Evaluation of the Corrosion Risk of Duplex Stainless Steel UNS S82551 in Treated Seawater Injection Service

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Abstract

In seawater handling systems, the available well tubing materials are Glass Reinforced Epoxy lined low alloy steel or Corrosion Resistant Alloy’s (CRA) such as super duplex stainless steel. However, in treated seawater the corrosion risk can be controlled and lower grade alloys can be considered. Recent efforts have focused attention on better dissolved oxygen controls which permits the investigation and possible use of more cost effective materials such as the duplex stainless steel UNS S82551. Full scale testing of tubes joined together with a proprietary premium threaded connection was performed in controlled seawater loops simulating service conditions at 30°C. The flow rate and dissolved oxygen were controlled at 5 m/s and <20ppb, respectively. Weekly dissolved oxygen excursions corresponding to 24h at 100ppb followed by 1 hour at 300ppb were performed during the 5 months exposure. Corrosion results of UNS S82551 tubing were compared to UNS S31803 and UNS S39274. In parallel, laboratory exposures of coupons were performed in dissolved oxygen controlled cells with and without CREVCORR crevice formers, allowing the measurement of electrochemical potentials as function of dissolved oxygen content (e.g. biofilm ennoblement monitoring) and the related corrosion resistance. The results showed that dissolved oxygen content should be properly controlled below critical values to avoid crevice corrosion of the lesser alloyed duplex stainless steels. In the full scale loop test, UNS S82551 tubes did not show crevice corrosion at threaded connection interfaces under the defined test conditions.

Keywords: Crevice corrosion, duplex stainless steels, treated seawater, dissolved oxygen
**Introduction**

In treated seawater injection wells (e.g. with dissolved oxygen removed), the corrosion risk can be controlled and permits low alloy steel to be considered for equipment and tubing, provided the dissolved oxygen concentrations (DOC) are held below 20 ppb. Nevertheless, previous experience has shown that treated seawater injection systems if not correctly operated, can lead to high DOC in the seawater injected into the wells resulting in corrosion failures. The time to failure can also be exacerbated further by high shear stresses or erosion-corrosion caused by high injection rates creating unacceptably high velocities within the tubing. Publications by Nice et al [1,2] identified the effect of alloying grade L80 steel with small quantities of chromium (0.5 to 1.0%) could provide improved tubing longevity in treated seawater injection systems. Silverman et al [3] work further supports these findings for grade Q-125 tubing. But again unacceptably high injection rates will have a negative impact on this improvement. Therefore limiting seawater flow velocities to below 5 m/s has shown through both laboratory testing and Field experience to give enhanced tubing lifetimes. Silverman [3] findings would support this limit w.r.t tubing longevity with the reported flow velocities in the order of maximum 4 m/s.

In the situation when DOC concentrations are controlled (below 20 ppb) or even variable (which is the norm) but seawater flow velocities are above 5 m/s then the usual alternatives for the tubing to be considered are either GRE lined steel tubing or 25Cr super duplex stainless steel. The former has in our experience excellent performance in both treated and natural seawater injection wells [4,5] with no failures reported to date. However, GRE lined steel tubing cannot be used:

1. For well equipment e.g. down hole safety valves (DHSV), pressure and temperature gauges, etc.
2. Within all locations in a well, notably in the lower or liner section and also where well intervention equipment or plugs are required to be anchored.
3. When through tubing drilling or coiled tubing well intervention operations are planned.

Therefore a corrosion resistant alloy (CRA) has to be used for natural seawater applications, provided that the Pitting Resistant Equivalent Number (PRENw) is greater than 40. Thus treated seawater injection wells use 25Cr super duplex stainless steel tubing/liner sections and equipment. Unfortunately this Alloy is very expensive and therefore in order to reduce well construction costs more economic alternatives for treated seawater injection wells have to be sought. In this respect, the question arises for a treated seawater injection well: is it necessary to use an alloy with a PRENw > 40 or could a more cost-efficient PRENw > 30 be sufficient? UNS S31803 (22%Cr with PRENw > 34) has been used successfully in treated seawater topside pipework systems for over 10 years without failure. Lower grades (PRENw<30, e.g. UNS S31603) are however not considered for these applications due to the known very high risk of initiating localized corrosion in chloride containing media.

In an attempt to address this question a seawater test program was designed to determine the pitting and crevice corrosion performance of a new alloy UNS S82551 [6]. It has a PRENw> 30 and its performance was compared to UNS S31803 and UNS S39274. This paper describes the test program performed, the results and their implication w.r.t. the use of alloy UNS S82551 as tubing in treated seawater injection wells.
**Objectives**

In the present study both full scale and laboratory exposure tests were performed. The main objectives of the laboratory exposures were:

- To determine the evolution of stabilized open-circuit potential of the three tested alloys (UNS S82551, S31803 and S39274) in natural seawater, as a function of dissolved oxygen content
- To assess the risk of crevice corrosion for the three tested alloys in natural seawater as a function of dissolved oxygen content (DOC), using a standard crevice assembly, and using the actual pipe-coupling premium connection (PCPC) crevice configuration

In parallel, full scale exposures were carried out with the aim of evaluating the internal crevice corrosion resistance of the PCPC tubes, under simulated service conditions in a full scale treated seawater loop.

**Experimental**

**Alloys and tested coupons**

Three duplex stainless steel alloys, all provided by the same manufacturer, were evaluated: UNS S31803, UNS S39274 and UNS S82551. The tube geometry and the exact alloy composition is given in Table 1, together with calculated Pitting Resistant Equivalent Number (PRENw). The compositions are in the range of standard requirements.

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade name</th>
<th>Chemical Composition (mass %)</th>
<th>PRENw*</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNS S31803</td>
<td>S31803</td>
<td>C 22.4 Cr 5.1 Mo 3.20 W N</td>
<td>36.0</td>
</tr>
<tr>
<td>UNS S39274</td>
<td>S39274</td>
<td>0.016 C 24.9 Cr 6.8 Mo 3.14 W</td>
<td>43.2</td>
</tr>
<tr>
<td>UNS S82551</td>
<td>S82551</td>
<td>0.020 C 24.8 Cr 4.9 Mo 1.10 W</td>
<td>31.5</td>
</tr>
</tbody>
</table>

*PRENw = Cr + 3.3(Mo + 0.5W) + 16N*

Metallographic investigation was performed on the 3 tested alloys. Results are given in Figure 1 which confirms the duplex microstructure of the 3 tested alloys. The austenite/ferrite spatial distribution (50/50) and the microstructure of the inspected alloys showed no abnormal deviations from expected microstructure features.
For laboratory exposures in seawater cells, specimens were sampled from the provided tubes. The geometry of the coupons was about 60 mm x 60 mm and specimens were machined at all faces. A 3mm-diameter hole was drilled in the corner of each coupon to allow the handling and the electrical continuity with titanium wires for potential monitoring. For the coupons used for crevice corrosion testing, a central hole of 9 mm diameter was drilled to allow the mounting of crevice formers. The roughness measurements gave similar results for all coupons whatever the tested alloy, with averaged roughness of 0.18 ±0.02 µm for all tested samples.

Laboratory exposure of real PCPC connected tubes in quiescent conditions was also performed. A schematic representation of the PCPC samples is given in Figure 2. Under these conditions, the actual crevice configuration (i.e. threaded connection with copper anti-galling treatment) can be evaluated in the desired environment. A total of 7 samples (i.e. PCPC tubes) were used for this testing.

After cleaning and degreasing of the inner surfaces (with ethanol and acetone), transparent caps were sealed at tube-ends with adapted inert mastic. The cells were designed to allow gas
bubbling, seawater inlet and outlet and measurements of the open-circuit potential and dissolved oxygen content.

Full scale PCPC tubes were tested in the treated seawater flow loop. The geometry of the S82551, S31803 and S39274 coupons is shown in Figure 3. Photographs showing the typical exterior and interior aspects of a PCPC tube are given in Figure 4.

![Figure 3: Schematic drawing (cross section) of the tested PCPC tubes for flow loop exposures](image)

**Figure 3: Schematic drawing (cross section) of the tested PCPC tubes for flow loop exposures**

![Figure 4: Photographs of a tested PCPC tubes for flow loop exposures, (a) exterior and (b) interior aspects](image)

**Figure 4: Photographs of a tested PCPC tubes for flow loop exposures, (a) exterior and (b) interior aspects**

It is important to underline that PCPC are copper plated for anti-galling purposes. The presence of copper may influence the potential and the corrosion resistance of stainless steel tubes (due to galvanic action of copper on stainless steel). The thickness of the copper-plating could range from 7 to 20 µm according the manufacturer information. Two PCPC coupons per tested alloy and per tested conditions were used (i.e. 4 coupons per tested alloy).

**Set-ups and conditions of exposure**

**Open-circuit potential versus DOC**

The objective was to measure the stabilized open-circuit potential (OCP) of the tested alloys as a function of DOC, and to define a critical range of DOC for which the so-called biofilm ennoblement is observed. The criterion for stabilized potential was arbitrarily fixed to no potential evolution of more than +/-5mV over 48h (after a minimum exposure time of 15 days). The principle of the set-up is given in Figure 5. Continuously renewed seawater (from the bay of Brest, France) was used to allow a continuous supply of bacteria and nutrient from natural seawater. The temperature was controlled at 30.0°C ±0.5°C (regulated by heating bands) and the renewal rate was about one complete renewal per day of the seawater in the cells (i.e. about 24L/day). Specimens were handled with titanium (grade 2) wires for electrical contact allowing OCP measurements. OCP were measured during minimum 15 days and until stabilization (+/-5mV over 48h). Several dissolved oxygen levels were selected from
<10 ppb to saturation (6 ppm) in order to draw the OCP versus DOC curves, using 6 ranges of DOC. The DOC was controlled with the use of oxygen scavenger and mass gas flow regulators connected to pure nitrogen and oxygen. Dissolved oxygen content was measured with Light-Dissolved Oxygen (LDO) probes. The OCP were measured with high impedance (>10^{11}\Omega) data loggers connected to gel reference electrode Al/AgCl/KCl. The electrodes were weekly calibrated with a certified saturated calomel electrode.

![Figure 5: Principle of the set-up for dissolved oxygen control in electrochemical cells](image)

To assess the effect of copper coupled with stainless steel, assemblies made of super duplex stainless steel plates and pure copper plates were exposed in similar cells (i.e. DOC controlled cells containing quiescent renewed natural seawater at 30°C). To simulate the coupling ratios involved in the seawater loops, a surface anode (copper) to cathode (Stainless steel) ratio of 1:10 was used.

![Figure 6: Bi-metallic coupons used to simulate anti-galling copper treatment](image)

The mixed potentials were measured together with the galvanic currents. Galvanic current were measured with the zero-resistance ammeter. The systems were exposed for at least 2 weeks until stabilization of potentials and currents.

**CREVCORR Crevice Corrosion versus DOC**

Crevice corrosion was evaluated with the use of CREVCORR-type assemblies in the dissolved oxygen-controlled cells. The CREVCORR-type assembly has the following characteristics: crevice formers are made of polyvinylidene fluoride (PVDF), all fasteners are
made of titanium grade 2 and are electrically isolated from the tested specimen. Disc springs are used to calibrate and keep a measurable and constant pressure between the crevice formers and the specimen [7]. A schematic representation and a picture of the crevice assembly are shown in Figure 7.

![Schematic representation and picture of the CREVCORR crevice assembly](image)

From previous programs it was demonstrated that the use of CREVCORR-type assemblies can provide rather conservative results (when used with adapted gasket pressure) to assess localized corrosion of passive alloys in natural seawater [8,9]. This crevice corrosion testing is more realistic than ASTM-crevice corrosion testing (e.g. ASTM-G48) since service conditions are simulated on coupons offering sufficient anodic and cathodic surfaces. However, crevice corrosion results cannot be fully extrapolated to any field situation since it cannot simulate all specific parameters (e.g. high flow rates applications, environmental variations) and actual crevice geometries. According to the “CREVCORR” standard testing method, the crevice former should be tightened to the test specimens with a force of about 900N (i.e. pressure of about 3 N/mm²), which corresponds to a torque of 3 N·m on the used fasteners. Gasket pressure can be increased to 20 N/mm² to simulate more severe crevice configurations such as flanged parts or threaded connections [9]. For the present applications, CREVCORR-gaskets were adapted on curved specimens from tube sampling and both gasket pressures were used (i.e. 3 and 20 N/mm²). Several dissolved oxygen levels were tested from <20 ppb to 600 ppb. The tested conditions are given in Table 2.

![Table 2: Used conditions for CREVCORR testing in renewed natural seawater at 30°C](table)

<table>
<thead>
<tr>
<th>Desired DOC</th>
<th>S82551</th>
<th>S31803</th>
<th>S39274</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;50 ppb</td>
<td>20N/mm² (4)</td>
<td>20N/mm² (4)</td>
<td>20N/mm² (4)</td>
</tr>
<tr>
<td>50 ppb ±10 ppb</td>
<td>20N/mm² (3)</td>
<td>20N/mm² (3)</td>
<td>20N/mm² (3)</td>
</tr>
<tr>
<td>100 ppb ±20 ppb</td>
<td>20N/mm² (3)</td>
<td>20N/mm² (3)</td>
<td>20N/mm² (3)</td>
</tr>
<tr>
<td>200 ppb ±20 ppb</td>
<td>20N/mm² (2)</td>
<td>20N/mm² (2)</td>
<td>20N/mm² (2)</td>
</tr>
<tr>
<td>500 ppb ±20 ppb</td>
<td>20N/mm² (4)</td>
<td>20N/mm² (4)</td>
<td>20N/mm² (4)</td>
</tr>
<tr>
<td>600 ppb ±20 ppb</td>
<td>20N/mm² (3)</td>
<td>20N/mm² (3)</td>
<td>20N/mm² (3)</td>
</tr>
</tbody>
</table>
Exposure of PCPC tubes in quiescent conditions

After preparation of all tubes, the internal part of the PCPC tubes were filled with natural seawater regulated at 30°C. A schematic drawing showing the principle of the set-up is given in Figure 8.

Figure 8: Schematic drawing of the experimental set-up

A buffer cell with pre-deaerated seawater was installed upstream of the exposed tubes. The seawater, renewed at a rate of 6L/hour in the glass buffer cell, was heated at 30°C and pre-deaerated below 2 ppm. Then a peristaltic pump was used to renewed seawater in tubes at a rate of 1L/h. The temperature regulation was ensured by a controlled heating plate. The DOC was controlled with the use of precise gas flow regulators connected to pure nitrogen and pure oxygen bottles. The dissolved oxygen content was continuously monitored with LDO probes. The tested dissolved oxygen contents ranged from 80 to 500 ppb (7 DOC were used on 7 individual PCPC cells). For each tested sample, the exact DOC was measured together with the open-circuit potentials. For comparison purpose, all specimens were evaluated after 25 days of exposure.

Exposure of PCPC tubes in flow loops under simulated service conditions

The seawater loops were specifically designed to allow flow rates of about 5 m/s in the tested tubes and an accurate control of dissolved oxygen content, pH and temperatures. A schematic drawing of a controlled flow loop is given in Figure 9. The target exposure conditions were as followed: Flow rate 5 m/s – 30°C – DOC = <20 ppb with weekly DOC excursions at 100 ppb for 24h + 300 ppb for 1h. This DOC excursion was defined from field experience feedback as a possible critical and conservative value and frequency. The DOC was controlled using both N₂ bubbling and oxygen scavenger. Example of DO excursion control is given in Figure 10.
Figure 9: Schematic drawing of the treated seawater loop

Figure 10: DO excursion with DO \( \approx 100 \) ppb during about 24 hour followed by a peak at DO \( \approx 300 \) ppb during about 1 hour - Conditions out of excursions = DO < 20 ppb.

Two replicates per alloy were exposed in flow loop under the defined conditions during 145 days. The objective was to evaluate the internal crevice corrosion resistance of PCPC tubes under simulated service conditions in a full scale flow loop.

**Corrosion evaluations**

After exposure, the corrosion of all exposed specimens was visually evaluated using a binocular Leica M125 and an optical microscope Leica DM2500M. For PCPC tubes, the threaded connections were dismantled by cutting the systems into 4 pieces. These threaded sections were then separated from the tubes using a level arm. Corrosion depth measurements were performed by focalization technique using the optical microscope. Metallographic analysis was performed on selected specimens after electrolytic etching in NaOH 7N at 3V. According to the standard evaluation procedures, all corrosion attack deeper than 25µm were considered as crevice corrosion attacks [10,11].
Results

OCP versus DOC curves

The control of the temperature and of the DOC during exposures is given in Table 3 for all tested conditions. A good control of temperature and DOC in the desired ranges was obtained.

Table 3: Temperature and DOC control for OCP and CREVCORR testing in renewed natural seawater

<table>
<thead>
<tr>
<th>Desired DOC</th>
<th>Temperature [°C]</th>
<th>DOC [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;50ppb</td>
<td>30.2 ±0.1</td>
<td>18 ±11</td>
</tr>
<tr>
<td>50 ppb ±10ppb</td>
<td>30.1 ±0.1</td>
<td>47 ±7</td>
</tr>
<tr>
<td>100 ppb ±20ppb</td>
<td>29.9 ±0.1</td>
<td>105 ±15</td>
</tr>
<tr>
<td>200 ppb ±20ppb</td>
<td>30.0 ±0.1</td>
<td>197 ±12</td>
</tr>
<tr>
<td>500 ppb ±20ppb</td>
<td>30.0 ±0.1</td>
<td>513 ±9</td>
</tr>
<tr>
<td>6000 ppb</td>
<td>30.0 ±0.1</td>
<td>6000 ±180</td>
</tr>
</tbody>
</table>

The stabilized open-circuit potentials versus DOC are given in Figure 11 for all tested alloys. No significant differences were observed between the tested grades of stainless steels. In the tested conditions (i.e. continuously renewed quiescent seawater at 30°C) the biofilm ennoblement occurred at DOC of 100 ppb ±20 ppb and above. From 0 to 50 ppb the open-circuit potentials increased with the DOC but potentials at 50 ppb ±20 ppb remained below -100 mV/SCE, which is far below typical potentials which are measured after biofilm ennoblement (i.e. typically equal or above +200 mV/SCE). From these results it can be considered that the risk of initiation of crevice corrosion on stainless steels in natural seawater at 30°C is significantly decreased at DOC below 50 ppb. This risk is further decreased at lower DOC. These conclusions are confirmed in the next section (Crevice corrosion testing). When potential ennoblement occurred (i.e. at DOC = 100 ppb and above), the potential increase occurred at the same time independently on the DOC or the tested grade, i.e. after about 3 days of exposure at 30°C.
Crevice corrosion results

The CREVCORR corrosion results are summarized in Table 4 for all tested conditions. Crevice corrosion occurred for S82551 and S31803 at DOC of 100 ppb and above, while none of the tested specimens showed crevice corrosion at DOC<50. Corrosion was initiated on S39274 for DOC of 600 ppb. This confirms that the risk of crevice corrosion is significantly increased in conditions promoting potential ennoblement. With the tested configuration (curved machined surface with low Ra) no significant difference was found between the 2 gasket pressures at 3 and 20 N/mm². Regarding the PRENw numbers (cf. Table 1) of the tested alloys the better corrosion resistance of S39274 compared to S31803 and S82551 was expected.

The typical aspect of specimens after exposure is given in Figure 12 and Figure 13 showing corroded and corrosion-resistant coupons, respectively. When initiated, the corrosion features (i. e. below crevice formers) were similar whatever the tested conditions and alloy. The propagation of the corrosion cannot be determined accurately in this short-term exposure test, which only aimed at detecting the risk of initiation of crevice corrosion using a critical crevice configuration (YES/NO ranking test). It should be noted that crevice corrosion is rather stochastic and is known to often provide some variability in results.
Table 4: Crevice corrosion results of coupons with CREVCORR assemblies in continuously renewed seawater at 30°C (number of creviced specimens over total number of tested replicates, e.g., 0/4 = no crevice corrosion on 4 tested replicates).

<table>
<thead>
<tr>
<th>DOC (ppb ±ppb)</th>
<th>S82551</th>
<th>S31803</th>
<th>S39274</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;50ppb</td>
<td>0/4 (20N/mm²)</td>
<td>0/4 (20N/mm²)</td>
<td>0/4 (20N/mm²)</td>
</tr>
<tr>
<td>50 ppb ±10ppb</td>
<td>0/3 (3N/mm²)</td>
<td>0/3 (20N/mm²)</td>
<td>0/3 (20N/mm²)</td>
</tr>
<tr>
<td>100 ppb ±20ppb</td>
<td>2/3 (3N/mm²)</td>
<td>2/3 (3N/mm²)</td>
<td>0/3 (3N/mm²)</td>
</tr>
<tr>
<td>200 ppb ±20ppb</td>
<td>2/2 (20N/mm²)</td>
<td>2/2 (20N/mm²)</td>
<td>0/2 (3N/mm²)</td>
</tr>
<tr>
<td>500 ppb ±20ppb</td>
<td>4/4 (20N/mm²)</td>
<td>3/4 (20N/mm²)</td>
<td>1/4 (20N/mm²)</td>
</tr>
<tr>
<td>600 ppb ±20ppb</td>
<td>3/3 (3N/mm²)</td>
<td>3/3 (20N/mm²)</td>
<td>2/3 (20N/mm²)</td>
</tr>
</tbody>
</table>

Copper/Stainless steel assemblies

The mixed potential of copper/stainless steel assemblies is given as a function of DOC in Figure 14. These mixed material assemblies were used to assess the effect of galvanic...
coupling induced by the anti-galling copper treatment of PCPC elements. The potential increased with DOC but copper has a significant influence on the potential, especially at high DOC. When compared to OCP of stainless steels, the mixed potential with copper coupling (1:10 ratio) decreased from +300 mV/SCE to -50 mV/SCE at saturated DOC. The galvanic action of copper on stainless steel is expected to decrease the risk of localized corrosion of stainless steel in case of DO excursion.

Figure 14 : Mixed potential of copper/stainless steel assembly (ratio 1:10) as a function of DOC

The galvanic current circulating from the anodic copper to the cathodic stainless steel is given in Figure 15. It is shown that the galvanic current increased almost linearly with the DOC.

Figure 15 : Galvanic current density between copper/stainless steel assembly (ratio 1:10) as a function of DOC in quiescent seawater at 30°C.

From these measurements, Faraday’s law was used to estimate the galvanic corrosion of copper as a function of DOC under the tested conditions (i.e. quiescent seawater at 30°C), assuming uniform corrosion. Results are given in Figure 16 and it confirmed that galvanic corrosion of copper will be highly dependent on DOC. From 20 ppb to 6000 ppb, the galvanic corrosion rate of copper (with a 1:10 anode to cathode ratio) will be from about 35μm/year to
more than 1000 µm/year, assuming that galvanic corrosion rate remain the same during longer exposure time. It should be underlined that in conditions with high flow rates, the cathodic reduction of oxygen is expected to increase, increasing the galvanic corrosion of copper. Considering that copper plating of PCPC is from 7 to 20 µm thick, the copper coating is expected to be completely dissolved with time. Remaining coating will however act as galvanic protection of the adjacent stainless steel parts (until complete dissolution).

**Figure 16**: Calculated galvanic corrosion of copper in copper/stainless steel assembly (ratio 1:10) as a function of DOC in quiescent seawater at 30°C.

**Laboratory exposure of PCPC tubes in quiescent conditions**

After exposure, all PCPC tubes were cut in 4 parts to mechanically remove the PCPC from the tubes, allowing visual and microscopic evaluations in confined threaded connections (i.e. critical areas for crevice corrosion). Figure 17 shows schematic drawings and photographs of this operation. After dismounting, the corroded areas were evaluated. From the evaluation, it has been observed that significant corrosion has occurred for all tested samples from 150 to 500 ppb of DOC. The second series of exposure were conducted at lower DOC close to 100 ppb for 3 replicates. The copper-plating significantly dissolved for 2 of the 3 samples but only one showed crevice corrosion at coupling-pipe end shoulder interface. The third replicate was not affected by corrosion and the presence of significant remaining copper was confirmed on that specimen. The differences between the replicates can be explained by the different copper-plating thicknesses but also by the “borderline” behaviour of S82551 when exposed close to 100 ppb of DOC (i.e. lack of statistics). This trend was also shown in the CREVCORR-results. Photographs of corroded and none corroded specimens after separation of the PCPC are given in Figure 18 and Figure 19, respectively. The corrosion depths, measured by microscopic focalisation technique are given in Table 5 for all tested conditions. The corrosion attacks were globally deeper at the higher DOC. This is an expected result since the dissolved oxygen content increases the cathodic reduction and thus the propagation rate of the crevice corrosion [12]. It is also important to notice that, for almost all samples, the propagation of the corrosion was generally more pronounced on the tubes than on the PCPC coupling (except for 1 sample). This can be explained by the presence of the initial copper layer on the PCPC which delayed the corrosion of the stainless steel at this location.
Figure 17: Dismounting of the PCPC tubes

Figure 18: Photographs of the corroded area of the S82551 PCPC tube in quiescent conditions with seawater at 30°C before and after separation of PCPC. Averaged DOC = 92 ppb ±15.

Figure 19: Photographs of the S82551 PCPC tube in quiescent conditions with seawater at 30°C. Averaged DOC = 82 ppb ±24. No corrosion – No potential increase.
Table 5: Maximum corrosion depth as a function of the dissolved oxygen content

<table>
<thead>
<tr>
<th>DOC (ppb)</th>
<th>Corrosion depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>copper-plated S82551 PCPC</td>
</tr>
<tr>
<td>500 ± 20</td>
<td>500</td>
</tr>
<tr>
<td>420 ± 50</td>
<td>150</td>
</tr>
<tr>
<td>190 ± 30</td>
<td>100</td>
</tr>
<tr>
<td>150 ± 50</td>
<td>200</td>
</tr>
<tr>
<td>92 ±15</td>
<td>170</td>
</tr>
<tr>
<td>88 ±25</td>
<td>0</td>
</tr>
<tr>
<td>82 ±24</td>
<td>0</td>
</tr>
</tbody>
</table>

When corrosion initiated at PCPC shoulders, the aspect and the location of the corrosion were similar for all tubes. Metallographic inspections were performed on the PCPC and the tubes affected by corrosion at 500 ± 20 ppb of DOC. Cross sections were performed on the corroded area of the tube and the PCPC and results are given in Figure 20. Micrographs show that the propagation of the corrosion occurred preferentially along of the ferritic phase, which is generally the case for duplex materials in such environment.

Figure 20: Micrographs of the corroded area of the S82551 connected tube exposed in seawater at 30°C. Average DOC = 500 ppb ±20

The main results from the corrosion tests of PCPC tubes in quiescent seawater are listed below:
- in prolonged exposure in seawater at 30°C with DOC ≥ 150 ppb, it exists a significant risk of crevice corrosion at PCPC shoulders of S82551;
- the risk of propagation is increased with the DOC (i.e. higher corrosion rates at higher DOC);
- at DOC close to 100 ppb, the corrosion results are rather stochastic (i.e. corrosion of 1 sample out of 3 replicates), confirming that 100 ppb is a borderline condition for the use of S82551 in seawater. Prolonged exposures are thus not recommended at DOC close to 100 ppb.

These results are in good agreement with the CREVCORR-results which also showed that 100 ppb is a borderline condition for crevice corrosion resistance of S82551 in natural seawater at 30°C. After dissolution, the copper plating cannot be considered anymore as a galvanic protection for the S82551. However, it has probably a role in delaying the corrosion initiation in case of prolonged DOC excursions.
Full Scale exposure of PCPC tubes in flow loops

The evolution of temperature, flow rate and pH during the 145 days of exposure in the flow loop simulating treated seawater is given in Figure 21. These parameters remained stable during the whole duration of exposure at 30.0°C ±0.9°C, pH 7.50 ±0.14 and flow rate 4.9±0.1. The pH of the seawater before treatment (i.e. N₂ bubbling and oxygen scavenger lower) was 8.1±0.1. The lower pH of the treated water in the loop is due to the very low pH of the oxygen scavenger (pH = 2) and is in agreement with the field experience. The DOC control is given in Figure 22 during the whole duration of exposure. Twelve DOC excursions have been achieved during the 145 days of exposure.

After exposure, all the PCPC tubes were cut into 4 pieces to remove mechanically the PCPC couplings from the tubes. Visual and binocular inspections were performed on all specimens after 145 days of exposure in the flow loop with treated seawater at 30°C and no corrosion initiated at any PCPC shoulders for S39274, S31803 and S82551. The typical aspect of S82551 PCPC tubes after destructive inspection is given in Figure 23. Similar aspect (no...
corrosion) was observed on replicates and on other alloys (S31803 and S39274). It is observed that copper plating on surface directly opened to the water flow completely dissolved.

Figure 23: Visual aspect of PCPC tubes made of S82551, destructive inspection after 145 days of exposure in flow loop at 30°C—No corrosion at PCPC interfaces, same aspect for S31803 and S39274

Conclusions
The corrosion resistance of S82551 was evaluated with PCPC tubes under different service conditions and compared to more alloyed alloys S31803 and S39274. In treated seawater for DOC control at 30°C the main conclusions are listed below:

- In simulated service conditions using flow rates of about 5 m/s and DOC < 20 ppb with weekly excursions at 100ppb for 24h + 1h at 300 ppb, no internal corrosion (i.e. pitting on tubes or crevice at PCPC shoulders) occurred on S82551 after 145 days of exposures (i.e. 12 DOC excursions). Similar results were obtained on S31803 and S39274 (i.e. no internal corrosion).

- In quiescent conditions, prolonged exposures of S82551 PCPC tubes at DOC close and above 100 ppb induced a risk of initiating crevice corrosion at PCPC tube shoulders of S82551.

- The criteria for avoiding DOC above 50 ppb (i.e. 100±20ppb) during prolonged durations for S82551 was confirmed with laboratory testing of crevice corrosion. The corrosion risk was related to the biofilm ennoblement which occurred under these conditions.

- With CREVCORR crevice assemblies, crevice corrosion occurred on S82551 and S31803 specimens at DOC = 100±20ppb. Crevice corrosion of S39274 occurred only at 500 ppb and above.
- No crevice corrosion occurred on S82551 when tested at DOC below 50 ppb, regarding that no potential ennoblement occurred at these DOC.
- The presence of copper-plating on PCPC coupling is expected to delay the corrosion risk at PCPC interface by galvanic action. However, the presence of copper is only temporary and life duration will highly depend on actual DOC during service conditions.

It should be underlined that crevice geometries (e.g., use of gasket, geometric configuration, surface treatment, etc.) can have very significant influence on crevice corrosion results. Crevice geometries of S82551 elements thus need to be well defined and controlled to avoid corrosion failure in treated seawater systems.

References