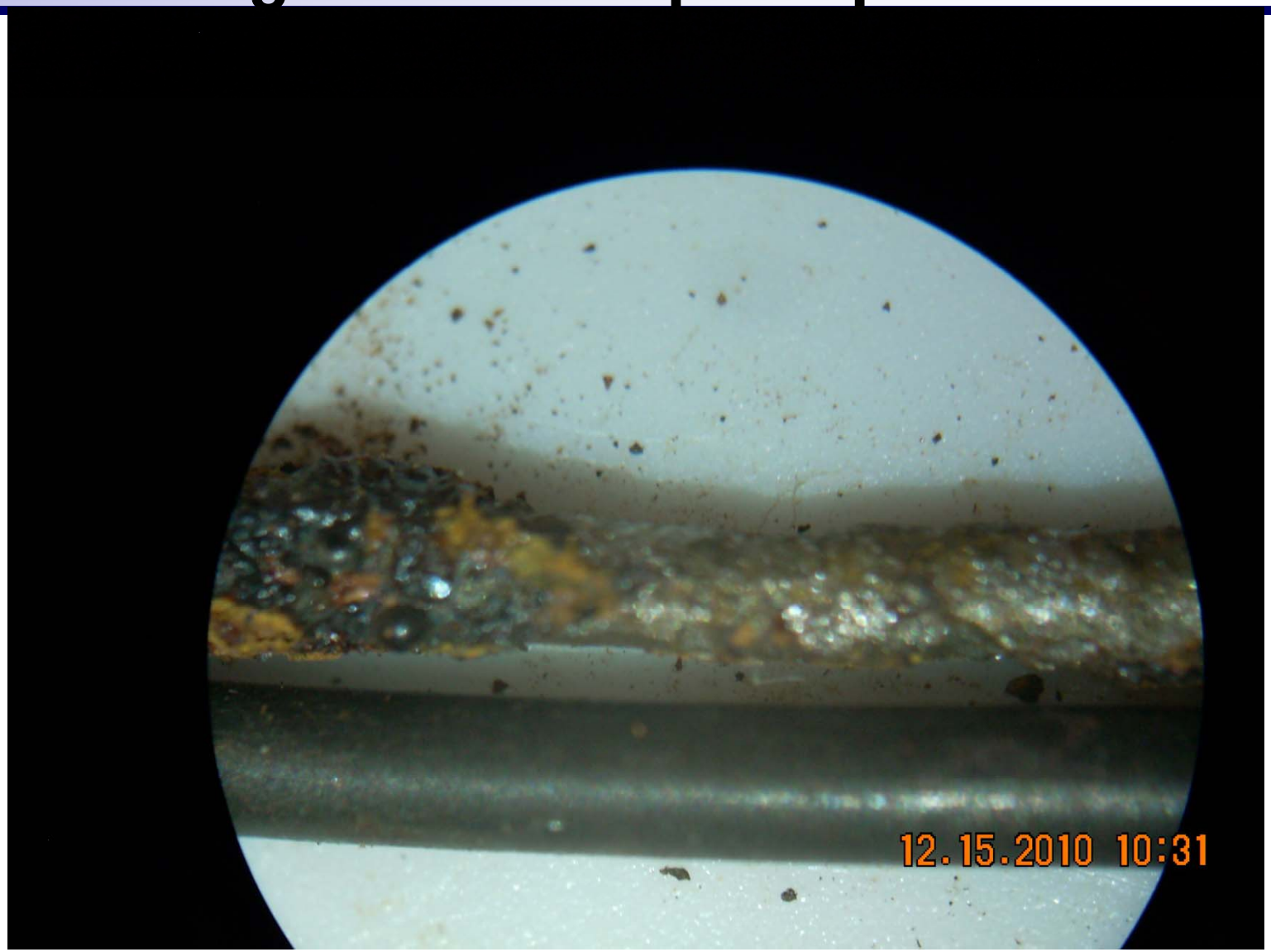
Regular E-10 sump three years old with possible white corrosion deposits on stainless flex?

How serious is the STP sump corrosion?

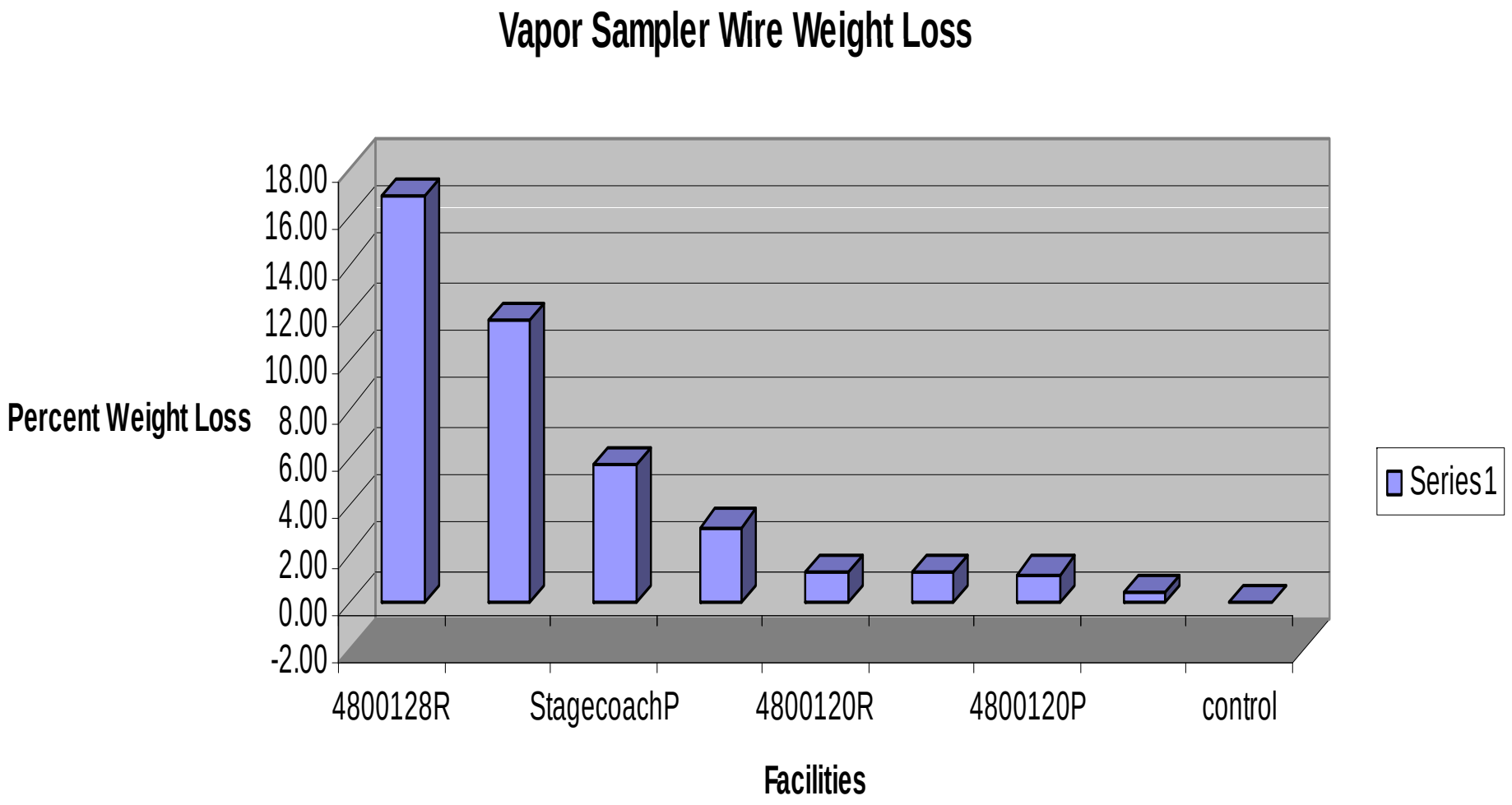
STP sump picture from Edwin C. French IV, Senior Env. Compliance Specialist, Storage Tank Section, Leon County, Florida

Corrosion on vapor sampler wire in sump for 66 days compared to control wire.

Corrosion on vapor sampler wire in sump for 66 days compared to control wire, notice the globular shape deposits.



VAPOR SAMPLER WIRE CORROSION



Vapor Sampler Wire Weight Loss

Vapor Sampler Wire Weight Loss

Sample	Length cm	Weight g	gram/cm	percent wire loss	days in sump
4800128R	23.3	2.9558	0.1269	16.80	68
4800128P	21.1	2.8416	0.1347	11.67	68
StagecoachP*	18.5	2.6602	0.1438	5.69	13
StagecoachR	22.5	3.3238	0.1477	3.11	66
4800120R	22.6	3.4025	0.1506	1.26	66
4560089R	20.3	3.0578	0.1506	1.21	66
4800120P	26.0	3.9183	0.1507	1.16	66
4560100P	24.2	3.6740	0.1518	0.43	66
control	27.4	4.1778	0.1525	0.00	68

*Due to rapid corrosion of wire in sump, wire removed after 13 days.

Corrosion Testing

- **Colorado School of Mines Grad. Students, Chase Williamson & Luke Jain, will be analyzing corrosion pipe samples taken from Stagecoach premium STP sump.**

SUMMARY

Rapid corrosion has been observed in <u>some</u> ethanol blended gasoline stp sumps with <u>limited ventilation</u>; these sumps contain high ethanol vapor concentrations with microbial activities forming acetic acid. Water condensate and temperature appear to influence rate of corrosion. Future studies need to be performed to determine the severity of the stp sump corrosion, and best ways to control the corrosion.

ACKNOWLEDGEMENT

I wish to thank the following individuals, agencies, and companies for their contributions to this presentation.

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QUESTIONS/BRAINSTORMING