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Sulfide Production and Corrosion in Seawater During Exposure to FAME Alternative Fuel

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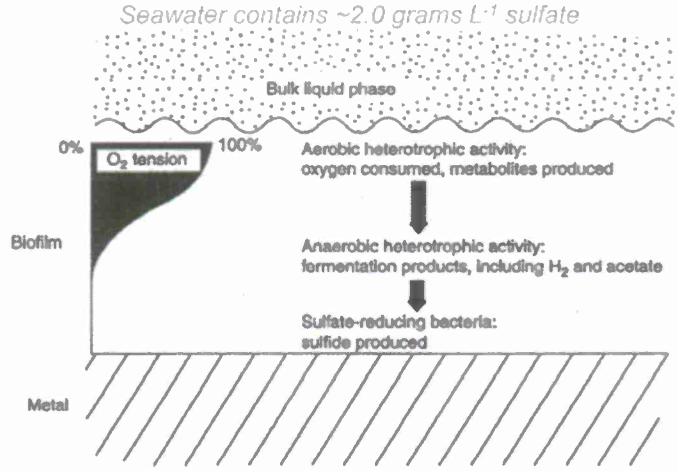
Sulfide Derivitization

Seawater contains ~2.0 grams L^{-1} sulfate



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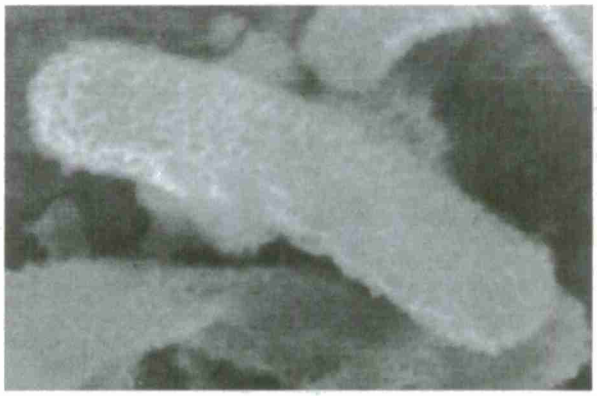
Sulfate-Reducing Bacteria



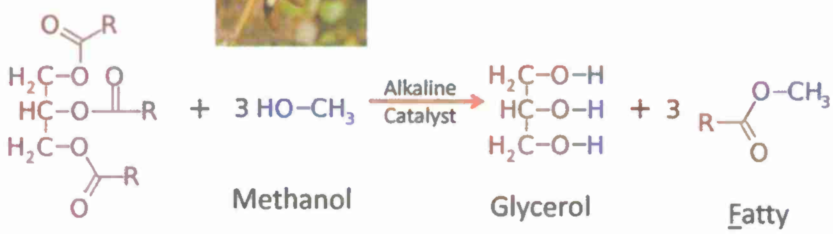
Initial Seawater Chemistries

Seawaters	pH	Salinity (g/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)
Key West	7.82	38	1.79	3864
Persian Gulf	7.98	44	1.94	4696

FAME

Soy
Beans

Transesterification



Triglyceride

Methanol

Glycerol

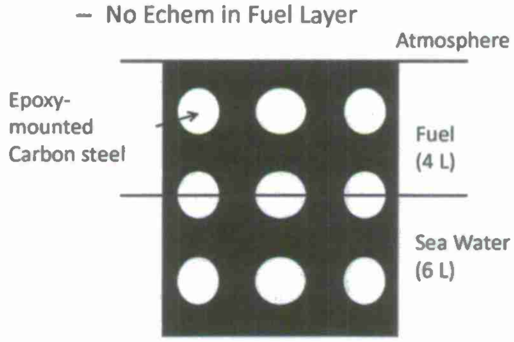
Fatty
Acid
Methyl
Ester

Exposure Chamber

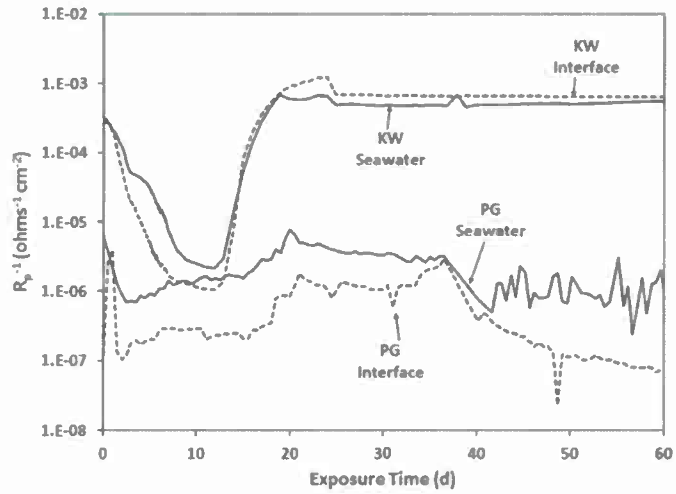
Anaerobic Chamber
- bal. N_2, 10% H_2, 0.1% CO_2 – maintain pH ~8

Polarization Resistance (R_p)

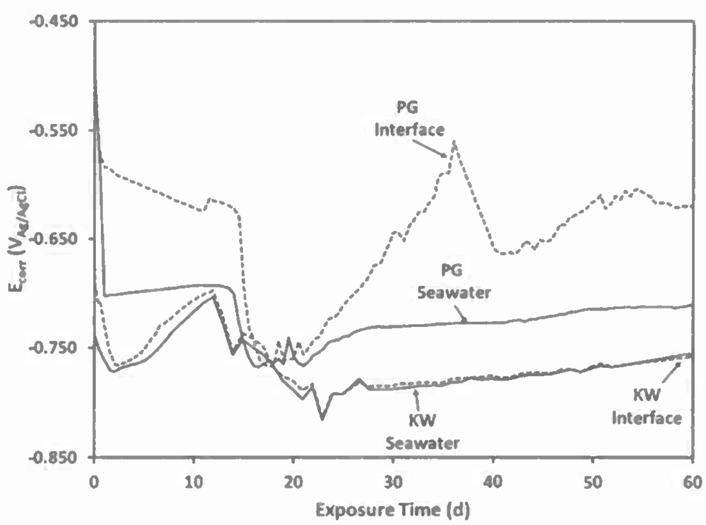
Corrosion Potential (E_{corr})
- No Echem in Fuel Layer



Corrosion Rate (R_p^{-1})

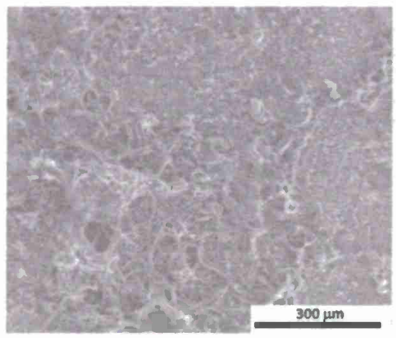


Corrosion Potential (E_{corr})

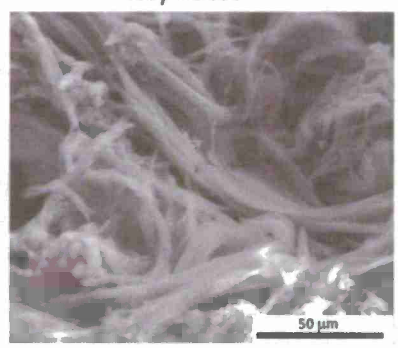


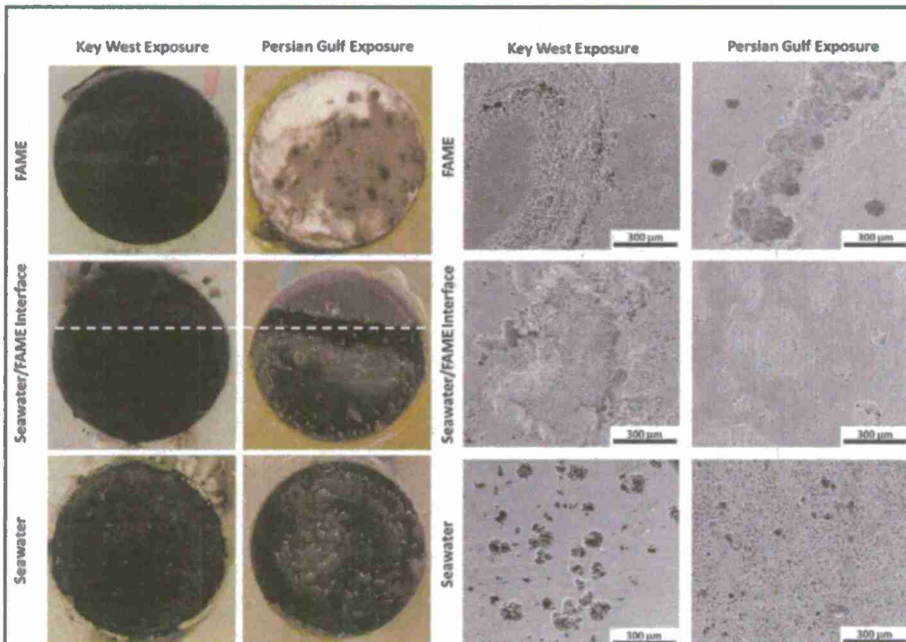
Fouling at the Interface

Persian Gulf



Key West





Corrosion Product Analysis

Energy Dispersive Spectroscopy

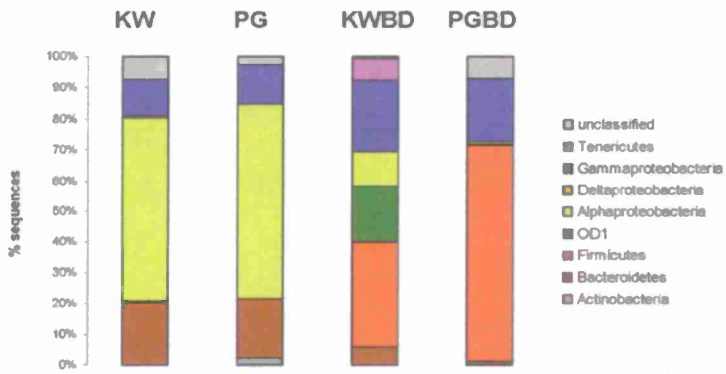
	Sulfur (wt%)		Chlorine (wt%)	
Electrode Position	KW	PG	KW	PG
FAME	19.7	1.7	4.5	0.49
FAME/SW Interface	23.6	0.5	4.7	0
Seawater	30.2	2.4	6.6	0

Sulfate reduction activity (SRA)

Sample	SRA µmol S /L/day	SRA µmol S /L/day
	Persian Gulf Seawater PG	Key West Seawater KW
in situ (no additions)	11.96 ± 1.33	17.7 ± 3.3
Amended with lactate	23.5 ± 1.7	115
Amended with crude oil*	10.3 ± 2.3	13.95 ± 0.75
Amended with crude oil and inoculated with strain Lake**	155 ± 6.7	264 ± 40
Sterile Control	7.95 ± 1.7	7.5 ± 3.5

* sterile crude oil
***Desulfoglоeba* strain Lake, an alkane-degrading sulphate-reducing bacterium

Bacterial 16rRNA Pyrosequencing



Quantitative PCR

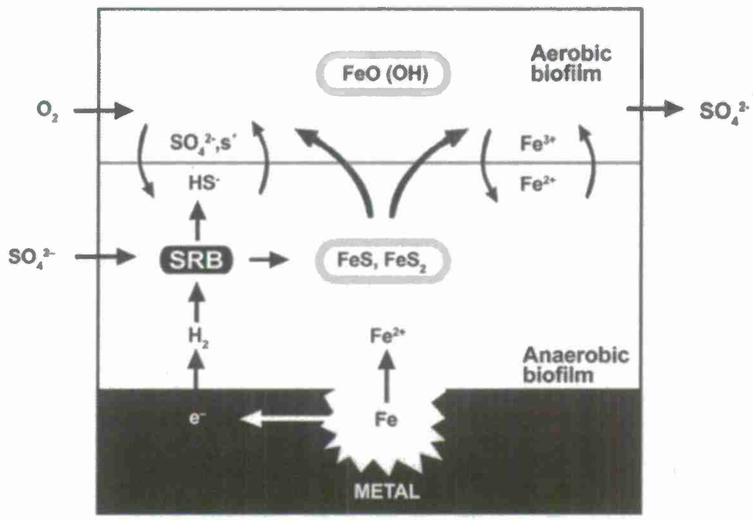
Estimates from qPCR	KW*	PG	KWBD	PGBD
Bacterial cells/ml	2.75×10^{7}	2.66×10^{7}	4.97×10^{5}	1.72×10^{5}
Dsr-bearing cells/ml**	3.17	BDL	BDL	BDL
Aps-bearing cells/ml***	BDL	BDL	BDL	BDL
Archaeal cells/ml	3.05×10^{3}	2.19×10^{3}	BDL	BDL
Mcr-bearing cells/ml****	2.48×10^{3}	2.48×10^{0}	1.21×10^{2}	4.74×10^{1}

*KW: Key West seawater; PG: Persian Gulf seawater; KWBD: FAME diesel incubated with KW seawater; PGBD: FAME diesel incubated with PG seawater.

** Dsr-bearing cells: cells that contain a copy of the gene coding for dissimulatory (bi)sulphite reductase, e.g. SRB.

*** Aps-bearing cells: cells that contain a copy of the gene coding for adenosine-5'-phosphosulphate reductase, e.g. SRB.

**** Mcr-bearing cells: cells that contain a copy of the gene coding for subunit *a* of methyl-S-CoM methylreductase, e.g. methanogens.



Hamilton et al., 2003

Conclusions

- Sulfide influenced corrosion rates of carbon steel exposed to seawaters and FAME diesel did not correlate with initial concentrations of sulfate, chloride or organic carbon in the seawater. KW >> PG
- A microbial community developed with low numbers of SRB after seawater was incubated with the alternative fuel
- Significantly higher elemental concentrations of sulfur and chlorine were detected in corrosion products in the KW exposure compared to PG
- Initially higher estimates of Dsr- and Mcr-bearing cells (i.e., SRB and methanogens) in KW compared with PG provide the only indication that KW seawater will support more sulfate reduction.
- The inability to predict corrosivity of particular seawaters from a limited set of chemical and microbial parameters demonstrates that simple models in which SRB abundance is directly associated with rate or extent of corrosion are inadequate.

MIC-5

MARINE CORROSION IN FUEL SYSTEMS

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The relationship between corrosion and biodegradation of bio- and petroleum-based fuels exposed to seawater is being evaluated. To date the fuels have included petroleum diesel (F76) and jet propellent (JP) 5, hydroprocessed (HP) bio-based lipids from renewable stocks (e.g. camelina and algae) and blends. Experiments have been conducted with aerobic seawater and unprotected carbon steel coupons under stagnant conditions. i.e., there were no attempts to influence the distribution or concentration of oxygen in the sealed vessels. In all cases the dissolved oxygen (DO) in the seawater was below the detection limits of the DO probe (100 ppb) within a few days of incubation, independent of fuel composition. Corrosion was due to microbiologically produced sulfides reacting with the carbon steel. There were few differences in electrochemically measured corrosion rates in incubations amended with any of the fuels or their blends. In the experiments that have been examined in detail, transient oxygen influenced the microbial biodegradation of fuels and resulted in a suite of characteristic metabolites. Detection of catechols confirmed the exposure of incubations to oxygen. Clone library analysis indicated higher proportions of Firmicutes, Deltaproteobacteria (primarily sulfate-reducing bacteria), Chloroflexi, and Lentisphaerae in incubations exposed to fuels than the original seawater. Relative proportions of sequences affiliated with these bacterial groups varied with fuel. Methanogen sequences similar to those of *Methanolobus* were also found in multiple incubations. Despite the dominance of characteristically anaerobic taxa, sequences coding for an alkane monooxygenase from marine hydrocarbon-degrading genera was observed, suggesting that organisms with this metabolic potential survived the incubation. The current hypothesis is that initial aerobic oxidation of fuel components resulted in the formation of a series of intermediates that were used by anaerobic seawater microbial communities to support their metabolism, sulfide production, and carbon steel microbiologically influenced corrosion. The more precise relationship between oxygen, microbial activity and corrosion is underway with more precise DO probes (4 ppb resolution).

MIC-6

SULFIDE PRODUCTION AND CORROSION IN SEAWATER DURING EXPOSURE TO FAME ALTERNATIVE FUEL

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Experiments were designed to evaluate corrosion-related consequences of storing/transporting fatty acid methyl ester (FAME) alternative diesel fuel in contact with natural seawater under anaerobic conditions. Coastal Key West, FL, and Persian Gulf seawaters, representing an oligotrophic and a more organic- and inorganic mineral-rich microbial coastal seawater environment, respectively, were used in 60-day studies with unprotected carbon steel. Despite low numbers of sulfate reducing bacteria in the original waters and after FAME diesel exposure, sulfide levels and corrosion increased markedly due to microbial sulfide production. The original microflora of the two seawaters was similar with respect to major taxonomic groups but with markedly different species. After exposure to FAME diesel the microflora of both waters changed dramatically, with Clostridiales (Firmicutes) becoming dominant. Microbial sulfide production was stimulated in both seawaters by the presence of FAME.