Microbial Influenced Corrosion (MIC) of Metals & Alloys in Fuel & Municipal Storage Tank and Piping Systems

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I. Introduction

The purpose of this paper is to describe:

A. The conditions leading to accelerated MIC (Microbial Influenced Corrosion) which is sometimes referred to as hydrocarbon utilizing microbes "HUMbugs" in fuel and municipal storage tanks and piping systems. MIC contributes to the accelerated corrosion of metals and alloys that are exposed to corrosive environments such as soils, water 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.

B. Laboratory, field testing and long term experience of corrosion protection provided by thermosetting plastic tanks and piping. This evidence will counter the misleading postulations that likely come from the fact that some polyesters are susceptible to biodegradation. Polyesters, both thermosetting and thermoplastic, can be purposely comprised of chemical segments that are biodegradable. These resins are designed to provide a material that can be composed in a landfill at the end of its useful life.

II. Background

A. Accelerated 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), and transmission systems including municipal sewer and drinking water piping. Anaerobic or aerobic MIC microbes require water (i.e., condensed moisture, fresh, saline, distilled) 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 plastics (e.g., seals, gaskets).

Microbes, bacteria and fungi are introduced into the storage tanks and piping systems along with dust particles and water condensed moisture through atmospheric 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.

a) Biofilms: 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 Bottom:** 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 takes 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.

Galvanic corrosion: In addition, biofilm accumulations create electro potential gradients between surfaces that are covered with biofilms and 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) **Water Removal**: Frequent water removal is important because microbes require water. However, reference ASTM D 6469 11.3.4 states, “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. 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 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.

D. AWWA Journal (2014): ***DNA Microbial Analysis and Potable Water Distribution***
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.

a) **Field studies:** Studies have shown that many microbes are able to pass through treatment barriers and survive to colonize in drinking water distribution systems. 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 and storage is subject to biofilms and MIC which will accelerate the corrosion of unprotected materials.

E. 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."

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

III. Thermoset Fiberglass Tanks & Piping ~ Resistance to MIC

A. Battelle Memorial Institute Aug, 2012 Report

Investigation of Corrosion in Systems Storing and Dispensing Ultra Low Sulfur Diesel (ULSD) in six (6) fiberglass underground storage tanks.

a) **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, acetic acid are 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." (underline added) [Fiberglass tank material was unaffected.]

B. US EPA ~ Corrosion in STP Sumps (3Q 2013) ***What Caused It and What can be Done About It?*** Headspace vapor testing from 64 tanks: Florida (35), Tennessee (16), Illinois (6), Wisconsin (4), California (2) and Iowa (1).

a) **US EPA Conclusions:** The three components that have resulted in tank sump MIC enhanced metal corrosion caused by acetobacter bacteria are:
   i. ethanol to provide the food source,
   ii. water (i.e., moisture) to live in, and
   iii. bacteria secretions of acetic acid that corrodes metals. (underline added) [Fiberglas material was unaffected]

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

a) **ASTSWMO Conclusions:**
   i. 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.

   ii. Higher water absorption means accelerated MIC metal corrosion.

   iii. Higher conductivity accelerates corrosion in the presence of cathodic metals (e.g., steel), anodic metals (e.g., brass, aluminum, copper).

   iv. "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. [underlining added]

C. NIST National Institute of Standards & Technology Corrosion Science (Jan.2014)
Corrosion of Copper and Steel Alloys in a Simulated Underground Storage-tank Sump Environment Containing Acid-producing Bacteria

a) "Carbon steel corrosion rate was significantly higher when in a vapor-phase exposure 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." (underlining added)

b) "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."

E. NACE Corrosion Expo. 2007 P.J Scott; CARIAD Consultants, Crete, Greece
Experiments on MIC of Steel and FRP Downhole Tubulars in West Kuwait Brines

a) **"**Laboratory tests showed that thermoplastics are resistant to attack by bacteria and fungi."

b) "FRP containing vinyl ester and epoxy resins were not attacked."

c) "FRP consisting of carbon fibers with epoxy resin has also been found to be susceptible to fungi."

d) "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." (underlining added)

F. Earlier Laboratory Studies: 1995 - 1998 *MIC & Fiber Reinforced Composites Microbial Growth on Fiber Reinforced Composite Materials*; Ji-Dong et al

a) 1995 Postulation that "…there may be degradation of the silane surface on glass fibers" ignores that microbes need a pathway to get to the glass, and the glass must de-bond from the resin in order for the 2 micron microbes to squeeze into a space between the fiber and resin of less than 1/2 of a micron.

b) Ji-Dong's 1997 later study concludes on page 368 "No significant difference of interlaminar shear strength was detected between the inoculated and the control composites." In spite of the foregoing test result, the paper theorizes that "fungi were shown to be responsible for the degradation of composite material" However, the material adhesion occurring between the fiber surface and the resin matrix." was in fact, unaffected in a standard industry test. (underlining added)

G. EPA Study Update (Sept. 2014 & 1Q 2015) *Investigating Corrosion Observations of Metal Components in Underground Storage Tanks Storing Ultra-Low Sulfur Diesel*

a) Tank vapor, bottom water and fuel collected from 42 UST sites (23 FRP & 19 steel) to analyze for corrosion factors and provided a preliminary hypothesis:
   i. Both ethanol and glycerol pathways viable.
   ii. Presence of corrosion does not appear to be influenced by tank material.
   iii. Corrosion observed in each of the minimal, moderate & severe categories.

H. Microbial Insights, Inc. (2015 website)

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 degradation 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 fuels.

I. Manufacturer Field Experience - 1982 to January 2015

a) Resin manufacturers Listed by UL as certified suppliers for the manufacturer of corrosion resistant tanks and piping state there is an unblemished history of resin protection against accelerated MIC in more than 20 years of application experience.
b) Glass manufacturers do not have any evidence that glass fiber sizing may leach and/or hydrolyze to contribute to ethyl acetate found in certain tank bottom analysis.
c) Fiberglass pipe manufacturers have a history of successful sea water piping applications since 1982 and have not experienced accelerated MIC corrosion.

IV. Conclusions: Microbial Influenced Corrosion of Metals & Alloys in Fuel & Municipal Storage Tank and Piping Systems

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 galvanic pitting corrosion in mild steel metals.

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

5. Mandated higher ethanol blended gasolines 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 laboratory 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 provides a food source for accelerated microbial influenced corrosion (MIC).

References: See Institute paper: *1995-2015 Review: Laboratory and Field studies of the Cause for MIC Accelerated Corrosion in Petroleum and Municipal Storage Tanks and Piping.*

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Attachment A

1. ASTM D6469-99 "Standard Guide for Microbial Contamination in Fuels and Fuel Systems"
2. Battelle Final Report (August 13, 2012) "Corrosion in Systems Storing and Dispensing Ultra Low Sulfur Diesel (ULSD), Hypotheses Investigation"
3. EPA Office of Research and Development (2013) "Corrosion In STP Sumps"
4. Oak Ridge National Laboratory: (May 2012) "Compatibility Study for Plastic, Elastomeric, and Metallic Fueling Infrastructure Materials Exposed to Aggressive Formulations of Ethanol-Blended Gasoline"
5. Oak Ridge National Laboratory: (July 2012) "Analysis of Underground Storage Tank System Materials to Increased Leak Potential Associated with E15 Fuel"
6. Oak Ridge National Laboratory: (August 2013) "Compatibility Study for Plastic, Elastomeric, and Metallic Fueling Infrastructure Materials Exposed to Aggressive Formulations of Isobutanol-Blended Gasoline's"
7. ASTSWMO (June 2013) "Compatibility of UST Systems with Biofuels"
8. ASTSWMO (June 2014) "Development and Implementation of State Tanks Core Programs"
9. NACE *Materials Performance* (January 2014) "A Closer Look at Microbiologically Influenced Corrosion"
10. NIST (National Institute of Standards and Technology) (January 2014) *Corrosion of copper and steel alloys in a simulated underground storage-tank sump environment containing acid-producing bacteria*
11. International Biodeterioration & Biodegradation (1995) *Microbial Growth on Fiber Reinforced Composite Materials* J-Dong Gru et al
12. NACE Corrosion 96 Conference and Expo (1996) *Fungal Degration of Fiber-Reinforced Composite Materials* Ji-Dong Gru et al
13. Journal of Industrial Microbiology & Biotechnology (1997) *Fiber-reinforced polymeric composites are susceptible to microbial degradation* Ji-Dong Gu
14. NACE Corrosion 2007 Conference & Expo *Experiments on MIC of Steel and FRP Downhole Tubulars in West Kuwait Brines* P.J.B. Scott
15. EPA Study Update (September 2014) *Investigating Corrosion Observations of Metal Components in Underground Storage Tanks Storing Ultra-Low Sulfur Diesel*
16. U.S. Dept. of Energy *Handbook for Handling, Storing, ad Dispensing E85 and Other Ethanol-Gasoline Blends* (2013)
17. Renewable Fuels Association (2009) *E 85 Fuel Ethanol Industry Guidelines, Specifications and Procedures*
18. U. S. Dept. of Defense (2005) *Microbiologically Influenced Corrosion a Bigger Problem than you think!*
19. Fiberglass Tank and pipe manufacturers:
    a. Owens Corning
    b. Containment Solutions Ltd.
    c. Xerxes Corporation
    d. NOV Fiber Glass Systems
    e. Hobas Pipe USA
20. Fiberglass reinforced thermoset plastic resin and glass manufacturers:

a. AOC resins
b. Ashland Performance Materials
c. Jushi Group
d. Syrgis Performance Initiators, Inc.
e. PPG Industries
f. Owens Corning