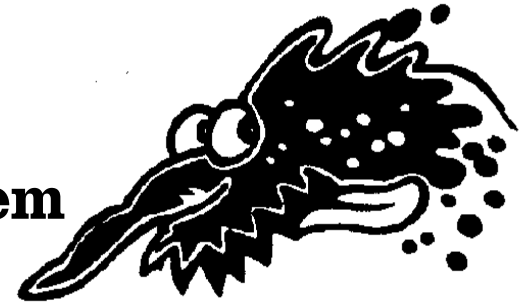
Leak Prevention

Microbes and Fuel Systems

The Overlooked Corrosion Problem



by Fred Passman

Microbes play an indispensable role in cycling both organic and mineral molecules essential to maintaining life on earth. We depend on the activities of microbes to breakdown wastes and convert them into nutrients to sustain the food chain. We use microbes to produce foods ranging from bread to sausage. Microbes within our intestinal tracts enable us to derive nutrition from the foods we eat. Suffice it to say we derive tremendous benefit from the various processes by which organisms break down both organic and inorganic materials.

When discussing material breakdown in positive terms, we use the terms of either *biodegradation* or *bioremediation.* Biodegradation includes all processes by which organisms break down materials. Bioremediation specifically refers to processes with which microbes or other organisms are used to fix a problem. With respect to leaking underground storage tanks (LUSTs), bioremediation uses microbes to degrade fuel that has seeped into the ground.

It's a short leap of understanding, then, to recognize that the same processes that serve our needs may also cause problems. The same biological processes that enable us to clean up spilled fuel using bioremediation can also degrade fuel stored in tanks. This undesired biodegradation is called *biodeterioration.*

During the past decade, government and industry have directed considerable effort and resources toward reducing the risk of soil and groundwater contamination from LUSTs. Although leak prevention technologies don't overtly presume that tanks fail from either inside or outside, most of the preventive measures address mitigation of the risk of failure due to corrosion or other insults working from a tank's outside towards its interior. In particular, leaks caused by galvanic corrosion have received considerable attention.

But there is another underappreciated corrosion process that I'd like to discuss. It takes place in all types of UST systems, and microbes play a key role. It's called *microbially influenced corrosion* (MIC).

Fuel and Corrosion Microbiology

The first report of gasoline biodeterioration was published in 1895 [1]. Subsequently, researchers demonstrated that microbes could degrade crude oil and all grades of liquid fuel. (See Davis's excellent 1967 monograph [2] and the 1984 compilation of papers edited by Atlas [3].) Fuel biodeterioration can be grouped into four general groups of processes:

- Microbes can attack the hydrocarbon and non-hydrocarbon fuel molecules directly, thereby changing the fuel's chemical and performance properties.
- Microbes growing in bottoms-waters or within biofilms (more on that in a bit) produce biosurfactants—detergent molecules—which can transport water-soluble molecules into fuel and disperse fuel molecules into water.
- Low molecular weight molecules excreted as microbial wastes may react with fuel molecules and accelerate particle formation. Some of these waste molecules are acidic and can make the fuel more corrosive.
- Microbial metabolism of sulfur molecules can make fuels more *sour* (fuel souring is directly related to the effect of reactive sulfur on its corrosivity as measured by the Doctor Test [4]).

Clearly, several of these processes change the chemistry of fuels to make the fuels potentially corrosive to materials used in UST construction. These are examples of indirect MIC.

Much of the seminal research on MIC was conducted in the 1940s. In 1945, Professor John Starkey proposed a model for MIC [5]. Starkey's model assumed that during MIC, iron ions dissolved from the metal at anodic sites on its surface. Electrons flowing from the anodic site to the cathodic site would attract hydrogen ions (protons), which would accumulate at the cathode. Were this hydrogen layer left undisturbed, electron flow would be arrested and the galvanic cell *passivated.*

According to Starkey, sulfate-reducing bacteria (SRB) used the hydrogen ions that would otherwise have accumulated at the cathodic end of a galvanic cell. This process, known as *depassivation*, accelerated the galvanic corrosion rate. As with most models, Starkey's was an oversimplification of the process; however, it was a major contribution to our understanding of MIC.

Research on the causes and dynamics of MIC remains a vital branch of microbial ecology. Today, we recognize a variety of processes that contribute to MIC. A number of microbes, in addition to SRB, depassivate metal surfaces. All of these microbes share a common class of enzymes called *hydrogenases.* The very process of colonizing surfaces creates chemical and electropotential gradients that drive corrosion. Moreover, weak organic acids can react with dissolved chloride salts to create locally high concentrations of hydrochloric acid that can acid-etch metal surfaces [6, 7]. Microbes most commonly create patterns of corrosion pits, as illustrated in Figure 1.

Microbial communities can attack polymers used in composites such as fiberglass-reinforced plastic (FRP) used for UST construction. As the polymers are attacked, gaps form between resin and fiber. Fluid seeps into these gaps and subsequent weakening of fiber integrity follows

■ *continued on page 14*

■ **Microbes and Fuel Systems**
from page 13

as the fluid goes through repeated expansion and contraction (freeze-thaw) cycles [8]. In contrast to the pitting pattern seen in steel tanks, MIC in FRP tanks is more likely to cause structural failure along a line of activity (more on this below).

How Do Microbes Get into Fuel Systems?

Microbes can get into fuel systems in various ways:

- **Vent lines:** All tanks are vented. As product is drawn from the tank, it creates a vacuum. Air drawn in through the tank's vent restores the air pressure within the tank to equilibrium with the air pressure (atmospheric pressure) outside the tank. Normal atmospheric air is full of water droplets and dust particles that carry microbes. Consequently, tank venting, essential to keep tanks from collapsing under atmospheric pressure, is a major entry route for contaminating microbes.
- **Fuel transport:** Microbes can be transported from refinery tanks or barges through pipelines and terminal tanks throughout the fuel distribution system.
- **Water in the system:** Relatively small volumes of water can support localized pockets or niches of microbial growth wherever a few milliliters of water can accumulate in the system.
- **UST fill-pipe sumps:** These are an excellent source of water containing high numbers of microbes. When surface water fills the sump and is subsequently drained through the overflow return valve, the fuel within the UST receives a significant dose of both water and microbes.

Where Do Microbes Grow in Fuel Systems?

Once a microbe has arrived within a fuel system, water is its key to survival. Good fuel may carry as much as 0.1 percent water. Most of this water remains dispersed in the fuel as *bound* or *associated* water. The amount of bound water that dissociates from the fuel depends on the fuel's additive package, its residence time in the tank, and the fuel's temperature. Some additives, such as ethanol, increase water's solubility or dispersiblity in fuel.

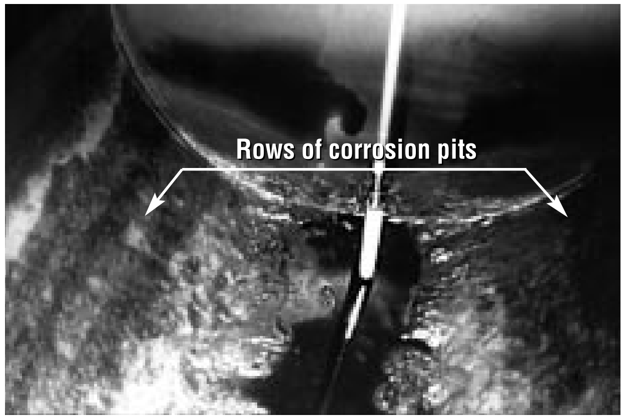


Figure 1. Corrosion pit pattern in UST. Notice concentration of pits in rows at the approximate low inventory level. Flash evaporation typically prevents biofilm development above this level.

As product stands, water will continue to dissociate—the longer the residence time in a tank, the greater the volume of water that is likely to fall out. Water's solubility in fuel increases with temperature. As fuel cools, it tends to reject water. It's the nature of fuel, then, to transport water into tanks at each stage of distribution, from refinery to end-user service tank.

Most of the water that dissociates from fuel during storage in a tank will fall to the bottom. Some will condense on the interior tank shell surface. If the surface is free of biofilm, the condensed water will run down the sides of the shell and accumulate as bottoms-water. Where biofilm is present, the condensed water is more likely to become entrained within this film.

If we were to follow our newly arrived microbe, we would see that initially it settles slowly down through the fuel, along with the particle with which it rode into the tank. If the particle's specific gravity (weight relative to that of water) is greater than that of the fuel, but less than that of water, the particle may come to rest at the fuel-water boundary *(interface).*

Alternatively, convection currents within the fuel may transport the particle to the fuel-shell interface. If the microbe is a slime-former, it will attach itself to the surface and begin reproducing. Similarly, at the fuel-water interface, it will begin to form a biofilm layer, sometimes referred to as a *skinnogen* layer. The slime enables the microbe to create a *microenvironment* that permits further growth and proliferation. The slime also traps other microbes that may be settling through the fuel.

Over time, a *consortium* develops. A consortium is a group of unrelated microbes that form a community that is able to carry out bioconversion processes that none of its individual members could carry out alone. For example, the SRB, mentioned earlier, require an oxygen-free environment in order to grow. Microbes that require oxygen do at least two things to create conditions favorable for SRB. First, they consume the available oxygen, creating the requisite oxygen-free conditions deep within the biofilm. Second, they metabolize large organic molecules that SRB can't use as food and excrete the smaller molecules on which SRB thrive. By consuming these small molecules, SRB prevent them from accumulating within the biofilm and becoming toxic to the microbes that generated them as wastes.

For microbes to thrive within fuel systems, they need to aggregate within biofilms that can form consortia, trap water and nutrients, and protect the resident populations from the potentially hostile outside environment. Biofilm communities are most likely to develop at the fuel-water interface, lower portions of the tank shell surface, and within bottom sludge and sediment.

In diesel and heavier grade fuel tanks, biofilms can cover the entire tank surface. Gasoline is more volatile. In this case, as product is drawn from the tank, exposing surfaces, gasoline evaporates from those surfaces fast enough to also dehydrate them. Consequently, biofilms tend to form at and below the tank's normal low ullage level. At most fuel retail sites, this is the bottom third of the tank (assuming 3,000 gallon [11,340 liters] minimum inventory in a 10,000 gallon [37,854 liter] UST).

Heaviest biofilm development is typically at the level where the fuel-water interface intersects with the shell surface. Most often this is the zone between 10° and 20° arc, on either side of bottom dead center.

How Do Microbes Attack Fuel System Components?

Steel USTs

With an understanding of how microbes enter fuel systems and where they tend to accumulate, we can revisit the biodegradation processes mentioned earlier. Some microbes can use fuel hydrocarbons as their sole source of organic nutrition. Others can use fuel additives and other non-hydrocarbon fuel molecules as food. Some microbes that thrive in fuel systems may not be able to use any molecules in fuel as food. As I illustrated above, for the SRB, these microbes rely on the byproducts of other microbes for nutrition.

In steel tanks, MIC is primarily an incidental consequence of microbial activity. Biofilms create chemical and electropotential gradients, thereby inducing galvanic corrosion. Conditions within biofilms are typically acidic and reducing, contributing further to metal dissolution.

Within corrosion tubercles, strong inorganic acids, particularly hydrochloric, can form from the reaction between chloride salts and weak organic acids. The tubercle crust prevents the aggressively corrosive hydrochloric acid from diffusing into the system outside the tubercle. Consequently, severe acid etching proceeds within the tubercle.

Additionally, if SRB are present, they generate hydrogen sulfide. The hydrogen sulfide then reacts with free iron ions to form ferrous sulfide. The net result is a characteristically spherical corrosion pit, resulting in a pinhole leak as the outer margin of the pit breaks through the tank's exterior.

Fiberglass-Reinforced Plastic USTs

As mentioned earlier, the dynamics of FRP UST biodeterioration are quite different. At this point, it is not certain whether microbes use composite polymers as food or if enzymes intended to break down other molecules (actually used as food) attack the polymers.

In the studies performed to date, other nutrients have always been available to the microbes degrading FRP. In the case of fuel USTs, the point is perhaps moot. Microbes colonizing FRP surfaces have the same cornucopia of nutrients available as those colonizing steel tank surfaces.

Regardless of whether FRP polymers are used as food, the end result is shortened polymer chain lengths. This translates into weaker structure and increased brittleness. It's possible for the bottom few inches of an FRP UST to separate from the rest of the tank (recall my comment about maximal biofilm development at the level where the fuel-water interface meets the tank shell).

Lined USTs

Steel USTs that have been lined with a coating are subject to a third type of biodeterioration. If a coating has even a single holiday (break in the coating's uniformity), water and microbes can gain access to the coating-shell boundary. Colonization begins at the holiday and spreads out from there. Biofilm development between coating and shell is particularly insidious because it's so difficult to detect until the coating begins to blister away from the shell. Although the process has not been studied thoroughly, it is likely that the biodeterioration mechanisms described above for both steel and FRP USTs are active when microbes live between coating and tank shell materials. Both the coating and underlying steel are attacked.

Detecting Microbial Contamination

My earlier discussion of where microbes tend to grow within fuel systems also illustrates the difficulty of recognizing microbial contamination before system components are destroyed. It is nearly impossible to retrieve swab samples of slime from tank walls without gaining direct access to the tank.

The methods described here cannot provide information as conclusive as that obtained by entering a tank, making observations, and collecting samples directly. However, the preentry process of making a tank safe for entry is costly and time consuming. Moreover, it destroys much of the evidence that would be useful to a microbiologist. The only practical alternative is to pull fluid samples and use them as surrogates to assess what may be happening on the tank shell surface.

Samples traditionally collected for fuel quality testing yield little information about either the presence of microbes or whether significant biodeterioration in underway within the tank. Moreover, many of biodeterioration's symptoms mimic those of non-biological deterioration. Notwithstanding these challenges, it is possible to monitor fuel systems for both microbial contamination and biodeterioration.

I refer readers to ASTM's *Standard Guide to Microbial Contamination in Fuels and Fuel Systems* (D6469 [9]) for a more detailed discussion of the topics covered in this section.

Sampling

Monitoring begins with collecting the best possible sample. A full chapter of the forthcoming ASTM *Manual on Microbial Contamination of Fuels and Fuel Systems* (due to be published in early 2002) is devoted to sampling strategies and techniques. Bottom samples from the low end of a UST are most likely to provide useful microbiological information. This is often the first challenge.

Regardless of the intentions of UST installers, many USTs settle by the tank's turbine (submerged pump) end. A well-designed system will have a sampling port or other access fitting near the turbine distribution manifold to permit both sampling and water removal from this end of the UST. I am always delighted on the rare occasions when I encounter such systems. More often, the turbine must be pulled in order to get a bottom sample from this end of a UST.

Unless the UST's trim has been measured (fuel ullage at fill and turbine ends) and determined to be trim (low) at the fill-end, bottom samples should be taken from both ends of the UST.

Samples should be collected with a Bacon bomb or similar true bottom sampler. Each sample is dispensed through a clean funnel into an unused glass sample bottle. The advantage of using glass will become

■ continued on page 16

■ **Microbes and Fuel Systems**
from page 15

evident in the next section.

If dispensers calibrated to deliver 10 gpm (38 liters/min) are delivering < 7 gpm (27 liters/min), pull the dispenser filter and save it for examination. Test the dispenser flow rate after installing a fresh filter. If the rate hasn't returned to normal (the actual rate may be < 10 gpm if customers are taking fuel while you are running the test), corrosion may have degraded valve operation. (Hint: if you discover corroded components between the UST and the dispenser, suspect UST biodeterioration.)

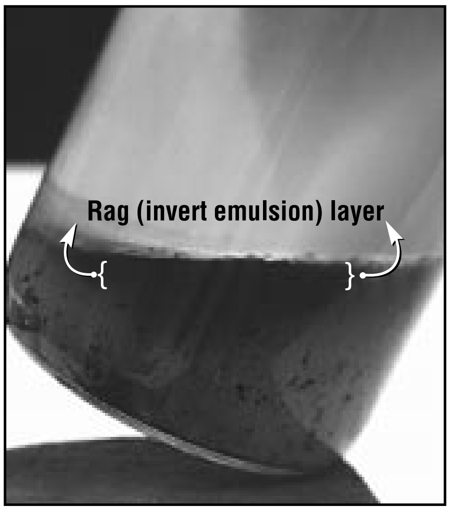


Figure 2. Fuel tank bottom sample showing haze 5 fuel over bottoms-water. Note the rag layer that has developed between the fuel and water phases. Similar to the tank shell biofilm, the rag layer is home to dense microbial populations.

Gross Observations

There are a number of simple observations that provide excellent indications as to whether significant biodeterioration is occurring within a particular system. Figure 2 illustrates a heavily contaminated bottom sample. Note the well-defined region between the bottoms-water and fuel. This invert-emulsion (water in fuel) zone is called the *rag layer.* It's caused by the production of biosurfactants and skinnogens at the fuel-water interface.

Rag layers may also be caused by chemical incompatibilities within the fuel. However, rag layers produced by microbes will (a) tend to adhere to the jar's side if you tilt the jar gently; (b) have stalactites of slime protruding into the water phase, stalagmites of slime projecting into the fuel phase, or both; and (c) will often be membranous or difficult to disperse. A well-defined rag-layer biofilm is a strong indicator of biofilm development on tank walls.

To determine if the sample's sediment contains lots of rust particles, dip the magnetic end of a stirring bar retriever into the sample bottle and swirl it gently on the bottom of the bottle for a few seconds. (A stirring bar retriever is a long, plastic-coated wand with a magnet that is encapsulated into one end; lab technicians use stirring bar retrievers routinely to pull magnetic stirring bars from test flasks.) Remove the retriever from the bottle and look for magnetic particles on its tip. If magnetic debris covers more than half of the bottom of the stirring bar retriever, then rust accumulation is significant and should be investigated further.

Bottoms-water samples from heavily infected tanks may also have distinctive odors. Strong sulfide or ammonia odors are characteristic of sulfate and nitrate reduction, respectively.

Open plugged filters for inspection. If the filter is plugged with rust or if the housing is corroding, suspect MIC activity within your system.

Other Tests

A complete diagnostic evaluation of biodeterioration in a UST requires a battery of physical, chemical, and microbiological tests [9]. Of these, the traditional microbiological tests—inoculating growth media to see what grows—are often the least useful. Many microbes that are perfectly content and thriving in the contaminated system may (a) not get captured in the sample; or (b) not grow in the medium into which we transfer them. Negative test results obtained with the various commercially available growth test kits may provide encouraging but misleading information. If MIC is suspected, a microbiologist trained in fuel and fuel system biodeterioration should be called in to perform a thorough assessment.

Controlling Microbial Contamination

Good housekeeping goes a long way toward preventing UST biodeterioration. Recognizing that water and sediment is going to be delivered with product, UST owners should institute regular monitoring and dewatering programs. As noted above, to be effective, samples and water draws need to be taken from the tank's low-end.

Although dry tankage is theoretically possible, it's impractical. Even in the aviation industry where fuel is filtered and dewatered at each step of the distribution process, water still reaches aircraft fuel tanks where it is dealt with through the use of deicing additives. Even if USTs were designed to permit water draw from the their lowest point, tank wall biofilms will entrain significant water (a 1/8-inch thick biofilm, covering 30 percent of the surface of a 10,000 gallon UST, can hold several gallons of water—a veritable ocean from the perspective of microbes). This means that over time, most tanks will develop microbe biofilms.

In fuel systems, biofilms may take three to six months to develop [10]. Since UST biodeterioration is unlikely to occur in the absence of a biofilm consortium, it makes sense to minimize the risk of biofilm formation. Periodic treatment with an antimicrobial pesticide can prevent biofilm maturation. I generally recommend treating tanks two or three times per year, depending on test data. All treatments should be data driven. If there's no evidence of biofilm development, the interval between treatments can be extended. If samples show that a rag layer forms within two months after treatment, I recommend treating more frequently.

The U.S. EPA approves only a limited number of antimicrobial pesticides for use in fuel systems. Before treating a UST with an antimicrobial pesticide, contact either a manufacturer or manufacturer's representative who is knowledgeable about treatment protocols, dosing, handling (all antimicrobial pesticides are treated as hazardous materials), and product selection.

Some products are primarily fuel soluble; others are only water soluble. The most effective products have at least some solubility in both fuel and water. Products also differ in their respective ranges of microbicidal activity. A few of the products approved for use in fuel systems have a secondary function as corrosion inhibitors. A reputable professional can help you determine what products and treatments are most likely to give you successful control.

If a tank is already heavily contaminated, chemical treatment alone is unlikely to be satisfactory. First, all antimicrobial pesticides are used up as they kill microbes. If a tank is coated with a thick biofilm, the microbicide is probably going to be used up before the tank is disinfected. Some microbicide molecules will get trapped in the biofilm without ever coming into contact with their targets.

Second, a successful microbicide treatment will disrupt the biofilm sufficiently to cause large pieces *(flocs)* of biofilm material to slough off of the tank's walls. A significant percentage of these flocs will be transported to the dispenser filters, which will consequently plug prematurely.

Heavily contaminated tanks should be cleaned within 24 hours after an initial "shock" treatment. There are a number of commercial systems for cleaning tanks. Some require direct access; others use tubing or hoses that are inserted into the tank.

The most effective systems recirculate and polish the fuel at high (> 200 gpm) flow rates and use directional nozzles to scour tank surfaces. Systems designed to operate at < 100 gpm are fine for pulling water, sludge, and sediment off of tank bottoms, but are ineffective against tank shell biofilms. Aggressive tank cleaning, as a biodeterioration control measure, should only be needed once every five to ten years, if it's accompanied by periodic preventive treatment.

Microbes ... in a Tank Shell

Left undetected and untreated, microorganisms can infect fuel systems, develop consortia communities, and cause fuel system component failures ranging from premature dispenser filter plugging to leaking USTs. Most UST installations do not make it easy to pull the bottom samples that are most useful for monitoring biodeterioration risk. Optimally, all USTs should be fitted with sample collection and dewatering access near each end of the tank. Currently, most USTs can only be sampled at the fill-pipe, unless service engineers pull the turbine, the electronic gauging device, or both. Consequently, significant volumes of water can accumulate in tanks undetected.

Microbes find all of the water and nutrients they require in fuel tanks. The erroneous conventional wisdom that gasoline is less susceptible to microbial attack is based on several decades of experience with product containing tetraethyl lead. Once tetraethyl lead (itself an effective unregistered microbicide) was removed from automotive gasoline, microbes reinhabited gasoline systems. In my experience, gasoline tanks support considerably higher numbers of microbes than do diesel tanks.

Microbes find all of the water and nutrients they require in fuel tanks.

The mere presence of microbes does not necessarily mean that system biodeterioration is occurring. Symptoms of system change are better biodeterioration indicators. Look for rag layer development or accumulation of rust particles in bottom samples. Smell for sulfide or ammonia. Keep track of filter-plugging rates. In a clean system, filters can process (filter) 250,000 gal or more without affecting flow rate. In an infected system, filters may start plugging before having processed 50,000 gallons of fuel.

Historically, MIC in USTs has received relatively little attention. Leakage caused by MIC probably accounted for 10 to 20 percent of all leaking USTs. Several watershed events over the past decade, however, may change these statistics. LUST regulations have reduced the risk of leaks caused by galvanic corrosion from the UST's exterior. The fuel industry has also changed.

While consumer demand has grown steadily at 5 to 7 percent annually, shell capacity has shrunk at approximately the same rate. This means that product throughput rates have climbed 10 to 14 percent annually. In other words, there's less time for water and sediment to settle out of the fuel at each stage of the distribution system. More water and sediment (along with passenger microbes) get transported through from refinery to end-user.

In response to clean air regulations, fuel chemistry has also changed. Although there is no general agreement so far, it's likely that the net effect of these chemical changes (in both basic product and additive packages) has been to make fuels more susceptible to biodeterioration. In short, history is not necessarily a good predictor of the future likelihood of UST biodeterioration.

Steel, composite, and lined tanks are all susceptible to biodeterioration. In the recent past, most UST owners invested heavily to ensure that their systems complied with LUST regulations. Relatively inexpensive good housekeeping, coupled with periodic preventive treatment, can minimize the risk of uncontrolled microbial contamination wiping out the return on the upgrade investment. ■

Fred Passman is an industrial microbial ecologist and owner of Biodeterioration Control Associates, Inc., a consulting firm dedicated to helping industry recognize and control microbial contamination in process fluid systems. He can be reached at
bca-fjp@ix.netcom.com

References

[1] Myoshi, M. J. J. *Wiss. Bot.* 1895. 28, 269-289.

[2] Davis, J.B. *Petroleum Microbiology.* Elsevier Publishing Company, Amsterdam. 1967. 604 pp.

[3] Atlas, R. M. Ed. *Petroleum Microbiology.* Macmillan, New York. 1984. 692 pp.

[4] ASTM. "D4952 Standard Test Method for Qualitative Analysis for Active Sulfur Species in Fuels and Solvents" (Doctor Test). *ASTM Annual Book of Standards,* Vol. 5.03. ASTM, Conshohocken.

[5] Starkey, R. L. and K. Wright. *Bull. Amer. Gas Soc. Tech. Sec.* 1945. p. 108.

[6] Dexter, S.C. Ed. *Biologically Induced Corrosion.* NACE, Houston. 1986. 363 pp.

[7] Videla, H. A. *Manual of Biocorrosion.* CRC Press, Boca Raton. 1996. 273 pp.

[8] Gu, J. D., C. Lu, R. Mitchell, K. Thorp and A. Crasto. *Material. Perform.* 1997. 36:37-41.

[9] ASTM. "D6469 Standard Guide for Microbial Contamination in Fuels and Fuel Systems." *ASTM Annual Book of Standards,* Vol. 5.04. ASTM, Conshohocken.

[10] Passman, F. J., B. L. McFarland and M. J. Hillyer. *Int. Biodet. Biodeg.* 2001. 47, 95-106.