CORROSION FAILURE IN A LINED SOUR GAS PIPELINE - PART 2: ROLE OF METHANOL IN CORROSION BEHIND LINER

R. MacDonald
Shell Canada Energy
Calgary, Alberta

L. Simon
Shell Canada Energy
Pincher Creek, Alberta

K. Goerz
Shell Canada Energy
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M. Girgis
Shell Global Solutions
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ABSTRACT

As part of a recent failure investigation on a lined sour gas pipeline (Refer to Corrosion Failure in a Lined Sour Gas Pipeline Part 1: Case History of Incident), the corrosion mechanism was key to understanding why this failure occurred, and provided important information on how to manage the internal corrosion threat in other pipelines. In addition to the failure analysis and comparison of attributes on other lined pipelines, corrosion tests were performed in order to understand the corrosion mechanism. The corrosion testing helped to determine the failure cause and also supported the revision of integrity reference plans for existing and new lined sour gas pipelines. The role of methanol in the corrosion process that led to this internal corrosion failure in a lined sour gas pipeline is described. The presence of formic acid is considered as a possible minor contributor to the corrosion experienced in the Screwdriver Creek Pipeline (SC pipeline), but not essential to the main threat of methanol with the sour gas.

Keywords: Methanol, formic acid, H2S, sour, CO2, corrosion, pipeline, liner, HDPE

INTRODUCTION

This paper is Part 2, relating to the Corrosion Failure in a Lined Sour Gas Pipeline - Part 1: Case History of Incident. In Part 1 details are provided on the operating conditions, operating history and contributing factors to the cause of the failure. Referring to relevant sections of the Part 1 paper, it appears that the protective iron sulphide scale had not existed in a uniform manner, and as a result corrosion was able to occur in localized patches. In those locations, a paste-like mixture of iron sulphide corrosion product suspended in an acidic liquid, was found sandwiched in the annulus between the HDPE liner and the steel pipe. The liquid component was believed to be primarily methanol, which was used in the pipeline for hydrate control. There was no evidence that chlorides, bacteria, or elemental sulphur played a role in the corrosion process.

CORROSION ANALYSIS

The cause of the failure was assessed through failure analysis of portions of the failed segment[1] of the SC pipeline as well as through a review of the design, construction and operation of the SC pipeline. This assessment has concluded that the failure occurred as a consequence of localized internal corrosion of the steel portion of the SC pipeline. Internal corrosion ultimately resulted in the failure of the steel pipe followed by a breach of the internal liner. There is no evidence of a breach in the liner prior to the failure of the steel portion of the SC pipeline. There was no evidence that chlorides, bacteria or elemental sulfur played a part in the corrosion process.

It was postulated that local areas of high methanol concentration within the annulus[2] could have acted to disrupt the formation of a uniform passive iron sulfide film at locations where corrosion was found. It was also suggested that organic acids (e.g. formic acid) may have been present and could have contributed to the corrosion. In addition, tests undertaken by Shell suggest that formic acid may lower pH in the annulus environment.

Assuming no breach in the HDPE liner, the following four possible scenarios were proposed to explain how water and other corrosive agents could be present in the annulus: (a) water and/or corrosive agents within the annulus at the time of HDPE liner installation; (b) introduction of water and/or corrosive agents into the annulus from external sources after the installation of the liner; (c) formation of water and other corrosive species in the annulus by chemical reaction; and (d) permeation of water vapour and other corrosive species from the produced fluids through the liner.

Based on the lack of evidence of chlorides and elemental sulfur (known scale disrupters) we considered other possible scale disrupters including methanol and organic acids. Potential sources of methanol include its common use to remove or prevent hydrates. Additional laboratory analysis showed evidence of formic acid in the dark gray scale taken from the annulus at the failure location.

The failure analysis found that much of the internal pipeline surface did not exhibit any visible evidence of corrosion and was coated with a thin protective iron sulfide film. It was postulated that local areas of high methanol concentration

[1] Segment refers to the specific length of the pipeline between two flange pairs.
[2] The annulus is the interstitial space that exists between the liner outside surface and the steel carrier pipe internal surface.

within the annulus could have acted to disrupt the formation of a uniform passive iron sulfide film at locations where corrosion was found. It was also suggested that organic acids may have been present and could have contributed to the corrosion.

Mackinawite, Fe_9S_8, was the dominant solid (corrosion product) in the dark gray scale. If sulfur or chlorides had been involved, other forms of corrosion products would have been present. The presence of mackinawite would therefore seem to support the role of other scale disrupters in this case.

Formic Acid

Regarding the organic acid, it was originally thought that formic acid may have contributed to the corrosion. At the time, formate ions had been detected in the annulus scale at and near the failure location. It was possible that the formate ions were remnants of the formic acid additive in the well acid stimulation program. During the investigation, formate ions had been detected in all annulus scales analyzed to date.

Formate ions present in the scale at the failure location and at other locations within the SC pipeline most likely originated from well stimulations, where it is commonly included as an intensifier. It would have flowed through the SC pipeline as a vapor and is likely to have permeated through the liner into the annulus.

Formic acid vapors can permeate the liner, similar to methanol or water. Results from some unrelated work in another of our sour gas operations has shown that organic acids carry as a vapor subsequent to well stimulations and result in formate ion concentrations of up to 1700mg/L within the condensed water. That work also shows that the concentration will decrease with time, but may remain as a small component for a considerable length of time.

Methanol Corrosion

Methanol used for hydrate control and de-icing was, and continues to be a common practice within the industry, and can be safely used for these purposes. The use of methanol in the Pipeline was not inconsistent with common industry practice. However, as a result of this investigation, it has been determined that methanol, under certain circumstances in HDPE lined sour gas pipelines, behaves somewhat differently than previously understood.

Methanol is a known disrupter of protective scale under certain circumstances. As discussed below, high methanol concentrations with the other contaminants in the annulus, promoted on-going corrosion in certain conditions.

Polyamide Liner Operation

During operation of the SC pipeline with the polyamide liner, methanol was used to prevent hydrates from forming during normal production and it was also used during the original hydrotest.

Methanol in the annulus could have come from either or both of these sources. The methanol used for hydrate control likely permeated the polyamide liner. In addition, some of the methanol used during the hydrotest was likely left behind in the pipeline after the completion of the test.

The failure occurred in the top half of the pipe. We believe this to be the result of corrosion that was initiated during operation with the polyamide liner. The polyamide liner, as learned in 2002, allowed gas pockets to form in the top half of the annulus. Based on this investigation, methanol and water collected in the gas pockets and remained in contact with the steel pipe.

Sources of Methanol During HDPE Liner Operation

During operation with the HDPE liner, methanol was continuously injected at the wellhead into the production flowing through the SC pipeline in order to control hydrates. It was anticipated that small amounts of methanol would permeate the HDPE liner into the annulus. As discussed below, our investigation concluded that greater than anticipated permeation of methanol vapours occurred during the operation of the SC pipeline.

Methanol may have also been introduced directly into the annulus from other sources during HDPE liner service:

1. Commissioning of the annulus vent system required methanol to de-ice vents, notably in the Segment with the failure. This segment was a particular problem due to pigging up the long incline between V6 and V7.
2. After startup, frequent manual venting on the SC pipeline to reduce the annulus pressure (ie: improve the poor annulus communication) introduced small amounts of inhibited methanol into the jumper vent tubing at the flange bellholes in order to de-ice the jumper vent tubing.

Process Modeling

In 2003, it was believed that the annulus would contain wet sour gas, but the amount of water and methanol would be small. It was believed that wet sour gas in the annulus, without chlorides, elemental sulphur and large amounts of methanol, would cause only a low corrosion rate and protective scale would develop, which would also reduce corrosion rates.

It is now understood that 90% of the liquid methanol injected into the production at the well site, is vaporized downstream of the well site heater. This creates a relatively high vapor pressure in the production fluids and leads to greater than expected permeation of methanol vapor through the HDPE liner into the annulus.

Subsequent to the failure, we developed the process model, which is a process engineering simulation, to better understand the operation of the HDPE liner and the conditions in the annulus. The process model shows that the gas that permeates through the HDPE liner into the annulus will include small amounts of methanol vapor and water vapor. The permeated annulus gas is below the dew point of water and methanol at all annulus pressures experienced. Therefore, it is now understood that the small quantities of methanol and water vapor that would permeate through the HDPE liner into the annulus would condense and collect within the annulus. Liquid methanol added directly into the annulus would also exist as vapor or liquid within the annulus, depending upon the pressure and temperature in the annulus.

The process model also suggests that the liquid condensed in the annulus will be dominated by water and methanol. Initially, the water volume would exceed the methanol volume, but the latter would still be significant. Subsequently, as annulus gas flows through the annulus vent system towards the scrubber (located at the end of the SC pipeline), more vapors may condense, as conditions allow. The process model shows that the long jumper vent tubing used at the flange bellholes would lead to condensation, due to greater cooling in this part of the annulus vent system. The process model shows that condensed liquids from this gas stream will have more methanol than water in the liquid. Other studies on the behaviour of methanol in unlined sour gas pipelines are consistent with the model results (1).

CORROSION TEST METHODOLOGY

Corrosion testing was completed for the purpose of achieving a better understanding of the corrosion mechanism. A series of tests were undertaken to simulate various environments and conditions in the annulus, including determining the impact of methanol and formic acid, and the presence of annulus scales on the corrosion mechanism and rates.

Autoclave tests assisted in establishing the roles of methanol and formic acid in the corrosion mechanism and rates within the annulus. Various conditions were tested, including:

- methanol and methanol plus formic acid
- un-breached versus breached liner cases
- high and low pressure annulus

The series of corrosion tests were conducted using 250ml stirred autoclaves. Figure 1 depicts the typical configuration of the autoclaves. Slow stirring (i.e. 120 rpm) was achieved using a Teflon-coated stir bar at the bottom of the autoclave.

Coupon Preparation

The test program was designed to address several scenarios that may give insight to the probable corrosion mechanism(s) that led to the pipeline failure. Some tests were conducted using bare carbon steel coupons (Figure 2) and others were conducted using lined carbon steel coupons (Figure 3).

Bare Carbon Steel Coupons

A specially designed flat, disc-like coupon (C1018 carbon steel) was employed and fitted in a custom-made holder. A 600-grit polished finish was applied to the coupon. The coupon was cleaned in an ultrasonic bath using a sequence of methanol and acetone. Following the test the coupon was cleaned and weighed. Corrosion rate was calculated based on weight loss data.

Lined Carbon Steel Coupons

For the tests conducted on the lined carbon steel coupons; a piece of 'grooved' HDPE was placed on the top of the coupon surface and tightly clamped to reflect the design of a lined pipeline. Following the tests, the coupons were cleaned and weighed as described earlier. Figure 3 shows the setup in detail.
For the tests simulating the breached liner scenario, a hole was made in the center of the liner sample.

Pre-Corrosion Test

Because the pipeline had been exposed to sour gas conditions for many years of production since the startup, it is assumed that iron sulphide scale was formed on the pipeline surface. To simulate this case, all the tests were conducted using pre-corroded coupons (pre-iron-sulphided) prior to exposure to test conditions. Pre-corrosion tests were conducted under pipeline conditions. The chloride level used for the pre-corrosion tests was 5000ppm. This chloride level was proven (based on prior lab experience) to give uniform iron sulphide scale. All the corrosion rates obtained throughout the study were reported based on the weight loss measurement at the end of the tests, including the 12hr pre-corrode period. A test was run to define what was the corrosion rate due to pre-corrode period. Comments on actual corrosion rates were based on subtracting the pre-corrosion rate from the total corrosion rate.

Samples obtained from the annulus and the failed sections of pipe provided clues as to what the annulus chemistry was like. The SC pipeline scenarios selected for the tests were chosen to evaluate the following:

1. Differentiate corrosion rates and appearance between a breached liner and the un-breached liner
2. The role of methanol and formic acid in the corrosion tests
3. The impact of annulus pressure

Table 1 summarizes the three scenarios selected to test.

Case I: Un-Breached Liner - Effect of Contaminants

A) Impact of Formic Acid

This test used un-breached HDPE liners to show a base case test under pipeline conditions and nothing put into the annulus. The impact of formic acid in the pipeline condition was tested for comparison. A pre-corrode corrosion rate is shown for rate comparison to the full 7 day corrosion tests completed under various conditions.

B) Impact of Non-Protective Scale

To test the effect of the presence of non-protective scale, testing was done using non-protective scale. Scale obtained from the SC pipeline was placed in the annulus within the test cell. The HDPE liner was un-breached for these tests and it was run under pipeline conditions.

Corrosion would be present from permeated species during the short test duration. This may simulate the system with a new HDPE liner, with no additions of liquid methanol or water into the annulus, but relying only on permeation from the pipeline.

The test condition is described in Table 2 and the summary of test results is provided in Table 3.

The test results indicate:

- without non-protective scale present, no pitting was observed (Figure 4)
- the test with the non-protective scale (Figure 5) from the SC pipeline showed pitting and corrosion damage similar in appearance to that which occurred at the failure location
- the test with the non-protective scale from the SC pipeline shows corrosion product that is predominantly mackinawite iron sulphide species.
- pitting corrosion was only observed where there had been no batch inhibitor applied to the coupon.
- the addition of a small amount of formic acid to the mix, increased the pitting corrosion rate in the non-protective scale from the pipeline slightly.

Case II: Un-Breached Liner Condition - Effect of Methanol

These tests were designed to simulate an un-breached HDPE liner and particular annulus conditions. The test pressure and fluids reflected annulus conditions with two different methanol concentrations with 100ppm chloride brine. Tests were completed under both high (4200kPag) and low (800kPag) annulus pressures to determine corrosion tendency under the SC pipeline condition as compared to a lower pressure annulus in other lined pipelines in the System. Table 4 summarizes annulus conditions under the different scenarios and the test results are provided in Table 5.

The test results indicate:

- 50% methanol-water mixtures were more corrosive than the 90% methanol-water mixtures under both pressures.
- The 50% methanol/water mixture showed pitting and corrosion damage similar in appearance to that which occurred at the failure location under both pressures (Figure 6)
- the results with 50% methanol/water mixture under high pressure show similar corrosion to the Case 1 tests with non-protective scale from the SC pipeline (Figure 7).
- pitting corrosion only occurs in the area on the coupon where no batch inhibitor was applied.

Case III: Breached Liner Condition

Although a liner breach was not believed to have occurred and did not cause the failure, tests were completed to demonstrate what corrosion damage would occur if a breach of the HDPE liner had occurred. The test conditions (Table 6) in these tests reflected SC pipeline and annulus conditions expected with a breached HDPE liner. The tests were to help us determine the corrosion rates and appearance for comparison with the actual failure.

The test results (Table 7) indicate:

- For a breached liner condition, the corrosion rate was found to be similar to the unbreached liner condition. (Figure 8)
- The presence of 1000ppm formic acid caused a significant increase in the pitting corrosion rates (5X). (Figure 9)
- Pitting corrosion only occurs in the area on the coupon where no batch inhibitor was applied.
- The appearance of the corrosion in these tests was noticeably different than either the corrosion noted in connection with the SC pipeline failure or the corrosion in the Case I and Case II tests.

Summary of Findings

Autoclave tests assisted in establishing the roles of methanol and formic acid in the corrosion mechanism and rates within the annulus.

The test findings can be summarized as follows:

- The corrodents, under both high and low annulus pressures were determined to be corrosive in the conditions experienced in the annulus, although the corrosive effect of the corrodents is slightly higher under high annulus pressures.
- Formic acid presence would exacerbate the corrosion rate, but is not required to be present in order for corrosion to occur in the annulus.
- The appearance of the corrosion in a breached liner scenario is noticeably different than either the corrosion noted in connection with the SC pipeline failure or the corrosion in the unbreached liner tests.
- The corrosion test results have shown that the presence of significant amounts of methanol with water leads to pitting and corrosion, ie; non-protective iron sulphide scale.

CORROSION MONITORING

Corrosion monitoring devices, in-line inspections and bell hole inspections are being used on the lined sour gas pipelines being returned to service to monitor corrosion of the steel pipe behind the liner.

Results from bell hole inspections have been used to select an area of internal pitting and an area with shallow corrosion wall loss to place real-time corrosion monitoring devices. The devices are designed as custom units in order to focus on corrosion aligned with the axial, external grooves in the HDPE liner.

Subsequent to restart of the pipelines, the corrosion monitoring devices have shown only short-term minor corrosion rate events correlated to the startups on the pipeline. After startup, the corrosion rate has decreased to a very low rate. With the use of the process model it is expected that any liquid methanol within the annulus will eventually weather off and no longer remain as a corrosion threat.

CONCLUSIONS

1. The methanol and water, under both high and low annulus pressures were determined to be corrosive in the conditions experienced in the annulus, although the corrosive effect of the methanol and water is slightly higher under high annulus pressures.
2. Formic acid presence would exacerbate the corrosion rate, but is not required to be present in order for corrosion to occur in the annulus.

3. The appearance of the corrosion in a breached liner scenario is noticeably different than either the corrosion noted in connection with the SC pipeline failure or the corrosion in the unbreached liner tests.

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TABLE 1:
Summary of the Various Pipeline Scenarios

Scenario #	*DESCRIPTION*	*Rationale*
I	LINED CARBON STEEL (UN-BREACHED)	This scenario represents the steady state operation of the pipeline and the impact of contaminants. The objective was to investigate: 1. The impact of the pipeline environment on the carbon steel surface behind the un-breached liner. 2. The impact of scale behind the liner
II	UN-BREACHED LINER - EFFECT OF METHANOL	Methanol was tested under two scenarios: 1. Low P annulus represents the annulus pressure during both the early stages of the pipeline operation (reflects design premise, P annulus << P line). 2. high P annulus due to restricted vent system flow (P annulus ~ P line).
III	LINED CARBON STEEL - BREACHED	This scenario represents the possibility of a breach in the liner.

TABLE 2:
Summary of Test Conditions

Parameters	*Data*
Temperature, C	45
Pressure, KPa	4500
H2S, mole%	25
CO2, mole %	11
Chloride, ppm	8000
Continuous Inhibitor, ppm	3000
Batch Inhibitor	Diluted 1:1 with Diesel
Methanol	Added in ratio of 1:1 methanol:brine. Methanol is injected at the wellhead for hydrate control.
Diesel	Saturated with sulfur. Diesel is injected at the well head to dissolve the elemental sulfur.

TABLE 3:
Scenario 1 Test Results

Test #	*Test - No Breach*	*General Rate (mm/yr)*	*Pitting Rate (mm/yr)*
1	Conditions with no Breach and No Scale	0.356	No pitting
2	No breach + 1000ppm formic acid	0.393	No pitting
3	Screwdriver Cr Scale	0.389	7.06
4	Screwdriver Cr Scale with 1000ppm formic acid	0.399	10.77

TABLE 4:
High and Low pressure annulus conditions

Parameters	*Low Pressure*	*High Pressure*
Temperature, C	45	45
Pressure, KPa	800	4200
H2S, mole%	36	36
CO2, mole %	11	11
Chloride, ppm	100	100
Batch Inhibitor	Diluted 1:1 with Diesel Coupons were "half batched"	Diluted 1:1 with Diesel Coupons were half batched
Methanol	Added in different ratios with water	Added in different ratios with water
Diesel loaded with sulfur	Added in equal ratios to methanol and brine	Added in equal ratios to methanol and brine

TABLE 5:
Summary of Corrosion Data under Low and High Pressure Conditions In the Presence of Methanol

		Low Pressure Annulus Conditions			***High Pressure Annulus Conditions***	
Test #	Test Conditions	General Corrosion Rate, mm/y	Pitting Corrosion Rate, mm/y	Test #	General Corrosion Rate, mm/y	Pitting Corrosion Rate, mm/y
5	No Liner Methanol:Water (1:1) Ratio	0.273	2.92 (many pits in Un batched section) Figure 5	**9**	0.510 Figure 6	9.92 (many pits in un-batched section)
6	Breached liner Methanol:Water (1:1) Ratio	0.196	1.89 (many pits in Un batched section)	**10**	0.225	2.25 (many pits in un-batched section)
7	No Liner Methanol:Water (9:1) Ratio	0.206	No Pitting	**11**	0.320	No Pitting
8	Breached liner Methanol:Water (9:1) Ratio	0.166	No Pitting	**12**	0.258	No Pitting

Table 6:
Summary of Test Conditions Under Breached Liner Scenario

Parameters	***Data***
Temperature, C	45
Pressare, Kpa	4500
H2S, mole%	25
CO2, mole %	11
Chloride, ppm	8000
Continuous Inhibitor, ppm	3000
Batch Inhibitor	Diluted 1:1 with Diesel
Un-inhibited Methanol: Brine: Diesel	1:1:1

TABLE 7:
Summary of Corrosion Data Under Breached Liner Conditions

Test #	***Test - Breached Liner***	***General Rate (mm/yr)***	***Pitting Rate (mm/yr)***
15	Conditions with Breach (Table 6)	0.413	4.02
16	With breach + 1000ppm formic acid	0.420	21.11

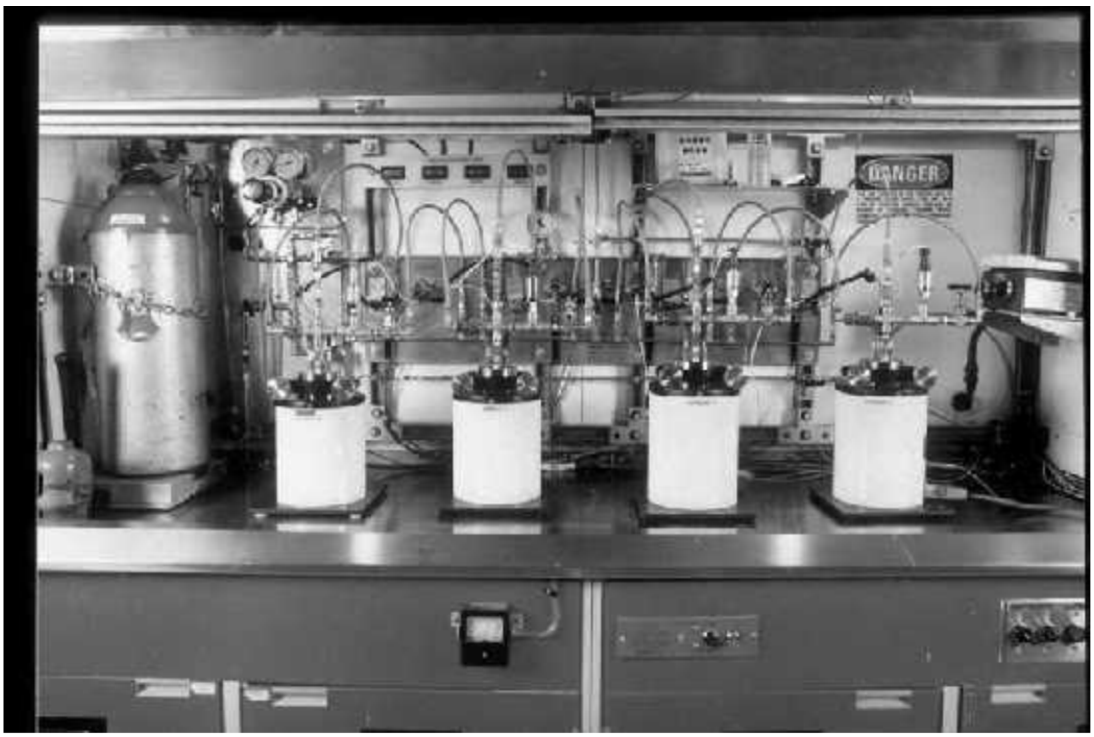

FIGURE 1 - Typical Laboratory Autoclave Configuration

FIGURE 2 - Bare Corrosion Coupon in Holder

FIGURE 3 - Setup used for corrosion tests in which HDPE was placed on the top of carbon steel surface

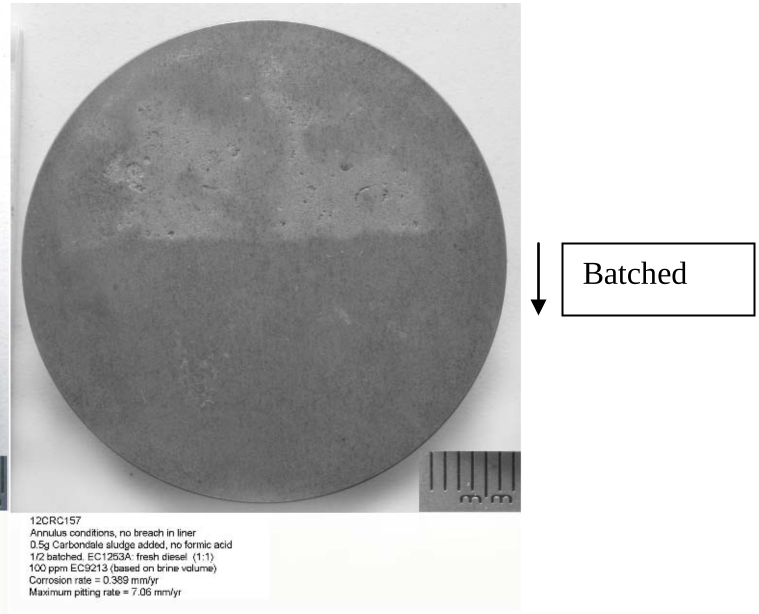

FIGURE 4 (left) - Surface morphology of a coupon exposed to pipeline conditions (Test #1)

FIGURE 5 (right) - Surface morphology of a coupon exposed to pipeline conditions (Test #3)

FIGURE 6 (left) - Surface morphology of a coupon exposed to low-pressure annulus conditions (Test # 5).

FIGURE 7 (right) - Surface morphology of a coupon exposed to high-pressure annulus conditions (Test # 9).

FIGURE 8 (left) - Surface morphology of a coupon exposed to breached liner conditions (Test #15).

FIGURE 9 (right) - Surface morphology of a coupon exposed to breached liner conditions in the presence of formic acid (Test # 16).