Development of a Test Program for Assessing the SCC, Pitting and Crevice Corrosion Behaviour of Selected Corrosion Resistant Alloy Liner Materials for Clad Pipe Offshore Applications

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Abstract

The development of a gas field located approximately 80 km offshore from Western Australia involves production of oil and gas from subsea wells in 150 – 250 m water depth. Design considerations for the subsea system has identified the maximum temperature for operations is greater than 130°C. Consequently, for large diameter (18") flowlines, this precludes the use of duplex stainless steels as corrosion resistant alloys (CRA’s) for service under the expected operating conditions. Attention has therefore focussed on alternative CRA’s such as austenitic stainless steels and Ni based alloys as mechanically clad or lined clad pipe for carbon steel subsea gas flowlines.

One design concern is the recognised temperature limit for CRA materials, such as 316L stainless steel and similar alloys in production fluids is taken to be 120°C. This then raises concerns surrounding their suitability for providing sufficient corrosion resistance / stress corrosion cracking resistance in gas environments containing CO₂ and H₂S at temperatures higher than 130°C.

It was recommended that specific testing should be completed at temperatures greater than 133°C to establish that candidate materials are still corrosion resistant. The focus of this study was to develop, implement and assess a testing program that would predict the suitability of a series of CRA’s alloys for use in mechanical clad / lined subsea gas flowlines, with respect to pitting corrosion, crevice corrosion and stress corrosion cracking. This paper will present the rationale adopted for this testing program to simulate the stringent operating conditions, the results from these findings and the overall assessment / integrity of the candidate alloys selected.

Keywords: Stress Corrosion Cracking, Crevice Corrosion, Pitting Corrosion, Corrosion Resistant Alloy

1. INTRODUCTION

Material selection for high temperature applications relies on corrosion testing to identify, validate, and verify the alloy to match the application. One of the obstacles in the selection of durable high temperature materials for aggressive high temperature and high pressure oil and gas production application is the lack of rapid and versatile standardized tests. While a substantial amount of work has evaluated the corrosion of high temperature materials, this field is still evolving. An understanding of the corrosion mechanism and behaviour of materials under test conditions that simulate the actual application provides a reliable tool for materials selection.

The current study has arisen as a result of materials selection concerns surrounding their use in subsea systems, particularly lined / clad flowlines for a gas field currently being developed, which is located approximately 80 km offshore from Western Australia, involving the production of oil and gas from subsea wells in 150 – 250 m water depth. Design considerations for the subsea system has identified the maximum temperature for operations is greater than 130°C. Consequently, for large diameter (18") flowlines, this
precludes the use of duplex stainless steels as corrosion resistant alloys (CRA’s) for service under the expected operating conditions. Attention has therefore focussed on alternative CRA’s such as austenitic stainless steels and Ni based alloys as mechanically clad or lined clad pipe for subsea gas carbon steel flowlines.

In addition to the operating temperatures varying between ambient seabed temperatures to relatively high temperatures (in excess of 130°C), typical operating flowline pressures are between 36000 to 43000 kPaa. The environment typically contains 5.5% CO₂ and can therefore be considered to be sweet, However, while no appreciable amounts of H₂S are to be expected, this may change during the anticipated design life of the project.

During the subsea tie-in process the liquid within the flowlines and tie-in spool will be exposed to the surrounding natural seawater prior to end caps being fitted. Dilution of the chemically treated liquid, due to natural seawater ingress, within the components is a cause for concern due to the potential for localised pitting and crevice corrosion of the CRA materials. There is also a risk of natural seawater ingress during linepipe installation [1]. With a carbon steel pipe natural seawater ingress would lead to a small amount of general corrosion over the entire internal wetted surface of the pipe. However if the internal surface is fabricated from a corrosion resistant alloy (CRA) material then random pitting can occur after a period of only a few days, depending on the actual CRA used.

In addition, biofilm formation and microbial influenced corrosion can further aggravate the situation. In the mid-seventies it was observed that stainless steels, independent of their composition, have a higher corrosion potential in natural seawater than sterile water [2]. This was attributed to a microbial slime layer, the biofilm, which is quickly formed on an inert surface. It was shown that the biofilm had a catalytic effect on the cathodic reaction in the corrosion process, i.e. the oxygen reduction and higher current densities at cathodic polarization than in corresponding sterile water. A high corrosion potential increases the risk for the initiation of crevice and pitting corrosion while a faster cathodic reaction means a higher propagation rate of attack. Consequently, natural living seawater is considerably more corrosive than artificial seawater or sodium chloride solutions [3].

As a consequence of the high operating temperatures and pressures, aggressive environment and flowline design (clad or lined carbon steel pipes), concerns have arisen surrounding their suitability for providing sufficient corrosion resistance / stress corrosion cracking resistance in gas environments containing CO₂ and possibly H₂S at temperatures higher than 130°C. In particular, higher temperatures are an issue as the recognised temperature limit for CRA materials, such as 316L stainless steel and similar alloys in production fluids are taken to be circa 120°C.

It was recommended that specific testing should be completed at temperatures greater than 133°C to establish the corrosion resistance / stress corrosion cracking resistance of the candidate materials. The focus of this study was to develop, implement and assess a testing program that would predict the suitability of a series of CRA’s alloys for use in mechanical clad / lined subsea gas flowlines, with respect to pitting corrosion, crevice corrosion and stress corrosion cracking under simulated flowline operating conditions and service strains. Three CRA’s, namely 316L (UNS S31603), 317L (UNS S31703) Stainless Steel and Alloy 825 (UNS N08825) were chosen as candidate materials for testing. A test program was developed which incorporated (i) pitting and crevice corrosion tests under worst case operating conditions and (ii) four-point bend tests, as per a modified ASTM G39 with maximum simulated in-service strain used to stress the material within a natural seawater environment. Simulated operating conditions were achieved using an autoclave system with varying concentrations of formation Cl, HCO₃, CO₂ and H₂S species for (i) worst case formation water maximum flowing conditions; (ii) worst case condensed water maximum flowing conditions; (iii) shut-in formation water conditions and (iv) shut-in condensed water conditions [4].

This paper will present the rationale adopted for this testing program to simulate the stringent operating conditions, the results from these findings and the overall assessment / integrity of the candidate alloys selected.
2. EXPERIMENTAL APPROACH

Three alloys were investigated, namely 316L stainless steel, 317L stainless steel and Alloy 825. These alloys are used in the oil and gas industry due to their high temperature, high pressure, corrosion and oxidation resistance. The compositions of the alloys are listed in Table 1. A series of screening tests were conducted on selected corrosion resistant alloys to determined resistance to, stress corrosion cracking (SCC), localized pitting and crevice corrosion, in conditions simulating service conditions for a subsea pipeline planned to be installed in the Northwest shelf in Australia.

The test program and specimen requirements for the various tests are summarized in Table 2.

3. TEST ENVIRONMENT

The various test conditions and test solution compositions adopted in this study are summarized in Table 3 and Table 4 respectively. These conditions were chosen to simulate 4 worst case scenarios, namely (i) worst case formation water maximum flowing conditions; (ii) worst case condensed water maximum flowing conditions; (iii) shut-in formation water conditions and (iv) shut-in condensed water conditions.
Tab. 3 Test Conditions

<table>
<thead>
<tr>
<th>Test</th>
<th>Condition Description</th>
<th>Cl Conc (ppm)</th>
<th>HCO₃ Conc (ppm)</th>
<th>ppCO₂ (bara)</th>
<th>ppH₂S (mbara)</th>
<th>Acetic acid (ppm)</th>
<th>Propanoic acid (ppm)</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Worst case formation water maximum flowing conditions</td>
<td>10,000</td>
<td>2000</td>
<td>13.2</td>
<td>0.03</td>
<td>810</td>
<td>118</td>
<td>150</td>
</tr>
<tr>
<td>2</td>
<td>Worst case condensed water maximum flowing conditions</td>
<td>250</td>
<td>0</td>
<td>13.2</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>150</td>
</tr>
<tr>
<td>3</td>
<td>Shut-in formation water conditions</td>
<td>10,000</td>
<td>2000</td>
<td>20</td>
<td>0.04</td>
<td>810</td>
<td>118</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>Shut-in condensed water conditions</td>
<td>250</td>
<td>0</td>
<td>20</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>25</td>
</tr>
</tbody>
</table>

The test solution had the following composition, as shown in Table 4.

Tab. 4 Test Solution for All Conditions

<table>
<thead>
<tr>
<th>Solution Test Condition 1 &amp; 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Species</strong></td>
</tr>
<tr>
<td>Chlorides</td>
</tr>
<tr>
<td>Bicarbonate</td>
</tr>
<tr>
<td>Propanoic acid</td>
</tr>
<tr>
<td>Acetic acid</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solution Test Condition 2 &amp; 4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Species</strong></td>
</tr>
<tr>
<td>Chlorides</td>
</tr>
<tr>
<td>Bicarbonate</td>
</tr>
<tr>
<td>Propanoic acid</td>
</tr>
<tr>
<td>Acetic acid</td>
</tr>
</tbody>
</table>

4. TEST SPECIMEN PREPARATION

4.1 Four Point Bend Test

Four Point Bend SCC specimens were prepared from the pre-strained test material, the approximate dimensions of the test pieces were 70 x 15 x 5 mm thick [5]. The internal clad pipe surface was the main test surface to be loaded in tension and left in the as received condition. Non-test surfaces were finished to 600 grit.
Test pieces were loaded in four-point bending using individual loading frames and PEEK contact points. The strain applied was equivalent to 100% of the 0.2% proof stress at the test temperature and calculated using the following formula:

\[ 0.2 = 0.002 + \left( \frac{R_p 0.2}{E} \right) \] (1)

Where 0.2 is the strain at the 0.2 proof stress and \( R_p 0.2 \) is the average 0.2% proof stress from three tensile tests conducted at the test temperature. \( E \) is the elastic modulus at room temperature of the material obtained from manufacturer's data sheets.

Strain gauges were applied and allowed to set for twenty four hours. The specimen was placed in a jig, and loaded slowly and carefully to avoid overloading. The specimens were monitored for 2 hours with the gauges in place to detect any relaxation, if necessary; the specimens were further stressed to maintain the target strain value. When the required stress (strain) had been achieved, and all data recorded, the gauges were removed and the surfaces of the specimen, where the gauges were located, abraded manually using 600 Grade silicon carbide paper. The surfaces were then cleaned with acetone. Actual strain measurements for test specimens are shown in Figure 1.

![Fig. 1 4-Point Bend specimen during stressing and after loading](image)

**4.2. Pitting and Crevice Test**

Pitting specimens were prepared from the same material as SCC test pieces. Dimensions were approximately 50 x 25 mm. The internal clad pipe surface was the main test surface and left in the as received condition. Non-test surfaces were finished to 600 grit. Coupons were degreased and weighed on an analytical balance reading to 0.1mg [6].

For crevice tests, two grooved PEEK multi-crevice assemblies were fitted to each SSC/SCC coupon fastener. Studding and nuts used were Hastelloy C276. Each sample was checked prior to testing to ensure no contact between the fastener and the test specimen. Testing was conducted in general accordance to ASTM G78-01 as shown in Figure 2.
4.3. **Autoclave Test Procedure**

The samples were loaded into the vessels twenty four hours prior to testing. Inert spacers were used to hold and isolate the specimens from each other and from the autoclave. The autoclaves were pressure tested with oxygen-free nitrogen, then evacuated and refilled with nitrogen to about 10 bar pressure, five times, to remove all traces of oxygen.

The test solution was deaerated with OFN grade nitrogen before charging into the autoclave vessel. The oxygen content was less than 10ppb, as measured by an Orbisphere oxygen meter. All the lines to the autoclave from the deaeration vessel were purged with nitrogen and evacuated. The test solution was transferred to the autoclave under pressure of CO\(_2\). The test solution was purged with N 4.5 grade CO\(_2\) in the autoclave for a further 30 minutes per litre of test solution.

The autoclave was then heated to the required test temperature and saturated with the appropriate gas mix:

- Test Conditions 1 and 2 used a gas mix of 25ppm H\(_2\)S balance CO\(_2\) at a pressure of 1.2 Bara 0 + 0.5 bar + vapour pressure (estimated at 5 bara at 150\(^\circ\)C) and then over pressured with CP grade CO\(_2\) to 13.2 Bara 0 + 0.5 bar + vapour pressure (estimated at 5 bara at 150\(^\circ\)C).

- Test Conditions 3 and 4 used a gas mix of 25ppm H\(_2\)S balance CO\(_2\) at a pressure of 1.6 Bara 0 + 0.5 bar + vapour pressure (estimated at 0 bara at 25\(^\circ\)C) and then over pressured with CP grade CO\(_2\) to 20 Bara 0 + 0.5 bar + vapour pressure (estimated at 0 bara at 25\(^\circ\)C).

To saturate the solution it was sparged with the gas mix at a rate of at least 100 mL/min for at least 20 min/L of test solution. At temperatures greater than 100\(^\circ\)C, the solution was sparged with the gas mix for short periods at low flow rates (30 – 60 minutes at 50-100 ml/min) to reduce loss of water and the concentration of the test solution. After sparging, the vessel was then sealed and the pressure in the vessel allowed stabilising. The process of sparging and stabilisation of pressure was repeated until the pressure within the vessel remained stable at the saturation pressure of the gas mix for at least 30 minutes. At this point the solution in the vessel was taken as being saturated with the gas mix. The gas head was subsequently refreshed with the test gas once per week.

The solution pH were measured at the end of the test period, at ambient temperature and saturated with 1 bar CO\(_2\). A sample of fluid was taken from the autoclave at the end of each test, cooled and the pH measured saturated with 1 bar CO\(_2\). Test temperature and pressure were recorded manually at least once each working day and electronically for the duration of the test. The test period was 720 hours at temperature and pressure.

Following the exposure period the autoclave was allowed to cool, the pressure was reduced and the vessel purged with nitrogen to flush out H\(_2\)S. The specimens were then removed for evaluation. Table 5 shows the pH values at the start and end of the tests.
Tab. 5 Solution pH measurements

<table>
<thead>
<tr>
<th>pH Measurement</th>
<th>Test Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Start</td>
<td>5.79</td>
</tr>
<tr>
<td>End</td>
<td>5.65</td>
</tr>
</tbody>
</table>

5. RESULTS

After removal from test the 4-point bend specimen surfaces were examined for general and localised corrosion and for cracks at up to 40x magnification, using a binocular microscope. Dye penetrant inspection was also performed to detect the presence of any cracks. Metallographic cross-sections were taken at any suspect locations; otherwise example sections were prepared in the area of maximum applied stress.

The results from the examination of the 4-point bend specimens showed no evidence of cracking. The results from the visual examination of the specimens for localised corrosion also showed no evidence of localised corrosion either pitting or crevice corrosion, in that no pit like features were observed on the as received test surface that were not pre-existing prior to testing. Evidence of localized corrosion was defined as “pit like” features deeper than 20 microns on the as received surface that were not pre-existing before the start of the test.

No evidence of crevice corrosion was observed on any specimens tested in any of the four environments, in that no pit like features were observed on the as received test surface that were not pre-existing prior to testing [7] and [8]. The specimens were tested in 4 different test conditions for SSC/SCC, localised and crevice corrosion. No evidence of SSC or SCC was observed in any specimens tested. Figures 3 and 4 show samples at the conclusion of the test.

Fig. 3 Samples (316, 317 and Alloy 825) After Completion of 4-point bend Test

Fig. 4 Samples (316, 317 and Alloy 825) After Completion of Crevice Corrosion Test
The findings from this study have revealed that 4 point bend tests and crevice / pitting corrosion studies on the three alloys were conducted in environments designed to simulate environments representative of the process conditions.

6. CONCLUSION
1. A series of tests were designed and developed to assess the stress corrosion cracking and localized (pitting and crevice) corrosion of three corrosion resistant alloys in simulated conditions designed for service of subsea pipelines scheduled for operation in a gas field located approximately 80 km offshore from Western Australia

2. Based upon the experiments performed, no evidence of localized (crevice and/or pitting) corrosion, SSC or SCC was observed in any of the specimens tested

3. The overall findings from these studies reveal that the three selected CRA’s were found to be suitable for operation as subsea flowlines within the intended gas field subject to the stringent “worst case scenario” test conditions adopted for this study

4. The test program and methodology were considered appropriate and suitable for assessing the corrosion behavior of these three alloys in the simulated subsea oil field environment

REFERENCES
[8] ASTM G-1 Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens