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CORROSION IN FUEL/NATURAL SEAWATER ENVIRONMENTS

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ABSTRACT

Experiments were designed to evaluate corrosion-related consequences of storing/transporting petroleum and alternative fuels in contact with natural seawater. Fuels included petroleum JP-5, camelina derived JP-5, petroleum F-76, and algal derived F-76 and mixtures of the petroleum-based and alternative fuels. Corrosion rates were estimated from polarization resistance measurements and corrosion was measured by weight loss. Corrosion attack morphology and corrosion products were analyzed by three-dimensional profilometry, environmental scanning microscopy, and energy dispersive spectroscopy. Alternative fuels stimulated sulfide production in seawater indicating that the alternative fuels were more biodegradable than the petroleum-based counterparts. Chlorides and sulfides could be detected in all corrosion products when seawater was present. Weight loss did not correlate with instantaneous corrosion rates or with dissolved sulfide concentrations in the seawater.

Keywords: seawater, carbon steel, fuel, biodiesel, sulfide, microbiologically influenced corrosion

INTRODUCTION

The chemical and microbiological compositions of hydrocarbon fuels have been studied for decades. Microbiologically influenced corrosion (MIC) has been evaluated for crude and distillate fuels during all phases of exploration, transportation, storage and usage.¹ It is estimated that damage due to MIC in production, transport, and storage of oil amounts to some hundred million dollars in the United States every year.² Russian investigators³ estimated that 30 percent of the corrosion damage in equipment used for oil exploration and production was directly attributable to MIC.

Alternative fuels have different chemistries and microbiological constituents than petroleum diesel and those differences may influence reactions with materials, i.e., corrosion. Petroleum diesel is made up of hundreds of different hydrocarbon chains, with residues of sulfur and crude oil remaining. Biodiesel is produced from vegetable oils by converting the triglyceride oils to methyl (or ethyl) esters with a process known as transesterification.⁴ The transesterification process reacts alcohol with the oil

to release three "ester chains" from the glycerin backbone of each triglyceride. The reaction requires heat and a strong base catalyst (e.g., hydroxide), for complete conversion of the vegetable oil into the separated esters and glycerin. Biodiesel contains no sulfur. In the United States the term "biodiesel" is standardized as fatty acid methyl ester (FAME) and is considered a first-generation biofuel. Biodiesel content is reported as the number of carbon atoms in the FAME backbone, e.g., FAME C17. Biodiesel mixes easily with petroleum diesel as a fuel additive for use in blends of up to 20%. In 1998, biodiesel as a 20% blend (B-20) with petroleum diesel was designated an "alternative fuel" under the Energy Policy Act. This designation allows government fleet services to purchase the B-20 blend for operation in normal diesel vehicles and receive credit for those vehicles. In Europe (EU), the Renewable Transport Fuel Obligation obliges suppliers to include 5% renewable fuel in all transport fuel sold in the EU by 2010.

Military grade petroleum fuels such as JP-5 and F-76 are of particular interest to the defense community. JP-5 (for Jet Propellant) is a kerosene-based fuel for use in aircraft turbine engines. Since the fuel is the primary aircraft fuel used aboard aircraft carriers, a substantially higher flash point (60 °C) is required over commercial ground-based aircraft with fire safety being a primary concern about vessels. F-76 is a distillate petroleum-based fuel used aboard ships in diesel engines, gas turbines and boilers. Like JP-5, F-76 has tight specifications including the 60 °C flashpoint requirement. These two fuels make up the bulk of the fuels used aboard military ships. Efforts have been made to supplement these petroleum-based with alternative fuels from renewable sources such as plant stock (e.g. camelina) and microbiological sources (e.g. algae). These fuels are referred to as "hydrorefined" (HR) biofuels where the fuel stock has been reduced with hydrogen with final products being straight chain hydrocarbons.

It is likely that alternative fuels will be exposed to seawater in compensated fuel ballast systems on U.S. Navy ships. Compensated fuel ballast systems are configured as a series of fuel tanks that automatically draw in seawater to replace fuel as it is consumed. Keeping the fuel tanks full in this manner enhances the stability of a vessel by using the weight of the seawater to compensate for ballast mass lost through fuel consumption. During refueling, fuel displaces the seawater, and the displaced seawater is discharged.

Some bacteria and fungi are naturally occurring in petroleum diesel; others are introduced as contaminants from air or water. Several investigators have reported that the microflora that persists in hydrocarbons depends on the formulation.^{5,6} The microorganisms most often associated with MIC in hydrocarbon fuels in contact with fresh water or seawater are the sulfate-reducing bacteria (SRB) and fungi (e.g., *Hormoconis resinae*). There are little data on the natural microflora in alternative fuels. Microbial interaction with both petroleum diesel and biodiesel is limited to water availability. Since water is sparingly soluble in both petroleum diesel and biodiesel, microbial growth is concentrated at fuel/water interfaces, i.e., emulsified water, and separate water phases. The presence of water increases the possibility of abiotic corrosion, growth of microorganisms and MIC.

Results presented in this paper represent a continuation of studies related to corrosion and fouling in alternative fuels, which started with soy-based biodiesels in contact with distilled water⁷ and seawater.⁸ Because of the hygroscopic nature of biodiesels and their biodegradability, it is unlikely that biodiesels will be used in marine applications. The present study evaluates corrosion of uncoated carbon steel exposed to HR fuels in contact with seawater.

MATERIALS AND METHODS

Fuels

Corrosion was evaluated in the following fuels:

- JP-5 Petro
- JP-5 Camelina HR
- JP-5 50/50 (50% Petro/50% Camelina)
- F-76 Petro
- F-76 Algal HR (*inadequate supplies for neat exposure*)
- F-76 50/50 (50% Petro/50% Algal).

Fuels were characterized using gas chromatography and mass spectrometry.

Metal Coupons

Corrosion coupons of UNS C10200 carbon steel (CS) (0.20% C, 0.47% Mn, 0.012% P, 0.013% Si, bal. Fe) were fabricated to dimensions of 5/8" (1.5875 cm) diameter and 1/8" (0.3175 mm) thick (5.5 cm² total area). A wire was attached to the backside of the coupons with conductive epoxy and carbon tape to achieve electrical connection. Coupons were individually mounted in epoxy to electrically isolate the wire connection and to establish an exposed area of 2 cm². Vacuum grease prevented epoxy intrusion between the coupon face and mount bottom, preserving the as-mill finish. Mounted coupons were sonicated in liquid detergent, rinsed successively with acetone, ethanol and distilled water and blown dry with nitrogen (N₂) gas.

Seawater

Key West (KW), FL, seawater was collected at the Naval Research Laboratory Marine Corrosion facility at a depth of 1.2 – 1.5 m by intake pipes powered by suction pumps. Seawater was shipped to the Naval Research Laboratory, Stennis Space Center, MS (NRLSSC), in three 19 L plastic containers. KW seawater has been characterized in more detail elsewhere.⁹⁻¹³

Exposure Conditions

Five chambers were constructed to expose CS electrodes to seawaters with biodiesel additions. The chambers were cylindrical (35.5 cm diameter and 27.9 cm height) and constructed from heavy gauge, chemical resistant, opaque black plastic. The chambers have been previously used for seawater-only exposures.^{9-11,13} Chambers were sealed by clamping the lid onto a rubber gasket. In this configuration, the chambers developed their own internal atmosphere but exterior gases could still enter the container through ports if required. The ports were 3/4" (1.9 cm) ball valves at the end of 3/4" dia. x 12" long (1.9 cm diam. x 30 cm) plastic pipe. Ag/AgCl electrodes and Pt/Nb mesh were used as reference and counter electrodes, respectively. For each chamber, 9 electrodes were arranged vertically so that triplicate coupons were exposed to three conditions (from top to bottom): 1) fuel, 2) fuel/seawater interface, and 3) seawater.

The chambers were filled with 4 L seawater and 6 L fuel and placed in an anaerobic hood with an atmosphere of 0.01% CO₂, 10 % H₂ and the balance N₂. CO₂ concentration was chosen to maintain a seawater pH of between 7.8 and 8.2.¹⁴ Ports were closed to limit condensation inside the anaerobic

hood. Anaerobic hood temperature was maintained at 23°C. No attempt was made to sterilize glassware, coupons, wires, or plastic mounts prior to introduction of fuel and water.

Hydrogen sulfide concentration $[HS^-]$ was measured after the 90-day exposure using the methylene blue method.¹⁵

Electrochemical Methods

A computer-controlled potentiostat/multiplexer was used for all electrochemical measurements. Polarization resistance (R_p) was determined by the linear polarization resistance technique (LPR)¹⁶ on each electrode once a day. For each LPR scan, corrosion potential (E_{corr}) was recorded vs. the reference electrode. Current density (i [$A\ cm^{-2}$]) was recorded as the potential of each coupon was scanned from -10 mV to +10 mV vs. E_{corr} at the standard scan rate of 0.1667 mV/s (0.6 V/hr).¹⁷ R_p was determined by a least-squares-fit of the slope of the potential (V)/ i curve using Ohms Law ($R_p = V/i$). Compensation for solution resistance (R_s) was not necessary because of the relatively high conductivity of seawater¹⁸ and low current densities. The inverse ($1/R_p$) is proportional to the instantaneous corrosion rate. The term 'instantaneous' is used here to distinguish it from a cumulative corrosion rate determination such as weight loss. LPR provides the corrosion rate at the instant in time of the measurement; it provides no information of corrosion that has occurred previously.

Post-Exposure Surface Examination

After the 90-day exposure period, electrodes were removed and imaged using a macro digital camera. Each electrode was fixed in cacodylate buffered 4 % glutaraldehyde in artificial seawater, rinsed in distilled water. Corrosion morphology and corrosion product composition were characterized with environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS), respectively.¹⁹ Electrodes were acid cleaned to remove corrosion products,²⁰ and re-examined with ESEM. Select electrodes were scanned using a non-contact optical profiler with a 400 μm optical laser pen to reconstruct high contrast 3-D digital images. Pit depths were measured from these reconstructed images.

RESULTS

The n-alkane portions of camelina- and algal- derived JP-5 and F-76 fuels were similar to the petroleum-based counterparts (Figures 1 and 2). In both cases, the petroleum fuels were more complex and both contained compounds that could inhibit microbial growth, e.g., phenols and aldehydes.

After the 90-day exposure, the chambers were opened. All chambers had a "rotten egg" sulfide smell. CS electrodes exposed to KW seawater with petro, camelina and 50/50- JP-5 additions are shown in Figure 3. Dark corrosion products were observed on all coupons in proximity to seawater whether fully immersed or at the seawater/fuel interface. Coupons in the fuel layer exhibited regions of localized corrosion surrounded by unattacked metal. Similar observations were made for exposures in F-76 (Figure 4). Corrosion products in both the water and fuel phases contained chloride and sulfur (data not shown).

Corrosion rates ($1/R_p$ [$1/ohm\cdot cm^2$]) initially decreased by an order of magnitude for all exposures in the first 7 – 10 days to JP-5 (Figure 5) and F-76 (Figure 6). Corrosion rates increased by 2 – 3 orders of magnitude after 30 days with the highest corrosion rate measured at the interface of the

camelina/seawater coupon. At the end of the 90-day exposure, the corrosion rate in the 50/50 JP-5 exposure was still increasing with time. Dissolved sulfide was detected in all seawaters with the highest concentration (150 ppm) measured in the seawater with 50/50 JP-5 addition. F-76 exposures resulted in the lowest electrochemically measured corrosion rates with little difference observed between the exposure to petro and 50/50 mixtures.

Table 1 lists the weight loss (g) of carbon steel after 90-days exposure and acid cleaning. For JP-5 exposures, the largest amount of metal loss was measured at the interface of petro JP-5 and seawater. The lowest amount of metal loss was at the interface in the 50/50 mixture. For F-76, petro-based fuel addition resulted in larger amounts of metal loss than in the 50/50 mixture.

Table 1. Weight loss (g) of carbon steel after acid cleaning.

	Seawater	Seawater/Fuel Interface	Fuel
JP5 Petro	0.1725	0.312	0.2275
JP5 Camelina	0.1451	0.1522	0.1568
JP5 50/50	0.199	0.129	0.2259
F76 Petro	0.1997	0.0668	0.2666
F76 50/50	0.0856	0.0891	0.1017

After acid cleaning, pits with depths in excess of 250 microns were observed in carbon steel exposed in the fuel layers (Figure 7).

DISCUSSION

Lee et al.⁹ documented corrosion of carbon steel exposed to stagnant natural KW aerobic and anaerobic seawater and the resulting mechanisms for corrosion. Predictably, corrosion occurred under both exposure conditions. Coupons exposed to natural aerobic seawater were covered with intact iron oxides and corrosion was uniform. Microorganisms were located on the surfaces, but did not appear to influence corrosion. In contrast, under anaerobic conditions, surfaces were covered with non-tenacious, microbiologically produced sulfides and localized corrosion in the form of pitting. Lee et al.¹² also documented differences in microbial sulfide production in two coastal seawaters, but did not determine the cause of those differences.

Lee et al.⁷ demonstrated that biodiesel in contact with aerobic distilled water (simulating water of condensation) supported the growth of both bacteria and fungi in the water phase. Biodiesel does not contain sulfur and no sulfur-related microorganisms, e.g., SRB, were detected in their experiments with biodiesel and distilled water. Furthermore, in their experiments with biodiesel and distilled water there were no indications of corrosion, biotic or abiotic, in either the fuel or water phases. The metals used in that work were unprotected carbon steel, aluminum and a stainless steel. Lee et al.²¹ concluded that under their experimental conditions, biodiesel had the highest propensity for biofouling and the lowest corrosivity.

Corrosion in the presence of the biodiesel/seawater combination could not be predicted from previous experiments with the individual components, i.e., seawater and biodiesel. Biodiesel is hygroscopic, absorbing water from the environment. Microbial growth in seawater can be limited by nutrients, including carbon. Biodiesel methyl esters are quite sparingly soluble in seawater, with a

saturation concentration of 7 ppm at 17 °C, but are readily biodegraded. The half-life for the biodegradation of the vegetable methyl esters in agitated San Francisco Bay water was less than 4 days at 17 °C. Lee et al.⁸ demonstrated corrosion of unprotected carbon steel exposed in either phase of a two-phase biodiesel and seawater combination under anaerobic conditions. Corrosion in either liquid phase was influenced by the presence of the other phase. Sulfur and chloride from the seawater were located on surfaces exposed in the fuel phase and biodiesel stimulated sulfide production in the seawater phase.

Similar results were observed for corrosion in HR and petro-based JP-5 and F-76 fuels. The plant-derived fuels contained the same distribution of n-alkanes as the petroleum-based products (Figures 1 and 2) and the resulting corrosion was similar (Figures 3 and 4). There were no significant differences in the instantaneous corrosion rates in the presence of the petro-based, plant derived and mixtures of the two fuels. However the high concentration of dissolved sulfides in the seawater in contact with the 50/50 blend of petro and camelina JP-5 may reflect the biodegradability of the plant-derived fuel. Chlorides and sulfides in the fuels could not be measured, but their presence in corrosion products in areas of the carbon steel exposed to fuel layers may be a cause of concern for the fitness of the fuel.

CONCLUSIONS

Corrosion of carbon steel was observed in the seawater and fuel phases of both petroleum-based and plant-based fuels JP-5 and F-76 fuels. Corrosion in the fuel phase was consistently associated with chloride and sulfur, originating in the seawater. The highest dissolved sulfide levels were measured in the seawater that had been in contact with the 50/50 mixtures of the petroleum and plant-derived fuels.

ACKNOWLEDGEMENTS

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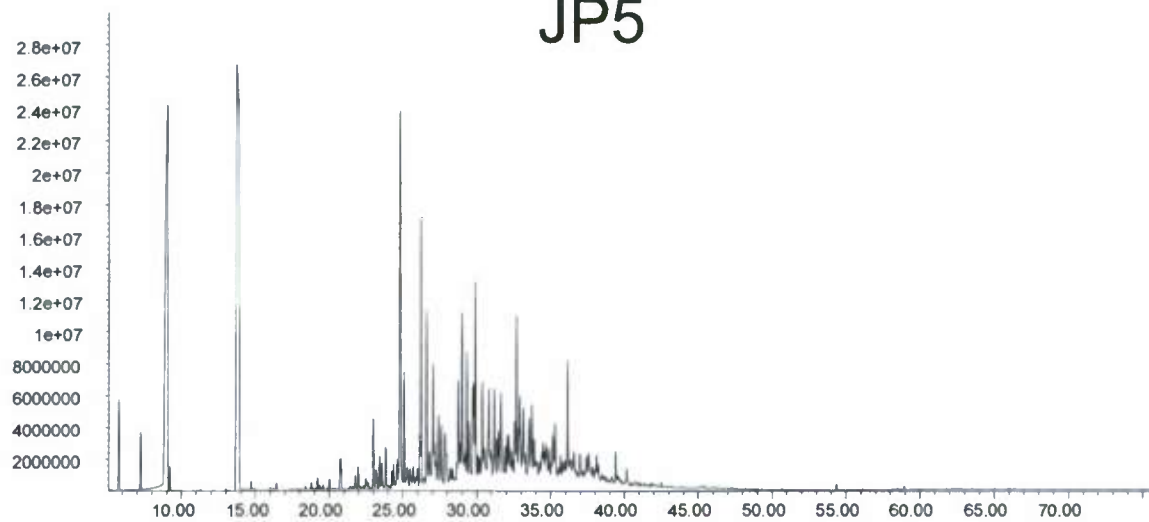
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	n-alkanes	i-alkanes	acids	others
JP5	C10-C15	some	C16 and C18	Many alkylated phenols
JP5 Camelina	C10-C18	C9-C20 (a lot)	C16 and C18	-

Abundance

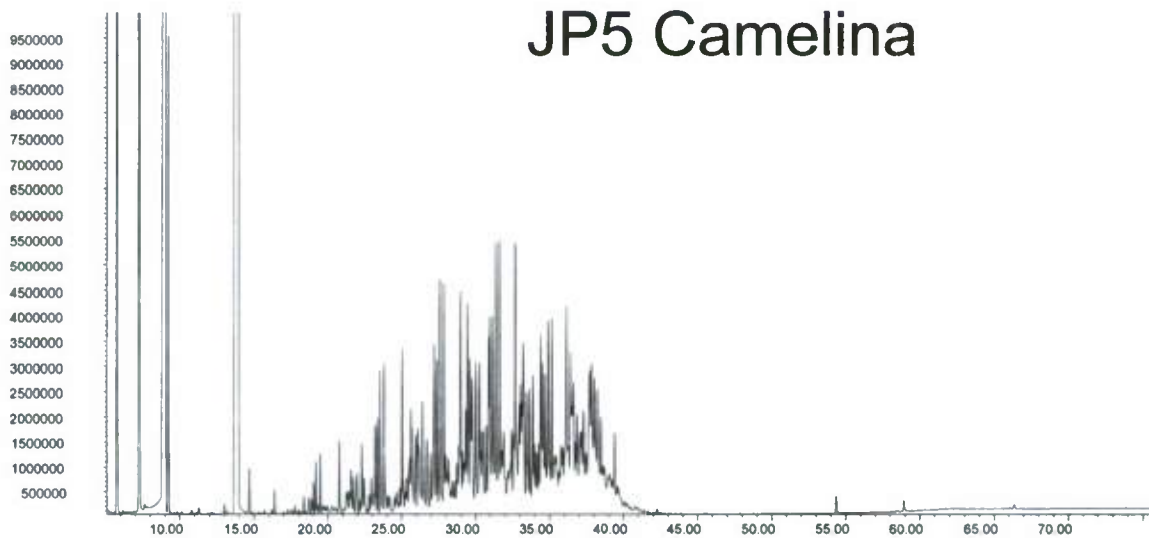
JP5



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Abundance

JP5 Camelina



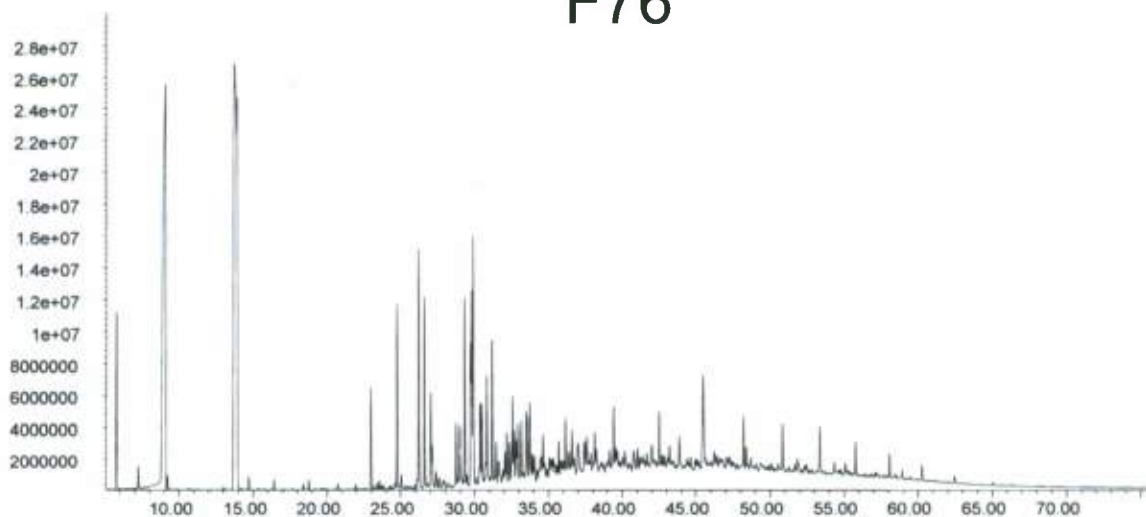
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Figure 1.

	n-alkanes	i-alkanes	acids	others
F76	C11-C15 and C22	-	C16 and C18	Naphthalene and alkylated naphthalenes Acetophenone Thiobenzoate nitrobenzaldehyde
F76 Algal	C10-C20 and C25	C11-C21 (a lot)	C16 and C18	

Abundance

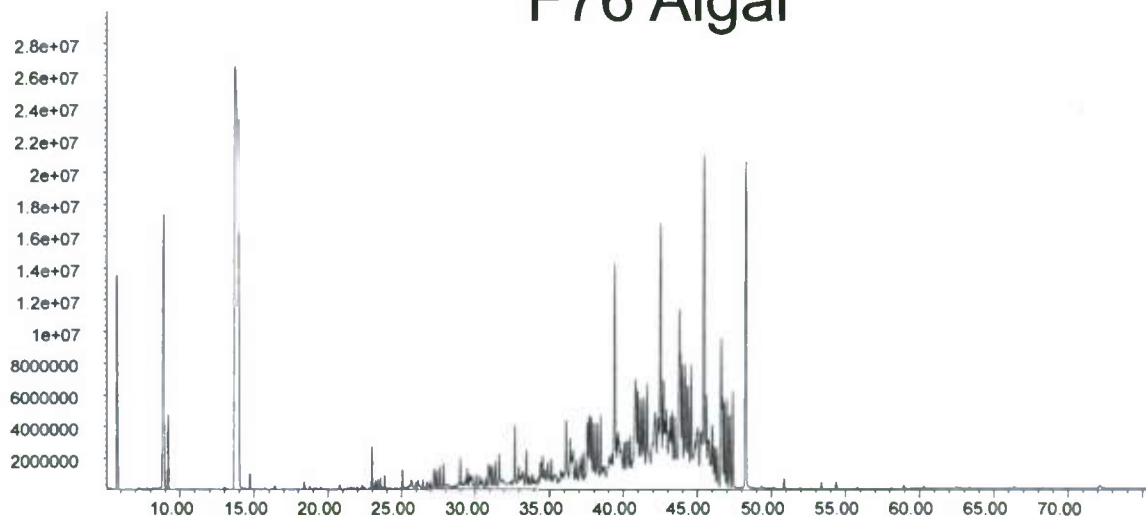
F76



Time-->

Abundance

F76 Algal



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Figure 2.

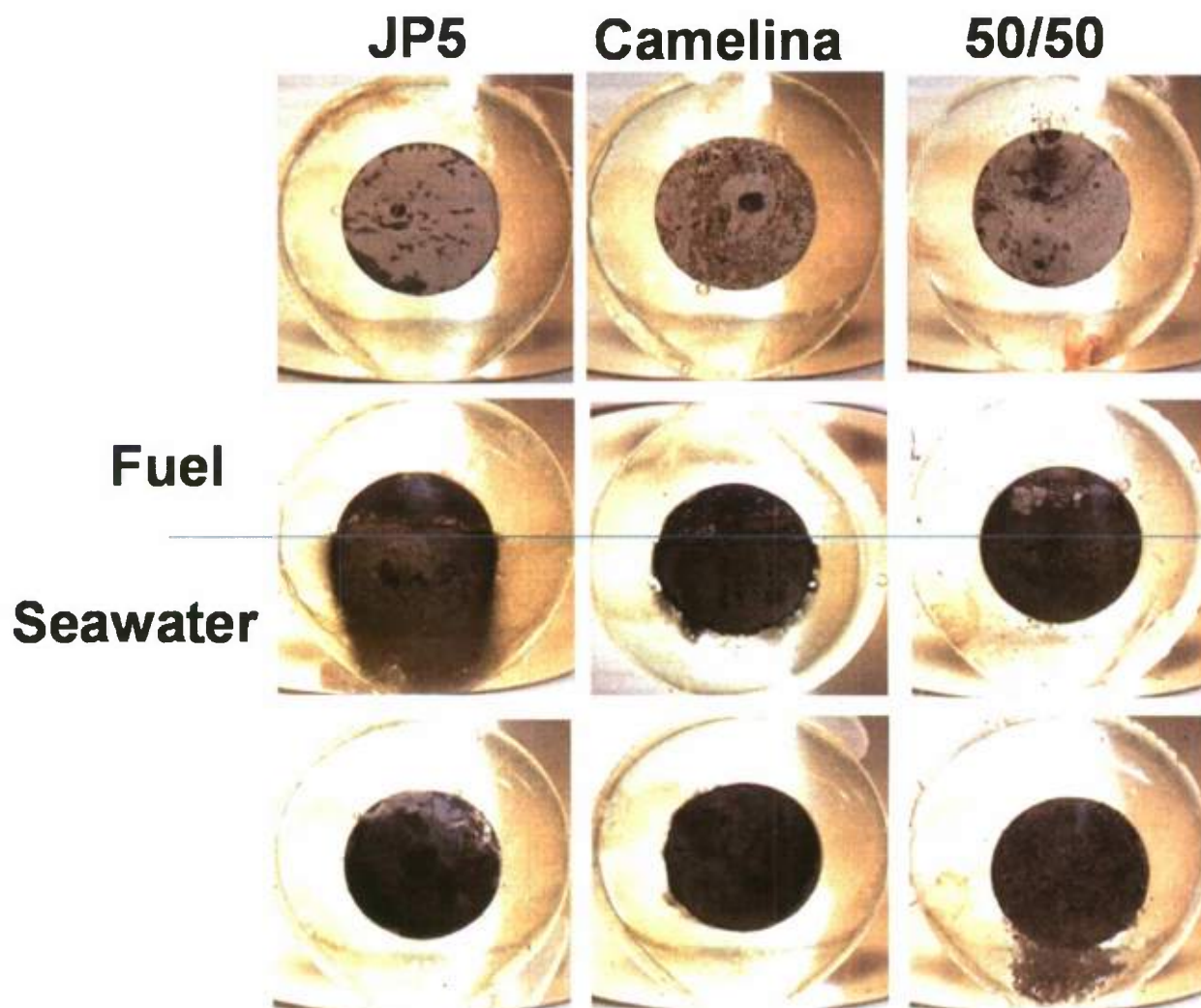


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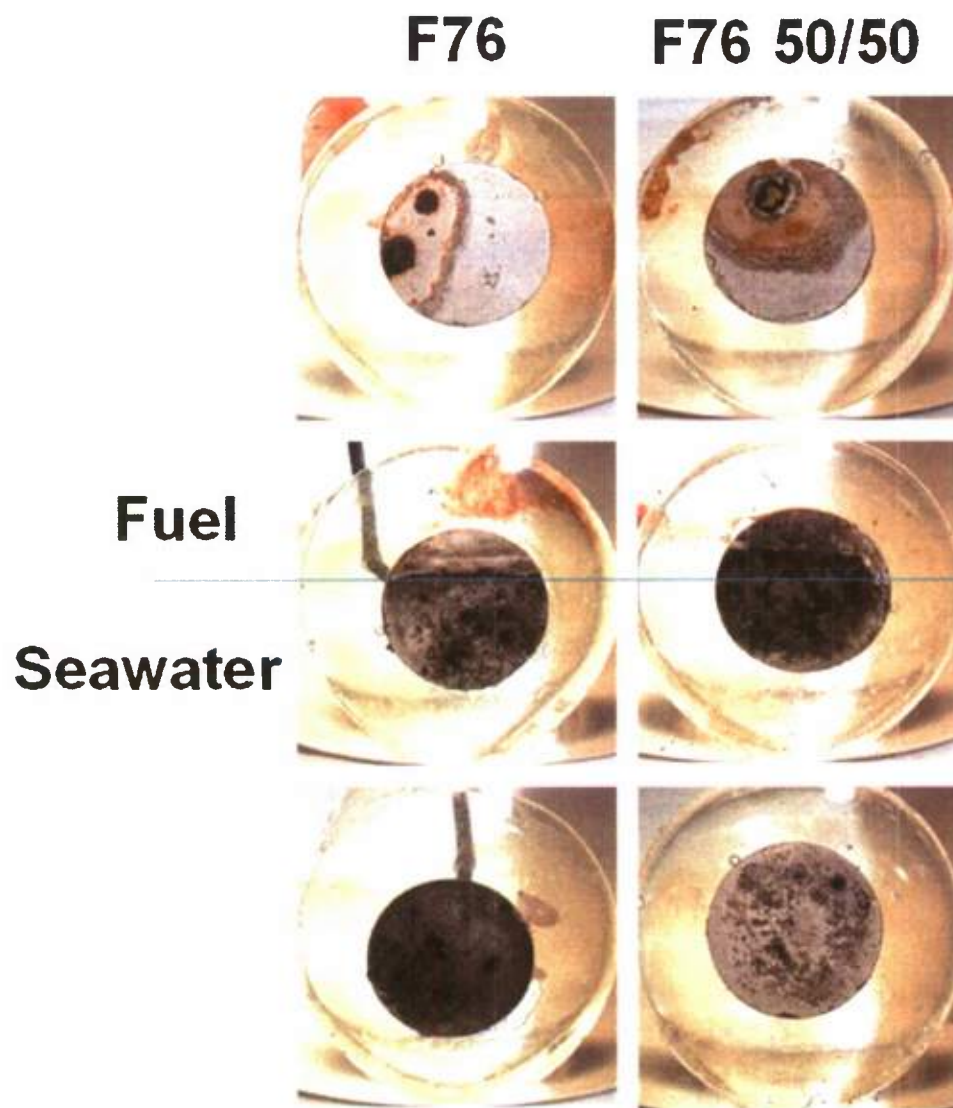


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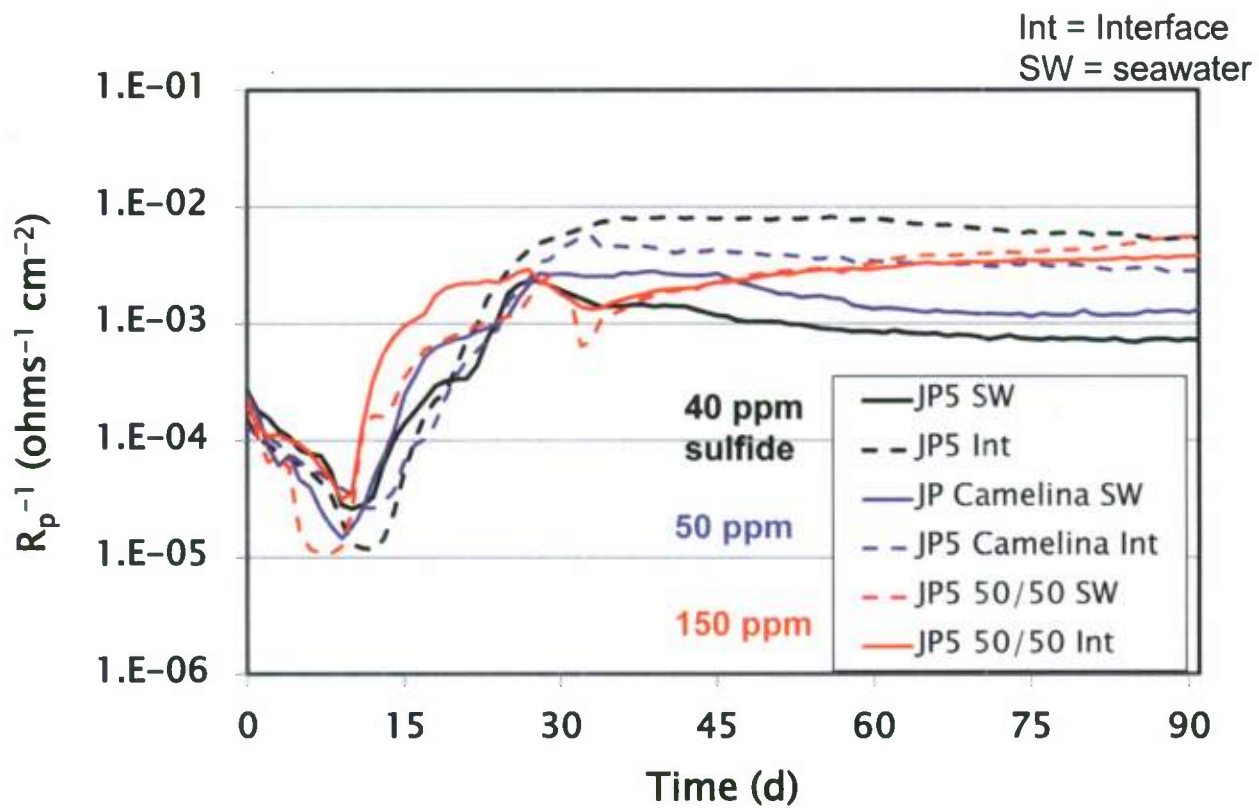


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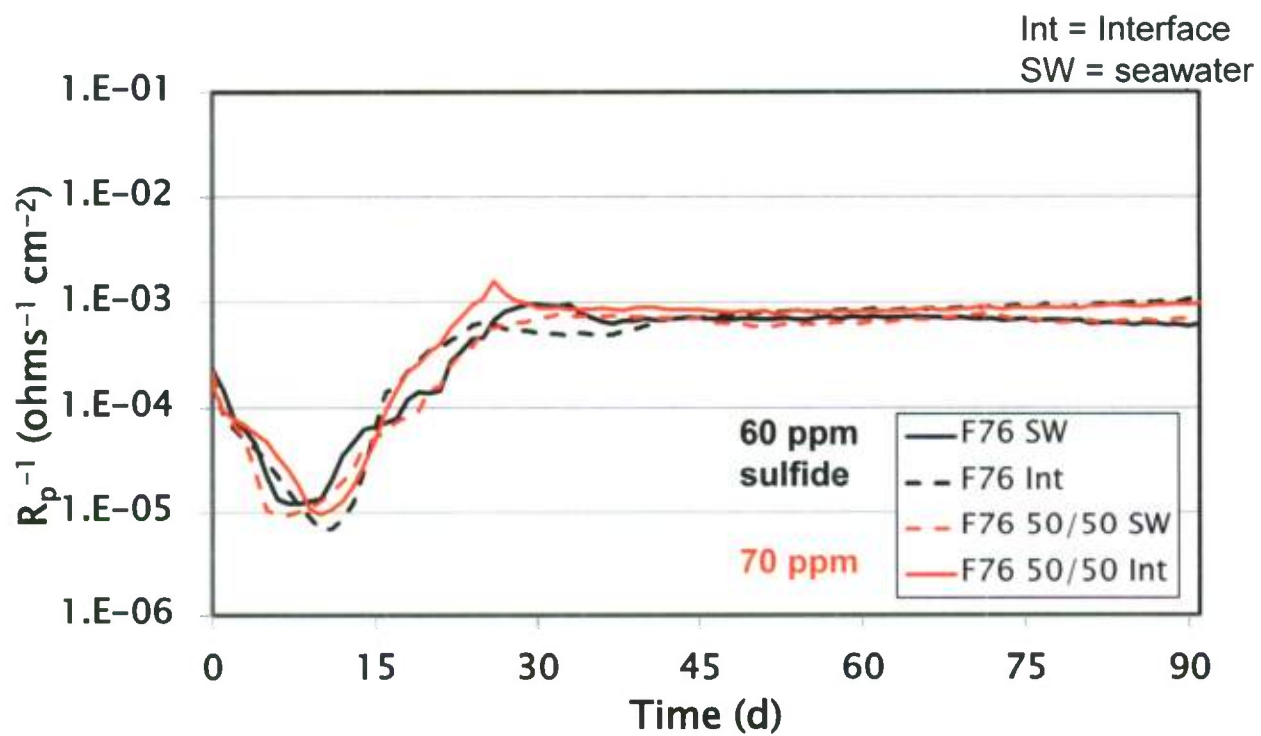


Figure 6.



Localized corrosion
in fuel layer

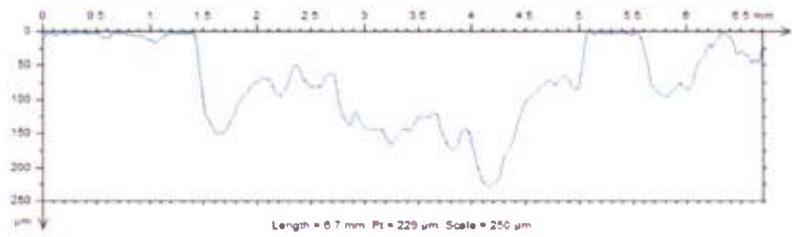
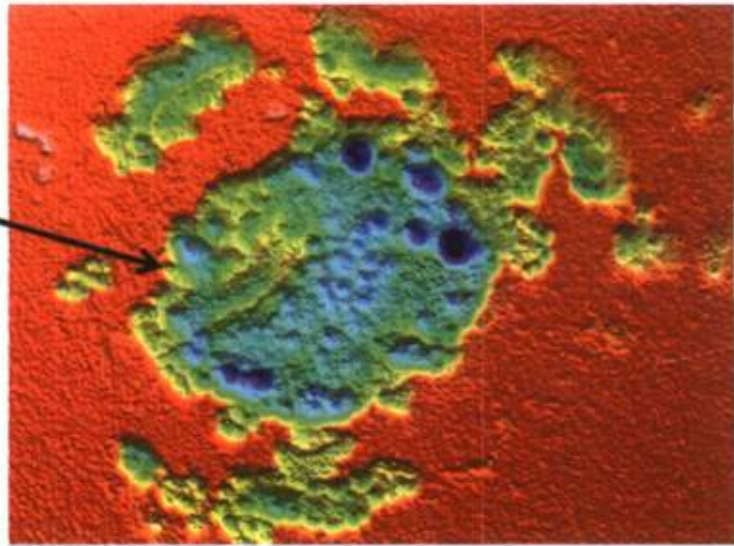


Figure 7.