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

(CRC Project No DP-07-13)

CRC Protocol for Selecting Sites with ULSD Systems Determined to Have Severe Corrosion

BACKGROUND

Severe and rapid corrosion has been observed in systems storing and dispensing ultra-low sulfur diesel (ULSD) since 2007. In addition, the corrosion is coating the majority of metallic equipment in both the wetted and un-wetted portions of ULSD underground storage tanks (USTs). To investigate this issue, multiple stakeholders in the diesel industry, through the Clean Diesel Fuel Alliance, sponsored a research study by Battelle Memorial Institute (hereafter termed "Battelle study"). That effort included the identification of retail fueling sites and the development of a protocol to ensure uniform and thorough sampling and inspections of fiberglass USTs. Fuel, water bottoms, vapor, bottom sediments, and scrape samples were taken from six sites across the country: one that was not supposed to have symptoms (but did to a much lesser degree) and five that were to have severe corrosion. Samples collected during the inspections were then analyzed for genetic material and chemical characteristics. These data, in combination with information on additives, allowed Battelle to draw conclusions with respect to three working hypotheses:

1) Aerobic and anaerobic microbes were producing by-products that established a corrosive environment in ULSD systems;
2) Aggressive chemical specie(s) (e.g., acetic acid) present in ULSD systems was (were) facilitating aggressive corrosion; and
3) Additives in the fuel were contributing to the corrosive environment in ULSD systems.

Based on the data collected, the Battelle study arrived at a final hypothesis that the ULSD stored in underground storage tanks was contaminated with ethanol, and the ethanol present in the systems was oxidized by *Acetobacter* into acetic acid which was diffused throughout the vapor and liquid space causing severe and rapid corrosion of metals associated with ULSD systems at retail stations. The study hypothesized that the presence of ethanol in the fiberglass USTs storing ULSD was the result of either tanker truck switch loading or legacy ventilation system connections to gasoline USTs allowing gasoline-ethanol vapors to back feed into the ULSD tank.

The Battelle study raises many questions that remain unanswered to date. For example, is accelerated corrosion only associated with fiberglass USTs or is it also present in steel USTs? Is the accelerated corrosion limited to the retail site level or is it present in upstream systems such as tanker truck, distribution terminal and associated equipment, pipeline, multi-product tanker ships or the refinery? Is a different contaminant (not ethanol) entering the fuel supply

before the retail site? Is acetic acid the major contributor or are other organic and inorganic contaminants present in the UST bottom water that are reacting synergistically and resulting in accelerated corrosion? Is the formation of acetic acid exclusively due to the oxidation of fugitive ethanol or are there other source(s) of acetic acid present in the UST?

A panel comprised of members of the Clean Diesel Fuel Alliance (and other stakeholders) has been formed under the auspices of the Diesel Performance Group of the Coordinating Research Council (CRC) Performance Committee (hereafter termed "the CRC Corrosion Panel") to develop and carry out research to: (a) address these unanswered questions, (b) facilitate a better understanding of the causes of observed corrosion in UST systems storing and distributing ULSD, and (c) assist in developing remedies.

GENERAL GUIDELINES FOR SCREENING AND SELECTING SITES FOR FURTHER STUDY

The CRC Corrosion Panel has developed a set of general guidelines and equipment maintenance history questions for use by researchers interested in screening and selecting sites for further testing and evaluation of potential causes of observed corrosion in ULSD storage and distribution systems. These guidelines, provided in Tables 1 and 2 on the following pages, are based on the cumulative technical knowledge of the Corrosion Panel members based on field observations, and they are not represented to be analytically-derived pass/fail cut points for defining whether or not a particular piece of equipment is corroded. The latter is intended to be the outcome of the subsequent detailed study of the screened sites selected for sample analysis.

Note also that the guidelines provided in Table 1 focus on the screening of corroded equipment based only on visual inspection as well as analysis of fuel and water bottom samples collected at the sites in ULSD storage and distribution service. Since the guidelines are intended only for site screening purposes, the collection and analysis of vapor phase samples for corrosion has not been included in order to minimize both time and cost.

Table 1
General Guidelines for Screening Aggressive Corrosion Conditions in ULSD Storage and Distribution Systems

I. Screening criteria:
   a. Pull the dispenser filter and inspect for metal degradation in the filter as well as in the filter housing. (The filter must have been in service for a minimum of three months)
      i. Does the dispenser filter housing show any corrosion?
         1. If yes, then go to step III
         2. If no, then cut open the filter's metal housing and examine the metal components. If any corrosion observed, then go to step III

II. If the filter housing is seemingly clean
   a. Pull out the submersible turbine pump (or alternatively use video equipment in situ) and inspect the riser:
      i. Use NACE Test Method 0172 to measure corrosion on riser pipe surface. If $\geq$ 5% then go to step III

III. Definition of aggressive corrosion in UST systems
   a. Increased replacement of equipment
   b. Is submersible turbine pump riser more than 50% corroded? (Alternatively, use video equipment to inspect.)
      i. Yes, aggressive corrosion
   c. If aggressive corrosion is observed then pull the following equipment and determine:
      i. Is the drop tube and/or flapper valve corroded?
      ii. Are any brass, copper, and/or aluminum components corroded?
   d. Aggressive corrosion conditions -- Aggressive corrosion is considered if 3 or more of the following conditions are met based on analyses of fuel and water bottom samples:
      i. Fuel (test procedures … (all samples are to be obtained from the lower third of fuel volume)
         1. NACE of C or worse
         2. Haze >2
         3. Particulate (filtration using 0.8 micron with >10 mg/liter)
         4. Karl/Fischer water content >200 ppm (mg/kg)
      ii. Water bottom (test procedures …
         1. pH less than 5
         2. Microbial growth > 10,000 cfu/ml
         3. Presence of low molecular weight (C_1 – C_5) acids (via GCMS scan)

Table 2
Questionnaire for Operators of ULSD Storage and Distribution Systems
Screened & Selected for Further Study

1. What preventive maintenance procedures, if any, do you use? How often?
2. Do you record water levels in your fuel tank? Do you have a Veeder-Root system? Can we get any V-R records?
3. How often is water drained from the tank?
4. Is there a dispensing filter on the tank? How often is it changed?
5. When a dispensing filter is changed, does anyone inspect the old filter? Has anyone ever noticed corrosion products?
6. Is your fuel ever treated with biocides? Which one? How often? Is the treated fuel allowed to remain quiescent in the tank for a prescribed period of time?
7. Do you add any additives to the fuel before or after it goes in the storage tank?
8. Have any of the components on the tank/pump/filter system ever been replaced? Which one(s)? How often? When?
9. a) Has the tank ever been emptied and cleaned or resurfaced? When? What was done? b) Has water/tank bottoms ever been sucked out of the tank? This is sometimes inappropriately referred to as “cleaning”.
10. Did the tank ever hold anything but ULSD? What was it? When?
11. Is this tank connected to other tanks in any way? Manifolds, vents, etc.?
12. Has anyone ever noticed strange odors coming from the tank or filters? Vinegar type smell?
13. Does the same fuel supplier typically fill this tank?
14. How often is new fuel added to the tank (turnover rate)?
15. How long has the tank been in the ground?