Final Report

This project was canceled by order of the Secretary of Transportation

Date of Report: *Oct 30, 2011*

Contract Number: DTPH56-09-T-000004

Prepared for: the U.S. Department of Transportation Pipeline and Hazardous Materials Safety Administration

Project Title: Stress Corrosion Cracking of Pipeline Steels in Fuel Grade Ethanol and Blends – *Study to Evaluate Alternate Standard Tests and Phenomenological Understanding* of *SCC*

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(a) Technical Status

Main aim of this project was to evaluate alternate standard test methods for stress corrosion cracking (SCC) and compare them with the results from slow strain rate test (SSRT) results under equivalent environmental conditions. Other important aim of this project was to develop an phenomenological understanding of SCC of pipeline steels in fuel grade ethanol (FGE) and FGE/gasoline blends. To achieve these objectives, tests were going on in all fours task areas of this project in the last quarter (July to Sept. 2011), when the project was terminated. Next sections describe the technical work done on these tasks. This report describes the technical work done on different tasks along with the summary of final status of these tasks in terms of key results.

1.0 <u>Task 1- Evaluate Tapered Tensile Tests to Determining Threshold Stresses for SCC</u>

Initial tests on tapered tensile samples were carried out with all sides polished. This to eliminate any effects of mill scale on the SCC susceptibility or threshold stresses in SFGE and FGE environments. Simulated fuel grade ethanol and fuel grade ethanol environments used in different tasks of this project are listed in Tables 1.1 and 1.2. Data in Table 1.3 shows all tapered tensile samples with all sides polished tested so far in this study. Previous results from this project, using tapered tensile test samples under constant loading, have shown that the surface stress corrosion cracks (SCC) were only seen in the samples tested in SFGE and FGE solutions with chlorides in the ethanolic test solutions. Further tests were carried out with the inner mill scale of the pipeline intact on one side of the sample.

Data from these tests is shown in Table 1.4. It is clear from these tests that the mill-scaled samples can be used to evaluate the SCC susceptibility of both polished and scaled surfaces. Results from both sets of samples have indicated that the plastic strain is required for the surface cracks to initiate on pipeline steel TTT samples in tested SFGE environments. Surface cracks only appeared in the areas of the TTT samples that showed Luder-bands. Pitting started on these Luder bands and then surface cracks followed the Luder band structure. No pitting or surface crack initiation was observed in areas other than area with plastic strain localization (outside Luder band areas). There were small pit-like structures at the Luder bands but the cracks that appeared at the surface did not propagate into the sample under tested loads during the 15-day test duration in tested environments. However, sectioned TTT samples indicated that the surface cracks observed on Luders bands did not propagate into the pipeline steel under constant load tests for 15 days.

Results showed that an increase in the water content (above ~2.5%) and decrease in pHe of ethanolic solutions led to pitting and general corrosion. Mill scaled surface (mill scale intact on one side) showed similar results to the ones seen from the polished surfaces. Oxide scale cracked under stresses above the yield strength of pipeline steel. However, we did not observe any adverse effect of mill scale on SCC initiation. Low pHe ethanol solutions showed higher dissolution of mill scale from the surface of tested samples.

Based on the previous results and observations, it was decided to do TTTM tests for longer time periods as well as under cyclic stresses to their effect on stress corrosion crack propagation. Therefore, tests in this quarter were done to evaluate the effect of chlorides, water , and pHe in the ethanolic solution on corrosion and SCC behavior of TTT samples exposed to chloride containing SFGE environments that showed SCC under slow strain rate tests. Variables were used to evaluate the effect of environmental factors of SCC susceptibility of X65 pipeline steel.

Table 1.1. Simulated Fuel Grade Ethanol (SFGE) Environments used in this study.

SFGE #	Chloride ppm	Water vol%	Methanol vol%	Acetic Acid mg/L
1	10.14	1.0	0.5	56
2	20.28	1.0	0.5	56
3	51.33	1.0	0.5	56
4	149.56	1.0	0.5	56
5	51.33	2.5	0.5	56
6	51.33	5.0	0.5	56
7	149.56	1.0	0.5	560
8	0	1.0	0.5	56
9	0	5.0	0.5	56
10	149.56	1.0	0	0
11	149.56	0	0	0
12	51.33	1.0	0.5	1120
13	150	1.0	0.5	112.4 NaOH
14	10	1.0	0.5	56
15	20	1.0	0.5	56
16	51	1.0	0.5	56
17	150	1.0	0.5	56
18	51	2.5	0.5	56

Table 1.2. Fuel Grade Ethanol (FGE) Environments used in this study.

FGE	Added Chloride ppm	Added Water vol%
Pure Ethanol	0	0
Pure FGE - S	0	0
Pure FGE - S	10	0
Pure FGE - S	51	0
Pure FGE - S	51	2.50
Pure FGE - S	51	5.00
Pure FGE - WOI	0	0
Pure FGE - WOI	10	0
Pure FGE - WOI	51	0
Pure FGE - WOI	51	2.50
Pure FGE - WOI	51	5.00

Pure Ethanol - 200 proof
"WOI" - Without Inhibitor - P C # 017608
"S" – Standard (Commercial Grade) - P C # 017609

Table 1.3. Summary of Tapered Tensile Sample tests where samples were exposed under constant load for 15-days. Samples listed in this table had all sides machined (no mill scale at the surface.

TTT-SP #	Test Environment	Gas Purge	Max. Stress (as % of Yield Stress)	SCC/Corrosion Susceptibility
1	SFGE-1	Air (continuous)	100	No (after optical Microscopy) TBD
2	SFGE-2	Air (continuous)	100	No (after optical Microscopy) TBD
3	Air			**No**
4	SFGE-3	Air (continuous)	100	**Yes** (Small cracks originating from corrosion Pits at flow-lines)
5	SFGE-1	Air (continuous)	110	**Yes** (few at flow lines)
6	SFGE-2	Air (continuous)	110	**Yes** (few at flow lines)
7	SFGE-3	Air (continuous)	110	**Yes -** Two types of film, Random pits everywhere , cracks at flow lines
8	SFGE-4	Air (continuous)	100	**Yes**, Pits & cracks on flow-lines, fewer flow lines, some large random pits
9	SFGE-5	Air (continuous)	100	**No SCC**-Bluish film, Pits on flow-lines
10	SFGE-6	Air (continuous)	100	**No SCC**, General corrosion
11	SFGE-4	Air (continuous)	110	TBD
12	SFGE-5	Air (continuous)	110	TBD
13	SFGE-7	Air (continuous)	100	**No SCC**, General corrosion starting from random pits
14	SFGE-3	Air – Not continuously purged	110	Pits on Flow lines, Small crack initiations-
15	SFGE-4	Air – Not continuously purged	110	Small corrosion patches under optical microscope. Small pits on flow-lines. SCC TBC
16	SFGE-5	Air – Not continuously purged	110	Pits on flow-lines. Small cracks seem to originate from pits –TBC. No general corrosion
17	SFGE-3	N2 (continuous)	110	Corrosion at flow-lines. Few big orange colored patches of general corrosion. SCC - TBC
18	SFGE-4	N2 (continuous)	110	Pit at inclusions. Patches of accelerated corrosion on sample (preferential dissolution in these areas) Otherwise very little corrosion. SCC-TBC
19	SFGE-5	N2 (continuous)	110	Pits at Inclusions. One large pit (at inclusion. Areas around inclusion are attacked. Two type of pits. Less attack on polished surface. SCC-TBC
20*	SFGE-1	Air (continuous)	110	**Yes** (few at flow lines)

21*	SFGE-3	Air (continuous)	110	**Yes -** Two types of film, Random pits everywhere , cracks at flow lines
22*	SFGE-4	Air (continuous)	110	**Yes**, Pits & cracks on flow-lines, some large random pits
23	Pure FGE - S	Air (continuous)	110	**No SCC**
24	Pure FGE - WOI	Air (continuous)	110	**No SCC**
25	SFGE-3	Air (continuous)	110	**Yes -** Two types of film, Random pits everywhere , cracks at flow lines

**To see the effect of pre-strain on SCC initiation, these samples were loaded to the maximum load in dry-air for 24 hours before adding the SFGE solution to the cell.*

Table 1.4. Summary of Tapered Tensile Sample with Mill Scale (TAPM samples) retained on one surface. TAPM samples were exposed under constant load for 15-days.

TAPM-SP #	Test Environment	Gas Purge	Max. Stress (as % of Yield Stress)	SCC/Corrosion Susceptibility
1	SFGE-1	Air (continuous)	110	Few Surface Cracks at flow lines but no cracks observed after sample sectioning
2	SFGE-2	Air (continuous)	110	Few Surface Cracks at flow lines but no cracks observed after sample sectioning
3	SFGE-3	Air (continuous)	110	Random pits everywhere. Few Surface Cracks at flow lines but no cracks observed after sample sectioning
4	Pure Ethanol (200 proof)	Air (continuous)	110	**No corrosion activity visible**
5	FGE - S	Air (continuous)	110	Few Surface Cracks at flow lines but no cracks observed after sample sectioning
6	FGE – WOI (Without Corrosion Inhibitor)	Air (continuous)	110	Few Surface Cracks at flow lines but no cracks observed after sample sectioning
7	Pure FGE – S + 10 ppm Cl	Air (continuous)	110	**No SCC**
8	Pure FGE – S + 51 ppm Cl	Air (continuous)	110	Few Surface Cracks at flow lines but no cracks observed after sample

				sectioning
9	Pure FGE – S + 51 ppm Cl + 2.5% H_2O	Air (continuous)	110	Few Surface Cracks at flow lines but no cracks observed after sample sectioning
10	Pure FGE – WOI + 10 ppm Cl	Air (continuous)	110	**No SCC**
11	Pure FGE – WOI + 51 ppm Cl	Air (continuous)	110	Few Surface Cracks at flow lines but no cracks observed after sample sectioning
12	Pure FGE – WOI + 51 ppm Cl + 2.5% H_2O	Air (continuous)	110	Large pits, typically at flow lines
13	SFGE-4	Air (continuous)	110	Pits & surface cracks on flow-lines, some large random pits
14	SFGE-6	Air (continuous)	110	**No SCC**, General corrosion
15	SFGE-7	Air (continuous)	110	**No SCC**, General corrosion and random pits
16	SFGE-8	Air (continuous)	110	**No SCC, No Corrosion**
17	SFGE-9	Air (continuous)	110	**Light film but no general corrosion**
18	SFGE-10	Air (continuous)	110	**Very few pits on flow lines**
19	Pure FGE - S	Air (continuous)	110	
20	Pure FGE - WOI	Air (continuous)	110	
21	SFGE-11	Air (continuous)	110	
22	SFGE-12	Air (continuous)	110	
23	Pure FGE - S	Air (continuous)	110	
24	Pure FGE - WOI	Air (continuous)	110	
25	SFGE-3	Air (continuous)	120	**Failure due to Overload**
26	Pure FGE - S	Air (continuous)	120	
27	SFGE-1	Air (continuous)	110	
28	SFGE-3	Air (continuous)	110	
29	Pure FGE - S	Air (continuous)	110	
30	Pure FGE - WOI	Air (continuous)	110	

<u>Effect of cyclic stresses on crack initiation</u>

Cyclic stress tests with TTT samples were started to see if stress corrosion cracks will propagate into the steel under fluctuating stresses. Frequency of these fluctuations was ~1-cycle per hour. Load was held at the maximum load for ~15 minutes before the sample was unloaded, as shown in Figure 1.1.

Table 1.4. Summary of x-65 pipeline TTTM samples with mill scale tested under cyclic stress conditions in different ethanolic environments.

Cyclic TTTM #	SFGE #	Gas purge	Max Stress (ksi)	Min. Stress (ksi)	Number of Cycles	Exposure Time (hrs)	Comments
1	SFGE-3	Air (cont.)	74.67	28.56	360	360	Few Small cracks
2	SFGE-4	Air (cont.)	74.67	28.37	360	360	Large pits and a few small cracks

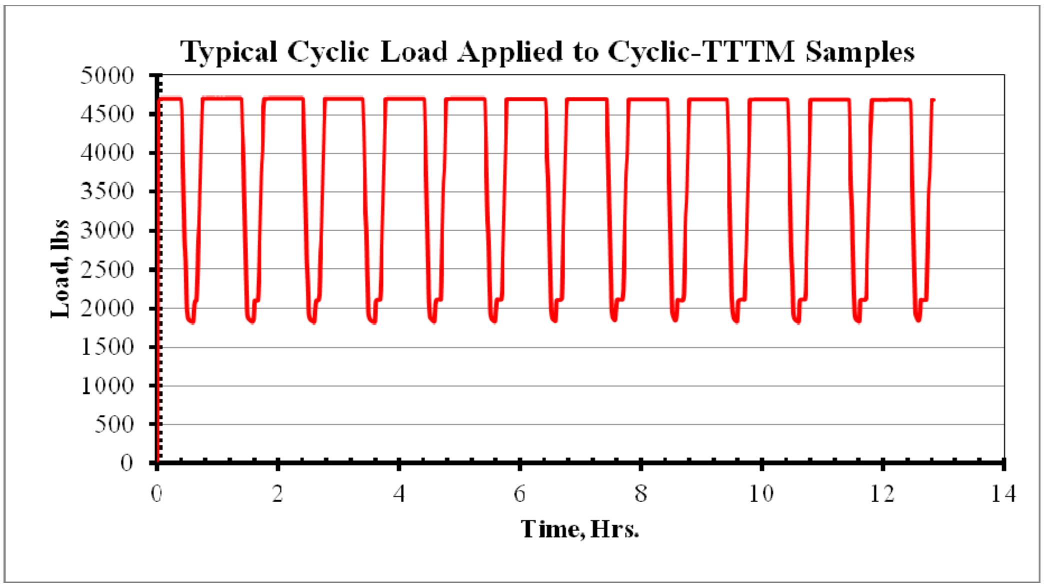


Figure 1.1 Typical cyclic loading used to test TTTM samples.

Data from cyclic loading TTT tests have shown small SCC propagating into the steel. This was not seen under constant loading tests. Although very few and small, but stress corrosion cracks were more prominent in SFGE solution containing 51ppm chlorides, as is shown in Figure 1.2. TTTM sample tested in SFGE with 150ppm chlorides showed large and deep pits, as shown in Figure 1.3. Some small cracks had originated from these pits. Number of cracks was fewer for the sample tested in SFGE-4 with 150ppm chlorides, which had more and deeper pits, compared to the one tested in SFGE-3 with 50ppm chlorides. Effect of cycling on TTTM sample's response to SCC susceptibility is same as that seen for the four-point bend (FPB) tests, as described in later sections.

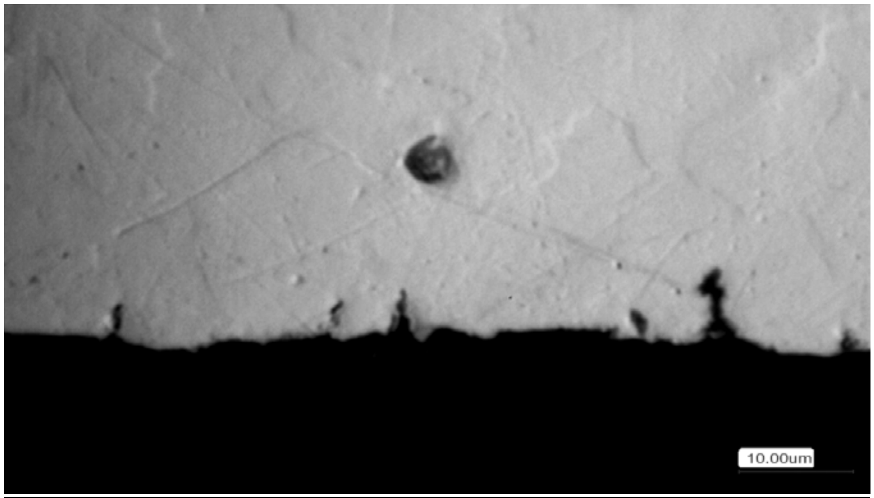


Figure 1.2. Cyclic TTTM sample exposed to SFGE-3 (50 ppm Cl^-) for 15 days. Sample showed small pits and small SCC propagating from these pits. Equivalent constant load tests did not show crack propagation.

Summary of TTT and TTTM Tests

Based on the TTT samples exposed to the selected environment for 15 days, following general summary/conclusions can be drawn:

- Data generated in the previous quarters had shown that the surface cracks were only seen in the samples tested in SFGE and FGE solutions with chlorides in the test solution.
- Increase in water content (above ~2.5%) and decrease in pHe led to pitting general and general corrosion.
- It was also shown that the plastic strain was required before surface cracks could be observed on pipeline steel TTT samples in tested SFGE environments.
- Surface cracks only appeared in the areas of the TTT samples that showed Luder-bands. Pitting started on these Luder bands and then surface cracks followed the Luder band structure. We did not see any signs of SCC initiation at any other area without plastic strain localization (outside Luder band areas.
- Sectioning of samples, that showed signs of surface cracks, did not show any well developed crack in the sample. There were small pit-like structures at the Luder bands but the cracks that appeared at the surface did not propagate into the sample under tested loads during the 15-day test duration in tested environments.
- Samples tested with the mill scaled surface intact on one side did not show any different results from the ones seen from the polished surfaces.
- Oxide scale cracked under stresses above the yield strength of pipeline steel. However, we did not observe any adverse effect of mill scale on SCC initiation.
- Film or corrosion deposits formed at the pipeline steel surface were strongly a function of the composition of the fuel grade ethanol solutions.

1.1 <u>Task-1 Slow Strain Rate Tests in SFGE</u>

All published data on SCC of pipeline steels in FGE and SFGE from this group and other research groups was done by slow strain rate test (SSRT). To get equivalent data for SCC susceptibility by SSRT, equivalent tests were done under all ethanolic environments tested in this study to compare with other test methods. The work on this sub task for the task-1 was primarily focused on tests in SFGE and commercial grade FGE, with and without corrosion inhibitors added, as shown in Table 1.1 and 1.2 respectively.

These tests were done to produce equivalent data to compare with other test methods under equivalent environments. Data from the SSRT, tests done in this quarter as well as previous data for comparison, is shown in Table 1.5. It clearly shows that pure ethanol did not show any signs of SCC. However, SFGEs containing chlorides above 10 ppm showed SCC or corrosion, depending on the water content and pHe of the solution. Data from samples tested in solutions containing varying amounts of chlorides, water, and acetic acid which affected the crack density and crack length is shown in Table 1.5. Results are no signs of SCC when ethanol is mixed with water, methanol, acetic acid, but no chlorides (e.g.SFGE-8 and SFGE-9). With increase in water content of SFGE above about 5%, which contains chlorides, changes from SCC to pitting or/and general corrosion, as shown by data in Table 1.5.

Results from these SSRT clearly show that the chlorides are very important but also the pH of the solution is important in determining the SCC susceptibility of pipeline steels in fuel grade and simulated fuel grade ethanol environments.

Table 1.5. Summary of x-65 pipeline steel samples tested by slow strain rate test method in different ethanolic environments.

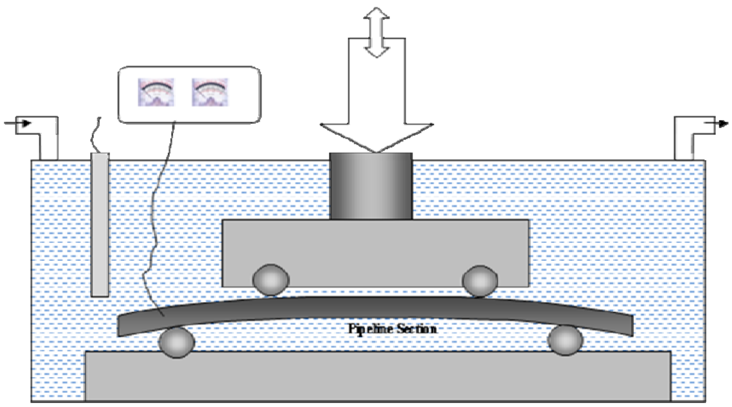
Test #	SFGE Tested	Gas Purge	Crack Density /mm	Crack Length (mm)	Crack Velocity mm/sec	Remarks
1	200 Proof		0	0.000	0.E+00	No Cracking
2	SFGE-1	Air(cont.)	16	0.091	4.E-07	SCC
3	SFGE-2	Air(cont.)	19	0.134	3.E-07	SCC
4	SFGE-3	Air(cont.)	24	0.226	6.E-07	SCC
5	SFGE-4	Air(cont.)	27	0.194	2.E-06	SCC
6	SFGE-5	Air(cont.)	8	0.064	2.E-07	SCC
7	SFGE-6	Air(cont.)	0	0.000	0.E+00	Pitting but No Cracking
8	SFGE-7	Air(cont.)	30	0.145	4.E-07	SCC
9	SFGE-8	Air(cont.)	0	0.000	0.E+00	No Corrosion
10	SFGE-9	Air(cont.)	0	0.000	0.E+00	No Corrosion
11	SFGE-10	Air(cont.)	11	0.093	4E-07	SCC
12	SFGE-11	Air(cont.)	14	0.072	2E-07	SCC
13	SFGE-12	Air(cont.)	30	0.119	3E-07	SCC
14	SFGE-11	Air(cont.)	TBD	TBD		TBD
15	SFGE-13	Air(cont.)	0	0	0.E+00	No Corrosion
16	SFGE-14	N_2(cont.)	0	0	0.E+00	No Corrosion
17	SFGE-15	N_2(cont.)	0	0	0.E+00	No Corrosion

18	SFGE-16	N_2(cont.)	0	0	0.E+00	No Corrosion
19	SFGE-17	N_2(cont.)	0	0	0.E+00	No Corrosion
20	SFGE-18	N_2(cont.)	0	0	0.E+00	No Corrosion

2.0 Task 2- Four-Point Bend (FPB) Tests on Pipeline Sections to Simulate Pipeline Loading

Static and cyclic loading of FPB samples

Four point bend tests were performed to simulate stresses on the inside surface of an operating pipeline. Test rig for FPB tests was designed to test a section of a pipeline, without any further sample preparation, especially without removing the mill scale, as shown in Figure 2.1



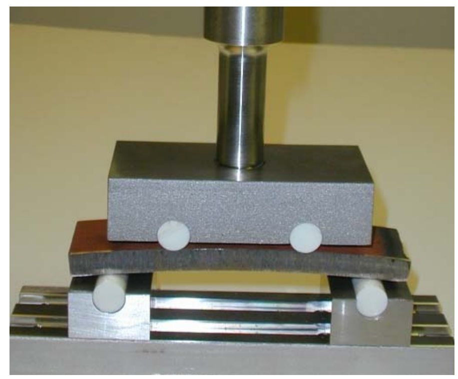


Figure 2.1 Four point bend tests on pipeline sections for SCC initiation under pipeline operating conditions, with and without mill scale.

Initial tests showed that there were areas where the mill scale had cracked and the SFGE got in touch with the bare metal, as shown in Figures 2.2 and 2.3. Corrosion products formed in these local areas. New corrosion product formed during FPB tests was lighter gray in these micrographs whereas the old mill scale is brownish. Earlier results from four-point bend (FPB) tests with constant strain or stress tests showed that SCC did not initiate at the mill scaled surface of pipeline steel, as is shown in Table 2.1. Results from the static FPB tests (with constant stress or strain) with mill scaled surface in SFGE and FGE were very similar to the one obtained from tests with TTT samples.

Pressure in these pipelines fluctuates from the operating loads or pressure fluctuations in the pipe. To see the effect of fluctuating stresses on SCC susceptibility, low frequency cyclic stresses were applied to pipeline samples with oxide scale intact at the surface. Typical cycle applied to these samples is shown in Figure 2.4.. Cyclic stress was applied for 15 days, similar to the static stress FPB tests described earlier. Maximum load was varied but the minimum load was kept constant in different tests at 200 lbs, as is show in Table 2.2 and 2.3. Corresponding tensile stresses at the internal pipe surface were calculated from the beam deflection based on ASTM G-39.

FPB tests with low frequency fluctuating stress (cycle per 2-hours) showed SCC in simulated fuel grade ethanol, as shown by results in Table 2.2 and 2.3. Figure 2.5 shows that the mill scale at the surface had cracked and when the surface film was removed with Clark's reagent without affecting the metal, surface cracks in the pipeline steel were clearly visible, as shown in Figure 2.5 (b). Cyclic loading, produced severe SCC in the form of long, branched cracks in all cases where the maximum stress was above the yield stress, as shown in Figures 2.6 to 2.8. Cracks were observed under the cyclic conditions at stresses which did not show any SCC under static loadings. Stress corrosion cracks were mainly transgranular in nature, as shown by SEM micrograph in Figures 2.7 and 2.8. Examples of polished cross sections of several four-point bend tests are depicted below for cyclic loading conditions. Based on that, tests were continued with low frequency- four point bend tests in fuel grade ethanol (FGE) environment.

Data from low frequency FPB tests so far has shown SCC of pipeline steel (with mill scale) in SFGE. Tests in this quarter were done to determine the threshold stress required under fluctuating stresses for four point bend tests. Data in Table 2.2 shows that the cyclic stresses, with maximum stress above the yield strength of pipeline steel, can cause SCC of pipeline steels in chloride containing FGE and SFGE. Whereas equivalent FPB tests, without cyclic stresses, did not show SCC in our previous tests from this study.

Interesting results from our recent tests have shown SCC susceptibility of pipeline steels in commercial fuel grade ethanol (FGE) without added water or chlorides under cyclic stress tests. Solution was analyzed after the test to see if some chloride contamination entered the cell but the chloride levels were below 0.5 ppm in these solutions.

Tests were done to determine the threshold stress required for four point bend tests, at which stress corrosion cracks (SCC) are initiated and propagated with application low frequency cyclic stress tests in FGE and SFGE with different compositions. Data so far indicates that the FGE without addition of chlorides under cyclic conditions have a threshold stress (maximum stress) just above the yield stress of steel. Whereas equivalent FPB tests without cyclic stresses did not show any signs of SCC in our previous tests from this study, even with SFGE with 51ppm chlorides.

Table 2.1. Summary of Four Point Bend (FPB) tests done in SFGE and FGE environments

FPB sp#	SFGE	Displacement (mm)	Maximum Stress (MPa)	Exposure Time (hrs)	SCC (Y/N)	Max. Crack Length (µm)
1	SFGE-3	0.25	134	360	N	NA
2	SFGE-3	1.00	537	360	N	NA
3	SFGE-3	2.50	1342	360	N	NA
4	Pure FGE - S	2.50	1342	204	N	NA
5	Pure FGE - WOI	2.50	1342	360	N	NA

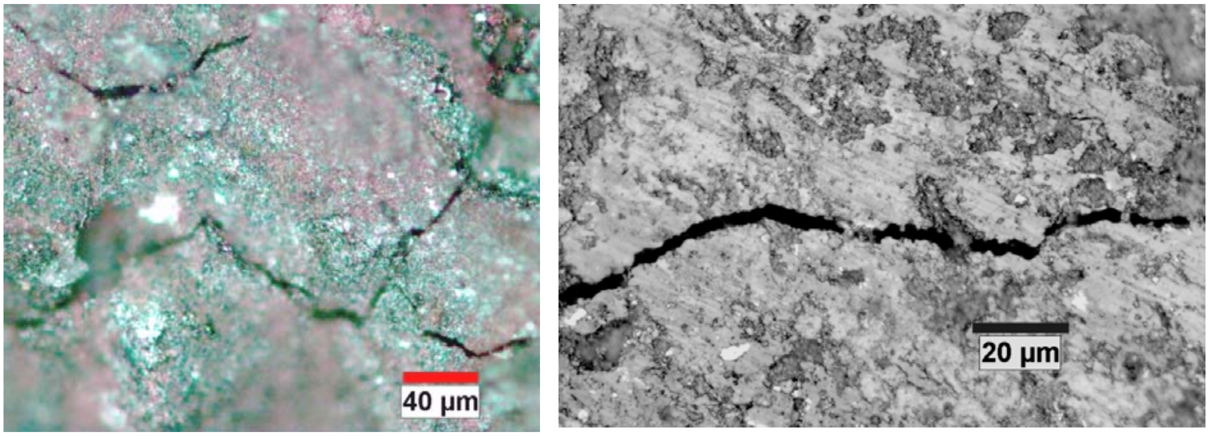


Figure 2.2 Surface cracks in the mill scale of tested four-point bend samples.

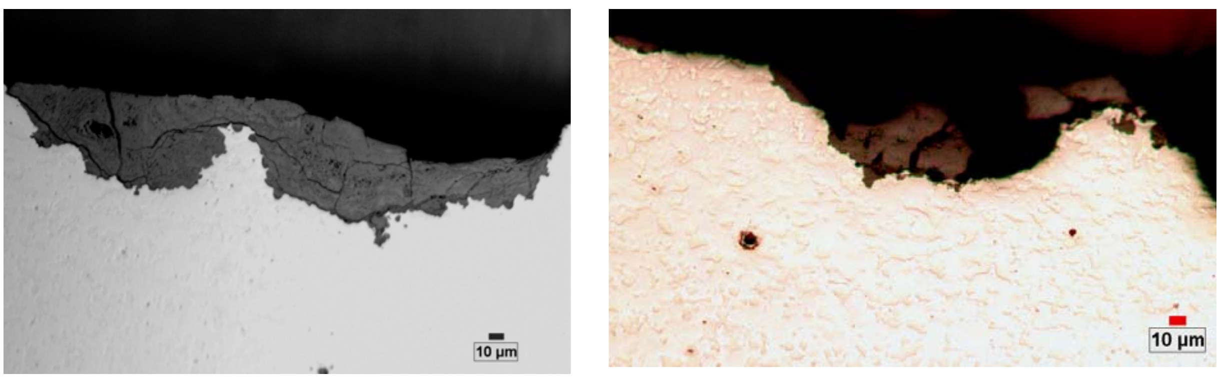
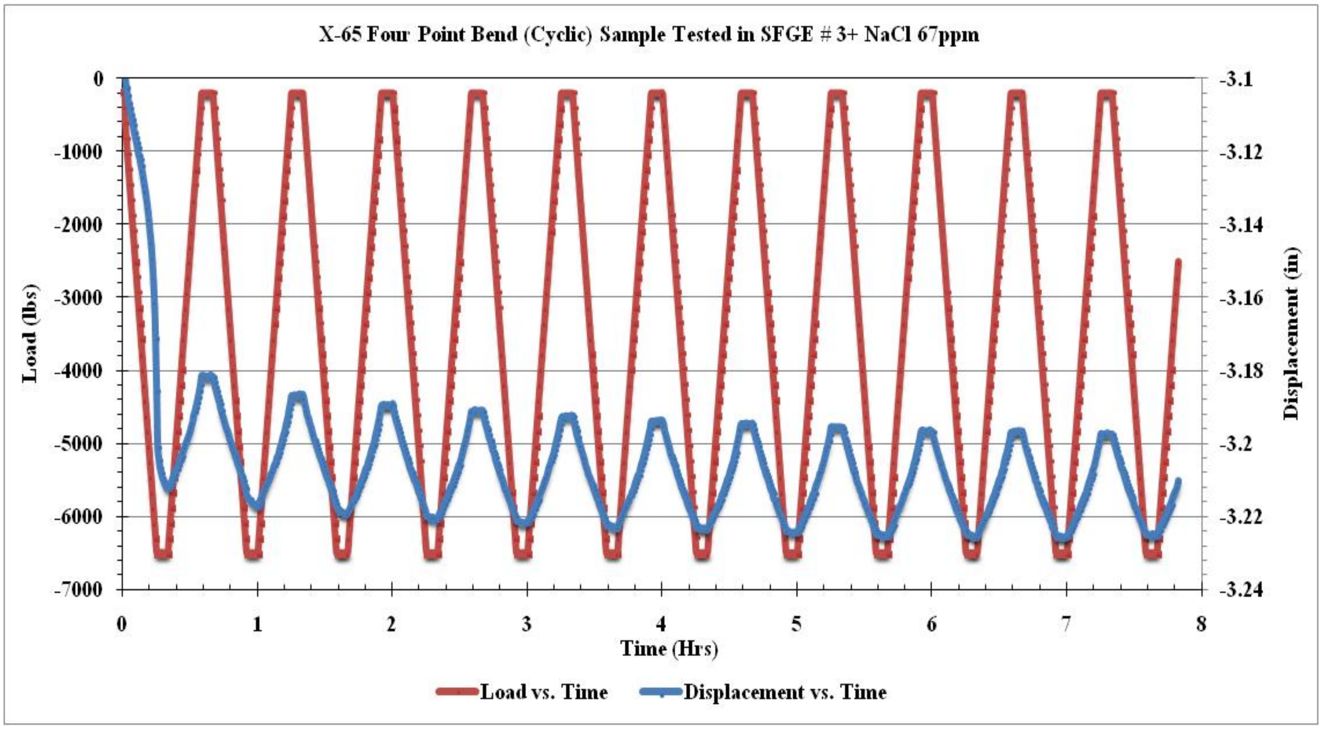


Figure 2.3 Cross section of FPB sample tested under monotonic strain conditions did not show any crack propagation in the metal for any tested pipeline steel sample.

2.1 Task-2 Effect of Low frequency Cyclic Stresses on SCC Susceptibility



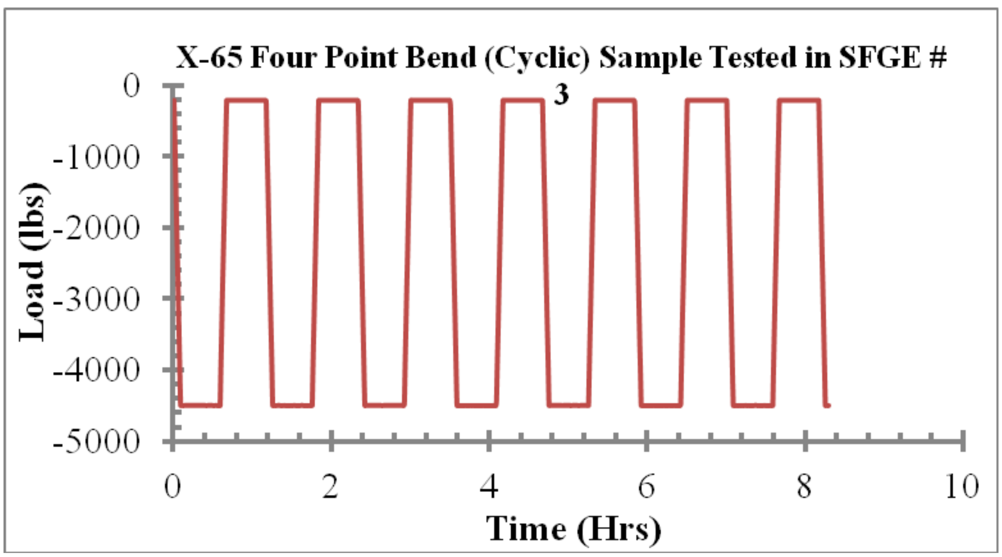
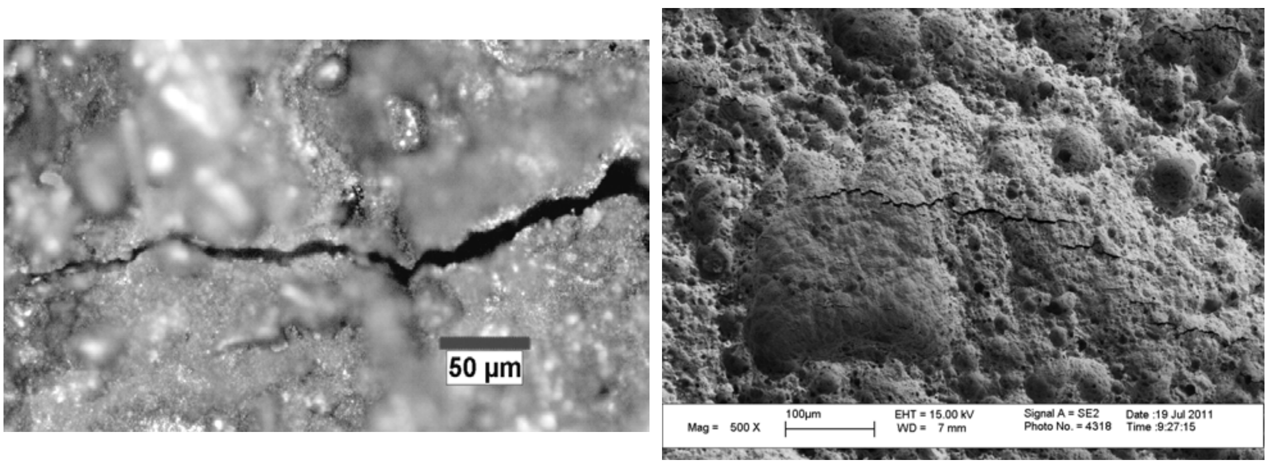


Figure 2.4. **Showing typical cyclic load/displacement conditions used for cyclic FPB tests in this study. Maximum load was varied for different test samples but the minimum load was kept constant at 200 lbs.**

Table 2.2. Summary of Cyclic Four Point Bend (FPB) tests done in SFGE environments.

FPB SP #	Environment	Purged Gas (Cont)	Min Load lbs	Max Load lbs	No of Cycles	Max. Crack Length (µm)
6	SFGE-3	Air	200	4500	360	No Cracks
7	SFGE-3	Air	200	6500	240	110
11	Air	Air	200	6500	240	No Cracks



(a) (b)

Figure 2.5. Surface cracks in the mill scaled surface of Cyclic FPB tests on pipeline sample (sample#7), a) with mill cracked mill scale at the surface, b) After mill scale removal, showing SCC in the pipeline steel

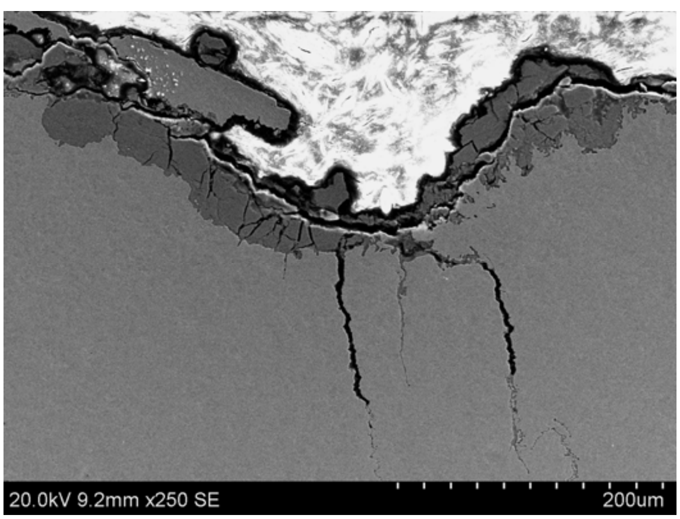
Preliminary observations from the crack morphology show that the cracks are predominately transgranular, as shown in Figures 2.7 and 2.8. In FGE and SFGE solutions with added Cl^-, the cracking appears transgranular, traversing the sample with a fairly straight path (4PBT samples #7 and #9), shown in Figures 2.6 to 2.8. This is consistent with findings in recently published literature on SCC in FGE. However, in the FGE environments (without any addition of chlorides) stress corrosion cracking assumes some mixed-mode appearance, changing direction at sharp angles (4PBT sample#8, 10), as shown in Table 2.3.

Table 2.3. Cyclic Four Point Bend (FPB) tests done in standard fuel grade ethanol (FGE-S) environments.

FPB SP #	Environment	Purged Gas (Cont)	Min Load lbs	Max Load lbs	No of Cycles	Max. Crack Length (μm)
8	FGE - S	Air	200	6500	240	184
10	FGE - S	Air	200	6000	240	83
12	FGE - S	Air	200	5500	240	98
13	FGE - S	Air	200	5000	240	No Cracks
16	FGE - S	Air	200	5000	167	No Cracks

Table 2.4. Summary of Cyclic Four Point Bend (FPB) tests done in Standard fuel grade ethanol (FGE-S) with Chloride added environments.

FPB SP #	Environment	Purged Gas (Cont)	Min Load lbs	Max Load lbs	No of Cycles	Max. Crack Length (μm)
9	FGE – S + 51 ppm Cl	Air	200	6500	240	102
14	FGE – S + 51 ppm Cl	Air	200	5000	240	41
15	FGE – S + 51 ppm Cl	Air	200	4500	240	No Cracks



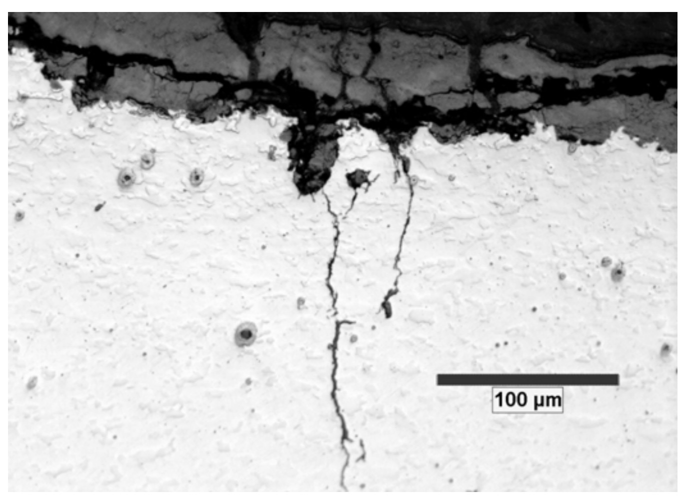


Figure 2.6. Cyclic Four Point Bend (FPB) tests on pipeline sample (sample#7), with mill scale intact on the inner surface, in SFGE-3 (with 50 ppm Cl). Maximum cyclic load of 6500 lbs. Examination of surface or the sectioned sample did not show any signs of SCC on these samples in SFGE-3

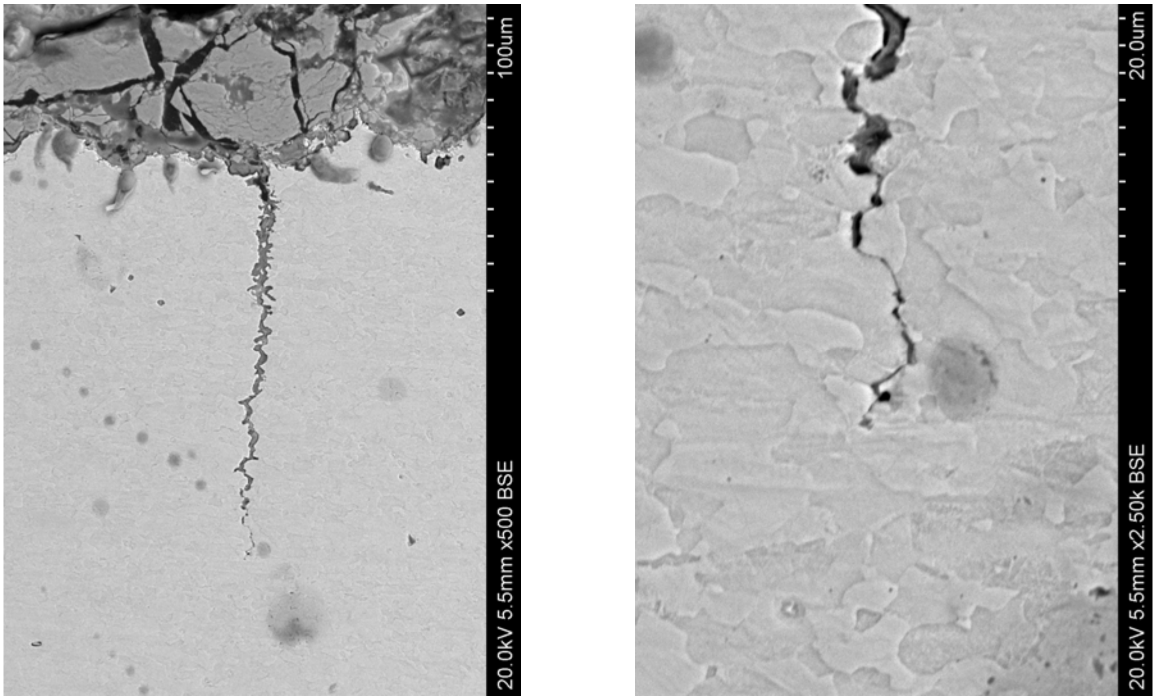


Figure 2.7. Cyclic Four Point Bend (FPB) tests on pipeline sample (sample#8) tested in commercial grade fuel grade ethanol (FGE) without any addition or modification. Maximum load per cycle was 6500 lbs. Notice that the SCC originated from notches of mill-scaled surface.

Stress corrosion cracks were observed in standard FGE solution (without addition of chloride) when the maximum cyclic load met or exceeded 5500 lbs, as in Figures 2.7. No SCC was observed on sample tested at maximum cyclic load of 5000 lbs, as shown in Table 2.3. and Figure 2.10. However, when an equivalent test at maximum cyclic load of 5000 lbs was carried out in the standard FGE with 51ppm chloride, sample showed small SCC initiating from the mill-scaled surface, as shown in Figure 2.11. However, test done wirh FGE-S with 51 ppm Cl at maximum load of 4500 lbs did not show any sign of SCC. This clearly shows that the threshold stresses depend on the environmental factors, where chlorides decrease the threshold stresses for SCC in ethanolic environments for pipeline steels.

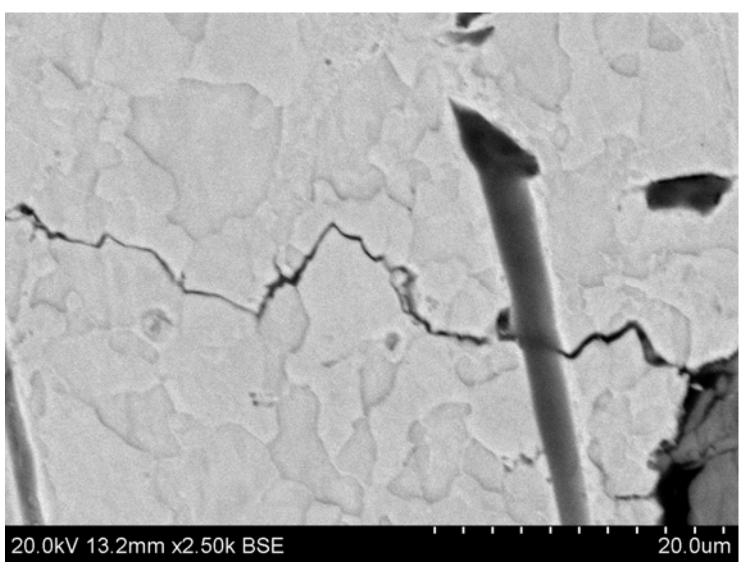


Figure 2.8. Cyclic Four Point Bend (FPB) tests on pipeline sample (sample#9) tested in FGE-S with 51ppm Cl added, showing a small SCC originated from mill-scaled surface. Maximum load per cycle was 6500 lbs.

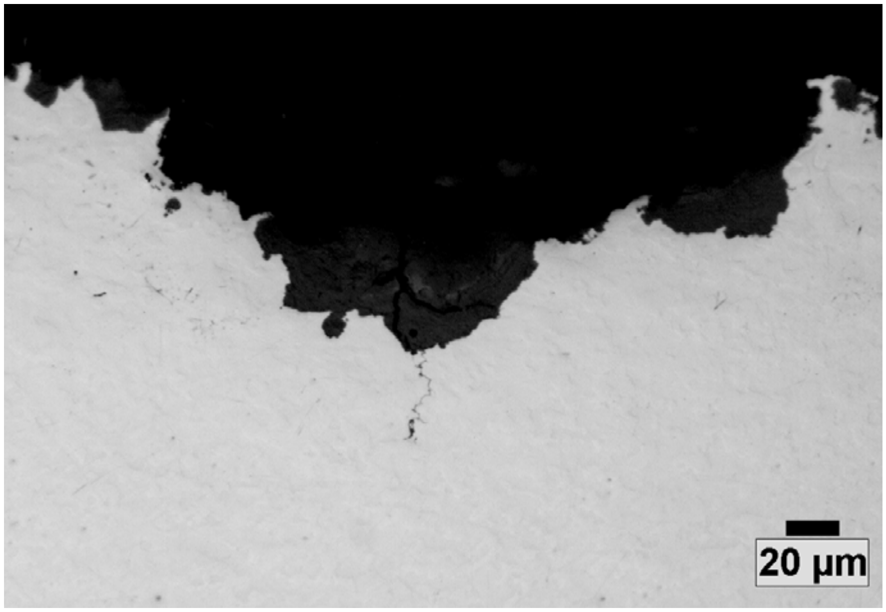


Figure 2.9. Cyclic Four Point Bend (FPB) tests on pipeline sample (sample#12) showing a small SCC originated from mill-scaled surface tested in commercial grade fuel grade ethanol (FGE-S) without any addition or modification. Maximum load per cycle was 5500 lbs.

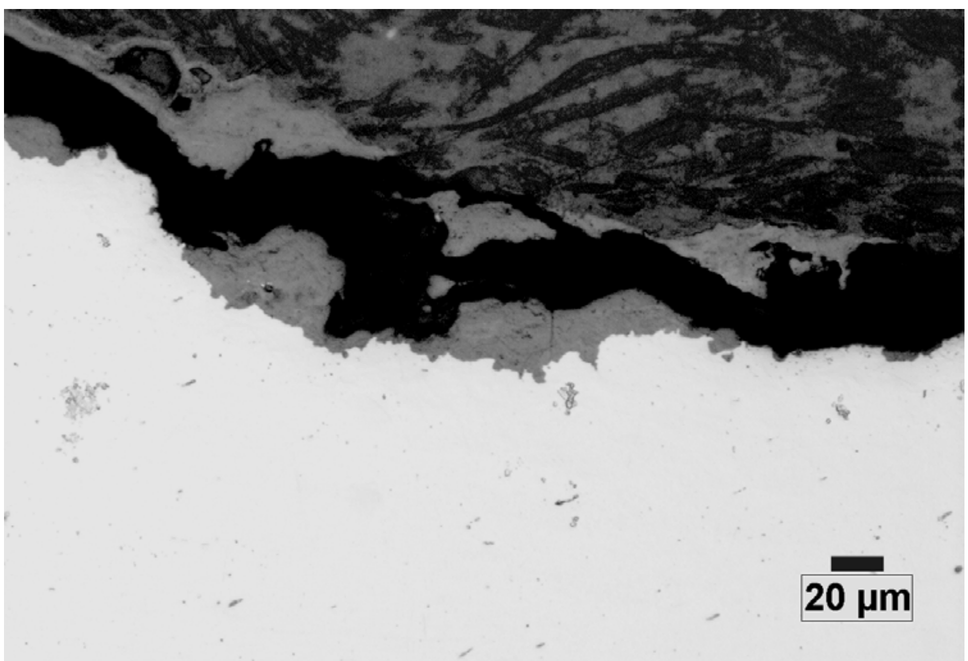


Figure 2.10. Cyclic Four Point Bend (FPB) tests on pipeline sample (sample#13) showed no SCC in commercial grade fuel grade ethanol (FGE-S). Maximum cyclic load for this test was 5000 lbs.

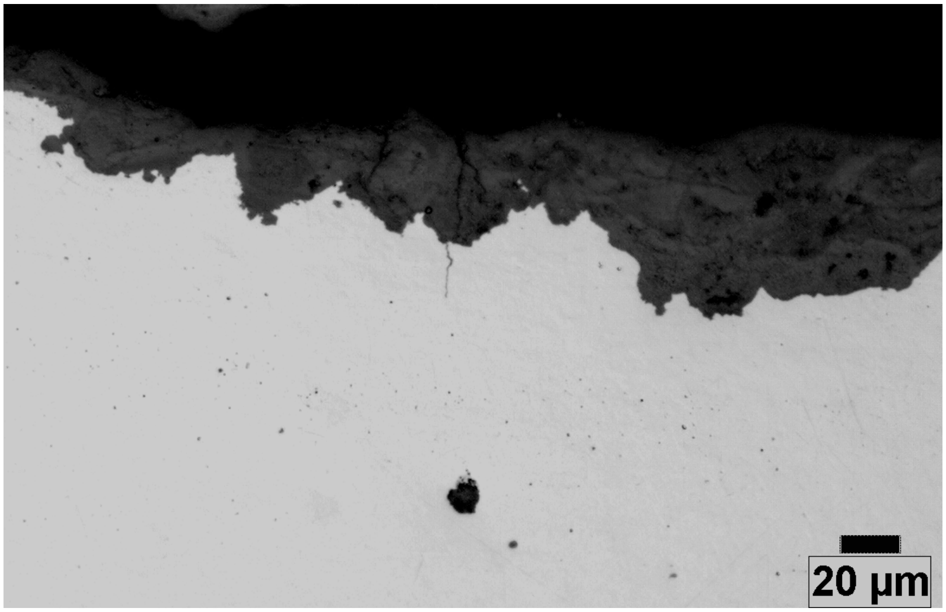


Figure 2.11. Cyclic Four Point Bend (FPB) tests on pipeline sample (sample#14) tested in commercial grade fuel grade ethanol (FGE) with 51ppm chloride showed SCC even at the Maximum cyclic load of 5000 lbs.

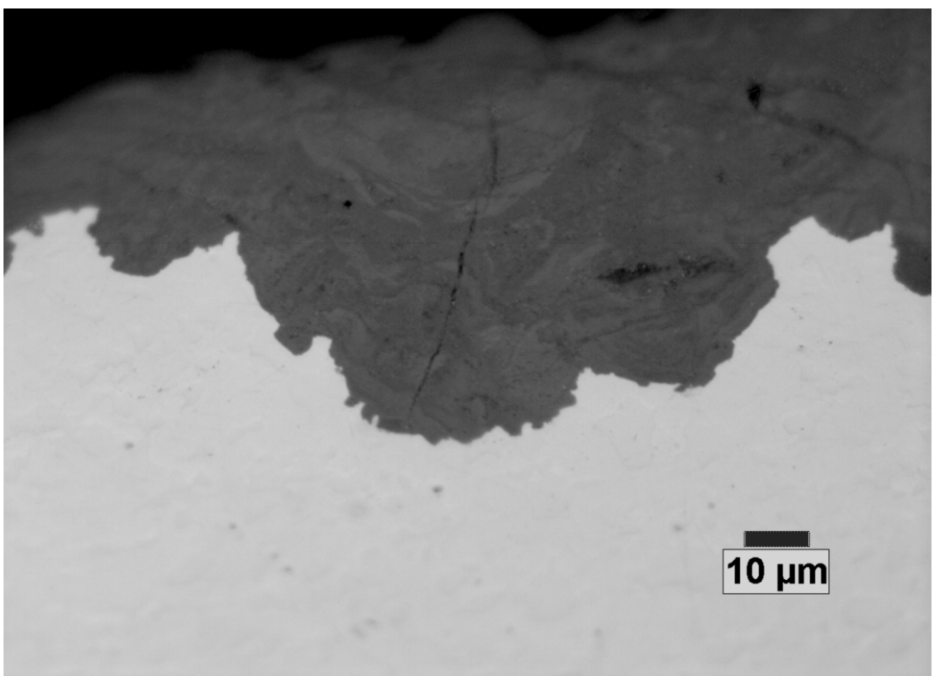


Figure 2.12. Cyclic Four Point Bend (FPB) tests on pipeline sample (sample#14) tested in commercial grade fuel grade ethanol (FGE) with 51ppm chloride tested at maximum cyclic load of 4500 lbs. This sample did not show any SCC

2.2 Key Results from Four Point Bend Tests:

- No SCC in SFGE of FGE was observed for FPBs tested under constant Load/Displacement
- Low-frequency cyclic loading (~1cycle per hour) resulted in SCC on mill-scaled FPB samples
- Threshold stresses (maximum cyclic stress) for SCC in FGE and SFGE was around YS of pipeline steel
- SCC was observed in commercial grade FGE (without chlorides) for the 1st time in our laboratory
- Crack growth rate increased with an increase in the maximum load
- Chlorides in FGE lowers the threshold stress for SCC initiation
- Threshold stresses are affected by the environmental constituents of fuel grade ethanol. For example, threshold stresses decrease with presence of chlorides even under cyclic conditions.

3.0 Task 3 K_{ISCC} and Crack Growth Rate Measurements (Fracture Mechanics Approach)

If there are preexisting cracks in pipeline or if cracks initiate, will they grow or when will they grow in FGE or FGE/gasoline blends? To answer this question it is important to determine the threshold stress intensity value for (K_{Iscc}) under different environmental conditions. To determine the values of threshold stress intensity for a single crack of a given dimension under different environmental conditions, standard fracture mechanics approach is adopted. Standard wedge loaded double cantilever beam (DCB) samples were machined out of the section of a X-65 pipeline.

Multiple pre-cracked DCB samples were prepared where the precrack was produced in air. The DCB samples are used in this study as multiple wedge loaded DCB samples can be exposed simultaneously to determine the K_{ISCC} and crack growth rates and crack morphology after each test can be evaluated. Precracked DCB samples were exposed to a given environment (SFGE-3 and SFGE-4) at different initial stress intensity factors (K) in different FGE environments to determine the K_{ISCC} under those conditions. Values of stress intensities tested for the two environments are listed in Table 8.

Double cantilever beam (DCB) samples were pre-cracked in dry lab air and loaded to different stress intensity (K) values. Crack length is measured under optical microscope, as shown in Figure 20. In first set of tests precracked DCB samples were loaded samples to different K_{ISCC} values and exposed to the SFGE environment (SFGE-3) with 51 ppm chlorides. Stress intensity factor for precracked samples was varied by wedge-loading the sample using loading bolts. Crack mouth opening displacement. ASTM G-168-00 was followed to calculate the stress intensity factor.

Sample are frequently examined to measure the crack growth on each sample and quantify the crack growth rate as a function of applied stress intensity and to determine the threshold stress intensity factor for SCC (K_{ISCC}). To do so, the samples are taken out of the chamber at regular intervals (in a special container to keep test environment in the crack) and examined using an optical microscope for crack growth. Crack growths on these samples are found to be slow. Tests will continue till the crack growth rate is less than 10^{-9} cm/s for a given sample. At the end of these tests, DCB sample will be fractured using MTS and the fracture surface will be examined to measure for crack length and determine stress corrosion crack morphology.

Table 8 DCB samples loaded to different stress intensity values and exposed to different SFGE solutions

DCB Sample #	Test Environment	Crack Mouth Opening Displacement (Vo) in mm	Starting Crack Length (ao) in Meter	Stress Intensity Factor at Crack Arrest (K_{Ia}), MPa-m^1/2
1	**SFGE#3**	**0.60**	0.038428	**48.27**
2	**SFGE#3**	**0.53**	0.036447	**45.34**
3	**SFGE#3**	**0.48**	0.03642	**40.42**
4	**SFGE#3**	**0.42**	0.036374	**35.56**
5	**SFGE#3**	**0.36**	0.036376	**30.43**
6	**SFGE#3**	**0.30**	0.03621	**25.84**
7	**SFGE#4**	**0.93**	0.03959	**70.40**
8	**SFGE#4**	**0.85**	0.039478	**65.25**
9	**SFGE#4**	**0.67**	0.037312	**54.89**
10	**SFGE#4**	**0.62**	0.037509	**50.32**
11	**SFGE#4**	**0.52**	0.035859	**45.14**
12	**SFGE#4**	**0.48**	0.036306	**40.03**

Initial data from DCB samples has shown that the K_{ISCC} for SFGE#3 is above 45 MPa-m$^{1/2}$. Samples are polished such that the intentionally put scratches, perpendicular to the crack path, help in determining the crack growth. DCB samples were examined under optical microscope at magnification of x1000, but significant crack growth was not observed under tested conditions on these samples even after about month long exposure. These samples will be fractured under liquid nitrogen and then the fracture surface will be observed in SEM to determine if there was any crack growth from the precrack under tested environmental conditions under applied stress intensities.

Tests in SFGE#4 are continuing and are expected to be over in next month. Typical crack tips of samples exposed to these environments are shown in Figure 21.

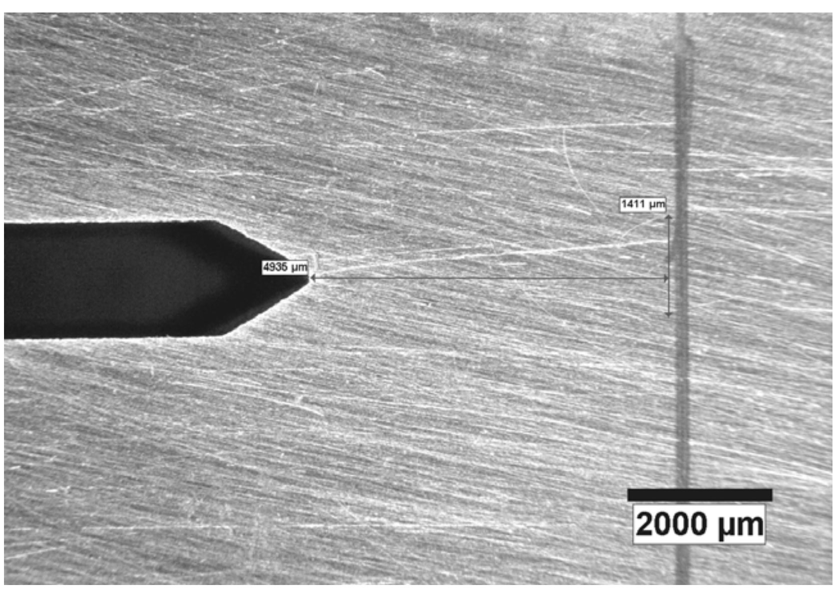


Figure 20. **Precracked DCB samples used in this study. Crack length and sample dimensions are measured to calculate the stress intensity after wedge loading.**

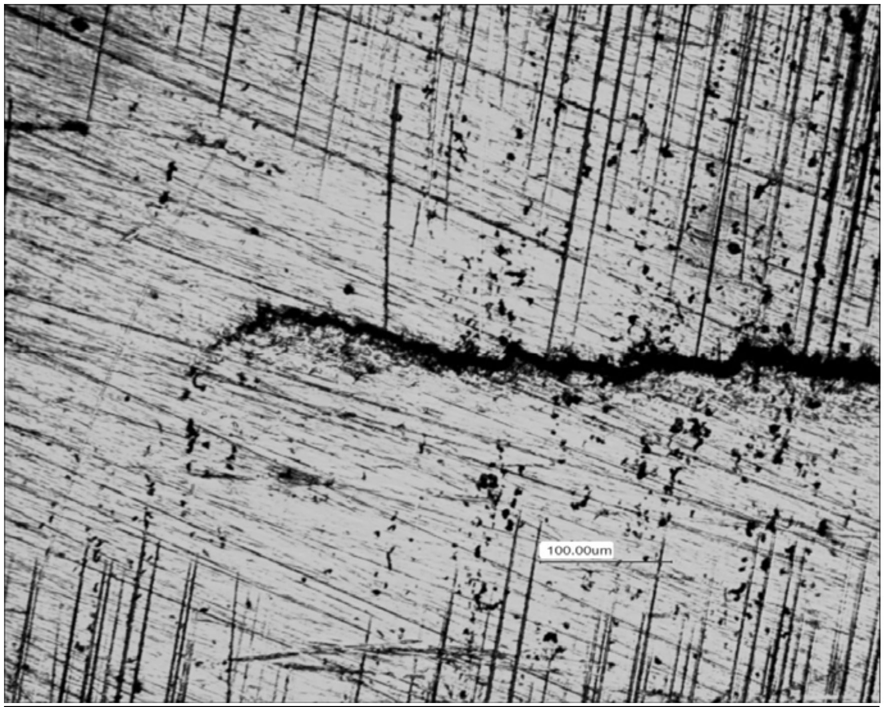


Figure 21. **Crack tip of DCB samples#12 after exposure to SFGE-4 for 12 days.**

4.0 <u>Task 4 – Phenomenological Understanding of SCC in FGE</u>

To understand the phenomenon of stress corrosion cracking of pipeline steels in ethanolic environments, especially in SFGE and FGE environments, tests were continuing. This involves evaluating the effect of environmental parameters, stress effects and alloy related effects. Results have shown clear effects of water, chlorides and pHe on repassivation of steels. Molecular dynamics (MD) modeling work is also continuing see how the water-ethanol mixture interacts with the steel surface or how the water soluble constituents get concentrated at the steel surface in these environments.

4.1 Cyclic SSRT to Understand its Effect on SCC initiation and Propagation

The overall goal of performing cyclic slow strain rate tests was to try to reproduce the cracking that occurred in the cycled 4-point bend tests. Thus far, five total samples have been tested. Initially, one test was performed in an FGE with no inhibitor (FGE-WOI) and a high amount of added chloride, because this had proven to be a potent cracking environment in the previous non-cyclic smooth and notched SSRT. The remainder of the cycled tests were done in the commercial ethanol that led to the one and only instance of SCC found in the early round robin tests, lot 8 (#1641499).

Table 4.1 **Composition of the environments used for cyclic tests:**

Environment	Chloride (ppm)	Water (vol%)	pHe (ASTM method)
FGE WOI	150	1.1	7.9
FGE Lot 8 (1641499)	<1	0.67	7.9

Table 4.2 Cyclic SSRT Conditions Tested

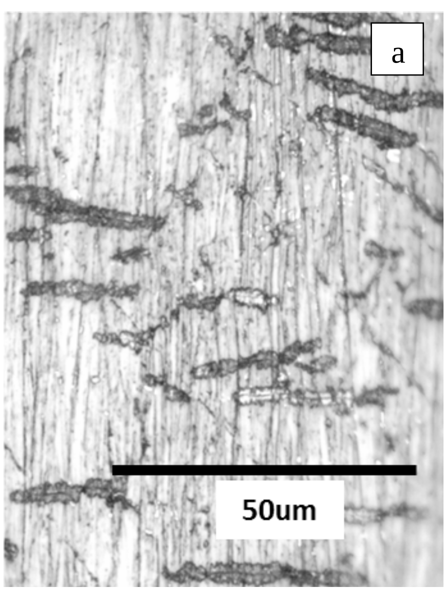
Test #	Environment	Time cycled	Elongation rate	Minimum load	Maximum load	R value
1	FGE Lot LG+150ppm Cl	8 days	5e-7in/s	1.09V (437lbs)	2.19V (875lb)	0.5
2	FGE Lot 8	15 days	5e-7in/s	1.09V (437lbs)	2.19V (875lb)	0.5
3	FGE Lot 8, pre-filmed	14 days	5e-6in/s	1.09V (437lbs)	2.19V (875lb)	0.5
4	FGE Lot 8, Rusty couple	14 days	5e-6 in/s	1.09V (437lbs)	2.19V (875lb)	0.5

Maximum load was chosen so that maximum stress of 71ksi was applied to each sample, which is above yield stress (65-70ksi) but below UTS. Cycling rate was increased by an order of magnitude after the first two tests to match that of the 4-point bend test cycling rate. Additionally, one sample was pre-filmed and the other galvanically coupled to a rusty piece of pipe steel because it was brought to our attention that these additional factors acted to raise the open circuit potential of the steel, boosting it into the SCC-susceptible range. Thus, it was expected that the loading schedule and environmental conditions would produce a potent cracking environment for samples 3 and 4.

After being cycled, sample surfaces were examined in optical microscope to identify possible crack initiation sites. Half of the gauge section of each sample was cross sectioned, polished, and examined for crack growth.

Results

No cracking was observed in any of the samples. The test# 1 sample surface did have many bands of localized corrosion, oriented perpendicular to the applied load (Figure 4.1 a). However, the cross section did not show any signs of crack propagation. There were one or two instances where the corrosion did penetrate into the steel, producing a deep crack-like pit (Figure 4.1 b).



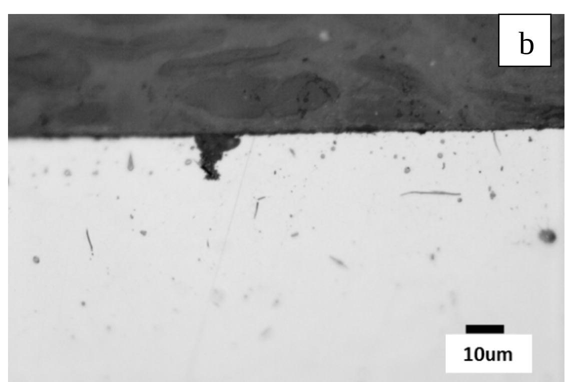


Figure 4.1. Surface (a) and cross section (b) of SSRT in Cl- containing FGE-WOI

The sample cycled in as-received Lot 8 FGE did not exhibit any areas of localized corrosion or crack initiation. The polished cross section appeared smooth (Figure 4.2)

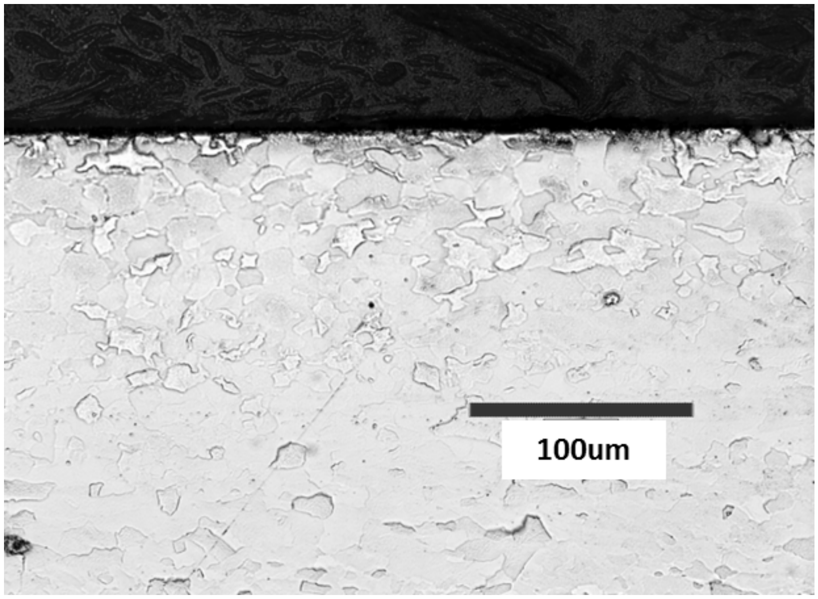


Figure 4.1. Polished cross section of sample cyclically strained in FGE lot 8

The pre-filmed sample developed deep pitting during the pre-filming process, which consisted of potentiostatically polarizing the sample to 641mV vs SCE in an aqueous NaOH solution, pH = 10.5, for several minutes. This procedure was suggested by Hanninen et al. (*Welding and Cutting*, Vol 10 (2011): pp.188-193.) as a technique to grow a corrosion scale on the surface of the specimen to simulate a pre-existing scale that would be found in field conditions. The pre-filmed sample did not appear to develop any new pits during the cyclic test (Figure 4.3 a and b). Existing pits may have grown in size, but did not initiate any stress corrosion cracks.

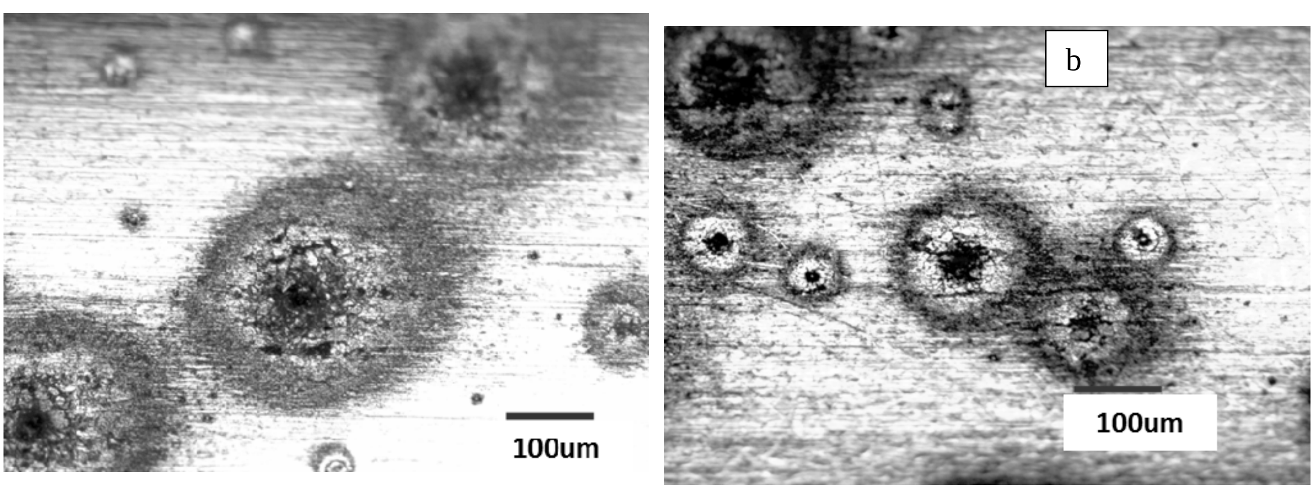


Figure 4.2. Test#4 sample surface before (a) and after (b) testing

Similarly, galvanic coupling of the sample to a pre-scaled or rusted piece of the same steel was discussed in a study done by Sridhar et al. (*Corrosion*, vol. *62* (8) (2006): pp. 687-702) as a method of

simulating a pre-existing scale on the pipe surface. The study concluded that this galvanic coupling did increase the SCC susceptibility of the steel in FGE environments. In our case, the cyclically loaded sample in test #4 was galvanically coupled to a rusted piece of the same steel, with the rusted steel: polished steel surface area ratio of approximately 1:1, identical to the ratio used in the study. After cycling for 14 days, areas were observed on the sample surface that resembled small fissures (
Figure **4.3** a). The fissures were encircled by a dark area, most likely a small amount of corrosion product. When the cross-section was examined, none of the fissures appeared to propagate as cracks into the bulk, and the surface appeared smooth throughout the section (
Figure **4.3** b).

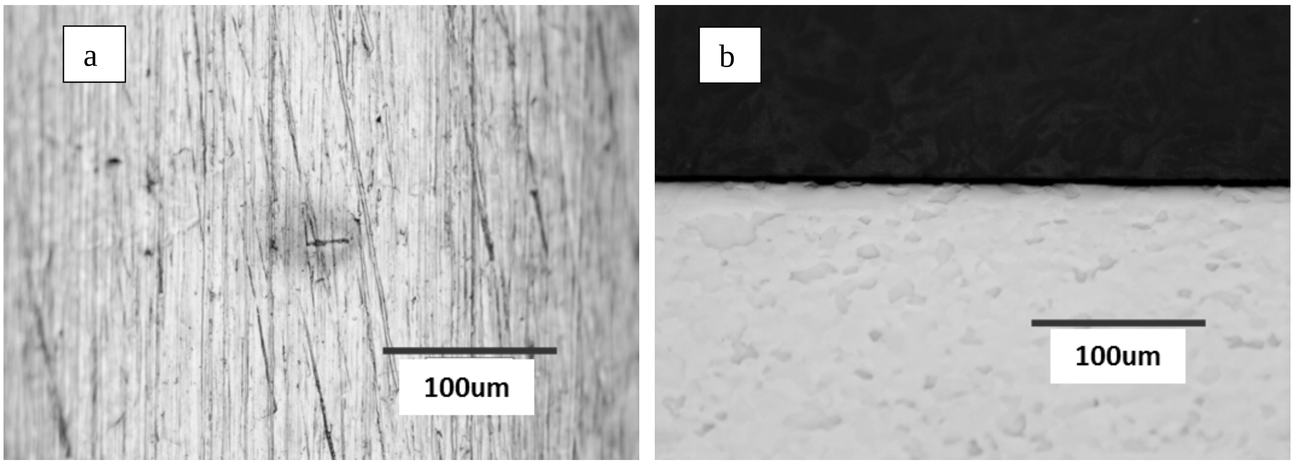


Figure 4.3. Galvanically coupled sample surface (a) and cross-section (b)

4.2 Key Results from Cyclic Slow Strain Rate Tests

- Stress corrosion crack propagation did not occur during any of the 2-week cyclic tests.
- Crack initiation sites did appear in the sample in high-chloride-content FGE-WOI and the galvanically coupled sample in FGE lot 8.
- A deep crack-like pit formed in the chloride environment, but no cracks resembling any of the cracking seen in 4PBT specimens in similar environments and loading conditions were observed.

(b) Business Status – Project was on schedule in all aspects when a decision was made by the DOT/PHMSA to terminate the project in August 2011. We were making a good progress in understanding the role of environmental parameters on the SCC and corrosion behavior of pipeline steels in different ethnolic environments. Project spending this quarter was also close to the proposed budget for this quarter.

(c) Schedule – Tasks for this project were on schedule. Now the project is terminated, so this is the final status report for the project.

(d) Payable Milestones –
Technical Summary of this project describes our results from this quarter. We were on schedule for all Tasks and had done extra work to make sure that the phenomenological understanding was complete for this phenomenon. Below is the summary of our progress against the payable milestones for the 8th quarter of this project

Payable Milestones for 8th Quarter	**Project Progress**
Task-1 Slow Strain Rate Tests	On Schedule
Task-1 Tapered Tensile Tests (TTT) in Gasoline Blends	More work was done on long term TTT test and cyclic effects using TTT samples in SFGE as well as FGE as we did not get SCC in TTT samples in these environments. Gasoline blends will be done in ethanolic environments that cause SCC
Task-2 Four point bend tests in SFGE	On Schedule
Task-2 FPB tests in Gasoline blends	More work was done on SFGE as well as FGE using cyclic FPB as static tests did not show any crack initiation or growth. Gasoline blends will be done in ethanolic environments that cause SCC
· Task 3 KISCC and Crack Growth Rate Measurement	On Schedule (extra work on cyclic tests was started)
Task 4 – Phenomenological Understanding of SCC in FGE - Role of Microstructure on SCC	On schedule
Task 4 – Phenomenological Understanding of SCC in FGE -	On schedule
Submit 8th quarterly report (Now Final Status Report)	