Corrosion of 1018 carbon steel in fuel/seawater incubations

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Polished carbon steel sputtered ~700 nm

ASTM specifications of 1018 carbon steel in wt%:
- C: 0.15 - 0.2
- Mn: 0.6 - 0.9
- S: 0.05 (max)
- P: 0.04 (max)
- balance: Fe
MnS inclusions are long micro-wires extending hundreds of microns along the rolling direction of the steel.

1. MnS inclusions imaged on clean steel coupon cut **perpendicular** to rolling axis of rod.

2. MnS inclusions imaged on clean steel coupon cut **parallel** to rolling axis of rod.
Pit statistics:

in 1018 Carbon steel:

pH ~ 7.4

6000 inclusions per mm$^2$

When exposed to ALDC for 12 days:
1 out of ~3000 is susceptible to initial pitting attack

When exposed to abiotic sterile Widdel media for 2 weeks:
1 out of ~12,000 is susceptible to initial pitting attack

Derivative of orientation is **residual strain** in crystal lattice.

1. EBSD map of lattice orientation.
2. EBSD map of residual strain over same field of view.

Strain varies within and among the different grains.

Legend:
- **No strain**
- Highly strained
- Intermediate strain
FEM image of polished carbon steel exposed to ALDC filtrate for 14 days, then stripped by chemical reagent to remove corrosion deposits.

Each grain corrodes at a slightly different rate. We hypothesize that high corrosion rates are correlated with high residual strains.
Pitting initiates around the inclusions

Auger maps (10 nm sputter)

Field of view = 1 µm across.

SEM image

Sulfur map

Oxygen map

MnS after 11 days exposure in Widdel medium with $[H_2S] = 0.05$ mM, $[Cl^-] = 300$ mM

**Strained dissolution of Fe**

$Fe^0 \rightarrow Fe^{2+} + 2 e^-$

**Hydrolysis of Fe$^{2+}$**

$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$
Pit development

1. Pits (~5 µm diameter) on coupon surface exposed to Widdel medium for two weeks (0.05 mM H₂S)

2. Pit on coupon surface corroded by ALDC for two weeks (~16 mM H₂S). Note lack of thick biofilm.

ALDC is a slow growing organism that does not form thick biofilm.
Pit initiation around MnS inclusions is due to local strain on the iron matrix due to stress exerted by the imperfections and impurities at these locations.

Pit growth and development is due to the acidification of pits through the hydrolysis of Fe$^{2+}$

At lower pH dissolution of MnS inclusions ($\text{MnS} + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + \text{Mn}^{2+}$) increases the local H$_2$S abiotically, which promotes local corrosion along MnS micro-wires

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Pitting corrosion

Large and deep pits generated around long MnS microwires after corrosion with or without SRB at pH 7

Low pH: abiotic H₂S:

\[
\text{MnS} + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + \text{Mn}^{2+}
\]

Hydrolysis of Fe²⁺:

\[
\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+
\]

Large pit developed around MnS after 2 weeks exposure to Widdel medium (0.05 mM H₂S, 300 mM Cl⁻)
Severe pitting: Occlusion by biofilm

Pits on coupons corroded by *Desulfovibrio alaskensis* g20 much larger than those on ALDC & Widdel medium.

*Desulfovibrio alaskensis* is a fast growing organism that does form thick biofilm.
MnS + 2H⁺ → H₂S + Mn²⁺

Abiotic H₂S production around MnS:

Fe²⁺ + 2H₂O → Fe(OH)₂ + 2H⁺

Hydrolysis of Fe²⁺ and Acidification

MnS + 2H⁺ → H₂S + Mn²⁺

Anodic reaction:

Fe → Fe²⁺ + 2e⁻

Cathodic reactions:

2H⁺ + 2e⁻ → H₂
2H₂S + 2e⁻ → 2HS⁻ + H₂
The presence of heavy biofilm accelerates pit initiation and growth

Steel coupons exposed *D. alaskensis* in Dr. Fields’ bioreactor for 2 days (A) biofilm / corrosion deposit ; (B) view after biocorrosion deposits are removed exposing the high densities of pitting.

**Occlusion by biofilm maintains acidic environment; creating auto- catalytic pitting mechanism.**
Conclusions so far:

- We hypothesize residual strain can be correlated with localized corrosion on carbon steel.

- Each MnS (or other) inclusion, with its surroundings, has a unique material property, and the Fe matrix at the immediate surroundings of each inclusion suffers from residual strain due to metallurgical processing.

- The presence of biofilm accelerates pit growth because the biofilm creates a barrier between the pit and the outside of the biofilm, giving rise to acidic conditions which leads to dissolution of all (active and inactive) MnS inclusions, increasing pitting density and promoting pit growth.

- Metabolic products of SRB contribute to the corrosion directly by production of additional electron acceptors.

- Electron acceptors are spread over a large 3-D space (FeS is good electrical conductor) the anodic processes are limited to small areas on the clean Fe surface and pits. This causes large current densities inside pits, which advances pit growth.

- Under highly acidic conditions inside pits, MnS locally and abiotically produces corrosive H₂S via MnS + 2H⁺ → H₂S + Mn²⁺, which accelerates the local corrosion process anaerobically and abiotically, causing pit growth and development along the MnS micro-wires. These then join pits to other pits, giving rise to macroscopic pitting.
Presence of thiosulfates cannot be ignored because when oxygen and sulfide react, thiosulfates form: 

$$2 \ S^{2-} + 2 \ O_2 + H_2O = S_2O_3^{2-} + 2 \ OH^-$$
**O$_2$ Transition across fuel/seawater interface in the presence of active aerobic bacteria**

Inoculum: JP5 Camelina/\textit{Marinobacter} ($\sim$4x10$^5$ cells per mL)

O$_2$ profile after 24 hrs of inoculation

(Pyruvate was \textit{not} removed from medium before inoculation)

![Graph showing O$_2$ profile](chart.png)

Sharp transition ($<$2mm)
A 10-mm-thick layer of JP5/Camelina blend placed over initially deoxygenated filtered seawater. The oxygen probe was kept ~5 mm below the fuel/seawater interface.
Corrosion in a JP5/seawater/Marinobacter environment


The corrosion is dominated by general erosion of the surface with no appreciable pitting.
Corrosion in grains and grain boundaries in fuel/seawater environment

F76: Grain boundary and pearlite attack. JP5 Camelina: Differential erosion of grains
Corrosion under JP5Camelina/KWSW bottom

Inoculum: *JP5Camelina/KWSW/Marinobacter/D. indonesiensis*. Exposure: 5 days.

The coupon at the bottom was colonized by microorganisms, a mixture of *D. indonesiensis* and *Marinobacter* (left). This gave rise to a highly complex corrosion process involving oxides and sulfides (XPS spectrum on the right).

Corrosion is dominated by oxides and sulfides
Complexity of corrosion in fuel/seawater environment

JP5Camelina/KWSW/Marinobacter/D. indonesiensis: ~18 days

Two images from different regions of the coupon at the bottom.

Highly heterogeneous and complex mixtures of oxides and sulfides as suggested by the images (above) and the EDX spectra (right).
Do the bacteria colonize coupons in fuel?

Inoculum: JP5Camelina/KWSW/Marinobacter/D. indonesiensis. Exposure: 2 days.

Bacteria colonizing Fe surface in fuel! View on the aqueous side.

Bacteria colonization on the fuel side accompanied by an oxide built up (left). Heavier biocorrosion on the aqueous side (right).
Conclusions of this section

• In the presence of active aerobic organisms, the oxygen concentration profile across a fuel/seawater interface shows a sharp transition within <2 mm.

• The diffusion rate of O\textsubscript{2} across a 1 cm layer of fuel is about 1 ppm/hr

• Corrosion in fuel/seawater environments is heterogeneous and complex, involving oxides and sulfide as well as intergranular and pitting corrosion.

• Removing the H\textsubscript{2}S from the SRBs before inoculation ensures that all the sulfides observed were produced by the metabolic activities of the SRBs.
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Thank you for your time

Microorganisms colonizing metal surface in JP5-Camelina