Corrosion of Copper and Steel Alloys in the Presence of *Acetobacter* sp. in a Simulated UST Sump Environment

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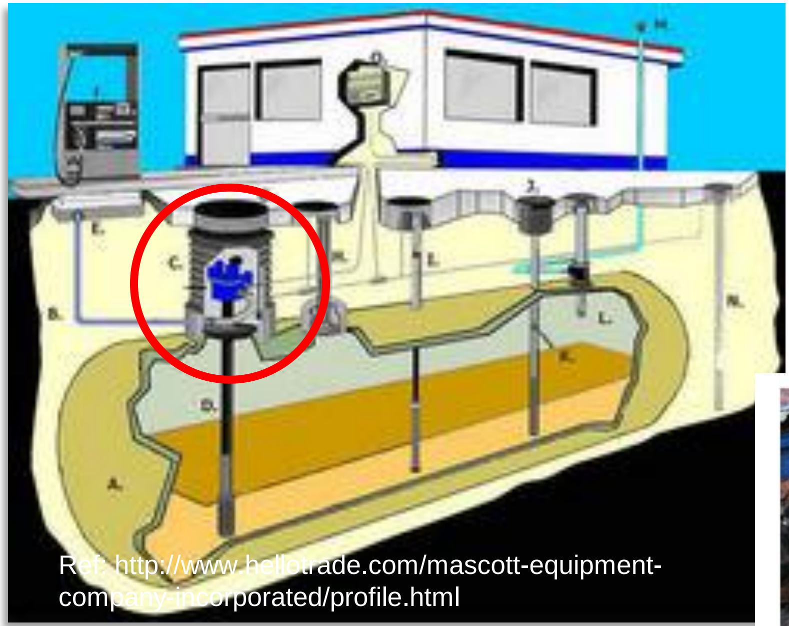
CIVIL&ENVIRONMENTALENGINEERING
COLORADO SCHOOL OF MINES

Problem: Rapid UST Corrosion



Ref: http://www.hellotrade.com/mascott-equipment-company-incorporated/profile.html

Underground Storage Tank (UST) sump components are susceptible to rapid corrosion at stations dispensing gasoline-ethanol blends and ultra-low-sulfur diesel fuel. Components include copper tubing, brass valves, and steel submersible turbine pumps (STP) and piping.

According to the U.S. EPA "There are approximately 584,000 underground storage tanks (USTs) nationwide that store petroleum or hazardous substances. The greatest potential threat from a leaking UST is contamination of groundwater, the source of drinking water for nearly half of all Americans."

Steve Pollock, Presentation, 23rd National Tank Conference: http://www.neiwpcc.org/tanks2012/presentations/Tuesday%20Presentations/pollock.biofuels.tuesday.pdf

Photo courtesy: Florida DEP

E10 STP, unknown grade (Florida) – Feb. 2011

Photo courtesy: San Diego County - Dept. of Environmental Health (California)

91 octane STP (California) – August 2010

Photo courtesy: State of Tennessee, TDEC

Premium/E10 STP (Tennessee) – March 2010

Same sump!

Photo courtesy: State of Tennessee, TDEC

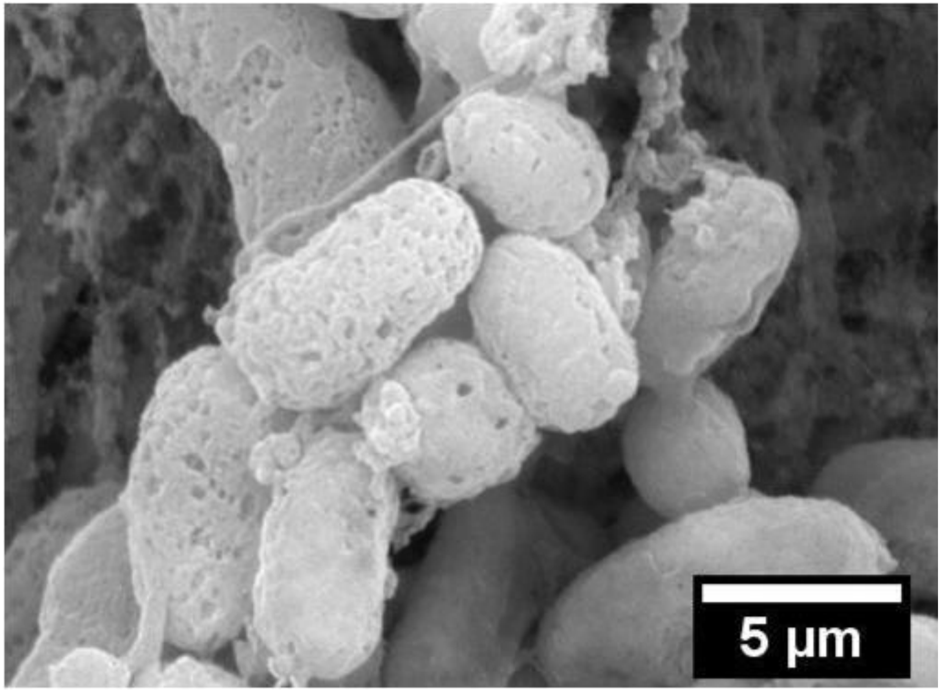
Premium/E10 STP (Tennessee) – August 2010

Current Objectives

Inspectors of USTs have noticed rapid corrosion and a vinegar-like odor when accessing the sumps. Microbiologically influenced corrosion (MIC) is suspected of contributing to the accelerated damage of UST systems dispensing ethanol-blended fuels.

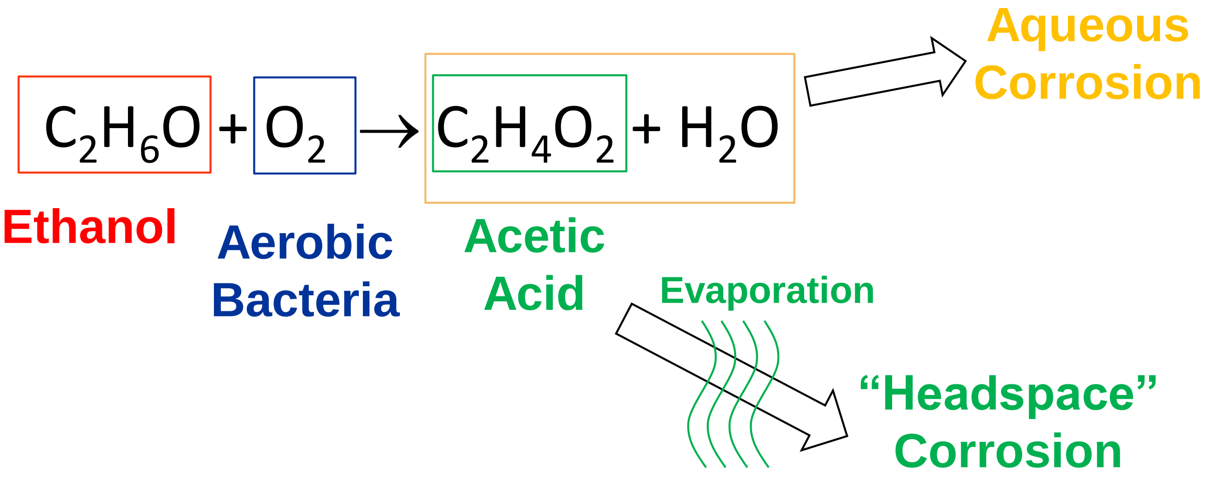
- *Test a Hypothesis*: Can *Acetobacter sp.* cause highly accelerated corrosion of UST components in the presence of ethanol?
- *Measure the corrosion rates* of various materials used in fuel handling exposed to biotically produced acetic acid
  - These data can aid in determining inspection intervals and other design protocols for systems handling ethanol fuel
- *Develop a test methodology* for evaluating corrosion in biofuel systems contaminated with microbes
  - Such a test will aid in selection of corrosion-resistant materials, coatings, inhibitors, and biocides
- *Improve measurement methodology*: Provide measurements to evaluate corrosion real-time and improve measurement strategies to improve predictive nature of measurements.
  - Such a test will aid in the selection of measurement strategies necessary to monitor corrosion effectively to prevent devastating failure.

Acetobacter Metabolism



Scanning electron microscope image of an *Acetobacter* biofilm on X52 pipeline steel after exposure to inoculated ethanol growth media solution.

Image courtesy of Luke Jain, Colorado School of Mines, Ph.D. Dissertation.



$C_2H_6O + O_2 \rightarrow C_2H_4O_2 + H_2O$

Ethanol

Aerobic Bacteria

Acetic Acid

Aqueous Corrosion

Evaporation

“Headspace” Corrosion

Premium/E10 STP (Tennessee) – August 2010

Bacteria Culture and Corrosion Experiments

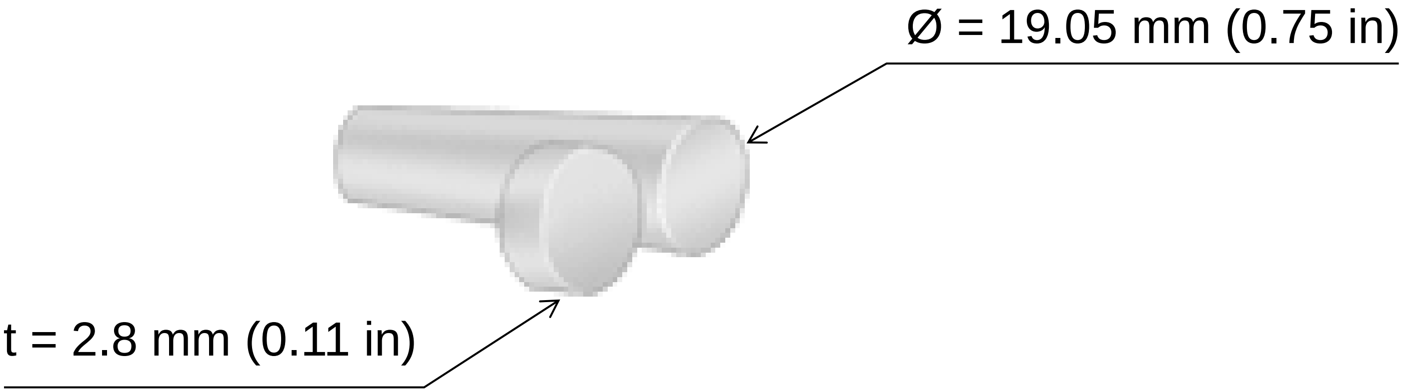
EXPERIMENTAL METHODS

Test Materials

Corrosion of copper and steel alloys are investigated in this study. The alloys tested were acquired from a commercial vendor in rod form and are representative of those used in tank components. Composition limits are shown below (wt. %). Both test materials are 'cold worked'.

Grade	Pb	Bi	O	P	Cu
110 Copper	0.05 max	0.005 max	0.04 max	0.04 max	Balance

Grade	C	Mn	Si	P	S	Fe
1018 Steel	0.15 – 0.20	0.60 – 0.90	0.15 – 0.30	0.04 max	0.05 max	Balance



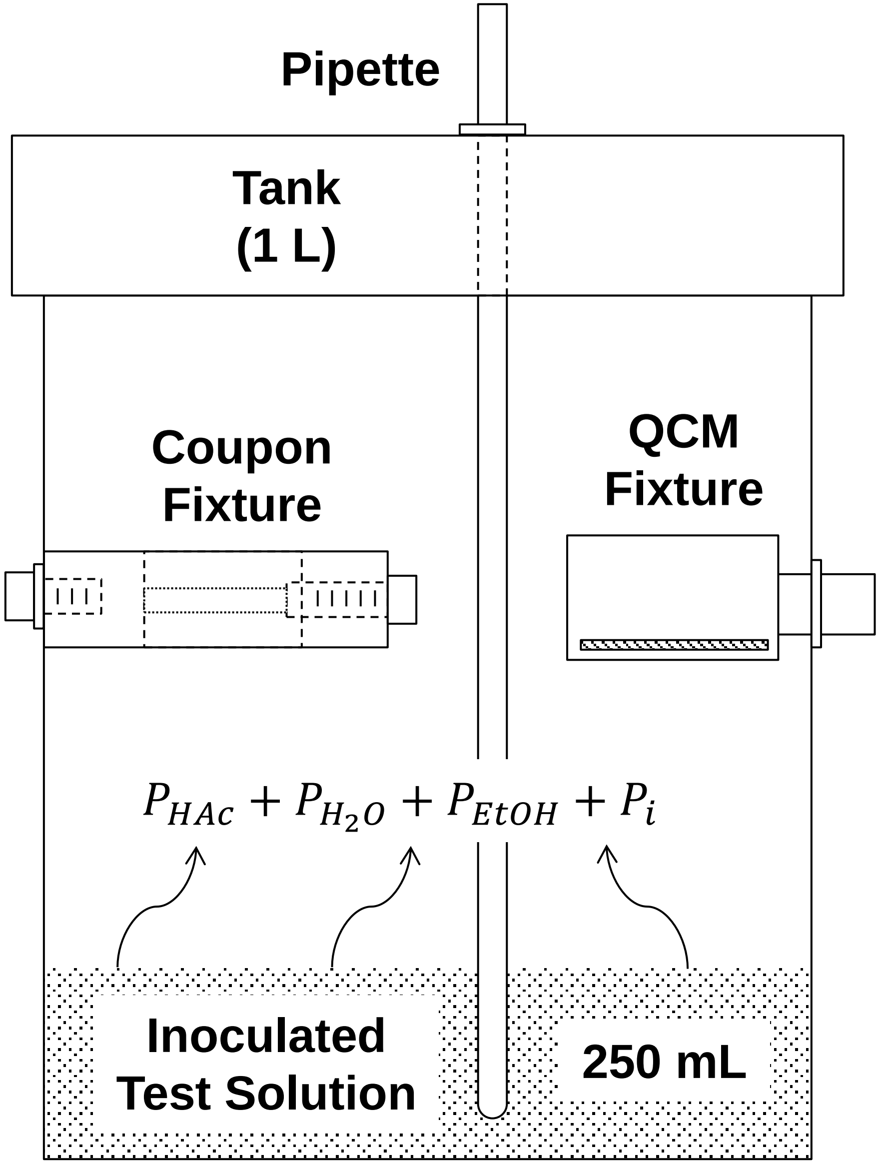
Bacteria Cultures

- *Acetobacter sp.* were isolated at an industrial ethanol production plant by our collaborators at Colorado School of Mines.
- Test Media simulates a mixture of e.g. groundwater and ethanol fuel:
  (5 % Ethanol – 95 % Bacteria Growth Media)
- In the future, we can likely control the microbial activity, and hence the pH by varying the ratio of this mixture. (What is relevant?)

Headspace Corrosion	**Aqueous-Ethanol Immersion Corrosion**
• Inoculate 250 mL of Test Media with *Acetobacter sp.* • Expose metal coupons to the vapor phase only • Expose Fe and Cu quartz crystal microbalances (QCM) and monitor frequency shift ($\propto$ mass change)	• Inoculate 500 mL of Test Media with *Acetobacter sp.* • Fully immerse alloy coupons in the liquid phase Test Media

- Pull coupons at regular intervals to investigate transient corrosion behavior
- Maintain culture by periodic feeding with fresh Test Media
- Monitor the solution acidity (pH meter) and solution absorbance with UV-Visible Spectroscopy:
  - $\text{Absorbance}|_{\lambda = 600\text{ nm}} \propto$ bacteria cell count
- Perform tests in triplicate

Headspace Corrosion Test Setup



Pipette

Tank
(1 L)

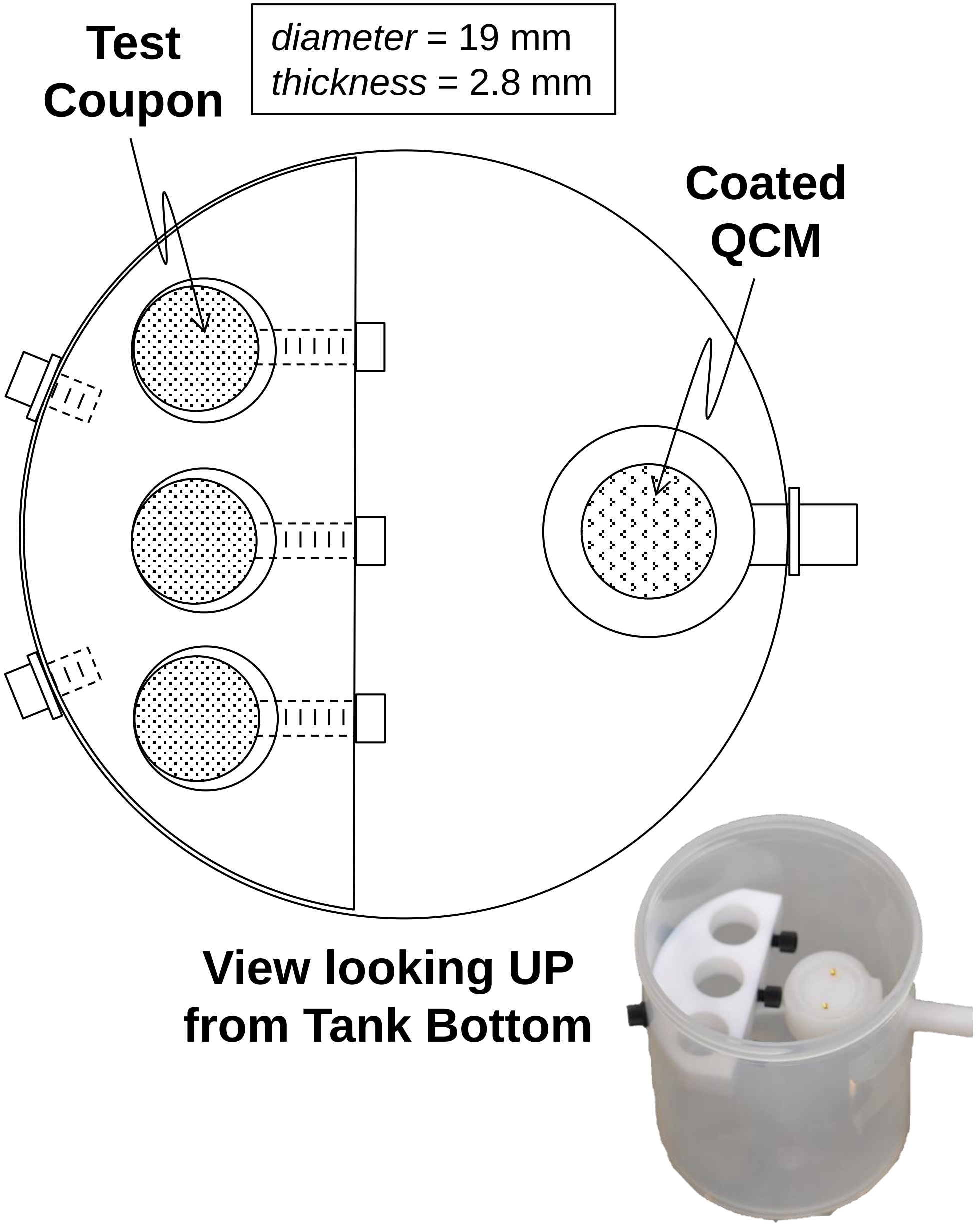
Coupon
Fixture

QCM
Fixture

$$P_{HAc} + P_{H_2O} + P_{EtOH} + P_i$$

Inoculated
Test Solution

250 mL



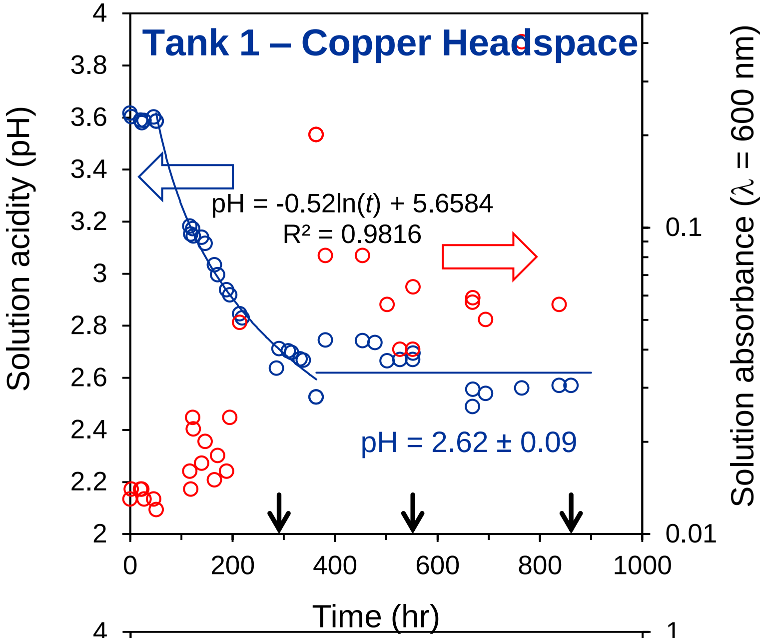
Test
Coupon

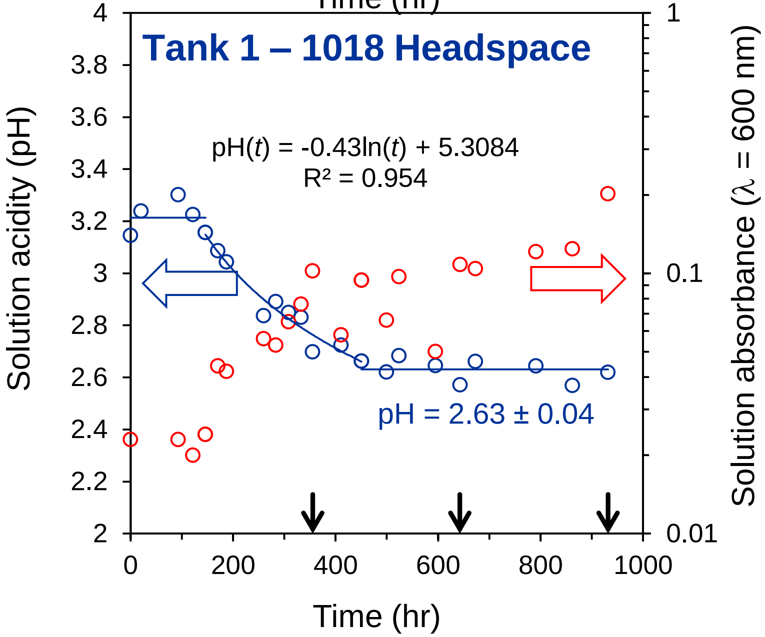
diameter = 19 mm
thickness = 2.8 mm

Coated
QCM

View looking UP
from Tank Bottom

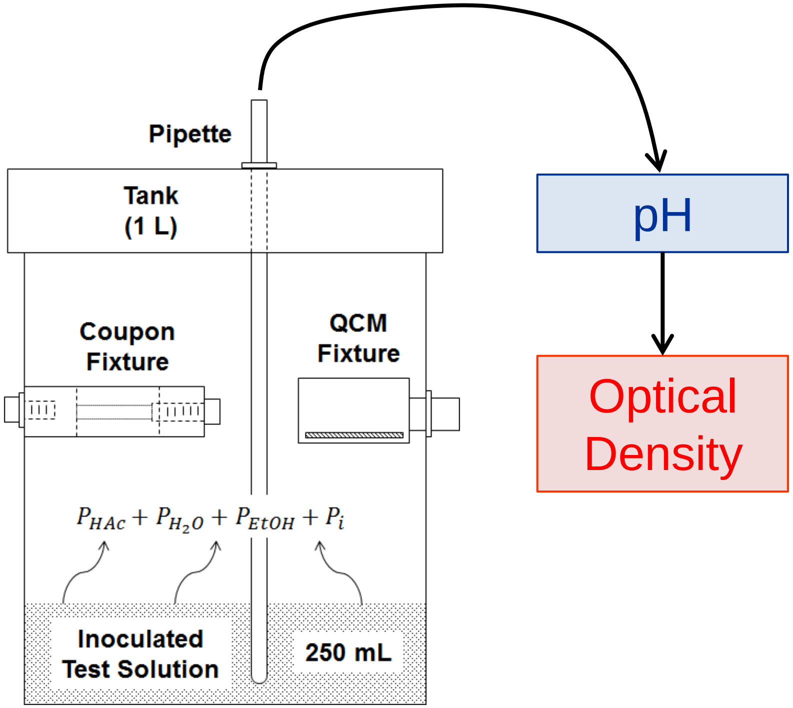
Measuring Bacteria Kinetics





Liquid samples were collected from the tank bottoms daily and acidity and *Acetobacter* cell density were measured.

- The initial pH was slightly higher in the copper tests; however, both series of tests decayed to similar pH levels in the solution.
- The tanks produced repeatable bacteria behavior in copper and steel corrosion tests.



Headspace Acetic Acid Concentration

The concentration of acetic acid in solution is dependent on pH according to:

$$\log[HAc] = -1.8561pH + 4.9674$$

Acetic acid vapor pressure is temperature-dependent (22 °C):

$$\log(P_0) = 4.68206 - \frac{1642.54}{-39.764 + T}$$

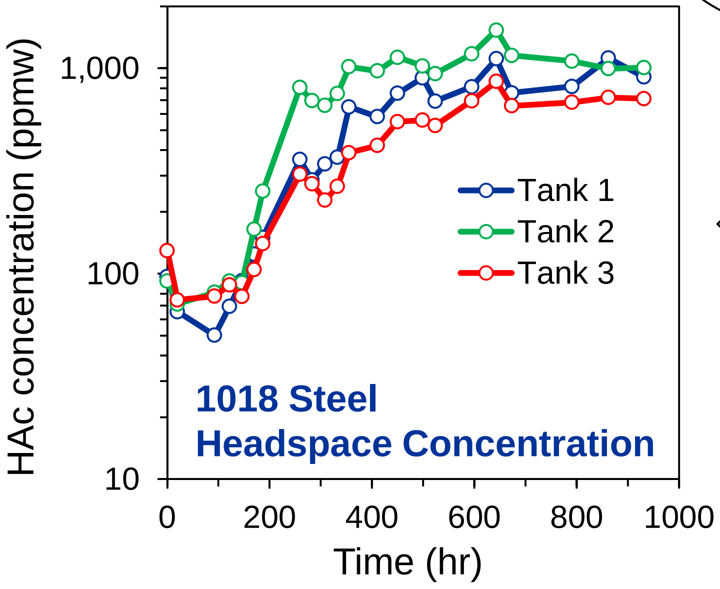
We assume that the partial pressure of acetic acid obeys Raoult's Law:

$$P_{HAc} = \chi_{HAc} \cdot P_0$$

The headspace is assumed to be an ideal gas:

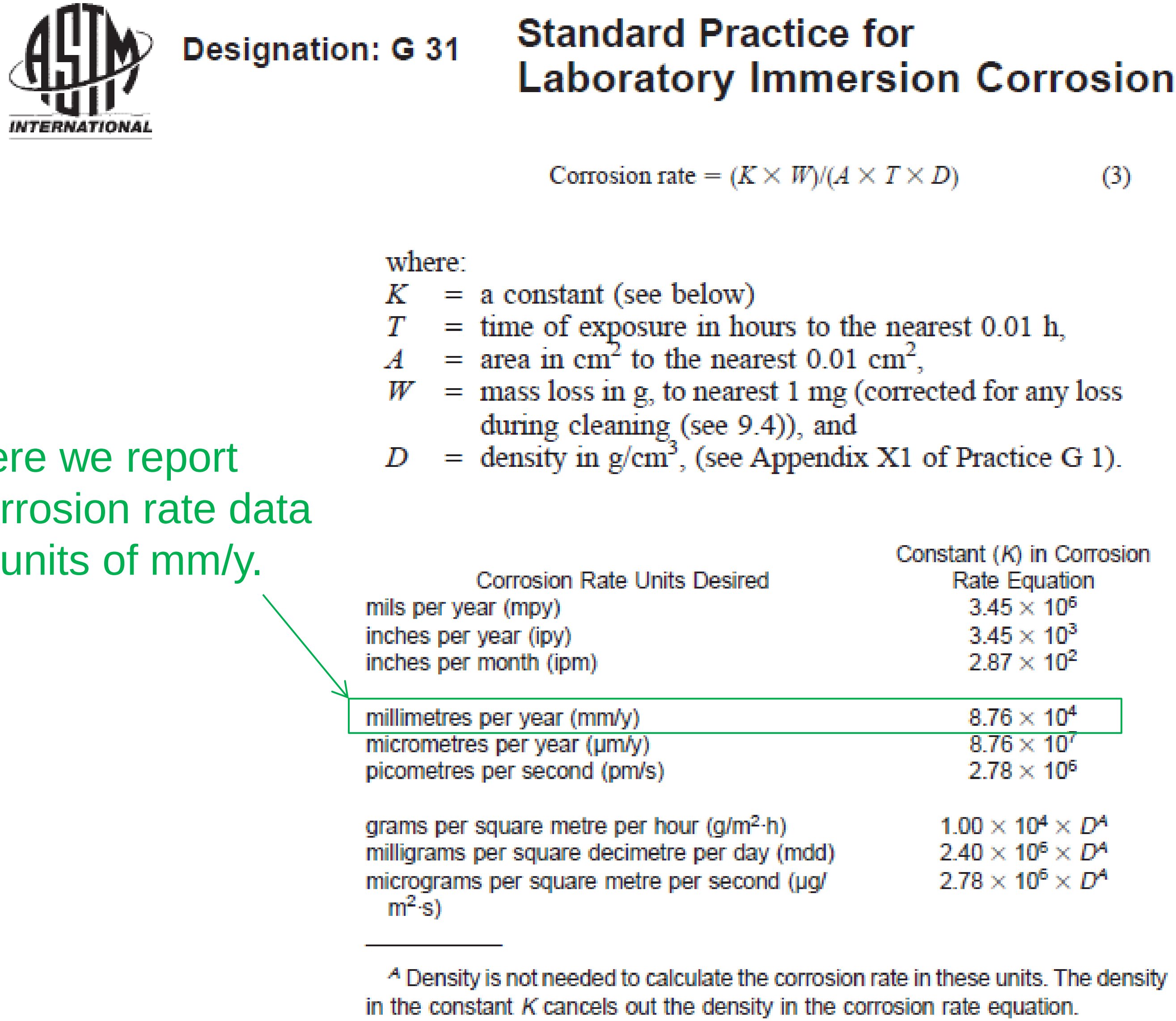
$$m_{HAc} = 10^6 \frac{P_{HAc} \cdot MW_{HAc}}{P_{air} \cdot MW_{air}}$$

P_{air} ≈ 650 mmHg in Boulder, CO
(15 % lower than at sea level)



- A solution with pH = 2.6 has an acetic acid concentration of 1.4 M and approximately 1000 ppmw in the space above the solution.

Corrosion Rate Measurements



Designation: G 31

Standard Practice for Laboratory Immersion Corrosion Testing of Metals

$$\text{Corrosion rate} = (K \times W)/(A \times T \times D) \qquad (3)$$

where:

K = a constant (see below)
T = time of exposure in hours to the nearest 0.01 h,
A = area in cm^2 to the nearest 0.01 cm^2,
W = mass loss in g, to nearest 1 mg (corrected for any loss during cleaning (see 9.4)), and
D = density in g/cm^3, (see Appendix X1 of Practice G 1).

Corrosion Rate Units Desired	Constant (K) in Corrosion Rate Equation
mils per year (mpy)	3.45×10^6
inches per year (ipy)	3.45×10^3
inches per month (ipm)	2.87×10^2
millimetres per year (mm/y)	8.76×10^4
micrometres per year (µm/y)	8.76×10^7
picometres per second (pm/s)	2.78×10^6
grams per square metre per hour ($g/m^2 \cdot h$)	$1.00 \times 10^4 \times D$[A]
milligrams per square decimetre per day (mdd)	$2.40 \times 10^6 \times D$[A]
micrograms per square metre per second ($µg/m^2 \cdot s$)	$2.78 \times 10^6 \times D$[A]

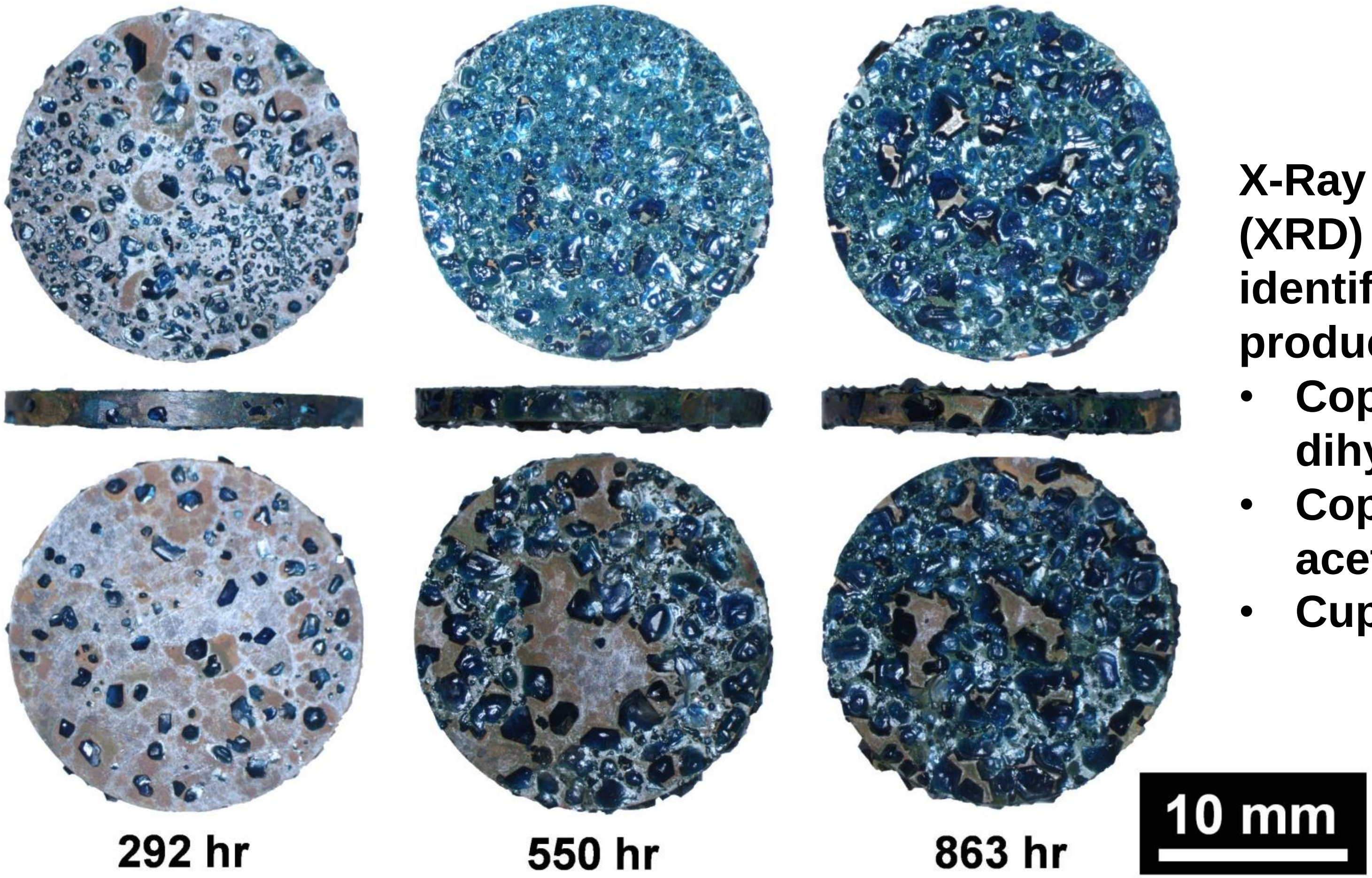
[A] Density is not needed to calculate the corrosion rate in these units. The density in the constant K cancels out the density in the corrosion rate equation.

Here we report corrosion rate data in units of mm/y.

Copper and Carbon Steel

HEADSPACE CORROSION

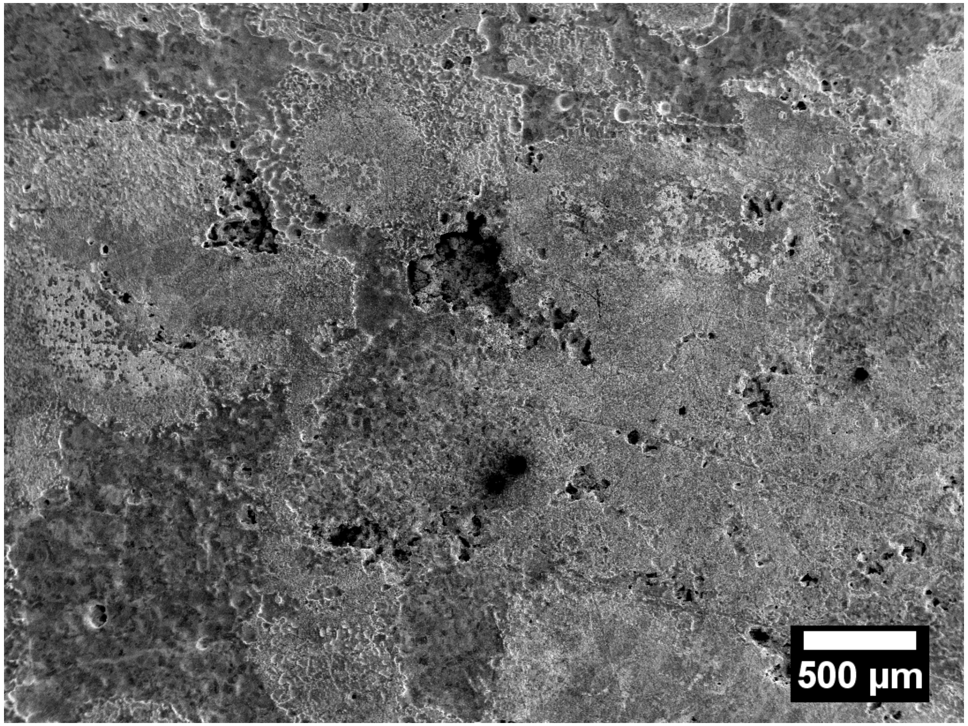
Copper Corrosion After Headspace Exposure



X-Ray Diffraction (XRD) was used to identify corrosion products:

- Copper acetate dihydrate
- Copper hydroxide acetate
- Cuprite

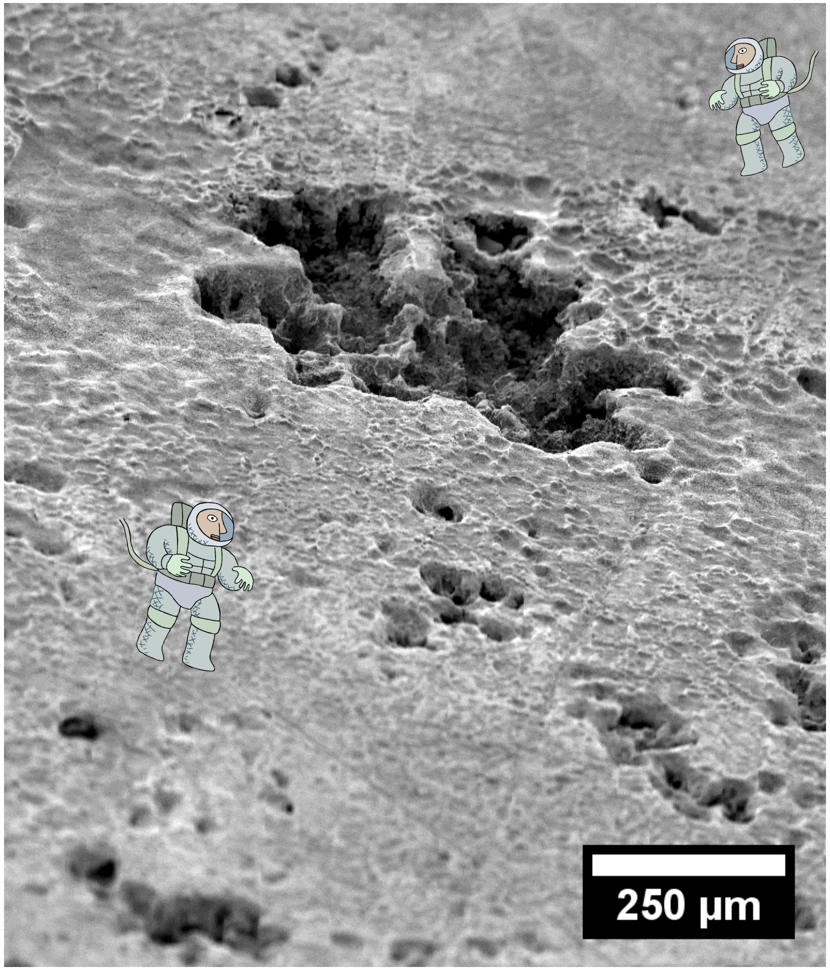
Headspace Corrosion Morphology



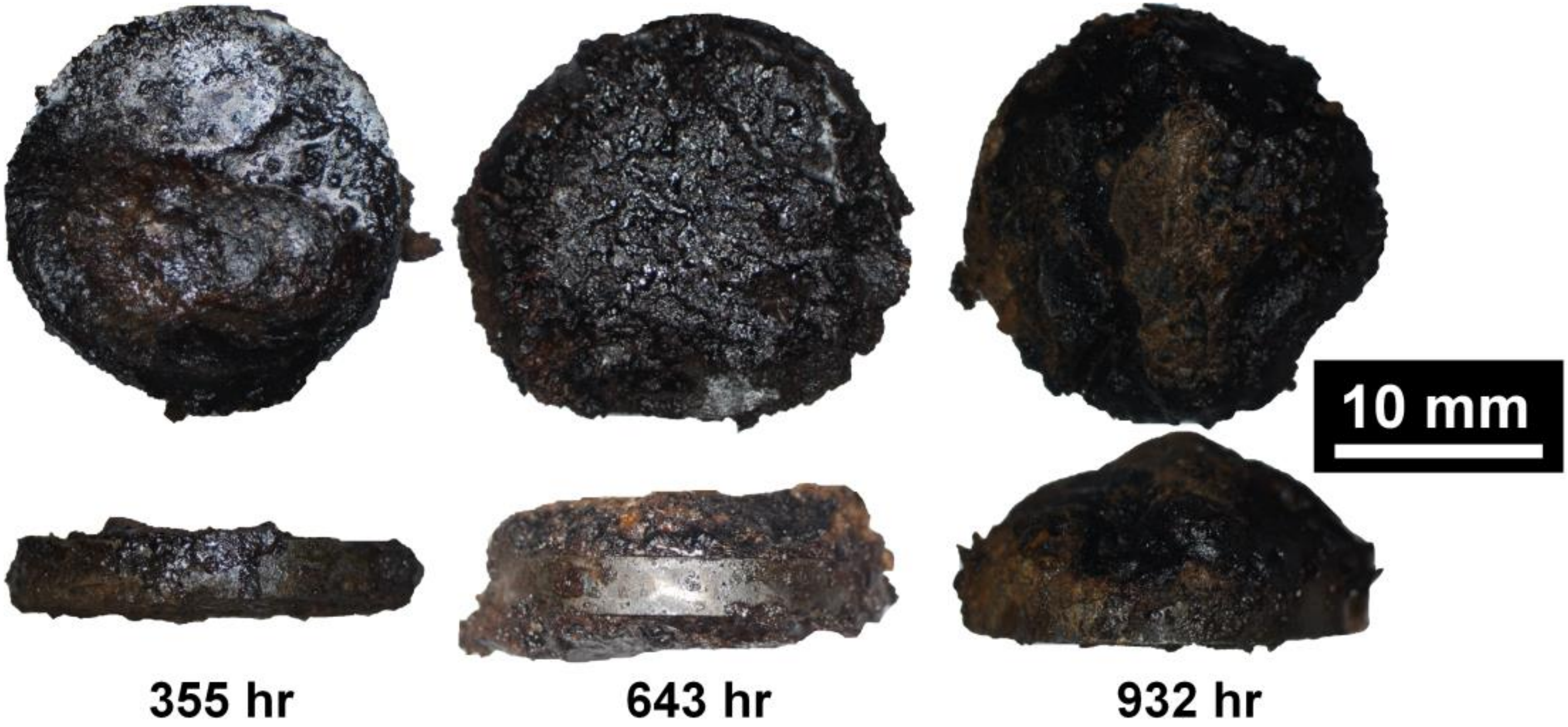
Removal of copper acetate revealed that general corrosion and pitting corrosion occurred under the crystals.

Small pits coalesced into larger pits with a wide, shallow appearance.

Pit Depth: Pit Width ≈ 1:2



Steel Corrosion After Headspace Exposure

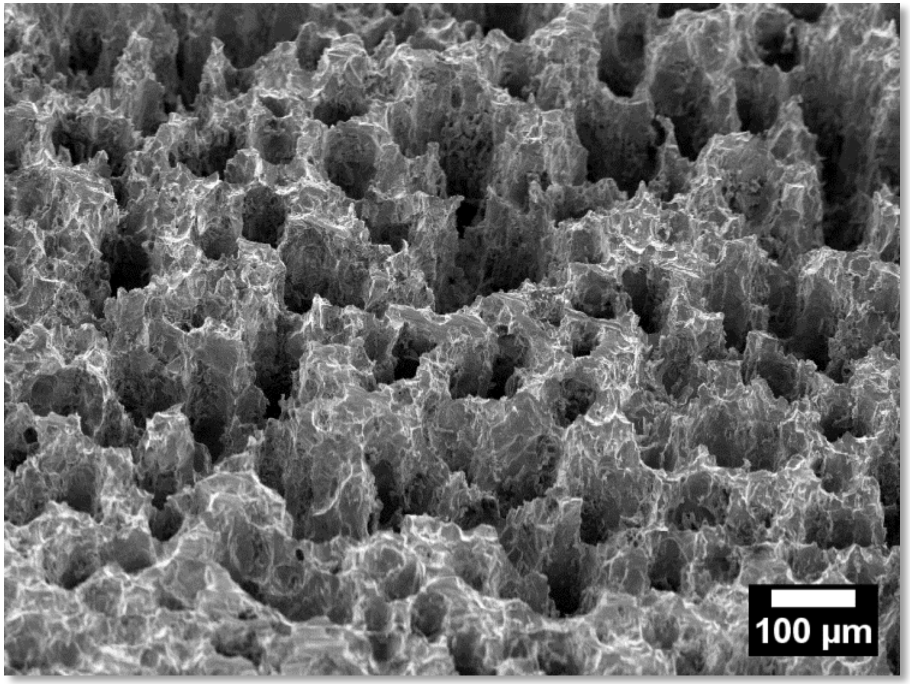


Corrosion product on the steel grew in thickness with longer exposure periods, and flaked easily from the coupons.

XRD was used to identify corrosion products:

- Iron oxides
- Iron hydroxides

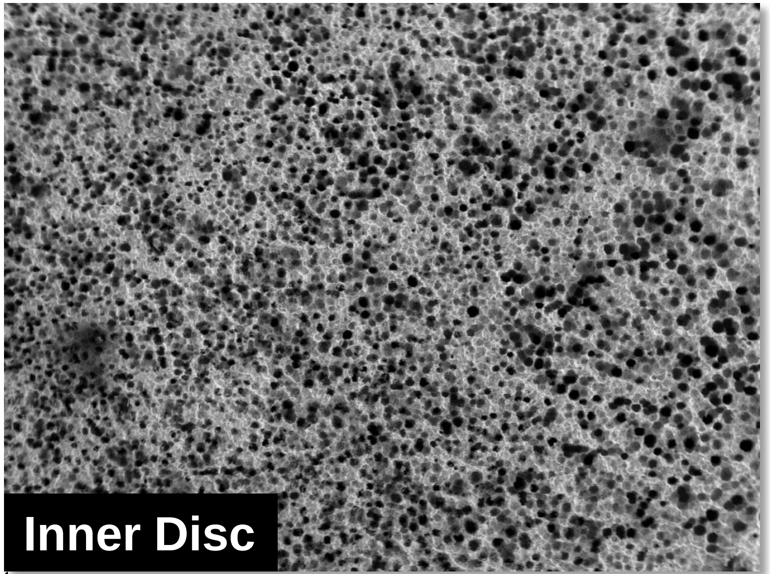
Headspace Corrosion Morphology

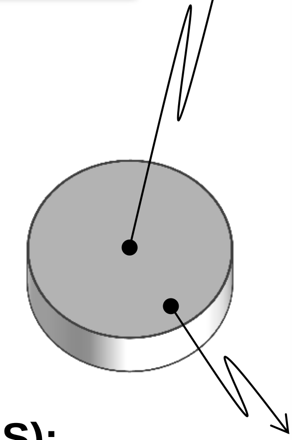


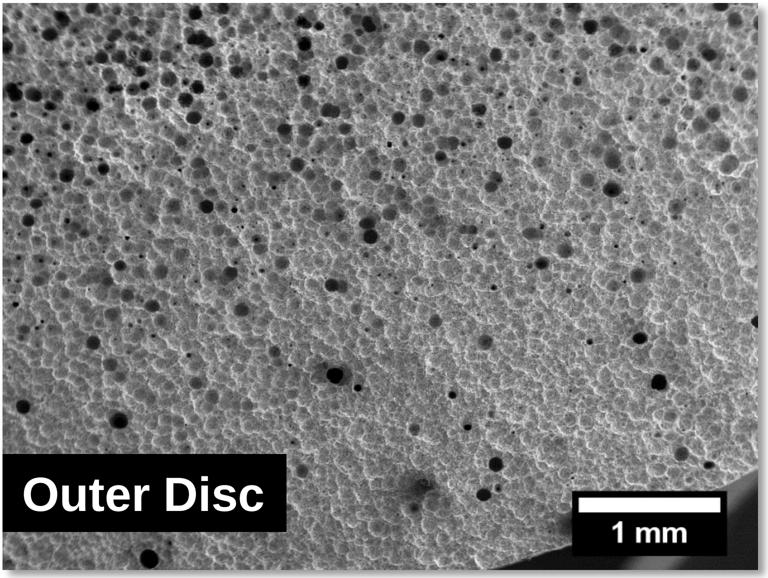
Removal of iron oxidation products revealed general pitting corrosion underneath.

Pit density varied spatially about the radial direction of the coupons.

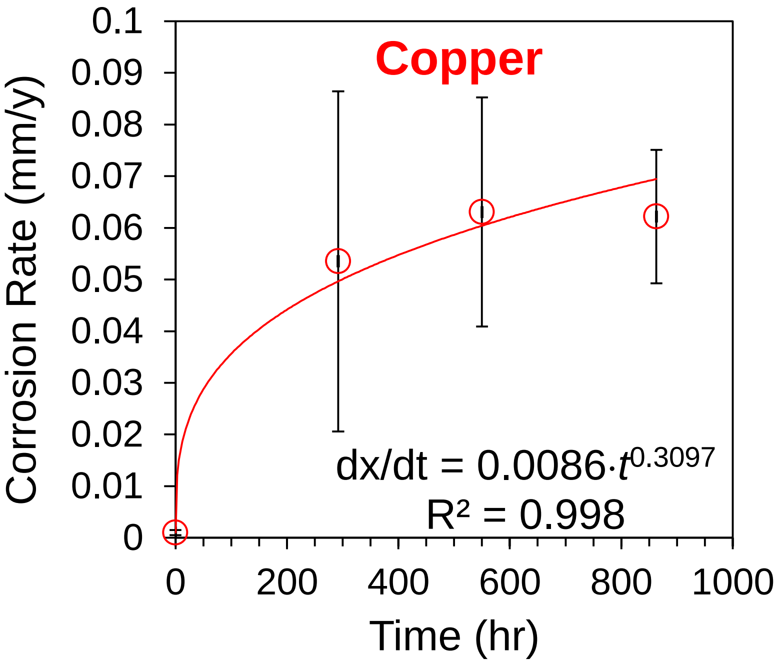
Pit initiation appear to be associated with non-metallic inclusions (e.g. MnS); therefore, alloy sulfur content may play an important role in pitting.

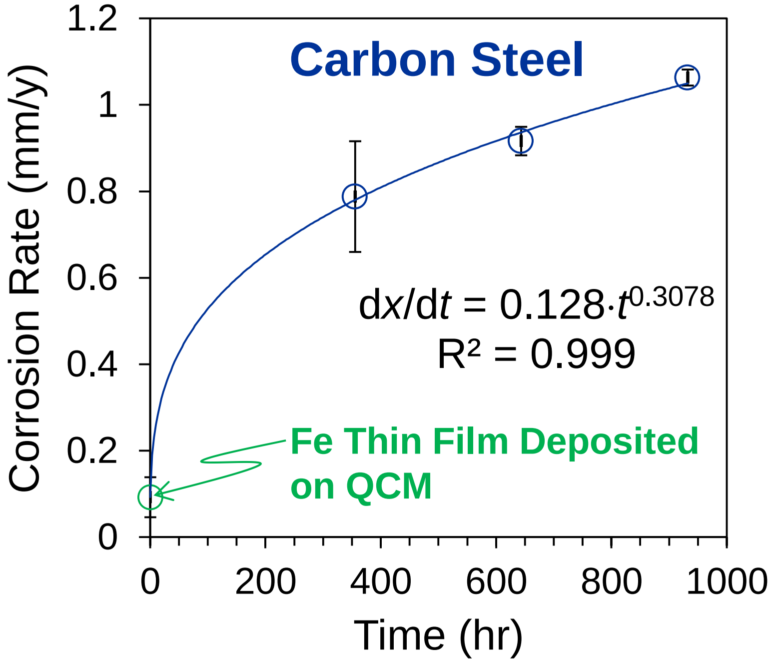






Headspace Corrosion Rate & Model





Fe Thin Film Deposited on QCM

Atmospheric Corrosion Empirical Model[1]

$$\frac{\Delta x}{\Delta t} = A_0 \cdot t^n$$

[1] C. Leygraf. Atmospheric Corrosion (2007).

$\Delta x/\Delta t$ = corrosion rate (mm/y)
A_0 = initial corrosion rate (mm/y)
t = exposure time (hr)

Lower $n \propto$ greater protectiveness of surface film

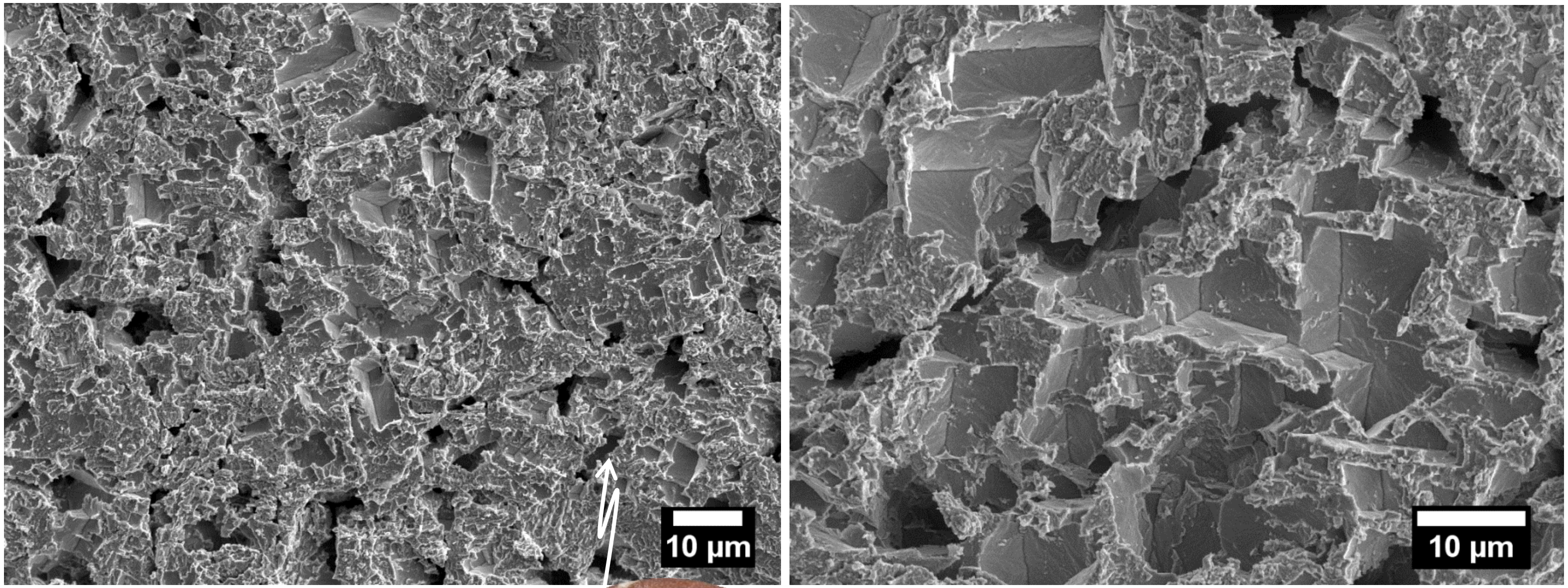
Material	A_0 (mm/y)	n	R^2
Copper	8.6×10^{-3}	0.3097	0.998
Steel	128×10^{-3}	0.3078	0.999

Copper and Carbon Steel

MIC IN AQUEOUS ETHANOL SOLUTION (SUMP BOTTOM)

Copper Corrosion Damage

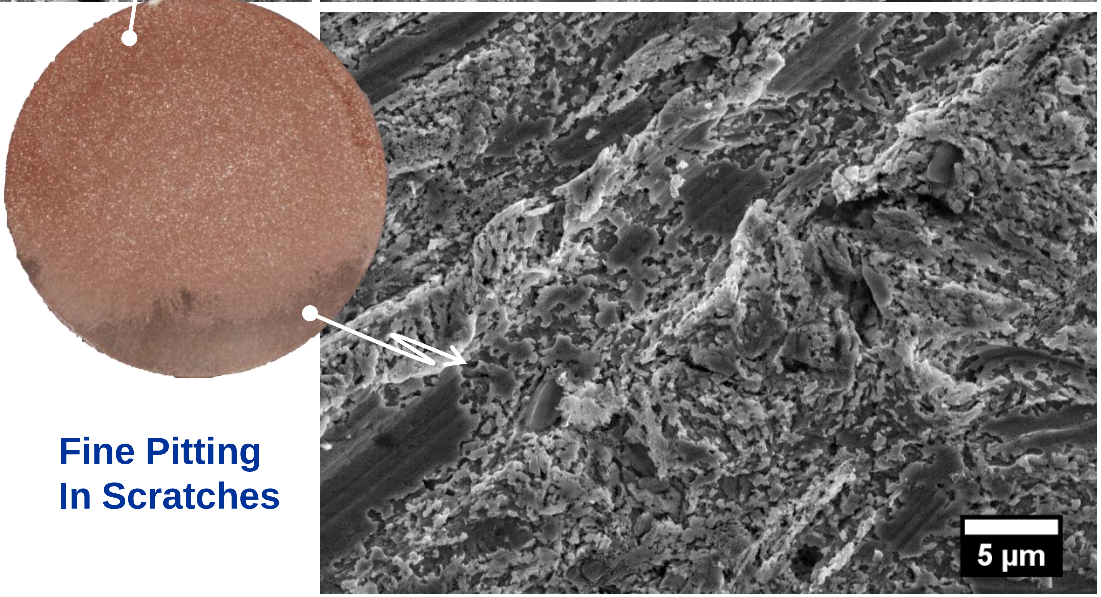
Intergranular Attack



Corrosion rate after 36 days exposure was:

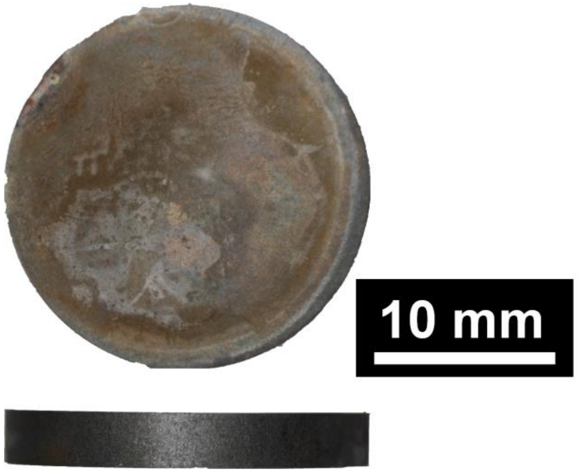
0.051 mm/y ± 0.010 mm/y

Deep intergranular attack was observed indicating that stress-corrosion cracking may lead to greatly accelerated perforation of copper tubing.



Fine Pitting In Scratches

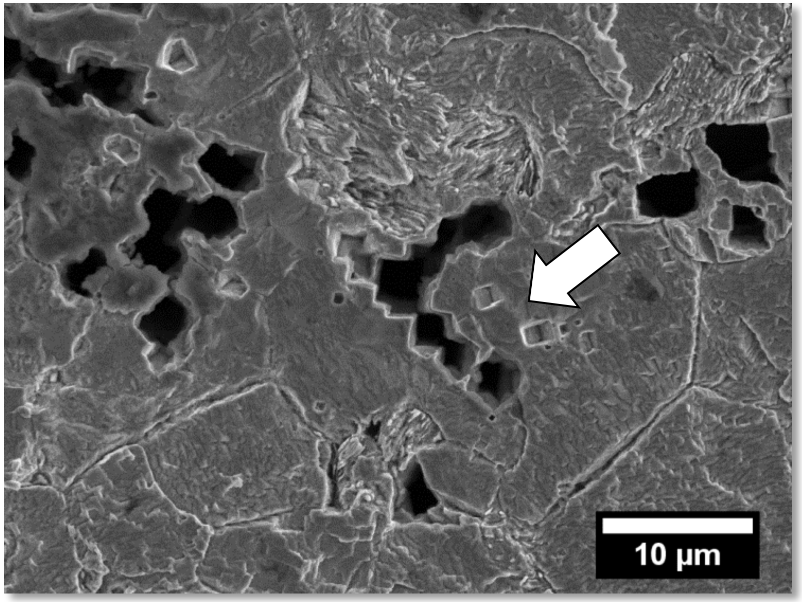
Steel Corrosion Damage



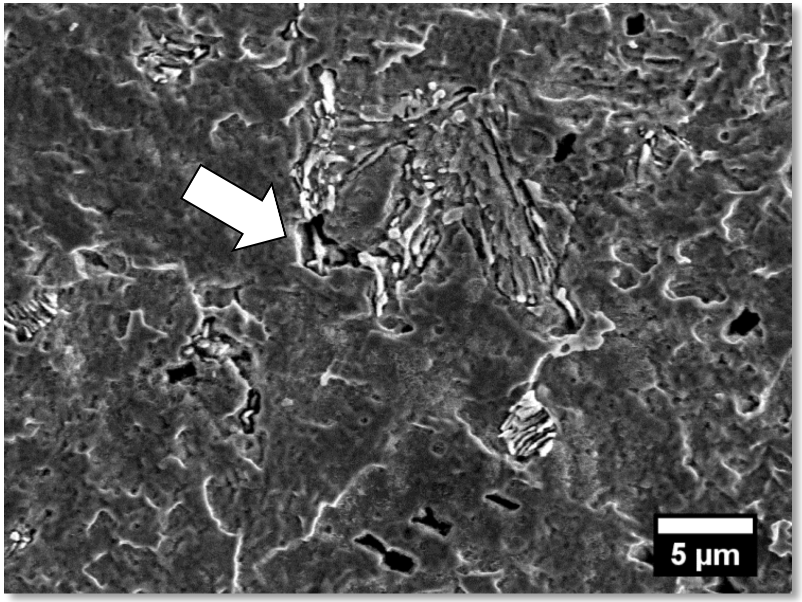
Corrosion rate after 39 days exposure was:
0.061 mm/y ± 0.003 mm/y

This is comparable to the copper headspace and immersion coupons. Such a low rate may be related to bacterial attachment, which could protect the steel by a passivation mechanism. However, the surface was covered with pits within ferrite grains, although some attack at interphase boundaries was noted.

Dislocation Etch Pits



Pearlite Boundary Attack



Summary

- In a controlled laboratory environment, *Acetobacter* sp. produced corrosion damage similar to that seen on UST sump components during field inspections.
- Corrosion rates of Copper and Steel alloys were measured after headspace exposure and exposure to inoculated ethanol growth solution.

Copper Corrosion

- Corrosion rates of ~0.06 mm/y were measured in the headspace and while immersed in solution.
- At this rate it would take ~15 years to corrode through a copper tube with 1.2 mm wall thickness.
- Localized corrosion was observed on the cold-worked copper material! Therefore, stress-corrosion cracking is a likely concern in bent copper tubing and would greatly reduce the tubing life and lead to leakage.

Steel Corrosion

- Corrosion rates of Steel in the headspace were severe(> 1 mm/y).
- The submersible pump casings are steel (or cast iron) and total replacement will be both necessary and costly at thousands of filling stations.
- *Acetobacter* Biofilm may actually decrease corrosion as demonstrated by the low corrosion rate of steel (~0.06 mm/y) while immersed in the solution.

- We developed a test method that can be used to screen materials and assess various techniques to prevent corrosion.

What Next?

- Standard Practices for Headspace Biocorrosion Testing
- Biocide Efficacy
  - Glutaraldehyde has already shown effectiveness in controlling *Acetobacter* corrosion of steel
- Coatings
  - Organic coatings need good acid resistance and good solvent resistance
- Inhibitors
- Headspace Gas Analysis
- *In situ* Monitoring/Detection with e.g., QCM

Test Materials

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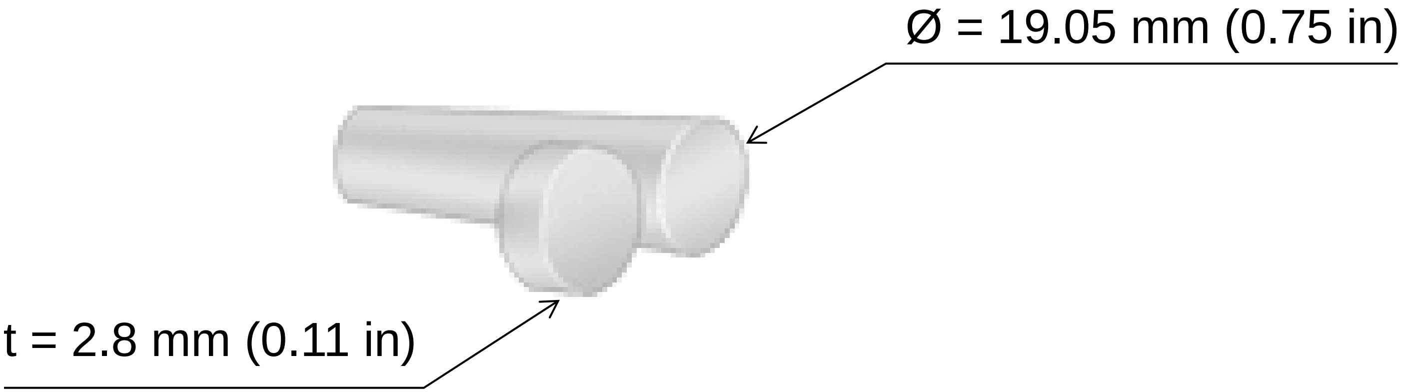

Bacteria Cultures

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- Test Media simulates a mixture of e.g. groundwater and ethanol fuel:
  (5 % Ethanol – 95 % Bacteria Growth Media)
- In the future, we can likely control the microbial activity, and hence the pH by varying the ratio of this mixture. (What is relevant?)

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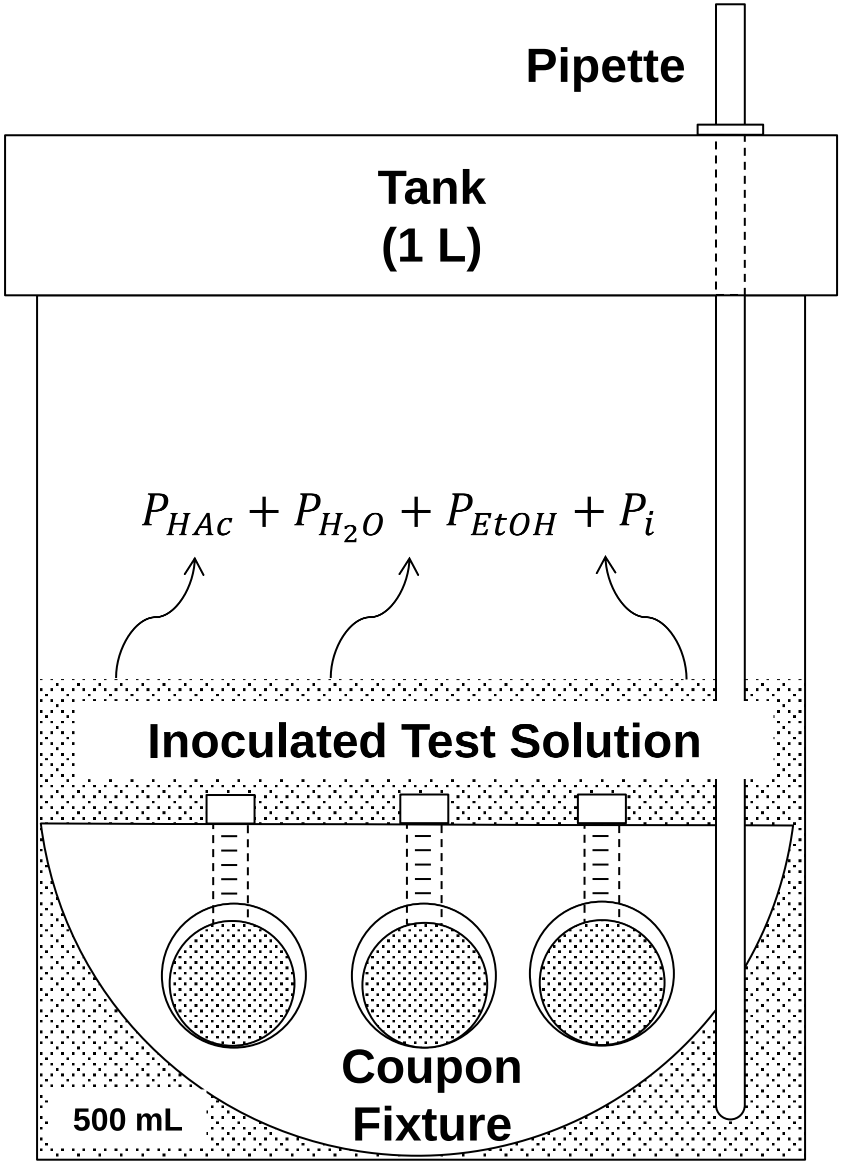
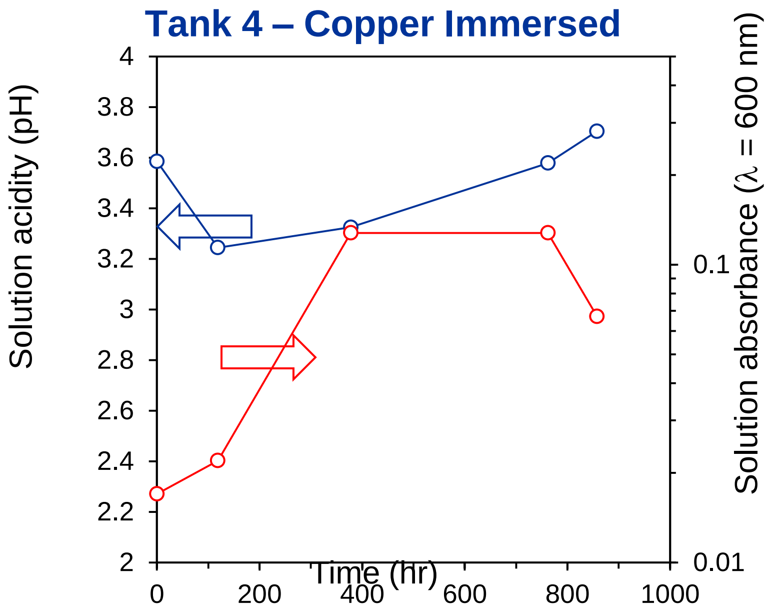
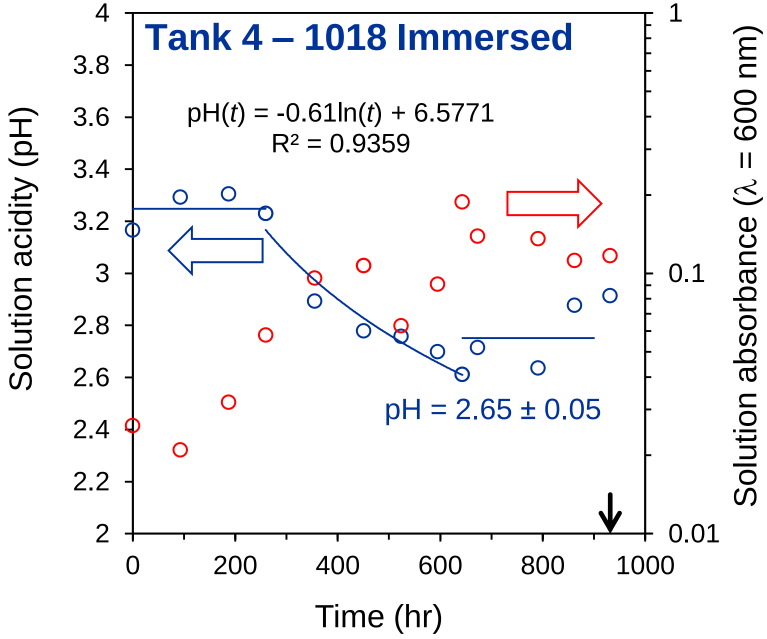
- Pull coupons at regular intervals to investigate transient corrosion behavior
- Maintain culture by periodic feeding with fresh Test Media
- Monitor the solution acidity (pH meter) and solution absorbance with UV-Visible Spectroscopy:
    - $\text{Absorbance}|_{\lambda\,=\,600\text{ nm}} \propto$ bacteria cell count
- Perform tests in triplicate

Immersion Corrosion Test Setup



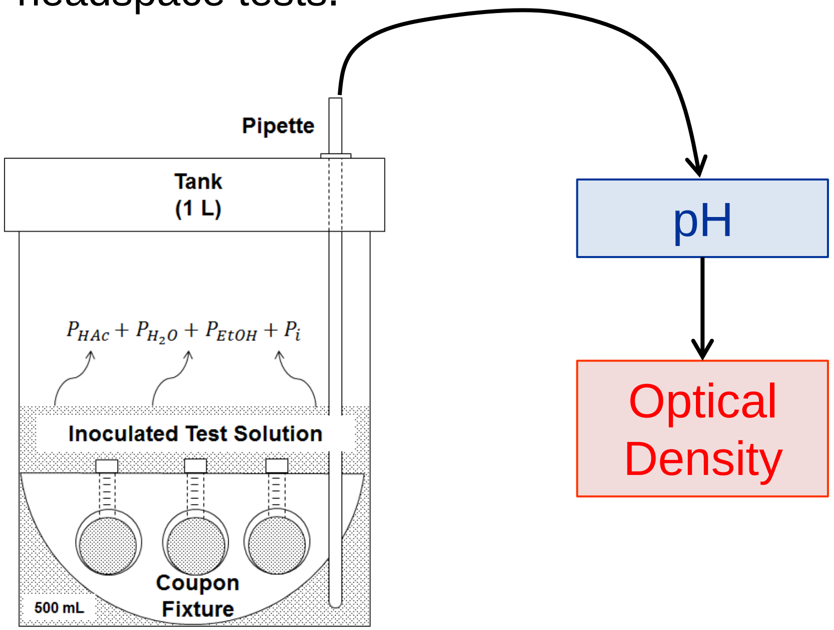
Measuring Bacteria Kinetics


Tank 4 – Copper Immersed

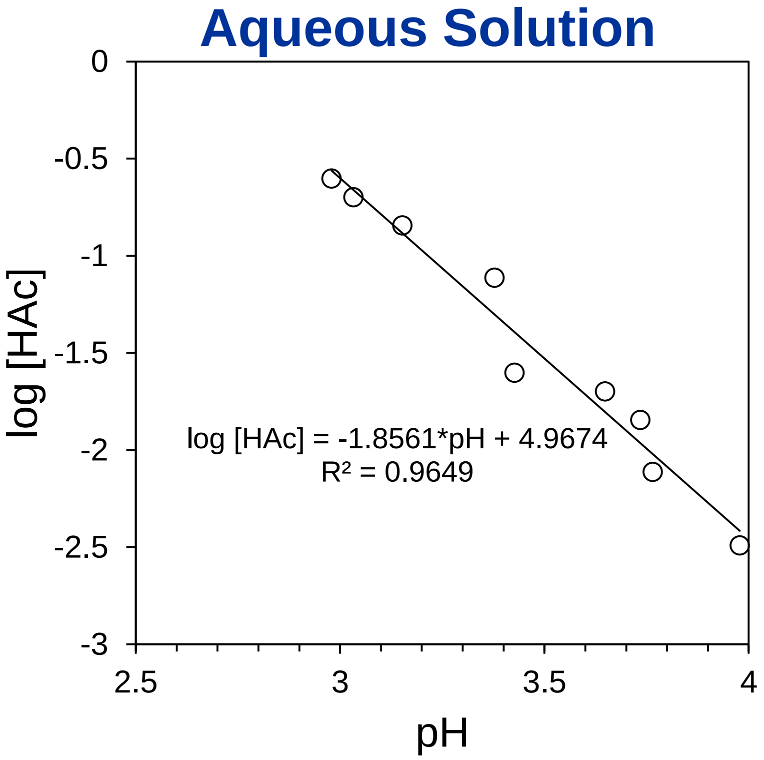

Tank 4 – 1018 Immersed

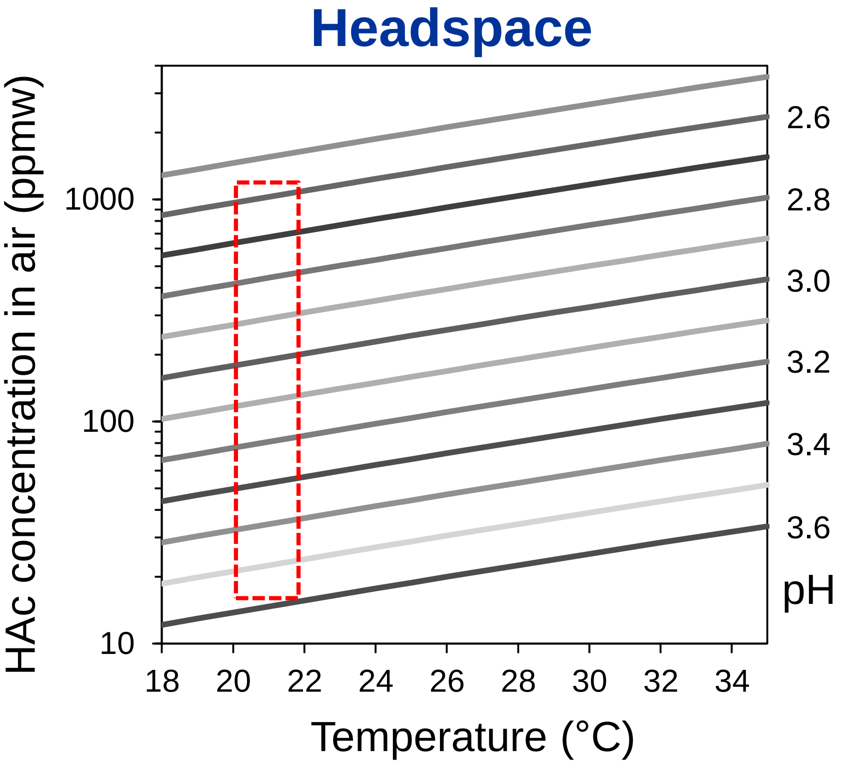
Liquid samples were collected from the tank bottoms and acidity and *Acetobacter* cell density were measured.

- When copper coupons were immersed in the test solution, the pH increased over time and bacteria tended to clump in an unusual morphology. Copper has some antimicrobial properties.
- When steel coupons were immersed, the bacteria kinetics were similar to the headspace tests.



Acetic Acid Concentration





- Acetic acid (HAc) is a weak acid and dissociates only partially in an aqueous-ethanol mixture; therefore, pH is not a direct reading of its concentration.
- Acetic acid headspace concentration is dependent on both temperature and solution pH. We determine concentration with calculations (next slide) and the presented here are merely estimates.

Headspace Acetic Acid Concentration

The concentration of acetic acid in solution is dependent on pH according to:

$$\log[HAc] = -1.8561pH + 4.9674$$

Acetic acid vapor pressure is temperature-dependent (22 °C):

$$\log(P_0) = 4.68206 - \frac{1642.54}{-39.764 + T}$$

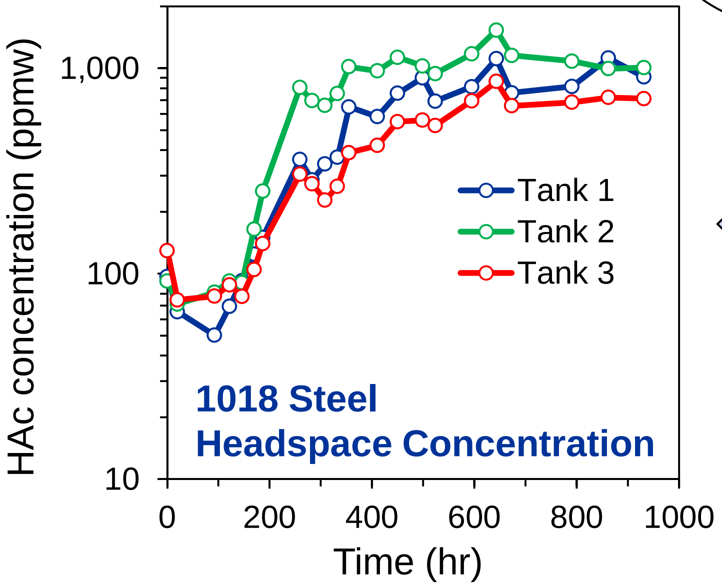
We assume that the partial pressure of acetic acid obeys Raoult’s Law:

$$P_{HAc} = \chi_{HAc} \cdot P_0$$

The headspace is assumed to be an ideal gas:

$$m_{HAc} = 10^6 \frac{P_{HAc} \cdot MW_{HAc}}{P_{air} \cdot MW_{air}}$$

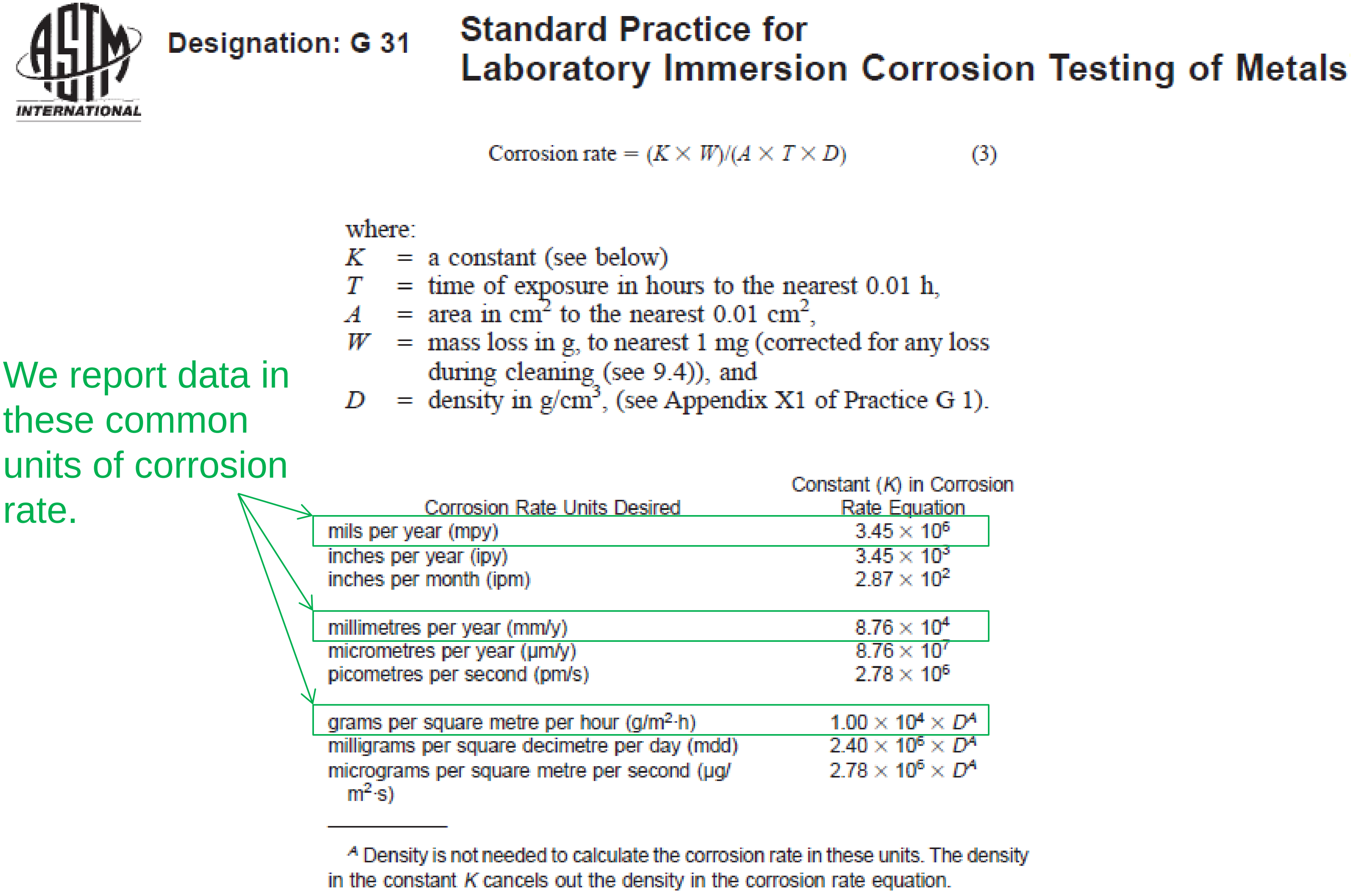
P_{air} ≈ 650 mmHg in Boulder, CO
(15 % lower than at sea level)



- A solution with pH = 2.6 has an acetic acid concentration of 1.4 M and approximately 1000 ppmw in the space above the solution.

Calculating Corrosion Rate

We report data in these common units of corrosion rate.



Designation: G 31

Standard Practice for Laboratory Immersion Corrosion Testing of Metals

$$\text{Corrosion rate} = (K \times W)/(A \times T \times D) \quad (3)$$

where:

K = a constant (see below)

T = time of exposure in hours to the nearest 0.01 h,

A = area in cm^2 to the nearest 0.01 cm^2,

W = mass loss in g, to nearest 1 mg (corrected for any loss during cleaning (see 9.4)), and

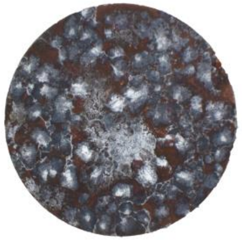
D = density in g/cm^3, (see Appendix X1 of Practice G 1).

Corrosion Rate Units Desired	Constant (K) in Corrosion Rate Equation
mils per year (mpy)	3.45×10^6
inches per year (ipy)	3.45×10^3
inches per month (ipm)	2.87×10^2
millimetres per year (mm/y)	8.76×10^4
micrometres per year (µm/y)	8.76×10^7
picometres per second (pm/s)	2.78×10^6
grams per square metre per hour ($g/m^2 \cdot h$)	$1.00 \times 10^4 \times D^A$
milligrams per square decimetre per day (mdd)	$2.40 \times 10^6 \times D^A$
micrograms per square metre per second ($\mu g/m^2 \cdot s$)	$2.78 \times 10^6 \times D^A$

[A] Density is not needed to calculate the corrosion rate in these units. The density in the constant K cancels out the density in the corrosion rate equation.

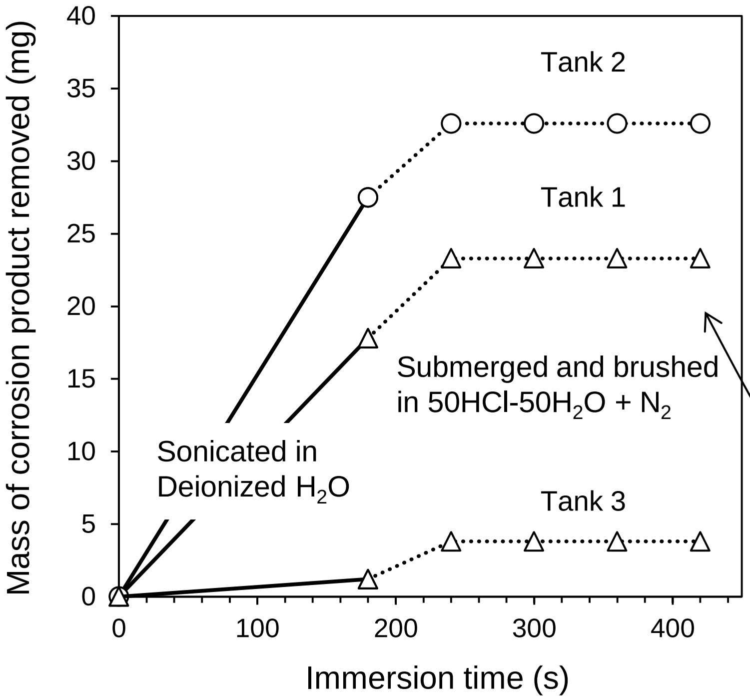
Corrosion Product Removal Procedure

As-tested condition removed from Tank 2

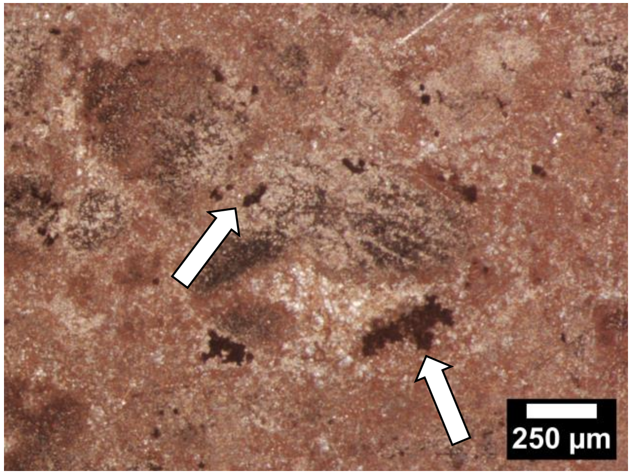


Sonicated for 3 minutes in Deionized Water

Brushed for 4 minutes in HCl/H_2O Solution



Removal of corrosion product reveals extensive pitting corrosion underneath the corrosion product.

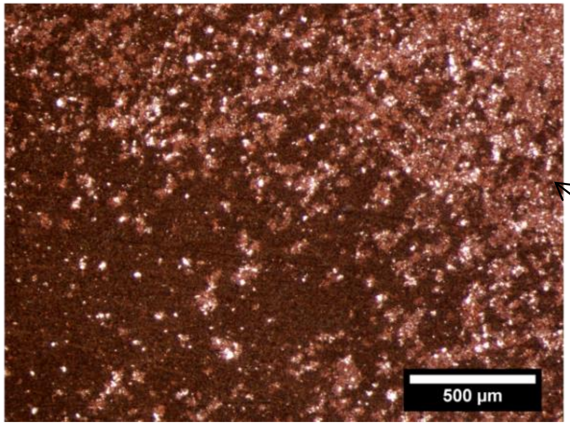


The cleaning process removes the corrosion product but does not corrode the underlying metal.

- **Blue crystals are removed with sonication**
- **Silver-colored corrosion product is more tenacious, and is removed mechanically and chemically by brushing in HCl/H_2O Solution**

Copper Corrosion After Immersion

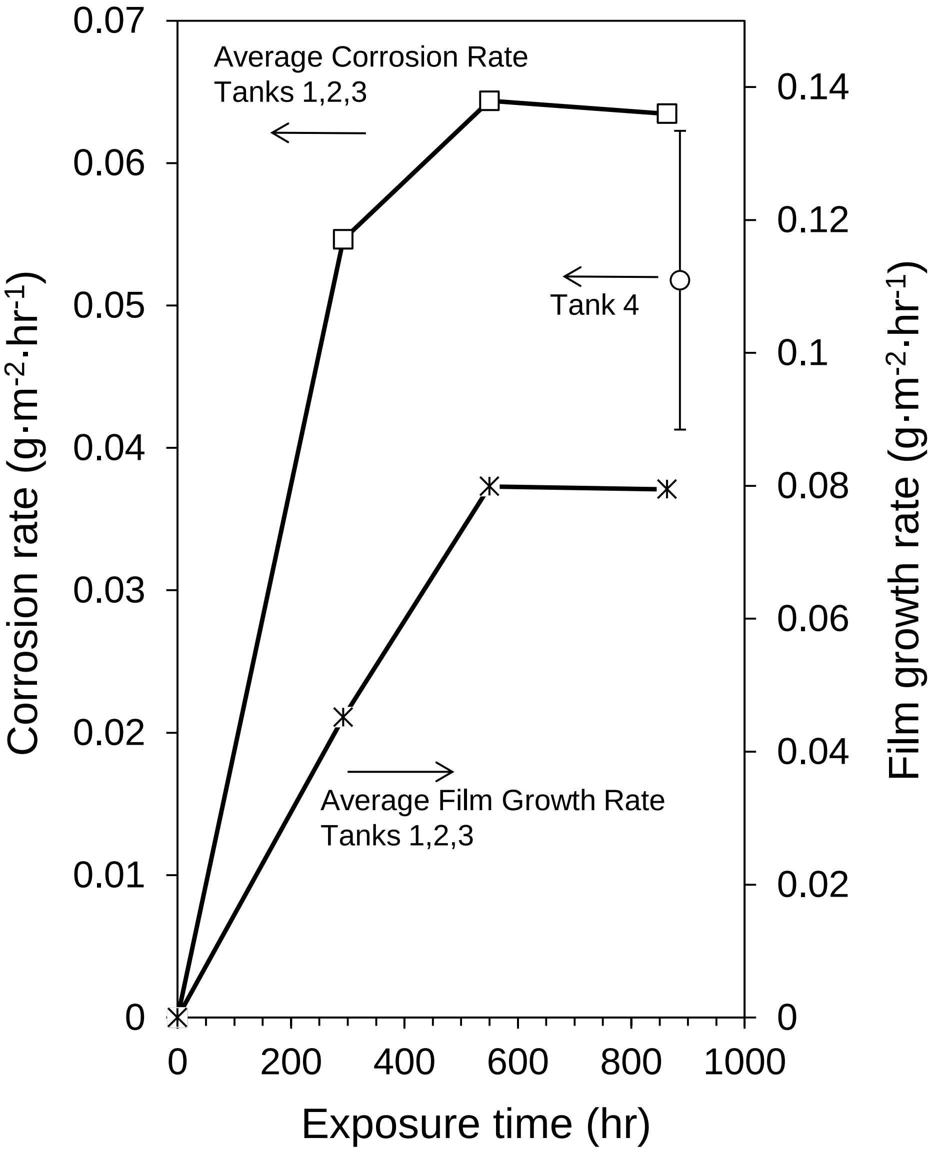
TANK 4



Surface Pitting

Corrosion was not as extensive on the immersion coupons as compared to the headspace coupons. Pit morphology exhibited a shallow and coalesced appearance. The test solution notably turned a blue color during testing, indicating the presence of dissolved copper acetate.

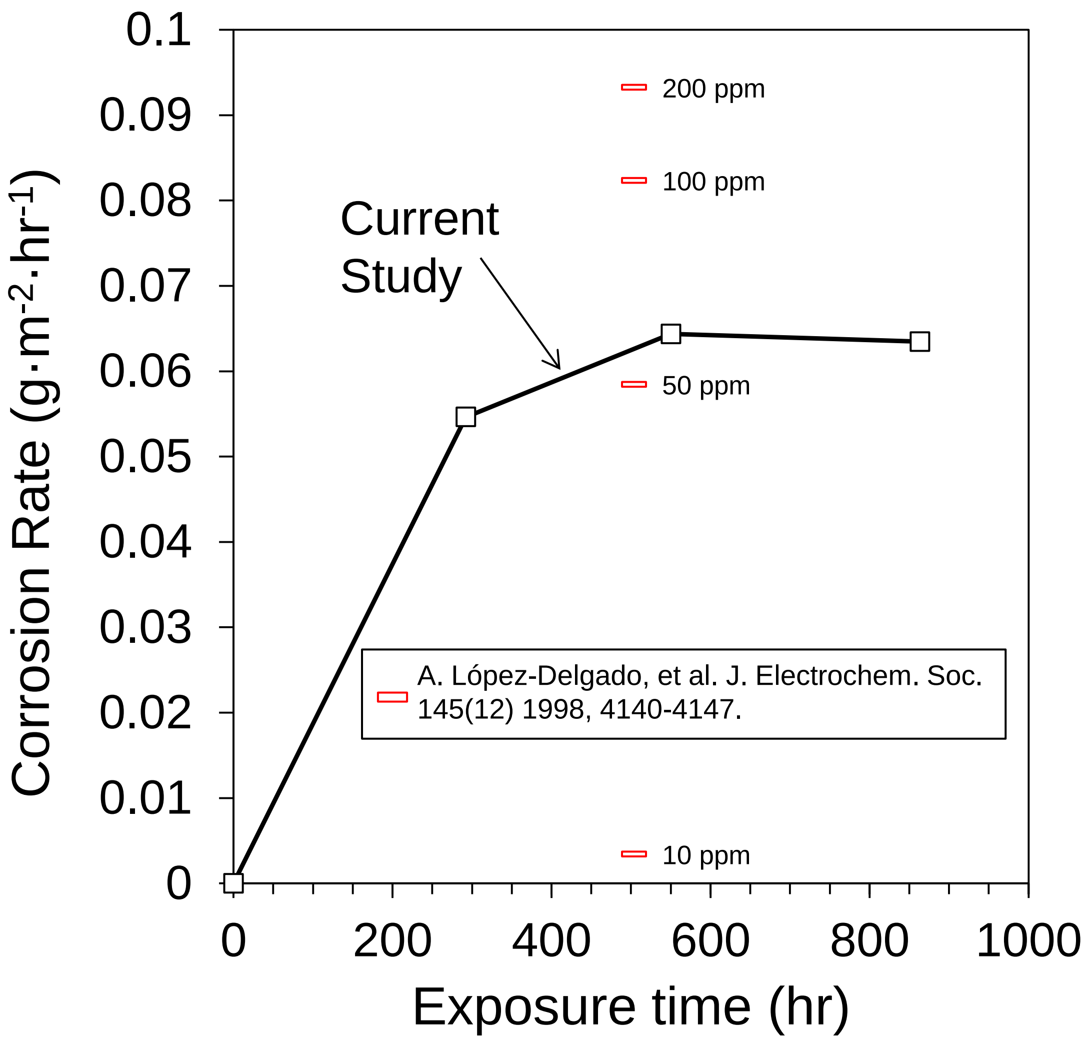
Copper Corrosion Rate



Corrosion rate and film growth rate in the headspace (Tanks 1, 2, 3) exhibit a plateau above a certain exposure period. This suggests that the copper corrosion rate increased until coupon surface was covered with the bluish corrosion product (i.e., a *steady-state* condition was achieved).

- Film growth rate is slightly higher than corrosion rate since mass is added to the system when acetate is captured at the copper surface.
- Immersed coupons (Tank 4) exhibited slightly lower corrosion rates compared to the headspace coupons.
- A typical corrosion rate of copper in water is about ~0.0025 mm/y (~0.1 mpy)
- An “acceptable” corrosion rate of copper in an open-loop system is typically less than 0.025 mm/y (<1.0 mpy)
- Corrosion rate of copper here is ~0.08 mm/y (~3.3 mpy)

Copper Corrosion in Biotic and Abiotic Acetic Acid Vapor

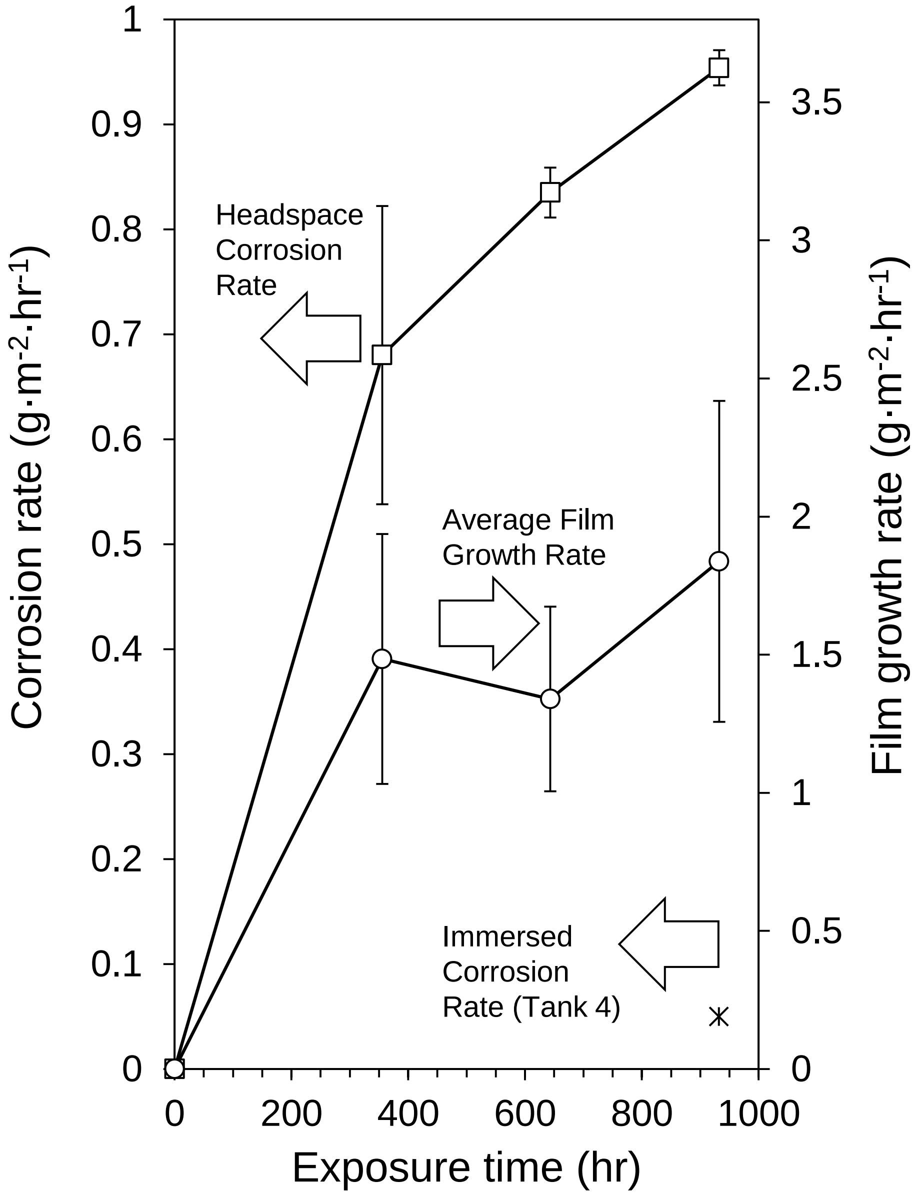


A comparison with abiotic acetic acid corrosion of copper is made here. Estimates based on this comparison suggest bacteria could produce acetic acid vapor concentrations in the range of 50 to 100 ppmw although calculated values suggest we may have significantly higher levels.

We have plans to develop a method for sampling the headspace[1] to determine acetic acid concentration. This could be used to monitor microbial activity and to develop a tank corrosion sensor.

1. T.J. Bruno. *J. Chromatogr. Sci.*, 47 2009, 569-574.

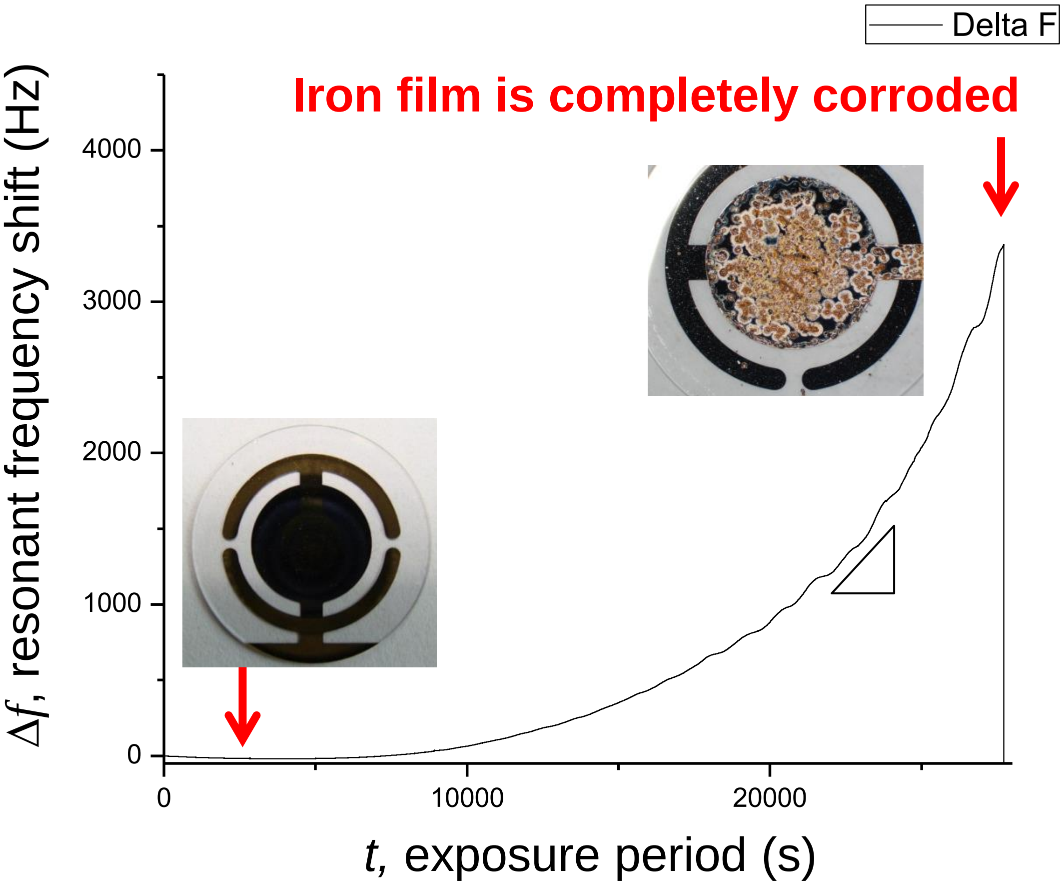
Steel Corrosion Rate



Corrosion rate likely has some dependence of the film growth as seen in the copper corrosion.

- Corrosion rate of 1018 steel coupons exposed to headspace was an order of magnitude greater than copper in the headspace and continuously increased with exposure time. (> 1 mm/y !!!)
- Film-growth rate on headspace coupons is higher since mass is added to the system when iron oxidation products are captured by the steel surface.
- Immersed coupons exhibited significantly lower corrosion rates than in the headspace. Microbial attachment (formation of a biofilm) may play a role in this behavior.

Corrosion of Fe Thin Film Sensor



Iron film is completely corroded

We deposit thin Fe films onto quartz crystals. The crystals are excited with an oscillating voltage so that they vibrate at their resonant frequency. The mass of the crystal can be measured real-time by monitoring the shift in the resonant frequency.

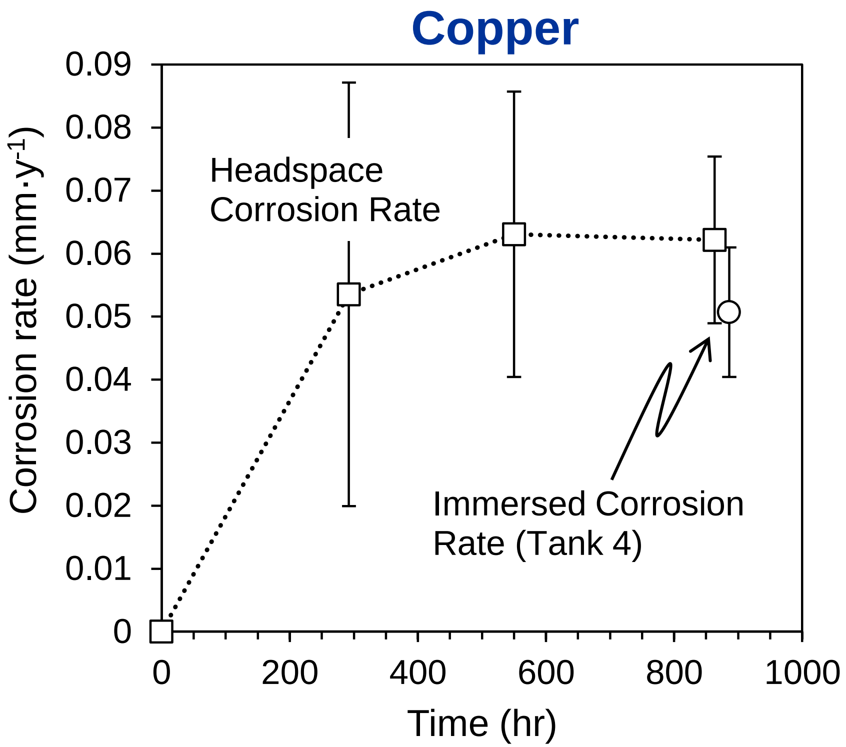
Mass change occurs due to oxidation of the thin iron layer as evident by the frequency shift.

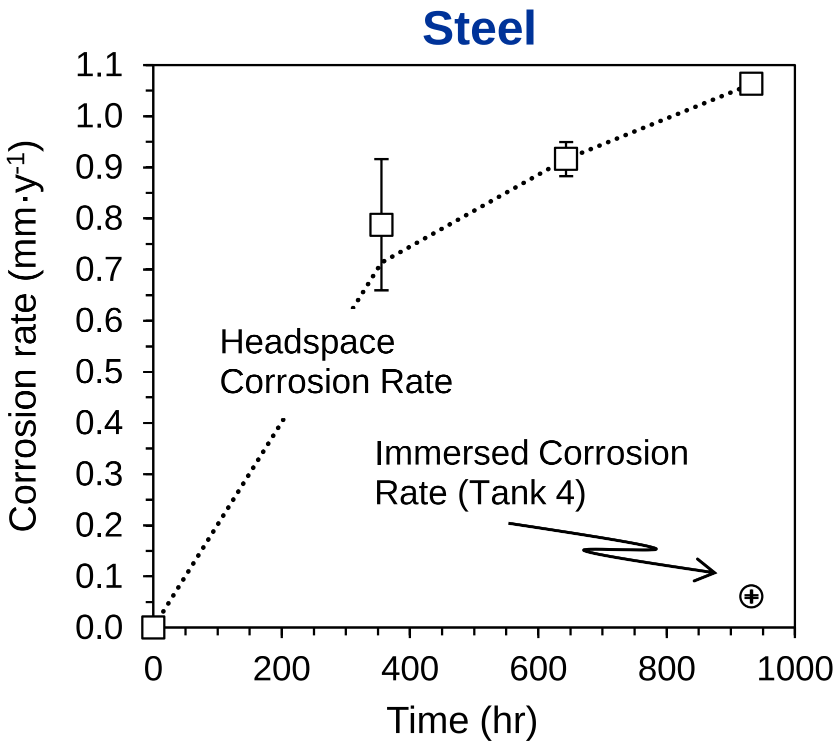
Sensor technology could be used as an early warning system for the onset of corrosion or to study corrosion in the field.

Constants

$$\Delta f = -\boxed{\frac{2{f_0}^2}{A\sqrt{\rho_q \mu_q}}} \cdot \boxed{\Delta m} \longrightarrow \frac{\Delta m}{\Delta t \cdot Area} = corrosion\ rate$$

Corrosion Rate in "Practical Units"





- Copper corrosion rate was up to ~0.08 mm/y in the headspace. It would take 15 years to corrode through copper tubing with 1.2 mm wall thickness.
- Deep grain-boundary attack was observed on the cold-worked copper immersed in solution!
- Stress-corrosion cracking is a likely concern, which would likely reduce the tubing life and lead to leakage of fuel into the environment and into the sump.

- Steel corrosion rate was above 1.0 mm/y in the headspace! This is an order of magnitude higher than that of the copper.
- Corrosion rate was lowest when the steel was immersed into the bacteria solution (~0.06 mm/y). This may be related to biofilm attachment on the steel corrosion coupons.

Summary

- In a controlled laboratory environment, *Acetobacter* sp. produce corrosion damage similar to that seen on UST sump components during field inspections
- Corrosion rates of Copper were measured in the headspace and immersed in inoculated ethanol growth solution
  - A general corrosion rate of ~0.08 mm/y was measured in the headspace and 0.06 mm/y immersed in solution.
  - 15 years would be needed to corrode through a copper pipe of 1.2 mm wall thickness <u>from the outside.</u>
  - Localized corrosion was observed on the cold-worked copper material! Therefore, stress-corrosion cracking is a likely concern in bent copper tubing and would greatly reduce the tubing life and lead to leaks, which exacerbate the MIC.
- Corrosion rates of Steel were measured and the data show severe corrosion in the headspace (> 1 mm/y)
  - The pump casings are steel (or cast iron) and total replacement will be both necessary and costly.
  - The UST are steel; therefore, bacterial contamination could degrade wall thickness and result in spillage.
  - A biofilm may actually decrease corrosion as illustrated by the low corrosion rate of steel while immersed (~0.06 mm/y).
- We developed a test that can be used to screen materials and investigate methods of preventing corrosion