1995-2015 Review: Laboratory and Field Studies on the Cause of Accelerated MIC Corrosion in Petroleum and Municipal Storage Tank and Piping Systems

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I. Executive Summary

The purpose of this paper is to provide information on the conditions that lead to microbial influenced corrosion (MIC) of metals and alloys and the corrosion protection provided by thermoset plastics, including the materials (i.e., glass, resins, additives) used in the manufacture of tanks and piping. MIC (sometimes referred to as hydrocarbon utilizing microbes, "HUMbugs") contributes to the rapid corrosion of metals and alloys that are exposed to corrosive environments such as soils, water (i.e., fresh, saline, distilled), hydrocarbon fuels, sewage and process chemicals. Certain microbe corrosive organic secretions (e.g., acetate) have been estimated to account for 20% of the total cost of such corrosion including reduced material strength and/or loss of containment.

Anaerobic or aerobic MIC microbes require water (e.g., condensed moisture) and food sources necessary for their growth. The food sources range from single carbon molecules (e.g., carbon dioxide and methane) to certain complex polymers that are known to break down (i.e., deplasticize) in certain thermo (e.g., seals, gaskets) versus thermoset plastics.

II. Introduction

A. Microbially Influenced Corrosion: MIC is corrosion accelerated by the action of microorganisms in the local environment. Facilities where MIC is prevalent include hydrocarbon and fuel (gas and liquid) storage (i.e., tanks), transmission systems including municipal sewer and drinking water piping.

Microbes, bacteria and fungi are introduced into the storage tanks and piping systems along with dust particles and water condensed moisture through atmospheric tank venting systems. Microbes require both water and nutrients to multiply. It is recognized that negligible traces of water are sufficient to support microbial populations and food sources are plentiful. These nutrients include carbon, hydrogen, oxygen, nitrogen, sulfur, phosphorus and lesser elements such as calcium, sodium, iron, magnesium and copper in trace quantities. As a result, fuel and municipal tank storage and piping systems will provide the prerequisite water and nutrients to support microbial growth and proliferation.

Microbial growth establishes communities, known as biofilms, which are a layer of microorganisms that proliferate at phase interfaces. They accumulate at the water/fuel interface as well as on tank walls and on equipment located above the liquid surface. The numbers of microbes within biofilms are orders of magnitude greater than microbes located elsewhere. For example, a 1-mm thick biofilm on a tank wall is 100 times the thickness of most fungi and 500 to 1,000 times the longest diameter of most bacteria. These biofilm communities are directly involved in MIC and result in accelerated metal corrosion.

B. Fuel Storage Tanks: Once inside the fuel tank the microbes may adhere to overhead surfaces and/or settle through the product. Some microbes will adhere to tank walls, some will collect at the fuel/water interface and others will accumulate at the tank bottom.

a) **Tank Bottoms:** Because microorganisms require both food and water for growth, the tank bottom interface is the most prevalent fuel/water interface. Thus, most growth and activity take place at the tank bottom. Such microbes grow anaerobically and produce low molecular weight organic acids (formate, acetate, lactate and others). These acids accelerate the corrosion process by chemically etching the metal surface. In addition, biofilm accumulations create electro potential gradients between the surfaces that are covered with biofilms and those surfaces that are not covered. This leads to different electrical potentials and the galvanic corrosion of the metal. Galvanic corrosion is known to cause a pattern of pinhole leaks in steel tanks and piping.

b) **Tank Ullage:** Tank refilling causes the ullage area to be replenished with hydrocarbon and water vapors, providing nutrients and moisture for microbial growth. Thus, there is a considerable area of fuel/water interface on the interior surface of the tank shell as well as on exposed in-tank equipment such as pumps and gauges. The biofilm that accumulates on tank walls is typically greater than 90% water. This water creates a substantial habitat for microorganisms.

c) **MIC Prevention:** Frequent water removal is important because microbes require water. However, reference ASTM D 6469 11.3.4 “Water removal is never 100% effective. Most tank configurations make it impossible to remove all water.” Water removal is never 100% effective for the following reasons:

i. **Most aboveground tank** configurations employ flat and convex bottoms which will retain water after draining.

ii. **While some underground tanks** were installed on a level plane, tanks settle in time, tilt and retain some water at the bottom. Even properly titled tanks will retain water at the bottom as the suction pump causes the fuel to visibly vortex into the discharge stream and signals the operator to cease pumping before all of the water is removed.

iii. **Daily diurnal breathing** of vented (atmospheric) tanks introduces moisture and water condensation in the tanks, introducing new water that replenishes the tank ullage, moisture water at the tank’s bottom and water at the fuel/water interface.

C. Fuel & Municipal Pipeline Corrosion Experience: NACE International's January 2014 *Materials Performance* publication reported on comments from selected knowledgeable NACE international members and other experts on the impact of MIC as a "contributor to rapid corrosion of metals and alloys exposed to soils, seawater, distilled water, freshwater, crude oil, hydrocarbon fuels, process chemicals and sewage." Following is a summary of their comments:

a) **MIC corrosion is underestimated:** "Systems where MIC is especially important include hydrocarbon and fuel (gas and liquid) transmission and storage systems, as well as hazardous materials transport and storage structures. These systems provide adequate environmental conditions and substrates for microbial development and the participation of microorganisms in corrosion has been clearly demonstrated and MIC failures documented. Utilities such as drinking water and sewer systems also provide adequate conditions for MIC development; however, in such systems MIC has often been underestimated, as has corrosion in general."

b) **MIC manifests as pitting corrosion:** "MIC typically manifests itself as localized (i.e., pitting) corrosion - with a wide variation in rate, including rapid metal loss rates - both internally and externally on pipelines, vessels, tanks, and other fluid handling equipment." "Often pitting is very isolated, with one hole surrounded by a number of shallower pits. Pitting rates range from a few mpy to more than 250 mpy." "In almost all cases MIC produces localized attack that reduces strength and/or results in loss of containment."

c) **Where MIC is most like to occur:** "...the places we expect MIC to occur experience rapid pitting, usually at interfaces where solids like scale, wax, and/or other solids can settle out or precipitate." In pipelines "areas downstream of welds, where cleaning pigs have difficulty removing deposits, as well as dead legs, low-velocity areas, and tank bottoms where solids and bacteria/biofilms can accumulate, are particularly susceptible to attack."

d) **MIC mitigation and its limitations:** "Biocides are still the chemicals of choice when mitigating MIC; however, biocides usually need to be combined with a mechanical or chemical cleaning program to enhance their effectiveness, especially if the biofilms and corrosion are already firmly established." (see below section D on Biocide Use)

   i. **Deposits and biofilm removal:** "...maintenance pigging (i.e., oil & gas pipelines) can be effective in removing deposits/biofilms that promote MIC" and ..." a further benefit of removing deposits is increasing the effectiveness of chemical treatment by allowing the chemical to reach the exposed metal surface."

   ii. **Chemical treatment:** "The main problem associated with the use of chemicals is the adaptation capacity of microorganisms that allow them to develop resistance mechanisms and, in some cases, the ability to biodegrade these products. Constant injection of the chemical products is necessary."

e) **MIC Corrosion Resistant Tanks & Piping:** "The threat of MIC needs to be considered in the design of new projects to enable monitoring and mitigation for managing MIC during the operational stage of the asset. <u>Materials selection</u>

should be based upon the anticipated operating conditions through the life of the asset and the intended design life." (underline added)

D. Biocide Use and Cleaning per ASTM D 6469: There are three major groups of fuel biocides: fuel soluble, water soluble and universally soluble.

a) **Fuel soluble biocides** are unstable or insoluble in water, where the microbes tend to grow.

b) **Water soluble biocides** are insoluble in fuel, tend to be inexpensive and are best used to shock-treat bottom-water contamination. However, water soluble biocides do not persist in fuel phase long enough to diffuse into system surface biofilms.

c) **Universally soluble biocides** are stable in both fuel and water and have the advantage of affecting both biofilm and bottom-water microbes. The principle disadvantage is the high cost relative to the other biocide groups.

d) **Tanks & pipe cleaning:** Heavily contaminated systems generally require tank and pipe cleaning in conjunction with biocide treatment and, after cleaning, the freshly charged fuel system should be retreated with a second biocide dose.

III. Battelle Memorial Institute Aug, 2012 *Investigation of Corrosion in Systems Storing and Dispensing Ultra Low Sulfur Diesel (ULSD)*

A. Objective: Conduct a research project to establish the factors leading to the accelerated corrosion of in-tank metal equipment (e.g., steel, copper) and deterioration of polymers (seals, gaskets) in ULSD storage and dispensing systems. Such in-tank metal equipment corrosion was identified in six non-corroded fiberglass underground storage tanks (USTs). The fiberglass tanks were free from deterioration, ranged in age of 13 to 24 years, and were located as follows: North Carolina (1), New York (2) and California (3). The hypothesis focused on MIC as the cause of accelerated in-tank equipment corrosion and the analysis of chemical constituents in the fuel, water and headspace vapor within the USTs. Also included was the question, if product additives (i.e. ethanol, biodiesel) were directly or indirectly a source for the microbe nutrients that result in the corrosive metabolites.

B. **Results:** Acetate was measured in all six bottom water samples and ethanol was identified in five of the six water bottoms. Four different tank DNA samples were of high quality and identified the presence of acetic acid produced by acetobacter bacteria, which requires oxygen and can use ethanol as an energy source. Thus, MIC is likely accelerating the other corrosive tank bottom water characteristics that included high conductivity, acidic pH and three tanks with high chloride concentrations.

C. Investigation Postulations and Responses: The Battelle study Table 10 "Summary of Water Bottom Sample Results" presented chemical analysis results on the water bottom samples. Glycolate was detected at four of the six sites and GC-MS scans indicated the presence of alcohols, acids and amines. It was postulated that these chemicals and methyl vinyl ketone (MEK) could have leached from the tank shells.

Following is a summary of the postulations and fiberglass tank material supplier responses to Battelle and work group questions:

a) **Glycolate and Acetic Acid: "**Glycolate, a related compound to acetic acid, was detected in appreciable amounts at four of six tank water bottoms."
   Note: (1) Glycolate was less than 100 ppm in two of the four tanks.
   (2) One of the tanks was a single wall tank that did not have an interstitial space [i.e. no liquid leak indicator.]

b) **#1 Question:** Is glycol used as a leak indicator in double wall tanks? And, if propylene glycol is used as a leak indicator in the double wall tank sump, could it leak into the tank bottom?
   Answers:
   i. Brine, not glycol, is used as the leak indicator in fiberglass double wall tanks.

   ii. While propylene glycol may be used in some double wall tank sumps, there is no communication between the sump and the tank interstitial spaces.

   iii. Glycolate/glycolic acid is not a decomposition product from propylene glycol.

c) **#2 Question:** Can polyester or vinyl ester resins hydrolyze to release glycol and acid if allowed to stay in contact with water?
   Answers:
   i. No quantified species in Table 10 can be derived from typical USTs unsaturated polyester or vinylester resin decomposition including acetic acid.
   ii. No leaching of acetic acid has been experienced in the history of fiberglass potable water storage tanks and fiberglass potable water transporting pipelines.

d) **#3 Question:** Two tanks may indicate components from resins. Table 10 shows MEK at one site and phthalate at another. Is it possible for MEKP and MEKPO to be responsible for the acetic and formic acids?
   Answers:

   i. The methyl ethyl ketone peroxide (MEKP) contains a simple phthalate, dimethyl phthylate. This phthalate is used as part of the safety diluents or phlegmatizers to increase the stability and product quality of MEKP. The dimethyl phthalate becomes immobilized within the thermoset resin. Resin testing includes boiling the thermoset resin sample in water. The amount of dimethyl phthalate extracted into the boiling water is not significant, typically below 100 ppm.

   ii. MEKP and MVK are very reactive materials that would polymerize and become immobilized within the thermoset resin during cure of the resin and/or post cure of the tank. Thus acetic and formic acids could not be coming from the thermoset resin tank.

e) **#4 Question:** Is glass fiber sizing a potential source of ethyl acetate and acetic acid? And, is Fluorine used in formulating the E-glass as a binder or adhesive (i.e., sizing)?
Answers:
   i. Ethyl acetate has not been used in any of the sizing systems in thousands of size formulations that manufacturers are aware of.

   ii. Acetic acid is used to adjust the pH of a silane coupling agent premix which is an important sizing ingredient. However, it and other VOCs (volatile organic compounds) are readily evaporated during the drying of glass fiber, forming cakes. The drying temperatures are generally in the 125 to 130 degrees C range, well above the boiling point of acetic acid (118-119 degrees C), methanol (65 degrees C) or ethanol (78.4 degrees C).

   iii. Fluorine was used more than 15 years ago, but to reduce air emissions of boron and fluorine as acid rain pollutants, it was reduced to 0.5-1.0%. Glass content in the tank corrosion liner is typically 25-35%, which makes the sizing amount less than 0.5% of the FRP laminate, hardly a plausible source of acetic acid.

D. Summary of fiberglass tank material suppliers to questions regarding potential tank wall material leaching of glycolate and acetic acid: Degradation of the unsaturated polyester resin leading to gycolate and/or acetate would be associated with significant tank degradation visible to the eye and measured by loss of structural properties. This was not the case with the six older fiberglass storage tanks (i.e. 13, 14, 21, 21, 22, & 24 years old) in the Battelle study.

E. Battelle Conclusion: The "final hypothesis is that corrosion in systems storing and dispensing ULSD is likely due to the dispersal of acetic acid throughout USTs. It is likely produced by acetobacter bacteria feeding on low levels of ethanol contamination dispersed into the humid vapor space by the higher vapor pressure and by disturbances during fuel deliveries when acetic acid is deposited throughout the system. This results in a cycle of wetting and drying of the equipment concentrating the acetic acid on the metallic equipment and corroding it quite severely and rapidly."

IV. US EPA ~ Corrosion in STP Sumps (3Q 2013)
What Caused It and What can be Done About It?

A. Objective: Confirm the hypothesis that acetic acid produced by acetobacteria biodegradation of ethanol was occurring in UST submerged turbine sumps and causing the accelerated corrosion of iron and copper equipment components. The research staff of the U.S. Environmental Protection Agency provided sampling kits to state regulators to measure concentrations of ethanol and acetic acid in the vapor space of underground storage tank STP sumps. The sample kits were returned to EPA's Ada, Oklahoma laboratory for analysis. Samples were acquired from Florida (35), Tennessee (16), Illinois (6), Wisconsin (4), California (2) and Iowa (1) for a total of 64.

B. Results: While standing water was in 7 sumps that exhibited corrosion, 61 of the sumps had high concentrations of ethanol or acetic acid in the vapor space samples (≥1,000 mg/L), with the remaining at lower concentrations. There was no appreciable difference between tanks that contained premium, regular E10 blended gasolines or E85 fuels.

Thirty nine photographs were available and showed iron or copper corrosion, typically in sumps where the air space in the sump included ethanol or acetic acid.

C. Conclusions: The three components that have resulted in tank sump MIC enhanced metal corrosion caused by acetobacter bacteria are (a) ethanol to provide the food source, (b) water (i.e., moisture) to live in and (c) bacteria secretions of acetic acid that corrode metals.

D. MIC Mitigation and its Limitations: Ideally the goal is to remove one of the following three components that encourage MIC growth:

a) Stop ethanol vapors from migrating into the tank sump from the tank ullage via STP, ATG and other riser pipes/fittings installed in the sump.

b) Stop the accumulation of standing water in the sump. However, sump standing water was in only 7 of the 61 sumps. It would be difficult to control the high concentrations of condensed water and resulting corrosion on the pump head and other sump equipment.

c) Retard the growth of microbes by adding biocides. This may be effective if standing water is present and biocides were added to standing water. However, without standing water, the addition of biocides may not reduce bacteria in the vapor space.

E. Comment: Designing and maintaining: (i) tight vapor free tank to sump accessory and pipe interfaces to prevent ethanol vapors from the tank ullage. This is likely a better alternative than maintaining a (ii) wet and humidity free sump or (iii) biocides to control microbial growth.

V. Assoc. of State and Territorial Solid Waste Management Officials (ASTSWMO) *Compatibility of UST Systems with Biofuels* June 2013

This ASTSWMO document was prepared as a resource for State UST Program staff, UST owners/operators, contractors and consultants for evaluating equipment compatibility when storing biofuels, pursuant to EPA's compatibility requirement (40 CFR Part 280.32). Owners and operators of USTs, regulated under 40 CFR part 280, are required to demonstrate compliance with EPA compatibility requirements when storing regulated substances, including biofuel blends containing greater than 10% ethanol or diesel containing greater than 20% biodiesel.

A. The document states that:

a) Biofuels are more soluble, have a higher water absorption capacity and are more conductive. Thus, higher solubility means seepage through non-metals (e.g., seals, thermoplastics) at the tank and sump interface.

b) Higher water absorption means accelerated MIC metal corrosion.

c) Higher conductivity accelerates corrosion in the presence of <u>cathodic</u> metals (e.g., steel), and <u>anodic</u> metals (e.g., brass, aluminum, copper).

B. Case Summaries: Fiberglass Tank Material Compatibility Observations

* 1: Phoenix, AZ: 24-yr old 10,000 gal double wall FRP tank; E-10 fuel.
Purported bottom cracks; tank lined and put back into service

2. Tucson AZ: 26-year old 10,000 gal single wall FRP tank; E-10 fuel
Purported end cap crack; tank removed

*3. Yuma, AZ: 28 year old 10,000 gal single wall tank: E-10 fuel.
Unknown source of purported leak; tank repaired and put back into service

*4. Yuma, AZ: 28 year old single wall FRP tank
Unknown source of purported leak; tank repaired and put back into service

14. Hobbs, New Mexico: 25-yr old 8,000 gal FRP tank; Non-leaker
Purported tank broke when removed

*18. Haleiwa, HI: 26-year old FRP tank; E-10
Non-leaking tank was cleaned prior to storing blended fuels,
Purported bottom crack; tank lined and put back into service

*19. Kailua, HI: 25-yr old FRP tank; E-10 fuel
Non-leaking tank interior cleaned prior to storing blended fuel
Purported <u>new</u> tank liner did not adhere to tank walls, tank relined
Tank put back in service

*20. Waipahu, HI: 23-yr old double wall FRP tank; E-10 fuel
Non-leaking tank interior cleaned prior to storing blended fuels
Purported <u>new</u> tank liner installed; tank put back into service
S<u>econd</u> liner failed; tank removed from service

21. Honolulu, HI: 26-yr old FRP single wall tank; E-10 fuel
Non- leaking tank interior cleaned prior to storing blended fuel
Purported failure of bottom gel coat; tank removed from service

22. Kihei, HI: 27 yr-old FRP single wall FP tank; E-10 fuel
Non-leaking tank interior cleaned prior to storing blended fuel
Purported failure of bottom gel coat; tank removed from service

C. Case Summary Comments:

a) Seven of the ten tanks (Note*) were structurally sound, lined and put back into service.
<u>Comment</u>: If MIC damage was prevalent, the tank interiors would <u>not</u> likely qualify for relining.

b) All case study tanks are over 20 years old (i.e., 24 to 28 years).
Prior to 1990, Institute member manufactured tanks were designed for E-10, the maximum legal gasohol blend. However, there is evidence that ethanol blended

E-10 was known to exceed the 10% ethanol blend ratio. Higher than 10% ethanol fuel blends were recognized in the following Oak Ridge reports:

i. May 2012 Oak Ridge report: (page xvi) "... water, trace levels of sodium chloride, acid and sulfuric acids "...are found in ethanol-gasoline fuels and represent potential high contamination conditions for fuel-grade ethanol."

ii. August 2013 Oak Ridge report (page 1, mid-paragraph 2) "....surveys indicated that the actual concentration of ethanol in E-10 dispensers has been noted to vary by as much as 2%." (underlining added)

Comment: Case studies of older than pre-1990 tanks where the ethanol blends were higher than the legal 10%, and/or other corrosion factors cited by Oak Ridge were present and detract from the Case study's usefulness to identify MIC tank damage. [Note: By 1990 Institute member manufactured FRP tanks were designed for up to 100% ethanol.]

c) Five of the ten tanks were located in Hawaii. In all five of the Hawaii cases an unknown interior tank cleaning method was used. The tanks were non-leakers prior to tank cleaning and then leaked after cleaning.

Comment: The tanks were likely damaged by tank cleaning, rather than MIC.

D. Unsubstantiated and Unendorsed Opinions on Fiberglass Tank Compatibility:

a) Page C-1: "The Workgroup has not done any material testing to verify that these observations were the result of compatibility issues between the equipment and the fuel used, does not endorse any of the findings, and is not responsible for the accuracy, completeness, or usefulness of any information presented in the case summaries." [underline added]

b) Page 6: "The views and opinions of case summary submitters do not necessarily state or reflect those of the ASTSWMO Alternate Fuels Workgroup." [underline added] However, it is purported that "....field observations also suggest there may be some impacts to fiberglass USTs." And it is purported that "In some regions of the country, mounting evidence from failure and field observations also suggests there may be some impacts to fiberglass USTs."

c) Page 7: It is purported that "Hydrocarbon Utilizing Microbes HUMbugs also can dissolve the resin holding the fibers together in a fiberglass tank, and use it for food, thus weakening the tank."

E. Comments on ASTSWMO Case Summaries and Opinion:

a) Case Studies: Superficial examination was in a narrow geographic range (i.e., AZ & HI) of tank bottom leaks, most of which were repaired and tanks put back into service. There was no supporting evidence of corrosive microbe biofilms or MIC.

b) While the Workgroup members did not agree "on any of the findings", the report makes the unsubstantiated statement that microbes can use FRP resin as a food source.

VI. *DNA Microbial Analysis and Potable Water Distribution*
AWWA Journal ~ March, 2014

This AWWA Journal paper discusses recent advances in DNA technology that will now allow nearly all microbes in a drinking water sample to be identified and quantified based on their DNA and be a likely substitute for the standard coliform tests which have been documented as failing to provide warning of public drinking water threats. Further, the cost of DNA testing is reduced and is being used in drinking water field studies.

A. Field Studies have shown that <u>many microbes are able to pass through treatment barriers and survive to colonize in drinking water distribution systems.</u> Microbes that survive the treatment process can attach to pipe walls and begin forming robust biofilms.

B. Pipe Corrosion: Initially pioneer bacteria attach and begin secreting extracellular polysaccharides (i.e., slime) that protects them from residual disinfectants and provides a more hospitable environment in which successor microbes can readily attach and begin to grow a more complex biofilm community. These biofilms may cause pipe corrosion.

C. Conclusion: Potable drinking water DNA field studies show that drinking water transmission piping is subject to biofilms and MIC which will accelerate the corrosion of unprotected materials.

VII. *Corrosion of Copper and Steel Alloys in a Simulated Underground Storage-tank Sump Environment Containing Acid-producing Bacteria*
NIST National Institute of Standards and Technology
Corrosion Science - January 2014

A. Problem: The consumption of alternative mandated fuels has increased significantly in the U.S. including ethanol and biodiesel and is projected to increase significantly. However, the current infrastructure was designed for unblended fuel and may not be compatible with these alternative fuels. Earlier studies revealed that there was rapid corrosion of steel metals and copper alloys in both the vapor (head space) and aqueous solution (tank bottom).

B. Objective: This NIST laboratory study used <u>new</u> equipment and test methods to study the corrosion of metal (steel and copper) tank sump components either immersed in ethanol-water solutions inoculated with bacteria, or exposed to vapors above the medium over a 30 day period. The <u>new</u> test methods included:

a) **Head Space testing chamber:** Used to evaluate metal components exposed to ethanol and acetic-acid vapor components in a pure atmosphere.

b) **Immersion and head space testing** with Acetobacter acetic to generate acetic-acid vapor with biological properties (e.g., bacterial attachment) versus acetic acid solution alone. Previous corrosion experiments used acetic acid from *abiotic* sources rather than a *biotic* source which may not replicate corrosion induced by microbes.

C. Conclusions: Copper corrosion when immersed in a test solution is on the order of that observed in the headspace. It is postulated that corrosion crystals form a more protective barrier to reduce corrosion.
<u>Carbon steel corrosion rate was significantly higher when in a vapor-phase exposure</u> as compared to immersed in a test solution. Carbon steel corrosion also consisted of pitting, which upon examination revealed pitting depths greater than those observed in the immersed condition. The NIST study confirmed metal corrosion damage in UST sumps similar to that seen by field inspectors.

VIII. 2007 NACE Corrosion Expo.

Experiments on MIC of Steel and FRP Downhole Tubulars in West Kuwait Brines P.J Scott; CARIAD Consultants, Crete, Greece

A. Problem: Oil field **s**econdary recovery is common in oilfields; however, the injection water will sour, cause plugging and corrosion in fields that had been previously trouble free. Brine water is known to contain dissolved inorganic salt which is higher than that found in sea water. Oil field secondary recovery involves injecting brine and sour water with the potential of MIC plugging and corrosion in oil fields previously uncontaminated.

B. Objectives: This laboratory study was to determine: (1) the growth of marine bacteria in brines, (2) the corrosion resistance of brine water in candidate steel alloys and FRP tubular materials and (3) the biodeterioration of fiber reinforced plastic.
FRP tubular samples including phenolic, vinyl ester and epoxy resins were exposed to acid producing bacteria. SEM examination showed that the vinyl ester and epoxy resins were not damaged; however, testing of the phenolic samples was inconclusive when the phenolic samples could not be properly prepared for SEM without damage.

C. Conclusions:

a) **"**Laboratory tests showed that thermoplastics are resistant to attack by bacteria and fungi."
b) "Predamaged areas of the gel coat of experimental coupons did not appear to be sensitive to attack by the bacteria."
c) "FRP consisting of carbon fibers and epoxy resin has also been found to be susceptible to fungi."
d) "FRP containing vinyl ester and epoxy resins was not attacked."
e) "Although some experimental data indicate that FRP might be attacked by bacteria, there have been no reported field cases of biodeterioration of pipelines, flow lines or tubulars to date."

IV. Earlier Laboratory Studies: 1995, 1996, 1997

Harvard University; Ji-Dong et al

A. ***Microbial Growth on Fiber Reinforced Composite Materials***

a) 1995 International Biodeterioration & Biodegradation paper

Laboratory study to determine if microorganisms pose a threat to the structural integrity of composite materials. The following five composite samples were exposed to a fungal consortium for 5 weeks and examined by a scanning electronic microscopy (SEM):

Resins: fluorinated polyimide Glass Fiber (P-25 Fisher Scientific, Pittsburg, PA)

bimaleimide	carbon (P-100) Amoco Performance Prod.)
poly (ether-ether-ketone)	carbon
epoxy	carbon
epoxy	carbon

Note: four of five samples used carbon fibers; but study postulated on glass fiber sizing.

The basis for the 1995 study is an earlier 1994 Wagner et al study that postulated there may be degradation of the silane surface on glass fibers and this disbonding may “result in fiber disbonding and delamination when a composite is under stress." [page 201] Thus, the paper hypothesized that "It is probable that the fungi were using the sizing materials as a carbon and energy source." (underline added) [page 203]

b) 1996 NACE Corrosion 96 Conference and Exposition

This 1996 laboratory study included the application of electrochemical impedance spectroscopy (EIS) to determine if glass and carbon fibers are susceptible to the growth of microorganisms. While the former carbon/glass fiber samples were used in this study, the difference is purported to be that "the former utilized a fungal consortium enriched from degraded polymetic materials while the latter used a constituted bacterial consortium of bacterial species having diverse physiological functions."

The paper hypothesized that "chemicals from the composites may serve as a carbon and energy source for the growth of fungi."

c) 1997 Journal of Industrial Microbiology & Biotechnology

This 1997 laboratory study included 179 days of monitoring EIS spectra purported to show that there was "a continuous deterioration of the matrix after inoculation. However, the composite held under aseptic conditions showed minimal changes of the impedance and phase angle." And "No significant difference of interlaminar shear strength was detected between the inoculated and the control composites.” The inability of the mechanical test to detect any differences between the inoculated and control composites is due to the insensitivity of the technique to a small proportion of disbonding over the whole composite matrix.

d) Comments on 1995, 1996 & 1997 Ji-Dong et al studies:

1) If sizing chemicals were attacked by microbes, the microbes would:
   i. need a pathway to get to the glass, and
   ii. the glass must de-bond from the resin in order for the 2 micron microbes,
   iii. to squeeze into a space between the fiber and resin of less than 1/2 of a micron.

2) See sizing discussion in section III. Battelle Memorial Institute Aug, 2012 *Investigation of Corrosion in Systems Storing and Dispensing Ultra Low Sulfur Diesel (ULSD)*

3) Four of the five study fibers are carbon versus glass fibers. Further, the resins and glass fibers are not used by Institute manufacturers of UL Listed 1316 fiberglass tanks UL 971 piping or Hobas pipe.

4) The foregoing Section *VIII Experiments on MIC of Steel and FRP Downhole Tubulars in West Kuwait Brines* study concluded: "FRP consisting of carbon fibers and epoxy resin has also been found to be susceptible to fungi." (underline added) Thus, fiberglass tanks and piping manufactured with glass fibers have not been shown as susceptible to fungi.

5) Ji-Dong's 1997 study concludes on page 368 "No significant difference of interlaminar shear strength was detected between the inoculated and the control composites." "The inability of the mechanical test to detect any differences between inoculated and control may be due to the sensitivity of the technique to a small proportion of disbonding over the whole composite matrix."

   In spite of the foregoing test result, the paper claims that "fungi were shown to be responsible for the degradation of composite material" when the material adhesion occurring between the fiber surface and the resin matrix was in fact unaffected.

e) Summary: The three Ji-Dong studies do not recognize that fiberglass thermoplastics are engineered products for their intended applications. For example, there are resins designed to be biodegradable and provide a material that may be composted in a landfill.

V. September 2014 – 1Q 15 EPA Study Updates
Investigating Corrosion Observations of Metal Components in Underground Storage Tanks Storing Ultra-Low Sulfur Diesel

A. Problem: Increase of ethanol in blended gasolines and biodiesel in Ultra-Low Sulfur Diesel are likely increasing microbiologically influenced corrosion (MIC). Inconclusive, *but likely, that ethanol, a food source for acetobacteria, is excreting acetic acid and* biodiesel containing glycerol is forming propionic acid. The acids may be the cause of accelerated corrosion in steel and copper metals in the tank liquid bottom and tank & sump vapor spaces.

B. Objectives: 1. Build on 2012 Battelle and EPA hypotheses and possibly come up with new pathways to identify the source of high level MIC corrosion.
2. Use tank vapor, bottom water and fuel collected from 42 UST sites (23 FRP & 19 steel) to analyze for corrosion factors.

C. Preliminary Hypotheses:
1. Both ethanol and glycerol pathways are viable.
2. Presence of corrosion does not appear to be influenced by tank material.
3. Corrosion observed in each of the minimal, moderate, and severe categories in both steel and fiberglass tanks.

VI. Microbial Insights, Inc.
Website Quantification of bacterial types implicated in MIC

MIC Bacteria Quantification:

A. Ethanol Utilizing Bacteria: Acetobacter catalyzes the oxidation of ethanol to acetic acid which can be a potential cause of corrosion.

B. Glycerol Utilizing Bacteria: Microbial degradiation of glycerol, a byproduct of biodiesel production from fats, lead to the generation of lactic and propionic acid both of which have been observed at high concentrations in diesel tanks.

VII. Conclusions: Microbial Influenced Corrosion

1. MIC accelerates the corrosion of metals, alloys and steel reinforced concrete by the action of microorganisms in hydrocarbon fuel & water storage tanks and transmission systems, including municipal sewer and drinking water piping.

2. Microorganisms require both food and water for growth, with both readily available in hydrocarbon fuel, water storage tanks and transmission systems.

3. MIC manifests itself as a pitting corrosion in mild steel metals.

4. MIC mitigation is limited. Mitigation requires biofilm removal (cleaning) and for chemical treatment to reach the exposed metal and alloy surfaces.

5. Mandated higher ethanol blends in gasoline and biodiesel blended diesel fuels are likely to experience accelerated metal and alloy corrosion in storage tank vapor and liquid spaces.

6. Earlier 1995 through 1997 MIC corrosion studies of fiberglass reinforced thermosetting plastics focused on carbon fibers as a MIC fuel source and non-applicable glass fiber sizing theories.

7. Fiberglass reinforced thermosetting plastic tanks and piping are not corroded by, nor provide a food source for, microbial influenced corrosion (MIC).

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sdc 3/19/14 rev 05/21/14 rev Oct. 2014 rev.Jan 1, 2015 rev.April 1, 2015