MATERIALS PERFORMANCE
CORROSION
INNOVATION OF THE YEAR AWARDS

2021 Award Nomination

Title of Innovation:

SM25CRU Cost-effective Duplex Tubing for Water-injection Wells

Nominee(s)

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Category:

(select one below)

Coatings and Linings
Cathodic Protection
[✓ **Materials Design**]
Chemical Treatment
Instrumentation
Testing
Modeling/Risk Assessment
Other—fill in

Dates of Innovation Development:

February 2016 to August 2020

Web site:

http://www.tubular.nipponsteel.com/
https://www.equinor.com/

Summary Description:

In Oil & Gas production fields for seawater handling systems such as water injection wells, the common solutions for tubing materials are low alloy steel, Glass Reinforced Epoxy (GRE) lined onto low alloy steel, or Corrosion Resistant Alloys such as super duplex stainless steel, which has pitting resistance equivalent number (PRENw) greater than 40. However, GRE would not be suitable for WAG (water alternate gas) applications and has limitations with respect to well interventions. Also, in treated seawater (e. g. dissolved oxygen removed), the corrosion risks can be controlled so that more cost-effective lower grade alloys can be considered. However, past experiences have shown that treated seawater injection systems if not correctly operated, can lead to high Dissolved Oxygen Concentrations (DOC) in the seawater injected into the wells resulting in corrosion failures. Experience has shown that this limits the use of low alloy steel tubing in seawater injection wells with lifetimes more than 10 years.

Recent efforts have focused attention on better DOC controls which permits the investigation and possible use of more cost-effective materials for both water injection and WAG applications. In this innovation, duplex stainless steels with PRENw above 30, have been considered to maintain both cost effectiveness and sufficient corrosion resistance in the treated seawater condition. SM25CRU duplex stainless steels, namely, UNS S82551 and S82541 (the latter is a higher strength version, but same PRENw) have been newly developed for this purpose. A seawater test program with controlled DOC, simulating real case conditions, was designed to demonstrate the corrosion performance of UNS S82551/S82541, replicating water injection service conditions with DOC excursions. Both UNS S82551/S82541 under treated seawater systems with some presence of DOC showed good corrosion resistance. The innovation has been achieved by the combination of fit for purpose material design and DOC control technology bringing important cost saving for Norwegian Continental Shelf wells.

(300 words)

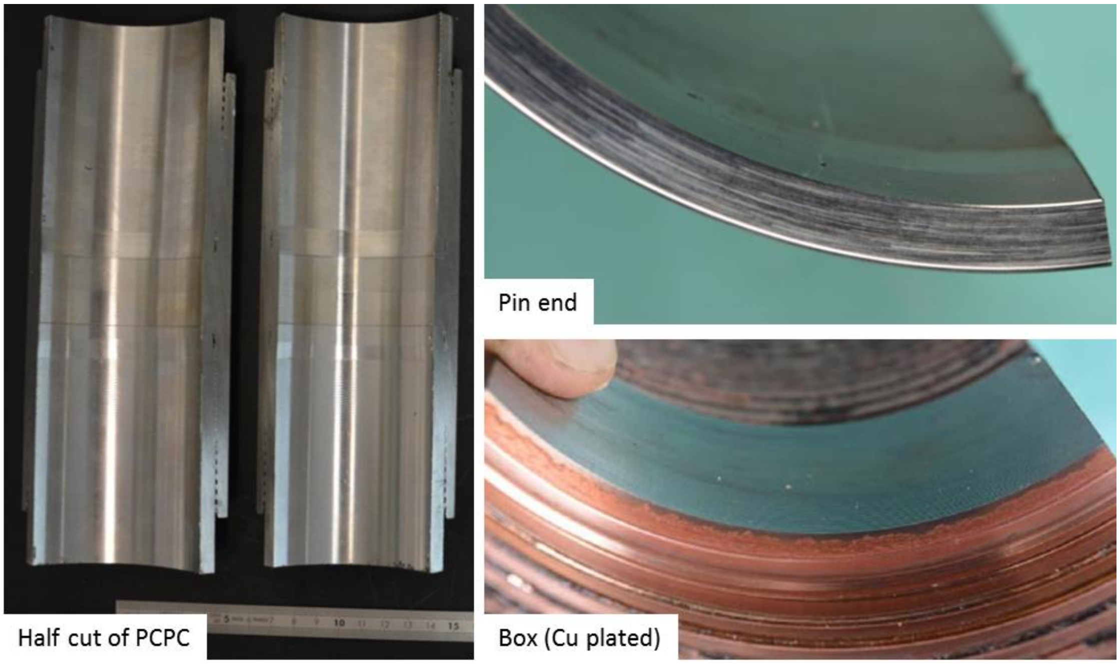


Figure: SM25CRU - good corrosion performance has been validated using pipe coupling premium connection (PCPC) set-up, through 145 days of treated seawater exposure in flow loop at 30°C.

Full Description:

(Please provide complete answers to the questions below. Graphs, charts, and photos can be inserted to support the answers.)

1. What is the innovation?

Cost-effective duplex stainless steels suitable for treated seawater injection well application.

2. How does the innovation work?

Duplex stainless steels with PRENw (= Cr + 3.3(Mo+1/2W) + 16N [mass%]) greater than 30 (actually, specified as min. 31.0) have been proved to be corrosion resistant in the treated seawater injection well conditions. The cost minimization can be realized using the combination of cost-effective duplex alloys UNS S82551/S82541 and DOC controlled system for the seawater injection service.

3. Describe the corrosion problem or technological gap that sparked the development of the innovation. How does the innovation improve upon existing methods/technologies to address this corrosion problem or provide a new solution to bridge the technology gap?

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

In the situation when DOC concentrations are controlled below 20 ppb, 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 (GRE) has, in our experience, excellent performance in both treated and natural seawater injection wells with no failures reported to date. However, GRE lined steel tubing cannot be used:

1. For well equipments e.g. down hole safety valves (DHSV), pressure and temperature gauges, cross-overs, 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/set.

3. When through tubing drilling or coiled tubing well intervention operations are planned.

In these instances, a Corrosion Resistant Alloy (CRA) must 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. Therefore, 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 enough? UNS (1) 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 and reported very high risks of initiating localized corrosion in chloride containing media.

To address this question a seawater test program was designed to determine the pitting and crevice corrosion performance of a new alloy UNS S82551, which has PRENw > 30.

The corrosion resistance of UNS S82551 was evaluated with actual pipe coupling premium connection set-up (called as PCPC to simulate a crevice set up) tubes under different service conditions and compared to alloys UNS S31803 and UNS S39274.

Through a comprehensive qualification program including full scale loop testing, an operational window for UNS S82551 has been established. The laboratory results proved that threaded and coupled UNS S82551 would not suffer from localized corrosion in seawater with dissolved oxygen concentrations up to and exceeding 50 ppb. That also included short excursions up to 100-300 ppb. The test program was designed to replicate oxygen concentrations typically seen in operations. The numbers presented are considered representative for such offshore process systems. Offshore de-aeration systems are typically designed to keep the dissolved oxygen concentration below 20 ppb, but excursions cannot be ruled out.

Based on the successful qualification program, UNS S82551 is already in use on two of the Company’s assets. Both assets have a good track record with respect to oxygen control. This has been part of the implementation strategy. Since the UNS S82551 obviously is more of a fit-for-purpose material selection than the 25%Cr super duplex stainless steel traditionally used, the Company has chosen to limit its use to assets with proven water treatment facility performance.

UNS S82541 has also been developed to fulfill the demand to allow the well design which needs the higher strength tubing. UNS S82541 contains higher Mn than UNS S82551 to achieve 80ksi Specified Minimum Yield Strength (SMYS) (UNS S82551 is available at 75 ksi SMYS). Since the PRENw of UNS S82541 is the same as that of UNS S82551, the corrosion resistance in treated seawater is the same, and its corrosion performance has been validated through the laboratory test using the novel crevice corrosion evaluation cell (called as remote crevice assembly). Using the remote crevice assembly, the re-passivation of UNS S82541 under creviced portion has been validated in the treated seawater condition.

4. Has the innovation been tested in the laboratory or in the field? If so, please describe any tests or field demonstrations and the results that support the capability and feasibility of the innovation.

Yes. Duplex stainless steel tubing alloys were evaluated: UNS S82551/S82541, UNS S31803 (standard duplex, 22Cr), and UNS S39274 (super duplex, 25Cr). The alloy compositions of UNS S82551 and UNS S82541 are given in Table 1.

Table 1: Chemical composition of UNS S82551 and UNS S82541 and specified minimum PRENw

Material	Chemical Composition (mass %)							
	C	Mn	Cr	Ni	Mo	Cu	N	PRENw*
UNS S 82551	max 0.03	max 1.50	23.5 – 25.5	4.5 – 6.5	0.75 – 2.0	2.0 – 3.0	0.10 – 0.35	min 31.0
UNS S 82541	max 0.03	1.5 – 7.5	23.5 – 25.5	3.5 – 6.5	0.75 – 2.0	1.0 – 3.0	0.10 – 0.35	min 31.0
* PRENw = Cr + 3.3(Mo + 1/2W) + 16N								

The stabilized Open Circuit Potential (OCP) of the tested alloys as a function of DOC was measured 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). 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). Several dissolved oxygen levels were selected from <10 ppb to saturation (6 ppm) to draw the OCP versus DOC curves, using 6 ranges of DOC.

The quiescent condition exposures of coupons with CREVCORR crevice formers and proprietary premium threaded connection (pipe coupling premium connection – PCPC) were performed in dissolved oxygen controlled cells, allowing the measurement of electrochemical potentials as a function of DOC for monitoring of biofilm formation and the related corrosion resistance.

Three alloys (UNS S31803, S39274 and S82551) were evaluated for CREVCORR testing, but only S82551 was used for PCPC type in the quiescent condition exposures.

Fit-for-purpose full scale corrosion testing of two tubes joined with a proprietary premium threaded connection was performed to investigate the risk of crevice corrosion in controlled seawater loops simulating service conditions at 30°C, as shown in Figure 1. The actual crevice configuration (i.e. threaded connection with copper anti-galling treatment) can be evaluated in the desired environment. 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 included during the 5 months exposure (Figure 2).

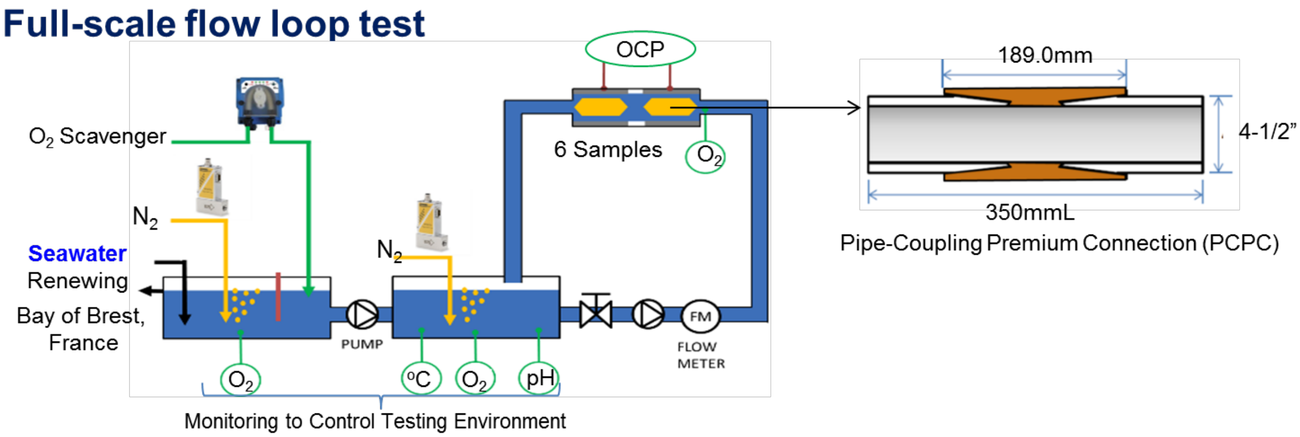


Figure 1 Schematic drawing of the treated seawater loop

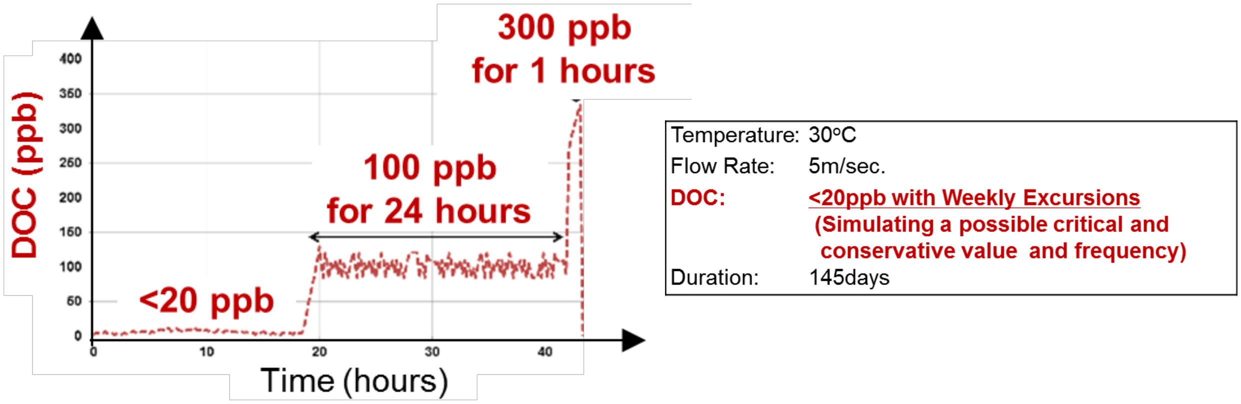


Figure 2 DOC excursions

OCP versus DOC curves:

The stabilized open-circuit potentials versus DOC are given in Figure 3 for all tested alloys. No significant differences were observed between the tested grades of stainless steels. In the tested conditions 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. When potential ennoblement occurred (i.e. at DOC = 100 ppb and above), the potential increase occurred at the same time independently of the DOC or the tested grade, i.e. after about 3 days of exposure at 30°C.

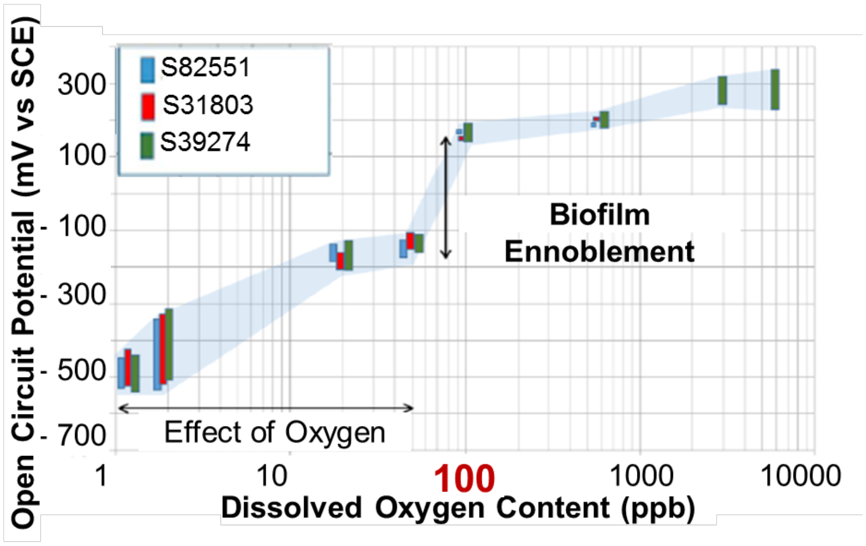


Figure 3 OCP versus DOC for All the Tested Stainless Steels with No Corrosion in Natural Renewed Seawater at 30^{o}C

Laboratory exposure in quiescent conditions:

The CREVCORR corrosion results are summarized in Table 2 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<50ppb. 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. No significant difference was found between the

2 gasket pressures at 3 and 20 N/mm². Regarding the PRENw numbers of the tested alloys the better corrosion resistance of S39274 compared to S31803 and S82551 was expected.

Table 2: 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).

	S82551	**S31803**	**S39274**
<50ppb	0/4 **(20N/mm²)**	0/4 **(20N/mm²)**	0/4 **(20N/mm²)**
50 ppb ±10ppb	0/3 **(20N/mm²)** 0/3 **(3N/mm²)**	0/3 **(20N/mm²)** 0/3 **(3N/mm²)**	0/3 **(20N/mm²)** 0/3 **(3N/mm²)**
100 ppb ±20ppb	3/3 **(20N/mm²)** 2/3 **(3N/mm²)**	3/3 **(20N/mm²)** 2/3 **(3N/mm²)**	0/3 **(20N/mm²)** 0/3 **(3N/mm²)**
200 ppb ±20ppb	2/2 **(20N/mm²)** 2/2 **(3N/mm²)**	2/2**(20N/mm²)** 2/2 **(3N/mm²)**	0/2 **(20N/mm²)** 0/2 **(3N/mm²)**
500 ppb ±20ppb	4/4 **(20N/mm²)**	3/4 **(20N/mm²)**	1/4 **(20N/mm²)**
600 ppb ±20ppb	3/3 **(20N/mm²)**	3/3 **(20N/mm²)**	2/3 **(20N/mm²)**

The results from the laboratory exposures of coupons with CREVCORR crevice formers and PCPC of UNS S82551 in dissolved oxygen controlled cells were summarized in Figure 4. The main results from the corrosion tests of PCPC tubes in quiescent seawater are;

- in prolonged exposure in seawater at 30°C with DOC ≥ 150 ppb, there exists a significant risk of crevice corrosion at PCPC seal of UNS S82551

- the risk of propagation is increased with the DOC (i.e. higher corrosion rates at higher DOC)

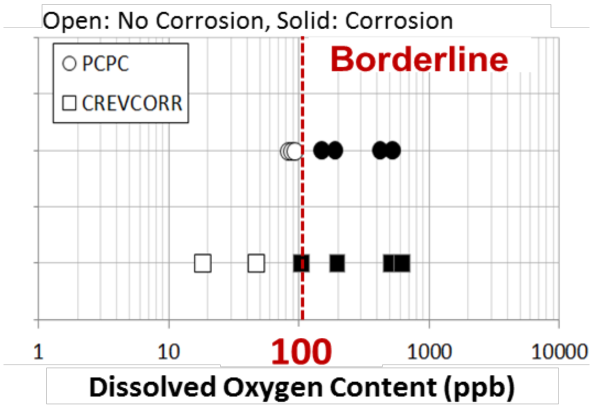


Figure 4: Results from quiecent exposure condition for CREVCORR and PCPC type specimens, UNS S82551

- 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 UNS S82551 in seawater.

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 UNS S82551 in natural seawater at 30°C.

The full-scale loop test using PCPC tubes:

The evolution of temperature, flow rate and pH were monitored and recorded during the 145 days of exposure in the flow loop simulating treated seawater. 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 m/s. The pH of the seawater before treatment (i. e. N_2 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 agrees with the field experience. The DOC control is given in Figure 5 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 as shown in Figure 6.

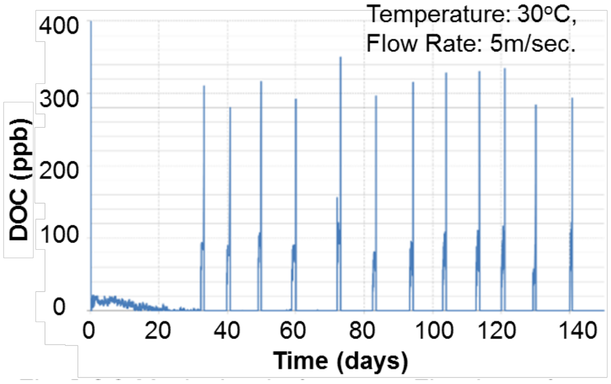


Figure 5: DOC monitoring in natural seawater flow loop at 30°C with controlled DO <20ppb + weekly excursions

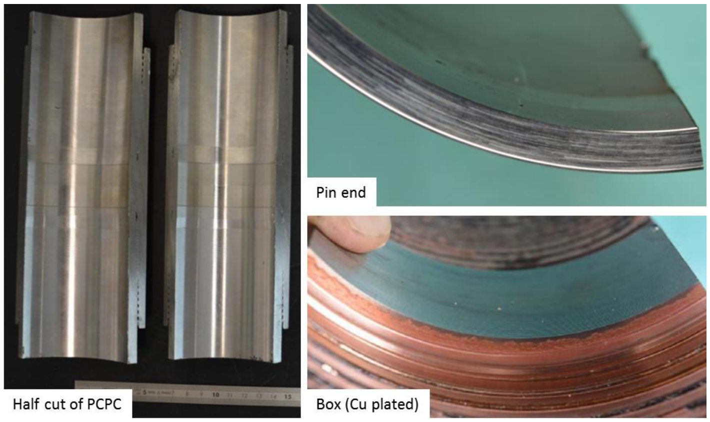


Figure 6: Visual aspect of PCPC tubes made of S82551, destructive inspection after 145 days of exposure in flow loop at 30°C

Re-passivation validation test using Remote Crevice Assembly

Since the PRENw of UNS S82541 is the same as that of UNS S82551, the corrosion resistance in treated seawater can be same. For UNS S82541 corrosion resistance was validated through the laboratory test using the novel crevice corrosion evaluation cell (Remote Crevice Assembly, RCA, Figure 7). Using the RCA, the re-passivation of UNS S82541 under creviced portion has been validated in the treated seawater condition.

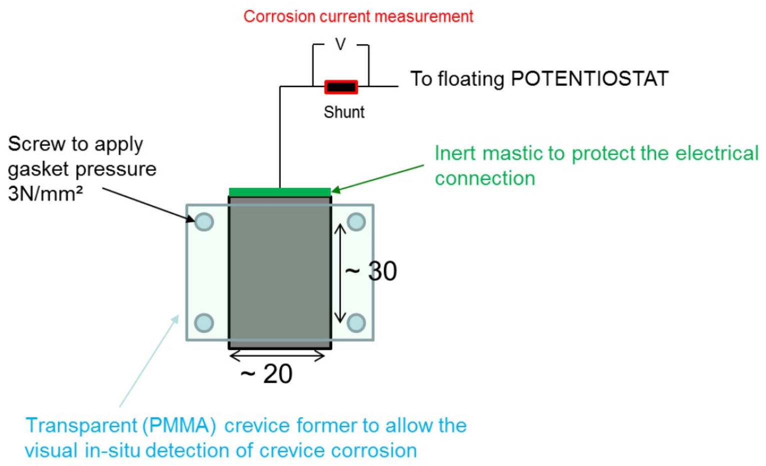
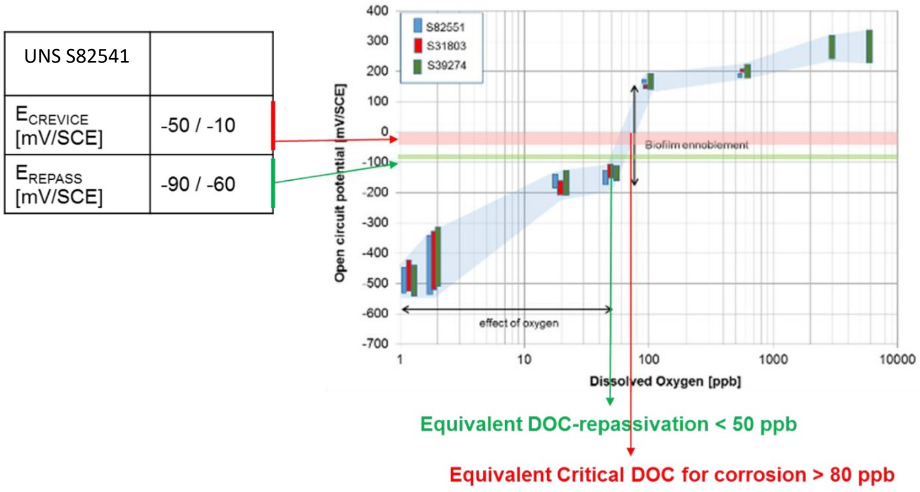


Figure 7 Schematic illustration for Remote Crevice Assembly (RCA)

In the previous study, the potential of different stainless steels (including SM25CRU) was measured as function of dissolved oxygen (ref. Fig. 3). It was shown that biofilm-induced ennoblement (leading to potentials >200 mV/SCE) was reached only at DOC above approx. 80 ppb. From this curve it is possible to correlate the potentials measured in the present study ($E_{activation}$ and $E_{repassivation}$), with associated DOC that are required to reach these potentials. The results from both studies on SM25CRU are summarized in Figure 8. The results of $E_{activation}$ and $E_{repassivation}$ are perfectly correlated with the conditions promoting biofilm-ennoblement: i. e. the corrosion is initiated at potentials that are reached just above the critical DOC for potential ennoblement, and the re-passivation occurs at potentials that are measured at DOC for which no biofilm ennoblement is measured. This corresponds to an equivalent $DOC_{activation}$ of about 80 ppb and an equivalent $DOC_{repassivation}$ < 50 ppb. At potentials that are reached below 50 ppb, the SM25CRU was confirmed to re-passivate. It can then be concluded that re-passivation occurred for UNS S82541 and also UNS S82551.



UNS S82541	
$E_{CREVICE}$ [mV/SCE]	-50 / -10
E_{REPASS} [mV/SCE]	-90 / -60

Figure 8 Correlation of OCP results versus DOC results for UNS S82541

5. How can the innovation be incorporated into existing corrosion prevention and control activities and how does it benefit the industry/industries it serves (i.e., does it provide a cost and/or time savings; improve an inspection, testing, or data collection process; help to extend the service life of assets or corrosion-control systems, etc.)?
This material fit-for-purpose development achieved substantial cost saving of the operator in Seawater injection applications. By fit for purpose we mean:

- Understanding the actual Injection conditions, specifically in terms of DOC and its excursions.

- Developing a material that could withstand the worst case scenario.

The same approach may be applied in other applications as long as the conditions are known and controlled by the operator.

6. Is the innovation commercially available? If yes, how long has it been utilized? If not, what is the next step in making the innovation commercially available? What are the challenges, if any, that may affect further development or use of this innovation and how could they be overcome?
Yes. Already deployed in a number the NCS seawater and WAG wells since 2017.

7. Are there any patents related to this work? If yes, please provide the patent title, number, and inventor.
Yes.

a) Patent Title: Duplex Stainless Steel, and Process for Production Thereof

Number: WO2012/111536

Inventors: Daisuke Motoya, Masahiko Hamada, Hisashi Amaya, Hiroyuki Nagayama, Kenta Yamada

b) Patent Title: Duplex Stainless Steel

Number: WO2013/191208

Inventors: Masayuki Sagara, Akiko Tomio