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Corrosion of copper and steel alloys in a simulated underground storage-tank sump environment containing acid-producing bacteria ☆

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ABSTRACT

We simulate corrosion observed in underground fuel storage tank systems by headspace and aqueous exposure to biotic organic acid. Carbon steel and copper were exposed to *Acetobacter* sp. inoculated into aqueous-ethanol solutions over a period of approximately 30 days. The steel alloy exhibited pitting corrosion and the copper alloy exhibited pitting and intergranular corrosion due to acetic acid produced by the microbes. Corrosion rates were dependent on formation of corrosion products and are ranked as follows in order of increasing magnitude: Copper-aqueous < Steel-aqueous < Copper-headspace < Steel-headspace. The laboratory test method developed here reproduces corrosion observed in practice.

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1. Introduction

Production and consumption rates of ethanol, biodiesel fuel, and other alternative fuels are projected to increase significantly in the U.S. in the coming years [1]. Usage of ethanol as an additive to gasoline is already quite high. In as recently as 2010, over 90% of the gasoline sold in the U.S. was reportedly blended with ethanol [2]. However, much of the current fuel infrastructure was designed for unblended gasoline, and there is growing concern that some of the materials used in the past may not be compatible with the emerging blended fuels [3,4]. One of the main concerns regarding material incompatibility is the potential for corrosion of fuel storage and dispensing infrastructure, which may result in leakage of fuels and subsequent pollution of the ground water supply requiring expensive clean-up and mitigation.

Since as early as 2008, inspectors in nine different U.S. states have reported an increasing number of incidents where underground storage tank (UST) components exhibited sudden and rapid corrosion [5]. The UST components that exhibited unexpected corrosion included sump pumps, submersible turbine pumps, risers, and ventilation pipes. Measurements of headspace chemistry revealed that high ethanol–vapor concentrations were associated with the corrosion, although the occurrence of corrosion was not exclusive to storage scenarios involving ethanol-blended gasoline fuels. The presence of acetic acid (measured in the form of acetate) and microbiological activity in the sump–pump environments was noted where corrosion occurred. Rapid corrosion of UST components associated with handling and dispensing of ultra-low-sulfur diesel (ULSD) fuels has also occurred [6]. In fuel storage scenarios involving ULSD, ethanol contamination was observed at many of the UST test sites [6]. The U.S. Environmental Protection Agency analyzed UST sump waters and vapors from many locations across the U.S., finding that high acetate concentrations (>1000 mg L^{-1}) were associated with the presence of ethanol in a variety of ethanol-blended gasoline and other fuels [7]. The levels of acetate were correlated to rust tubercles on steel and blue corrosion product on copper [7]. Analysis of all the UST components revealed the presence of acetic acid-producing bacteria (e.g., *Acetobacter* sp.) [5–7], a class of common microorganism that converts ethanol to acetic acid. These microorganisms likely caused or contributed to the accelerated corrosion [5–7] and were even identified as the predominant microbes found in the ULSD fuel systems [6].

Microbiologically-influenced corrosion (MIC) and microbial contamination have been associated with the usage and distribution of various liquid fuels for many years [8,9] and thus are not new problems in fuel-handling and dispensing scenarios. With respect to ethanol fuel in particular, industrial storage tanks have reportedly sustained microbial life including acid-producing bacteria (APB) and sulfate-reducing bacteria (SRB) [10]. APB, including *Acetobacter* sp., secrete organic acids during the fermentation of organic compounds, and are known to influence corrosion of metals [11]. *Acetobacter* sp. in particular, oxidize ethanol during the

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fermentation process, resulting in acetic-acid production according to the following reaction:

$$C_2H_5OH + O_2 \rightarrow CH_3CO_2H + H_2O. \quad (1)$$

APB have been shown to promote localized corrosion of steels at inclusion sites where the observed corrosion damage exhibits a distinct appearance from corrosion produced by a protic acid of the same pH [12]. Acetic acid is known to corrode metals while in its vapor form and when dissolved in an aqueous solution. Biotic acetic acid vapor that emanated from wood samples was shown to influence corrosion of copper, lead, and brass coupons [13]; however, most corrosion experiments to-date have considered acetic acid from abiotic sources. Abiotic acetic acid vapor has been shown to promote the corrosion of copper [14] and mild steel [15,16], which are two metallic materials used in mechanical components exposed to fuel vapors and aqueous phases contained in UST sump systems. The corrosion rate of mild steel exposed to aqueous mixtures of acetic acid was found to be quite high, and exhibited dependence on acid concentration, temperature, and the period of exposure [17]. The rate of copper corrosion exposed to aqueous acetic acid solutions was shown to be dependent on acid concentration [18], and was strongly influenced by relative humidity when exposed to acetic acid vapor [19].

This work reports on a corrosion evaluation study performed with a new testing methodology developed to simulate the MIC observed in UST systems. A headspace testing chamber was designed so that corrosion of sump–pump component alloys could be evaluated during exposure to ethanol and acetic-acid vapor components. *Acetobacter aceti* were used here to generate acetic acid in a simulated ethanol fuel environment to confirm that MIC is a plausible mechanism for the corrosion seen on UST sump–pump components. The biotic source of acetic acid is critical since abiotic substitutes might not replicate corrosion induced by microbes [12]. The use of *A. aceti* also provides information on biological properties (e.g., bacterial attachment) that would not be achieved with the addition of acetic acid solution alone. This test, while it did not incorporate blended fuels (e.g., E15, E85), could prove useful in evaluating MIC in fuel samples collected from field studies, including non-ethanol blended fuels. Furthermore, the test method could prove useful in investigating the growing number of microbes in fuels and crude oils that may be contributing to biodeterioration of fuels and fuel infrastructure [20,21].

2. Materials and methods

2.1. Materials

Two rod alloys (19.05 mm diameter) were obtained for this study from a commercial vendor, including a Type 1018 cold-drawn steel rod conforming to ASTM A108 specifications [22] and an Alloy 110 (H04 hard temper) copper rod conforming to ASTM B187 specifications [23]. Chemical compositions of both materials are reported in Table 1. Metal rods were saw-cut into disk-shaped coupons with a thickness of approximately 2.8 mm for corrosion tests.

2.2. Bacterial growth

Environmental isolates of *A. aceti* were cultivated from a fueling terminal tank [24]; samples were identified by 16S rRNA gene sequencing. *A. aceti* were maintained in a medium containing yeast extract (0.5 g L^{-1}), peptone (0.3 g L^{-1}), and sodium chloride (1 g L^{-1}) in distilled water [25] at pH 6. Ethanol (5% by volume) was added as a carbon source. A concentrated *Acetobacter* culture was established by growing the bacteria in 100 mL of culture media for 1 week. This established culture, which is in a stationary phase, was diluted for headspace experiments.

2.3. Preparation of headspace chambers

Saw-cut coupons were prepared according to ASTM G-1 Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens [26]. Coupons were progressively ground to a 600 grit finish with SiC paper immediately prior to testing, then degreased in acetone, then ethanol, and dried under flowing nitrogen gas. Coupons were weighed with a precision digital balance to the nearest 0.1 mg, then mounted in PTFE corrosion fixtures with polyethylene screws. Polymers were used for all coupon fixtures to prevent galvanic interactions. The fixtures were in turn placed in polyethylene test chambers as shown in Fig. 1. Fig. 1a and b shows the coupon placement during headspace exposure. All test chamber components were sterilized in an autoclave prior to corrosion tests. Fig. 1c shows the coupon placement during aqueous exposure; three coupons were placed in each test chamber, as indicated. Three chambers were loaded with coupons (3 coupons in each chamber, 9 total) during the headspace tests, and a single chamber (containing 3 coupons) was loaded during aqueous exposure tests. After coupons were secured in each chamber, 225 mL of growth media was poured into the bottom of each headspace chamber. An additional 25 mL of established *A. aceti* culture was pipetted into the growth media solution after lids were secured on chamber tops. The aqueous exposure chamber contained 450 mL of growth media inoculated with 50 mL of *A. aceti* culture to maintain an adequate solution volume-to-surface-area ratio suggested by the standard test method [27].

2.4. Sample collection

Acidity and solution optical density (proportional to cell concentration) were monitored periodically through the duration of the test by extracting test solution through a pipette after agitating the tank to ensure even distribution of the cultured cells. Uncertainty in pH measurements was ±0.03 pH units (1 s.d.) and optical density uncertainty was $\pm 1 \times 10^{-3}$ absorbance units for all measurements reported here. Optical density was measured with a UV–VIS spectrometer set at 600 nm wavelength. Growth media solution was replenished every two to three days by replacing the solution volume (typically 10 mL) extracted for pH and optical density measurements.

One coupon was collected from each headspace chamber at time points selected based on pH and absorbance readings (discussed below). The copper coupons were collected at 292 h, 550 h, and 863 h from the time of test initiation and the steel coupons were collected at 355 h, 643 h, and 932 h from the time of test initiation. All three coupons were pulled simultaneously from the aqueous exposure test chamber after 863 h (copper) and 932 h (steel) exposure time. The coupon mass was determined while corrosion product was still intact to determine mass gain due to film formation. Corrosion product was then removed according to

Table 1
Chemical composition limits of 1018 steel and copper alloy 110 (wt.%).

Alloy	Fe	C	Si	Mn	Cu	Pb	Bi	O	S	P
1018	Bal.	0.16	0.15	0.79	–	–	–	–	<0.05	<0.04
110	–	–	–	–	Bal.	<0.005	<0.005	<0.04	–	–