

**Applicability of 15% Cr and 17% Cr Martensite-Based Stainless Steel OCTG
Materials for Seawater Injection Service**

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ABSTRACT

This paper reports the applicability of 15% Cr-added (15-6-3-Cu-based; UNS No. S42625) and 17% Cr-added (17-4.5-3-Cu-W-based; UNS No. S42825) martensite-based stainless steel OCTG materials for seawater injection service. It is known that GRP (Glass-fiber Reinforced Plastic) lined carbon steel, 1% Cr-based low alloy steel and CRAs with a PREN (Pitting Resistant Equivalent Number) of over 40, e.g. Super Duplex stainless steels, are likely to be applied as a widely-accepted material selection for seawater injection, while L80-13Cr (13Cr-0.2C-based; UNS No. S42000) and Super-13Cr (generic 13Cr-5Ni-2Mo-based; e.g. UNS No. S41426) have been regarded as unsuitable for seawater injection. The 15% Cr-added and 17% Cr-added martensite-based stainless steels are positioned between Super-13Cr (generic 13Cr-5Ni-2Mo) martensitic stainless steel and duplex stainless steels in corrosion resistance in sweet (CO₂-containing) environments, indicating the potential of these stainless steels for application to seawater injection service.

These martensite-based stainless steels were evaluated by crevice corrosion tests under combined conditions of dissolved oxygen (D.O.) concentration and temperature in an artificial seawater solution simulating expected and/or over-excessive conditions of seawater injection service. A technique for estimating the D.O. concentration was also developed for higher temperatures than 80 °C (176 °F) to around 100 °C (210 °F), where dissolved oxygen cannot be detected with a membrane-penetration-based D.O. meter due to the instability of the membrane at these temperatures.

This study proved that 15% Cr-added and 17% Cr-added martensite-based stainless steels are free from crevice corrosion under most of the tested conditions within temperatures from 30 °C (86 °F) to 93 °C (200 °F) and D.O. levels of 35 ppb to 300 ppb., and those steels with PREN values in the 20s have the potential for application to seawater injection service, through corrosion test in static artificial seawater.

Key words: Seawater injection, Martensite-based stainless steel OCTG material, Dissolved oxygen, 15% Cr-added stainless steel, 17% Cr-added stainless steel, Crevice corrosion

INTRODUCTION

Generally speaking, titanium alloy, nickel alloy, duplex stainless steel, 1% Cr-added low alloy steel, GRP-lined carbon steel and carbon steel with appropriate inhibitors have often been adopted as regularly-used materials for water injection for Improved Oil Recovery (IOR). The material selection from among these materials depends on the corrosion environment under seawater injection due to the risk of oxygen contamination. These materials for water injection can be categorized into two groups, higher-alloyed CRA and carbon steel. L80-13% Cr stainless steel and modified 13% Cr steel (13Cr-5Ni-2Mo and 13Cr-4Ni-1Mo), which are categorized as intermediate-range materials between carbon steel and duplex stainless steels, have not been recommended for use in water injection applications because these 13% Cr-based stainless steel materials are susceptible to corrosion in oxygen contaminated environments, and especially pitting corrosion at dissolved oxygen (D.O.) levels of over 20 ppb¹, which can result in machine trouble and breakdown of the water treatment facility.

As a conventional concept, various standards and papers are available as guidance in the selection of materials for seawater injection. For example, Table 3 in NORSOK⁽¹⁾ Standard M-001 (Edition-5, 2014)² indicates that GRP-lined tubes and 22% Cr and 25% Cr duplex stainless steel should be selected for de-aerated conditions, and 25% Cr duplex stainless steel, GRP-lined tubes and titanium alloy should be used for aerated conditions. Also, based on the results of numerous corrosion tests of various materials under oxygen contaminated conditions, L. Scoppio and P.I. Nice mentioned that GRE-lined carbon steel, 25% Cr-based duplex stainless steel and titanium alloy should be used as tubing and liner materials for seawater injection³.

Martensite-based stainless steels of the 15% Cr-added type (15-6-3-Cu-based; UNS No. S42625) and 17% Cr-added type (17-4.5-3-Cu-W-based; UNS No. S42825) cover severer corrosion environments in oil and gas exploitation than Super-13Cr does, and also the less severe environments that had been covered and/or are often still covered by duplex stainless steels. Although these martensite-based materials have been used as tubing and production casings for oil and gas fields, no scientific paper has mentioned their availability for seawater injection application. This paper reports the crevice corrosion data obtained in laboratory experiments under combined conditions of temperature and D.O. level simulating the expected condition and/or over-excessive conditions at water treatment trouble and/or plant shutdown. The D.O. level in the experiment was monitored directly at temperatures of less than 80 °C (176 °F) throughout the test duration by using a ppb-level-detecting D.O. meter. However, the D.O. level cannot be measured correctly by this method at higher temperatures than 80 °C (176 °F). Therefore, a new technique (extrapolation-based method) was also developed to estimate the D.O. levels at higher temperatures. The results of this development are also reported in this paper.

EXPERIMENTAL PROCEDURE

Table 1 lists the details of the test conditions, and Figure 1 shows the position of each test condition as a function of temperature and D.O. level. In Fig. 1, the domain is divided into 4 regions. The first region

⁽¹⁾ NORSOK: Norwegian Standards for Oil & Gas Industry; NORSOK is an abbreviation of the official name “Norsk Søkkel Konkuranseposisjon” in Norwegian.

("Case (1)") is a D.O. level lower than 20 ppb and a temperature lower than 40 °C, representing regular injection service of "successfully" deaerated seawater. The region of "Case (2)" is covers the same temperature range but higher D.O. conditions. The test conditions of slightly-higher 35 ppb and 50 ppb D.O. levels (Tests No. 2 and 3) simulate short-term and small-scale trouble of deaeration systems. As the test duration for these D.O. conditions, "often-used" 720 h was selected, although this may be an overly-excessive condition. Tests No. 1 and No. 4 correspond to a large-scale shutdown of a seawater treatment system. The durations of these two tests are 720 h and 96 h, respectively. The region of "Case (3)" is higher temperature conditions which would be caused by interruption of water injection. The region of "Case (4)" is the combined risk case of "Case (2)" and "Case (3)." Conditions in this region have the highest corrosion risk for materials. The corrosion tests from No. 5 to No. 11 were performed to clarify the applicable limit of the stainless steels in such highest corrosion-risk cases. Only in the case of Test No.11, cyclic-switching D.O. control of "125 ppb D.O. for 2 h" and "50 ppb for 48 h" was carried out throughout the test duration of 720 h. Artificial seawater as specified in ASTM⁽²⁾ D1141⁴ was used for most of the tests. However, modified artificial seawater without heavy metal, which is composed of 3.8 mass% NaCl (23 000 ppm Cl⁻) and specified amounts of Na₂SO₄, Stock Solution No.1 and Stock Solution No.2 in ASTM⁽²⁾ D1141⁴ was used for Test No. 9, and a 21.5 mass% NaCl solution (130 000 ppm Cl⁻) was used for Tests No. 5 and No. 8, to simulate the injection of produced water.

Table 2 shows the chemical compositions of the materials used in this study. The PREN values of the stainless steels are calculated from the chemical composition. In calculation of the PREN values of L80-13CR, 15CR-125 and 17CR-110, a nitrogen concentration was regarded as zero. The target samples of this study were martensite-based stainless steels of 15% Cr-added (15-6-3-Cu-based; UNS No. S42625) and 17% Cr-added (17-4.5-3-Cu-W-based; UNS No. S42825) materials. These samples are based on mill production. Precisely speaking, the 17% Cr-added stainless steel surely has martensite as its main phase (around 60 %), but this steel also contains ferrite (around 30 %) and a small amount of austenite. However, in this paper, both the 15% Cr-added and the 17% Cr-added stainless steels are regarded as "martensite-based" materials. The reference samples were commercially-available seamless tube materials. Under most test conditions, duplex stainless steel, L80-1% Cr-based low alloy steel and L80-13% Cr were used as the reference samples.

Figure 2 shows a schematic diagram of the testing apparatus. The expected D.O. level was achieved by bubbling premixed O₂-N₂ gas. The premixed gas (oxygen ratio in nitrogen balanced gas) for each condition was determined in advance based on preliminary tests and theoretical calculations so as to achieve the target D.O. at the testing temperature. The D.O. levels at less than 80 °C (176 °F) were checked to be correct by using a D.O. meter. However, the D.O. meters at temperatures over 80 °C (176 °F) cannot measure precisely due to the instability of the membrane to pass oxygen. Therefore, as shown in Figure 3(a), candidate theoretically-calculated premixed gases for a test condition over 80 °C (176 °F) were prepared, the D.O. concentration at several temperatures below 80 °C (176 °F) was plotted against the temperature for each pre-mixed gas by measuring the real D.O. value with the D.O. meter, and the D.O. tendency was then extrapolated to the higher temperature range in order to estimate the D.O. levels at higher temperatures than 80 °C (176 °F). Figure 3(b) shows the relationship between the oxygen concentration of the premixed gas and the estimated D.O. concentration at 93 °C (200 °F) for each premixed gas. Based on this relationship, 0.85 % O₂ + bal. N₂ gas and 1.9 % O₂ + bal. N₂ gas were used in the experiments at 93 °C (200 °F) at the D.O. levels of 50 ppb and 125 ppb, respectively. It should be noted that the actual premixed gas blending ratios were set to slightly higher concentrations considering possible measurement error. Under all test conditions, the test solution was prepared so as to maintain a solution volume-to-surface ratio of 30 mL/cm² even in the minimum case.

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

Table 1: Summary of test conditions and tested samples.

Test No	Temp/C (temp/F)	Solution	Oxygen concentration (ppb)	Duration (hours)	Material Grade		Number of samples
					UNS No	Sample ID	
1	30°C (86°F)	Artificial seawater	100±10	720	S42000	L80-13Cr	Triplicate for each
2	42°C (108°F)		35 ±10	720	S42625	15CR-125	
					S42825	17CR-110	
					S31803	22CR-125	
					-	L80-1CR	
3			50 ±10	720	S42625	15CR-125	
					S42825	17CR-110	
					S32760	25CR-125	
4			115±10	96	S42000	L80-13Cr	
S42625	15CR-125						
S42825	17CR-110						
5	60°C (140°F)		21.5mass%NaCl (130,000ppm Cl ⁻)	300±10	720	S42625	
		S42825				17CR-110	
		-				L80-1CR	
6	70°C (158°F)	Artificial seawater	35 ±10	720	S42625	15CR-125	Triplicate for each
					S42825	17CR-110	
					S32760	25CR-125	
					S42000	L80-13Cr	
7	75°C (167°F)	21.5mass%NaCl (130,000ppm Cl ⁻)	300±10	720	S42625	15CR-125	
S42825					17CR-110		
S31803					22CR-125		
9	90°C (194°F)	Modified artificial seawater*	100±10	720	-	L80-1CR	
					S42000	L80-13Cr	
					S42625	15CR-125	
					S42825	17CR-110	
10	93°C (200°F)	Artificial seawater	50±10	720	S42625	15CR-125	
					S42825	17CR-110	
					S42625	15CR-125	
11			50±10 for 48hr 125±10 for 2hr	720	S42825	17CR-110	
					S42625	15CR-125	

(NOTE)

*: "Modified artificial seawater" for test no.9 is 3.8 mass% NaCl (23 000 ppm Cl⁻) and specified amounts of Na₂SO₄, Stock Solution No.1 and Stock Solution No.2 in ASTM D1141

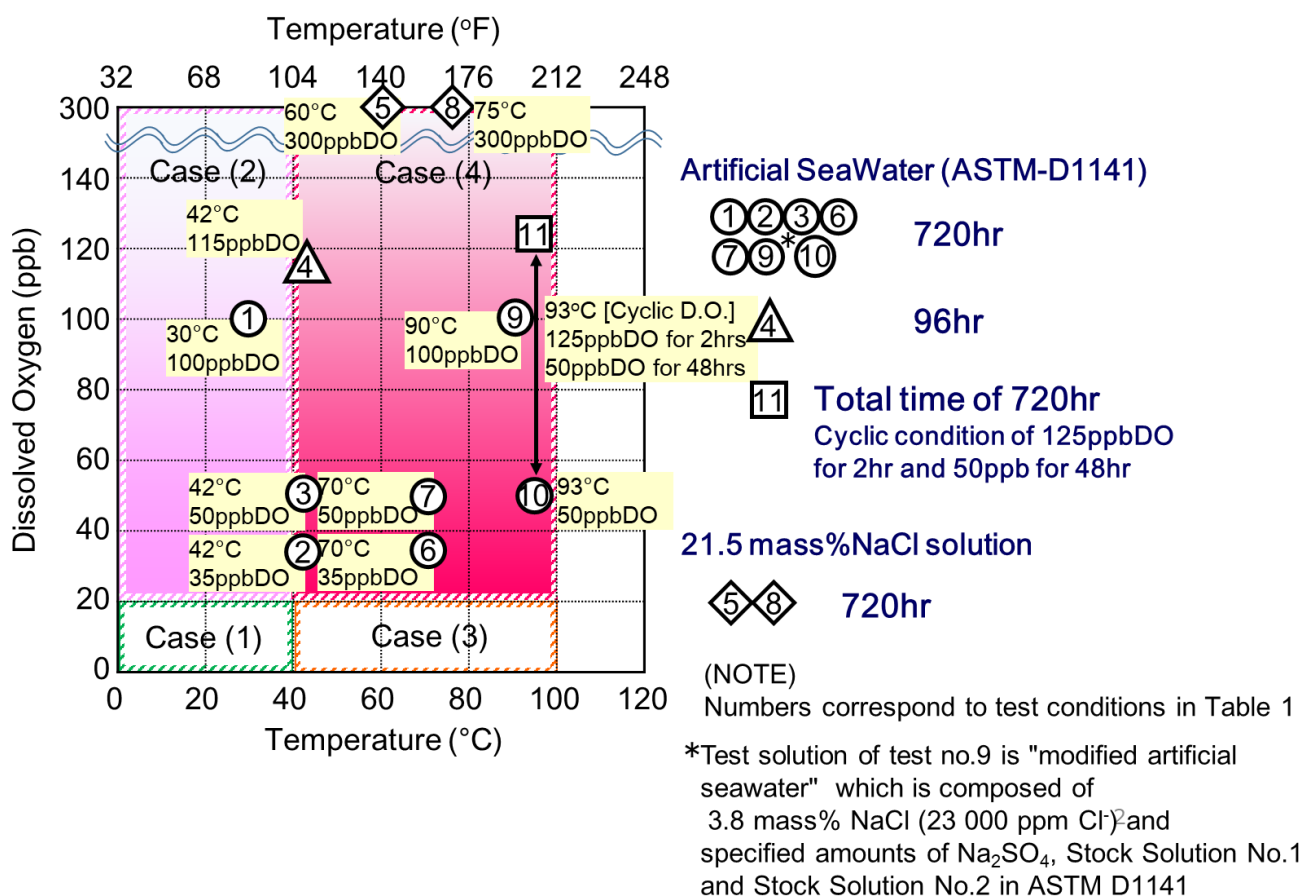


Figure 1: Test environments of dissolved oxygen and temperature in artificial seawater.

Table 2: Nominal chemical compositions (mass%) of tested samples.

	Sample ID	UNS No	Yield Strength grade	C	Cr	Ni	Mo	Others	PREN
Target materials	15CR-125	S42625	125ksi	0.03	15	6	3	1Cu-added	24.9*
	17CR-110	S42825	110ksi	0.03	17	4.5	3	1Cu and 1W-added	28.6*
Reference materials	L80-1CR	-	80ksi	0.2	1	-	-	Si-Mn-added	-
	L80-13CR	S42000	80ksi	0.2	13	-	-	-	13.0*
	22CR-125	S31803	125ksi	0.02	22	5	3	0.2N-added, Cold-drawn	35.1
	25CR-125	S32760	125ksi	0.02	25	6	3	0.6Cu-0.5W-0.3N, Cold-drawn	40.5

(NOTE)

$$\text{PREN} = \text{Cr} + 3.3 \times (\text{Mo} + 0.5 \times \text{W}) + 16 \times \text{N}$$

*N concentration was regarded as zero for calculation of PREN value of L80-13CR, 15CR-125 and 17CR-110.