

Materials Selection for Seawater Injection Service – Crevice Corrosion Testing of Stainless Steels Under Controlled Dissolved Oxygen

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ABSTRACT

Higher grade alloys such as super-duplex stainless steels have been the conventional choice when selecting corrosion resistant alloys (CRAs) for seawater or water-alternative gas (WAG) injection service. However, the use of less costly, leaner alloyed stainless steels has recently been given greater consideration in treated seawater systems where the dissolved oxygen concentration (DOC) is better controlled. Crevice corrosion exposure tests were conducted on nine (9) stainless steel alloys in synthetic seawater containing controlled DOC levels (100 ppb to 500 ppb range). The alloys ranged from a martensitic (13-Cr) stainless steel to higher alloyed duplex and super-duplex stainless steels (25-Cr). The stainless steel specimens were creviced using the CREVCORR configuration to produce tight and reproducible crevice geometries. The exposure tests were carried out in a stepwise process in which increasingly harsher test conditions (higher temperature, higher DOC) were applied after certain periods. The open circuit potentials of the specimens were monitored during the tests to indicate the onset of crevice attack as the conditions were altered. The results of this testing revealed that stainless steels containing 17-Cr or higher are not susceptible to crevice corrosion in synthetic seawater, even for dissolved oxygen levels as high as 500 ppb.

Keywords: Crevice corrosion, stainless steel, dissolved oxygen, seawater injection

INTRODUCTION

Treated seawater or WAG injection is commonly used as a means of enhanced oil recovery in the oil and gas industry. The seawater for injection is first treated with biocide (hypochlorite) at the lift-pump. Afterwards, the seawater is treated with mechanical deaeration followed by oxygen scavenger deaeration. The hypochlorite treatment at the lift-pump generally introduces a small concentration of free residual chlorine (0.5 – 1.0 ppm). Further downstream, biocide treatment may be required before the seawater enters the mechanical deaeration tower. The free residual chlorine content decays quickly after mechanical deaeration; at the lift-pump exit it is generally around 0.5 – 0.7 ppm but decays to trace amounts (0.01 – 0.03 ppm) at the injection head.

A low alloy steel, containing 1% Cr, combined with very tight control of DOC (< 20 ppb) is generally acceptable for injection that only involves seawater. However, the WAG injection poses a corrosion threat

to the integrity of low alloy tubing strings when switched from seawater to gas because the gas consists of acid gases such as H₂S or CO₂. Moreover, even when seawater alone is used, the injected water velocity should be maintained below 4 m/s to prevent erosion corrosion of the low alloy steel tubing string.¹ Therefore, selection of a proper CRA is often a better option to ensure that the tubing string will last for the entire design life.

Unfortunately, CRAs are expensive and not immune to corrosion failures in this type of application. When selecting a CRA material for WAG injection, the first consideration is to guard against sulfide stress cracking (SSC) and stress corrosion cracking (SCC) under acid gas conditions. Once it has been established that the candidate CRA is sufficiently resistant to SSC and SCC, the main concern becomes whether the CRA is sufficiently resistant to localized corrosion (e.g., crevice corrosion) in the presence of dissolved oxygen. Although the DOC of the seawater is kept at low levels in these systems, it is not uncommon to experience excursions in the DOC that could potentially lead to crevice corrosion. The target DOC in WAG injection systems is ≤ 20 ppb, which is achieved using both mechanical deaeration and oxygen scavengers. However, this level of DOC is not always ensured during operation and DOC excursions above the 20 ppb limit can frequently occur. Although it depends on the operator's experience, the DOC during operation is generally controlled as follows:

- DOC ≤ 20 ppb for around 70% of the operation time;
- DOC ≤ 50 ppb for around 90% of the operation time;
- DOC ≤ 100 ppb for nearly 100% of the operation time;
- DOC excursions above 100 ppb may occur but are not expected to last more than 24 hours.

Highly alloyed CRAs, such as super-duplex stainless steels (SDSS), are often considered necessary to address the localized corrosion risks associated with DOC excursions greater than 20 ppb. The SDSS class of alloys have a high pitting resistance equivalent number (PREN_w) that is typically > 40 . However, these alloys come with a high price tag and could be overly conservative for the intended application. Instead, less-costly duplex stainless steels (DSS) or even 17-Cr alloys could be suitable alternatives for WAG injection tubing strings provided that the localized corrosion susceptibility limits are better understood. The main purpose of the work presented in this paper was to examine these susceptibility limits in relation to the DOC level in synthetic seawater. This paper describes the testing program and key findings that were obtained from crevice exposure tests that were conducted under precisely controlled DOC conditions. The tests involved stainless steel alloys with PREN_w values ranging from 12 to 45.

EXPERIMENTAL

Materials and Specimens

Table 1 contains the chemical compositions and calculated PREN_w⁽¹⁾ of the alloys that were included in the crevice corrosion evaluations. Eight of the alloys were higher-alloyed stainless steels (PREN_w ≥ 25) that contained at least 17% Cr; these eight alloys were fabricated from tubular material that was supplied by the customer. The remaining two alloys were lower grade alloys (PREN_w ~ 12) that were fabricated from plate material. These two alloys (UNS K90941 and UNS S41000) were only included for comparative purposes. The exact chemical compositions of the 17-Cr alloys are excluded from Table 1 because of the proprietary nature of the alloy formulations.

Figure 1 shows the test specimen dimensions and geometry that were used for most of the tubular alloys that were evaluated. The specimen design and dimensions were modelled after those used in the

⁽¹⁾ PREN_w = Cr% + 3.3 x (Mo% + 0.5 x W%) + 16 x N%

CREVCORR test program². Two of the alloys (UNS S31803 and UNS S32750) could not be fabricated to the dimensions shown in Figure 1 due to limitations in the available tubular material. Consequently, the specimen dimensions for these two alloys were reduced to 38 mm x 38 mm. The other dimensions and features (thickness, hole diameters, etc.) were consistent with those specified in Figure 1.

Table 1
Compositions of tested alloys (wt.%) and associated PRENw values.

Alloy Type	UNS or Material ID	Chemical Composition, wt.%							PRENw
		Cr	Mo	N	W	Ni	Cu	C	
9Cr-1Mo Steel	K90941	8.75	0.97	–	–	0.18	0.11	0.04	12.0
13-Cr	S41000	12.24	0.03	0.01	–	0.23	0.13	0.13	12.5
17-Cr ®	3018*	16-18	2-3	–	–	4-5.5	2-3	≤ 0.03	25.1
17-Cr ®	2907*	16-18	2.3-2.8	®	0.8-1.2	3.5-4.5	≤ 1.5	≤ 0.04	27.0
DSS	S82551	25.04	1.03	0.18	–	4.99	–	0.01	31.3
DSS	S31803	22.64	3.18	0.18	–	5.2	–	0.02	36.0
DSS	S31260	25.06	3.04	0.18	–	7.09	0.39	0.018	38.0
SDSS	S32760	25.76	3.67	0.24	–	7.12	0.65	0.021	41.7
SDSS	S39274	25.28	3.18	0.28	2.14	6.78	0.46	0.018	43.8
SDSS	S32750	25.35	4 [†]	0.3 [†]	–	6.51	–	0.013	45.0

® = Proprietary, exact compositions omitted

* UNS designation does not exist

[†] Not contained in material test report, nominal compositions assumed

UNS K90941 and UNS S41000 specimens were not fabricated from customer-supplied, tubular material because they were not candidates for seawater injection service. Instead, the specimens were procured from the stocked inventory of specimens offered by a commercial vendor. UNS K90941 specimens were supplied with dimensions of 50.8 x 25.4 x 3.7 mm and UNS S41000 specimens were supplied with dimensions of 50.8 x 25.4 x 1.6 mm. The specimens were modified to include a center-hole for the crevice bolting and a corner-hole for an electrical lead. The hole sizes were consistent with those specified in Figure 1.

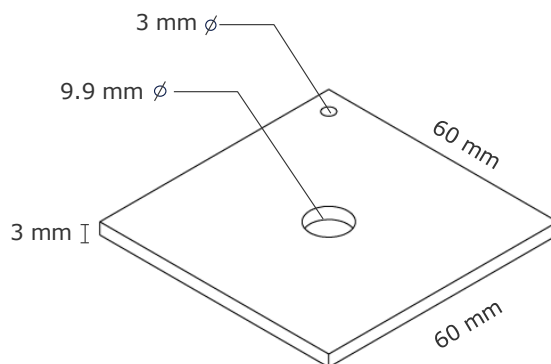


Figure 1: Drawing of crevice test specimen.

The specimens that were fabricated from tubular material were supplied with a US-600 (P-1200) finish and did not receive any additional polishing prior to testing. UNS K90941 and UNS S41000 specimens were supplied with a coarse finish; they were wet-ground to a US-600 finish within a few days prior to testing. All the specimens were thoroughly degreased with acetone and then rinsed with deionized water prior to crevice assembly and testing.

Crevice Assembly Configuration

The crevice configuration was based on the methodology established in the CREVCORR program as described by Kivisakk et al.² Figure 2 provides an assembled view and an exploded view of the crevice assembly and associated parts. The crevice formers were flat washers made of polyvinylidene difluoride (PVDF). The PVDF washers were wet ground with US-600 grit paper to remove all machining grooves. The fasteners (bolts, nuts, and washers) for the crevice assembly were made of titanium grade 2. An insulating sleeve, machined from Delrin® acetal tube, was used to sheath the titanium bolt and to center the washers. Fiberglass washers were used to electrically isolate the titanium washers from the disc spring washers, which were made of a nickel-base alloy. A set of six disc springs was used to maintain a constant force on the crevice formers. Two different disc spring configurations were used to maintain the crevice gasket pressures of 3 N/mm² and 12 N/mm²: a series stack of six washers (1-2-2-1) was used for the lower crevice pressure of 3 N/mm²; a parallel-series combination (3-2-1) of six disc springs was used for the 12 N/mm² crevice pressure to increase both the working load and deflection of the disc springs.

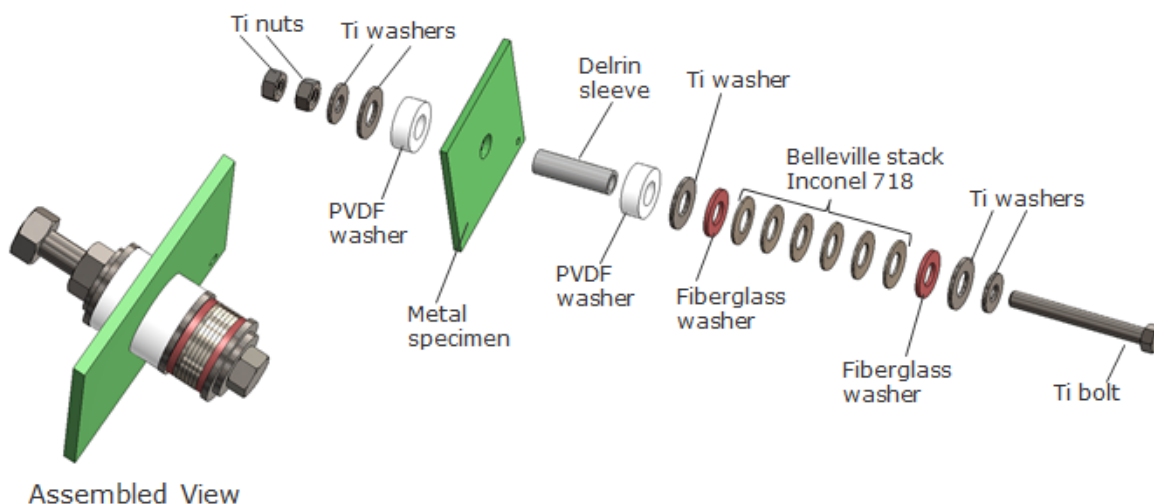


Figure 2: Assembled view and exploded view of crevice specimen configuration.

Load versus displacement tests were performed on mock-up crevice assemblies containing the different disc spring configurations to determine the amount of tightening/displacement that was required for each crevice pressure. A servo-electric test frame was used to generate the load versus displacement curves, which were used to correlate crevice pressure (load) to tightening distance (displacement). A calibrated dial indicator was used to measure the tightening distance as the crevice assemblies were tightened. Prior to recording tightening distance, the crevice assemblies received an initial torque of 0.2 N-m.

The total creviced area based on the PVDF washer dimensions was 5 cm². The ratio of cathodic area (non-creviced area) to anodic area (creviced area) was approximately 16 for the specimens that conformed to the dimensions in Figure 1. The alloys that did not conform to Figure 1 (UNS S31803, UNS S32750, UNS K90941, and UNS S41000) had cathodic to anodic area ratios that were around 6.

Test Solution and Test Gases

All testing was performed in synthetic seawater that was commercially procured. The synthetic seawater conformed to ASTM⁽²⁾ D1141³ and was procured in premixed, 20-liter quantities. Ultra-high purity nitrogen gas (99.999% purity) was used in all the tests. A mixed gas containing 1 mol% oxygen (balanced with high purity nitrogen) was used for tests requiring DOC levels below 300 ppb. Compressed air (ultra-zero grade) was used for tests requiring higher than 300 ppb DOC.

Gas Blending Calculations

The target dissolved oxygen concentrations were achieved by saturating the synthetic seawater solution with blended gas mixtures that were created by mixing two gases of the following types:

1. Gas 1: High-purity N₂
2. Gas 2: Pre-mixed N₂ + O₂
 - a. N₂ + 1 mol% O₂: for obtaining DOC of 100 or 200 ppb, or
 - b. N₂ + 21.7 mol% O₂: for obtaining DOC of 500 ppb

The gas-blend ratio (ratio of mass flow rates of Gas 1 to Gas 2) required to achieve the target dissolved oxygen concentration in synthetic seawater at a given temperature was modelled using OLI StudioTM software⁽³⁾. The input parameters for the OLI model consisted of the following:

- Chemical species and concentrations in the ASTM D1141 synthetic seawater solution
- Test temperature (30, 40 or 70°C)
- Gas 1: Pure N₂
- Gas 2: (N₂ + 1 mol% O₂) or (N₂ + 21.7 mol% O₂)

An OLI calculation was performed to study the variation of the aqueous-phase speciation as a function of the blend ratio of the two gases at each temperature. The gas-blend ratio predicted to yield the target DOC at the test temperature was determined from the results of the calculation. For a total gas flow rate of 100 sccm into the test cell, the individual mass flow rates of Gas 1 and Gas 2 were then derived from the predicted gas-blend ratio.

Experimental Setup and Test Procedure

The dissolved oxygen concentration in the tests was measured using an amperometric-type dissolved oxygen (DO) sensor. Based on the manufacturer specifications, the DO sensor had a detection limit ranging from 6 ppb to saturation and an accuracy stated as less than or equal to $\pm (1\% + 6 \text{ ppb})$. The DO sensor contained a thermistor in the sensor body to provide temperature compensation for the measurements. The DO sensor was placed directly inside the exposure vessel for Test 1. For the subsequent tests (Test 2 and Test 3), the DO sensor was placed outside of the test vessel in a recirculating loop in order to produce more stable readings. The recirculating loop was heated to maintain the proper solution temperature for the DO measurements.

The Test 1 and Test 2 crevice exposures were performed in a large, tubular vessel that contained a plastic rack for fixturing 48 crevice specimens as shown in Figure 3. The vessel was fabricated from a transparent acrylic tube, approximately 45 cm in height x 29 cm in diameter. The vessel contained roughly 25 liters of synthetic seawater for each test. The lid of the vessel was equipped with numerous ports to serve as feedthroughs for specimen lead wires, thermocouple, reference electrode, etc. The lid was sealed to the top flange of the vessel using an O-ring and fasteners. A heating band on the external surface of the vessel was combined with a controller and thermocouple to achieve thermostatic

⁽²⁾ ASTM International (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

⁽³⁾ OLI Studio, (Version 9.6.1, AQ Databanks): A commercial software for calculating the speciation and physical properties of aqueous solutions, within a thermodynamic framework; developed by OLI Systems, Inc., Cedar Knolls, NJ.