Corrosion in STP Sumps

What Causes It and What Can Be Done About It?

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(And His Co-Authors)

Figure 1
Corrosion on the turbine pump head in a sump in Florida. Photo provided by Chris French (Storage Tank Compliance Program, Leon County, Fla.).

Figure 1 depicts extensive corrosion seen in the sump for the submersible turbine pump (STP) of an underground storage tank in Florida. There is extensive corrosion of both the cast iron components of the turbine pump head and the copper line connecting the leak detector to the headspace of the tank.

What caused or is causing the corrosion? Acetic acid produced by biodegradation of ethanol that found its way into the sump is one plausible answer.

The first person to connect the dots in this mystery was Steve Pollock, a Compliance Inspector with the Petroleum Program in the Virginia Department of Environmental Quality. During his inspections, Mr. Pollock noticed odd corrosion in some of the STP sumps at gasoline service stations in Virginia. Accompanying the corrosion was the smell of vinegar.

The primary organic component of vinegar is acetic acid. Mr. Pollock speculated that acetic acid bacteria were degrading ethanol in the sumps to produce acetic acid. These are the same bacteria that turn wine into vinegar, using oxygen from the atmosphere to degrade ethanol to acetate.

If ethanol from the motor fuel could find its way into the sumps, this would provide a source of food for the acetic acid bacteria. Research staff of the U.S. Environmental Protection Agency (EPA) set out to evaluate the association between ethanol vapors in sumps and the production of acetic acid and, correspondingly, the association of acetic acid to corrosion in sumps.

To make this evaluation, EPA staff asked state regulators to collect samples from sumps at sites across the United States. To facilitate the work, EPA provided a sampling kit that allowed sampling of water from the sumps and vapors within the sumps. Participants were asked to sample sumps that showed evidence of corrosion and neighboring sumps that did not show corrosion. A passive diffusion sampler was installed in the sump to sample the concentrations of ethanol and acetic acid in air. Then the sampler was recovered and sent to the EPA's Ada, Okla. lab for analysis.

Data on vapor concentrations of ethanol and acetic acid were acquired from 35 sumps in Florida, 13 in Tennessee, six in Illinois, four in Wisconsin, two in California and one in Iowa. Some 27 of the USTs were labeled as regular gasoline, two as mid-grade gasoline, 26 as premium gasoline, five as E85 and one as diesel fuel. State regulators provided photographs for 48 of the sumps, with 39 of the photographs adequate to evaluate the presence or absence of corrosion products in the sumps. (The photographs and data on concentrations of ethanol and acetate in the sumps are available on request from wilson.johnt@epa.gov.)

Sampling Science

The vapor samplers were constructed using 40 ml Volatile Organic Analysis (VOA) vials filled with deionized water containing 1% trisodium phosphate to prevent growth of bacteria that might degrade ethanol or acetate in the sampler. The trisodium phosphate buffered the water to pH 10.5. Before the vials were placed in the sumps, the conventional Teflon-lined septum was replaced by a permeable membrane (0.2 µm Supor). While the vials were incubated in the sump, ethanol and acetic acid diffused across the permeable membrane and dissolved in the water in the sampler. When the samplers were retrieved, the permeable membrane was replaced with a Teflon-lined septum, and shipped to the laboratory for analysis. Then the samplers were analyzed for concentrations of ethanol and acetate in the water.

The vapor samplers were calibrated by comparing the rate of accumulation of ethanol and acetate when the samplers were exposed to air above water with known concentrations of ethanol or acetate. The accumulation of ethanol and acetate was linear over time, and proportional to the known concentration in the water. After 28 days, the average concentration of ethanol in the samplers was 37% of the concentration in the calibration water. The accumulation of acetate was 6.7%. The samplers were incubated in the sumps for approximately one month. To estimate the equilibrium concentration of ethanol or acetate in water that might condense on the fittings, the concentration of ethanol in the sampler was divided by 0.37, and the concentration of acetate in the sampler was divided by 0.067.

Major Findings

Figure 2 presents the distribution of ethanol and acetic acid in the air in 61 of the sumps in the survey. Many of the sumps had high concentrations of ethanol or acetic acid (>1,000 mg/L), and others had lower concentrations. There was no significant

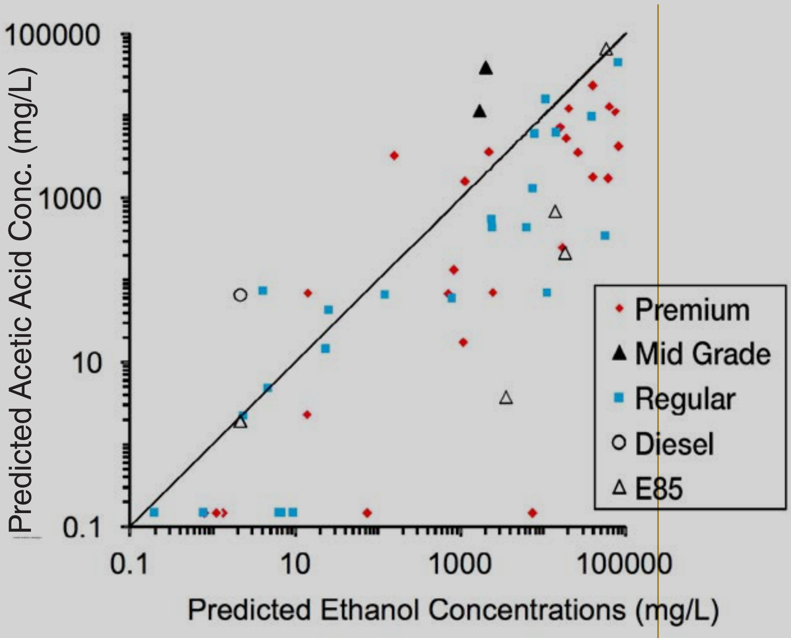

Figure 2

The concentrations of ethanol and acetic acid that would be expected to be dissolved in condensation water on the fittings in the sump based on the concentrations of ethanol and acetate acquired by the vapor samplers.

difference between tanks that contained premium gasoline, E85 and regular gasoline.

The available photographs were examined to determine whether rust tubercles or blue corrosion product was present: 37 of the photographs could be scored for presence or absence of rust tubercles; 36 could be scored for the presence or absence of a blue corrosion product; a total of 39 sumps could be scored for one corrosion product or the other. *Figure 1* shows tubercles of rust growing from the cast iron fittings and blue corrosion on the copper line in one of the sumps. The photo also shows water that has condensed on the fittings.

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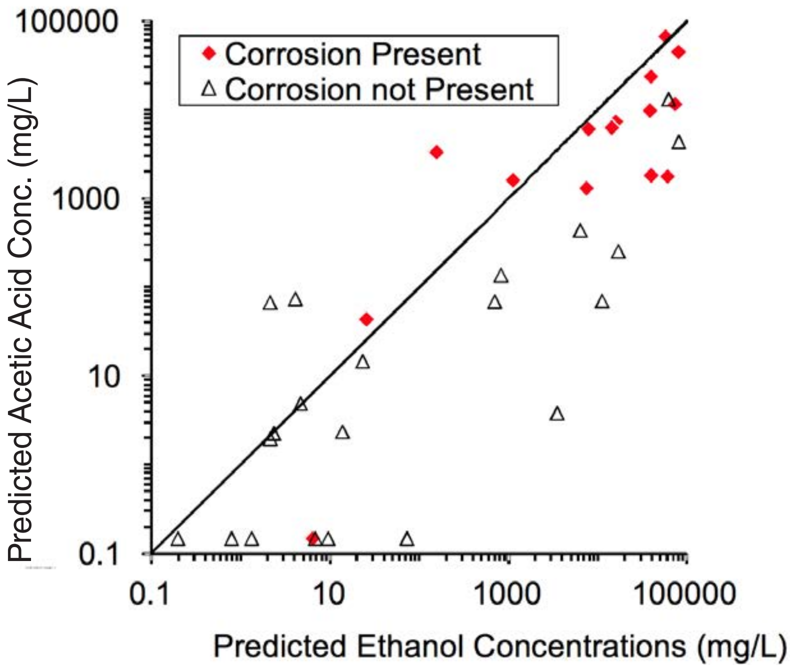

Figure 3

Relationship between the corrosion product in a sump and the predicted concentrations of ethanol and acetate in condensation water.

Figure 3 compares the concentration of ethanol and acetic acid in air in the 15 sumps with evidence of corrosion to the concentrations in 24 sumps without corrosion. In general, corrosion was associated with the higher concentrations of ethanol or acetic acid in air. However, there were exceptions. Two sumps with corrosion did not have high concentrations of ethanol or acetic acid at the time they were sampled. Two sumps with high concentrations of ethanol and acetic acid did not show corrosion.

Table 1 compares the geometric mean of the predicted concentration of ethanol and acetate in condensation water to the presence or absence of rust tubercles or blue corrosion product. The predicted concentration of ethanol and acetic acid in condensate was roughly 100-fold higher in sumps that had rust tubercles or the blue corrosion product. The rust tubercles or the blue corrosion product was associated with higher concentrations of ethanol or acetic acid in the air of the sump. There also

Sump Condition	Rust Tubercles	No Rust Tubercles	Blue Corrosion	No Blue Corrosion
	Geometric Mean of the Predicted Concentration of Ethanol in Condensate (mg/L)			
Wet	**5600** n=12 (36,000-850)*	**34** n=8 (580-2.0)*	**6,200** n=12 (41,000-910)*	**91** n=9 (1,500-5.5*)
Dry	**8900** n=4 (44,000-1,800)*	**11** n=13 (130-0.86)*	**7,300** n=1	**12** n=13 (160-0.88)*
	Geometric Mean of the Predicted Concentration of Acetate in Condensate (mg/L)			
Wet	**1,500** n=12 (11,000-200)*	**9.0** n=8 (170-0.48)*	**2,400** n=12 (18,000-310)*	**26** n=9 (300-2.2)*
Dry	**5,500** n=4 (33,000-940)*	**3.9** n=13 (24-0.64)*	**1,300** n=1	**6.9** n=13 (57-0.82)*

Table 1

Relationship between the presence of rust tubercles on the cast iron body of the STP, or a blue corrosion product on the copper line connecting the leak detector to the headspace of the tank, and the predicted concentration of ethanol or acetic acid.

* 95% confidence interval on the mean.

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was an association of corrosion with free water in the sump: 60% of the wet sumps had rust tubercles and 57% had blue corrosion, while 13% of the dry sumps had rust tubercles and 7% had blue corrosion.

The circumstances leading to corrosion in STP sumps in this study are similar to the findings of a 2012 Battelle Memorial Institute study to identify the causes of corrosion in six underground storage tanks that contained ultra low sulfur diesel (ULSD) fuel. In both studies, ethanol was available in the fuel. The water bottoms in the diesel tanks contained 9,000 to 22,500 mg/L of acetate. In this study, standing water was in seven sumps that exhibited corrosion. The concentration of acetate in the sump water varied from 1.4 to 72,000 mg/L. In five of the seven sumps, the concentration of acetate was greater than 1,600 mg/L (data available on request at wilson.johnt@epa.gov). The concentration of acetic acid in vapors in the ullage of the diesel tanks ranged from 570 to 16,000 ppbv, which corresponds to 190 to 5,300 mg/L dissolved in condensation water.

What It Means

The data point to a reasonable explanation for the corrosion in STP sumps. So what can be done about it? For ethanol to cause corrosion in a sump, three components are necessary: ethanol, bacteria to degrade the ethanol to acetic acid and water. Water provides the environment for the bacteria to live in and also is required for the actual chemical corrosion event.

In theory, corrosion can be prevented by eliminating any of the three necessary components.

Notice

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Ethanol

Corrosion can be stopped by stopping any leak that is allowing ethanol into the sump. If fittings are not fuel-tight and liquid fuel is entering the sump, this should be apparent from either free product or a petroleum sheen on water in the sump. The other possibility is vapors from the headspace of the tank migrating into the sump. One likely prospect for this is the copper vent tube and fittings between the leak detector on the turbine pump head and the tank vent port. Other possible sources of vapor leaks are manway gaskets, STP packer o-rings, ATG caps and cord grips, and other riser pipes and fittings installed in the sump.

In one sump with high concentrations of ethanol in the air, a state regulator used an infrared detector to locate a vapor leak at the compression fitting between the line to the leak detector and the vent port (Fowler, 2011). Vapor leaks also may be identified during pressure decay testing, and may be pinpointed with

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

helium leak location or ultrasonic leak detectors. Ensuring that all the lines, fittings and connections are either fuel tight or vapor tight, as appropriate, will keep ethanol from getting into the sump.

Water

It is more difficult to manage water in a sump. If the fuel is cold relative to the atmosphere, the fittings may sweat like a glass of water on a humid summer day. In such a case, water may condense on the fittings.

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Bacteria can grow in the condensate. To counteract this, at a minimum the seals and covers for the sump should be maintained in good condition and the sump elevated above grade to prevent the entry of rain water or snow melt. Water also may enter a sump through groundwater leaks. A sump testing and inspection program can help to identify and correct leaks in sumps and sump lids.

Adding a water absorbent to the sump may remove visible free-standing water, but it may or may not prevent the growth of the acetic acid bacteria.

Fowler (Fowler, 2011) noted that sumps that are ventilated through a secondary containment chase to the dispenser have less chance for corrosion. Ventilation will reduce the concentration of ethanol and acetic acid in vapor, and help keep the sump dry.

Bacteria

The third component is the bacteria. Biocides are designed to kill bacteria that might grow in a "water bottom" below the fuel in a tank. However, adding a biocide to the sump will only affect the bacteria that might grow in the water in the bottom of the sump. The biocide will not have access to bacteria growing in water that is condensing on the pump head or distribution lines in the sump. Using biocides, therefore, will probably not be as effective as stopping the leak of fuel or vapors that provide the ethanol to the acetic acid bacteria.

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