

Environmentally Assisted Cracking of Nickel-Based UNS N09955 in a Sour Wellbore Fluid for High-Pressure, High-Temperature Applications

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ABSTRACT

A thorough characterization of nickel-based UNS N09955 was performed in a simulated sour production wellbore environment for high-pressure, high-temperature (HPHT) subsea applications. The test environment chemistry was 1.14 mol% of carbon dioxide (CO₂), 0.4-psia fugacity of hydrogen sulfide (H₂S), 240,000 mg/L of chlorides, dissolved oxygen less than 10 ppb, and a pH of 4.2, at 400 °F (204 °C) temperature. Environmentally assisted cracking (EAC) susceptibility was evaluated by fracture toughness (FT) test using compact tension test specimens and rising displacement method. Fatigue crack growth rate (FCGR) and static crack growth rate (SCGR) were studied in the HPHT environment. FT testing indicated a moderate reduction in the initiation FT value of the alloy in HPHT condition compared with the in-air value. FCGR testing was performed at different frequencies and at maximum stress intensity factor (K_{max}) (or stress intensity range [ΔK]) values. At a K_{max} value of 55 MPa√m, FCGR increased at low frequencies, which may have been associated with the crack front sampling the susceptible orientation. However, at K_{max} values of 66, 75, and 85 MPa√m, there was no or little evidence of an increase in FCGR at low frequencies. Additionally, no evidence of a stable SCGR was observed over a range of K_{max} values from 55 to 85 MPa√m, supporting the fact that the threshold stress intensity factor (K_{th}) of Alloy 955 is greater than 85 MPa√m in the tested environment. Finally, scanning electron microscopy (SEM) was used to characterize the fracture surface morphology and crack-growth behavior of Alloy 955. Ductile features for in air FT test and evidence of dislocation slip band cracking and fatigue striations were observed for environmental tests.

Key words: precipitation hardened, nickel-based alloys, environmentally assisted cracking, sour wellbore fluid, fracture toughness, fatigue crack growth rate, static crack growth rate

INTRODUCTION

Precipitation-hardened nickel-based alloys have been used for decades in the oil and gas industry. Among these alloys, UNS¹ N07718 has received the most attention for use in upstream applications such as tubing hangers, production stab plate, multiphase flowmeter bodies, and valve stems because of its performance in sour wellbore fluids (SWFs) and hydrogen-charging environments. It has been reported that the alloy's performance is excellent for applications up to 350 °F (175 °C) to 400 °F (204 °C) in exposed wellbore environments such as sour production fluids and completion brines and when externally exposed to seawater with cathodic protection (SWCP) at seabed temperatures. However, at higher temperatures, it becomes vulnerable to localized corrosion and stress corrosion cracking, especially in low-pH and higher-chloride-containing environments.¹ Studies have shown that other well-known corrosion-resistant alloys (CRA's), such as Alloy 725 (UNS N07725) and Alloy 625+ (UNS N07716), are susceptible to hydrogen embrittlement in SWCP conditions.²⁻⁵ Therefore, these alloys, which have excellent resistance to localized corrosion and stress corrosion cracking in elevated temperature sour production fluids, are associated with higher risk for applications where the material is externally exposed to SWCP. With the development of HPHT fields, exposure to high-temperature wellbore fluids internally and SWCP externally becomes inevitable, and the industry needs to look for alloys that can withstand these complex situations.

Ni-based CRA's generally exhibit excellent resistance to uniform corrosion over a wide range of pH's, chloride concentrations, and temperatures. They can however be susceptible to localized corrosion, and SCC at elevated temperatures in the presence of aggressive environments containing chlorides/ and acid gases such as H₂S and CO₂. The susceptibility of these alloys to localized corrosion and SCC is related to the repassivation potential behavior. When the potential (applied or corrosion potential) is below the repassivation potential, alloys are generally found to be resistant to localized corrosion and SCC. However, when the potentials are above the repassivation potential, the alloys are susceptible to localized corrosion and SCC. In several cases localized corrosion sites such as pits, where found to be sites where SCC would initiate. SCC susceptibility is typically determined based on either slow strain rate (SSR) or constant deflection tests like C-ring test. Under the same conditions, SSR tests are more aggressive than the constant deflection tests. In addition, the susceptibility to SCC was found to be dependent on the applied strain rate in the SSR tests. These observations clearly suggest that the applied strain rate plays a critical role establishing the susceptibility of CRA's to SCC. In HPHT conditions, materials are subject to not only aggressive environments, but a complex set of loading conditions that involves high static loads coupled with low cycle fatigue events. Hence, to accurately reflect the material response in service conditions, it is important to determine the fracture toughness and FCGR and characterize the materials behavior under various loading regimes.

Alloy 955 (UNS N09955) was introduced recently and has shown low corrosion rates and less susceptibility to localized corrosion and stress corrosion cracking in NACE⁽²⁾ MR0175-3 VII sour environments with the addition of free elemental sulfur (S⁰) when tested per NACE Standard TM0177 and borderline elongation-to-failure ratio results in a hydrogen-charging condition when tested per NACE TM0198 standard.^{6,7} The microstructure and mechanical properties of Alloy 955 were characterized after different heat treatments. A transmission electron microscopy (TEM) study of the microstructure using image analysis techniques exhibited only γ'' particles when heat treated at 746 °C (1,375 °F). However, after an additional heat treatment at 621 °C (1,150 °F), a higher total volume fraction of $\gamma'' + \gamma'$ appeared in the microstructure, and the yield strength of the material increased by 15%.⁸

This study was designed to characterize the alloy's behavior in a defined sour production fluid mimicking an HPHT field chemistry. FT, FCGR, and SCGR tests and microstructure studies were carried out to characterize the alloy using advanced analytical tools.

EXPERIMENTAL PROCEDURE

The test program consisted of characterizing Alloy 955 in a sour production fluid using the following experiments and analysis:

- FT tests in air and in the sour production fluid at 204 °C (400 °F) using the rising displacement method
- FCGR test in the SWF

(1) Unified Numbering System (UNS) for Metals and Alloys. Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International).

(2) NACE (AMPP), 15835 Park Ten Pl., Houston, TX 77084, USA

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- SCGR test in the SWF
- Advanced microstructural characterization using SEM

Test Material

Experiments and studies were performed on a forged bar of Alloy 955-120K with a diameter of 483 mm (19 in). The chemical composition (from the product analysis) and mechanical properties of the material, reported by the mill certificate, are given in Tables 1 and 2, respectively.

Table 1: Chemical composition of the Alloy 955 (wt.%)

Element	C	Mn	Si	Cr	Ni	Mo	S	P	Cu	Co	Al	Ti	Nb	B	Fe
API 6ACRA	0.030 max	0.50 Max	0.50 max	20.0-24.0	55.0-60.0	5.5-7.0	0.0010 max	0.015 max	0.044 max	1.00 max	0.25-0.80	0.50-1.00	4.0-5.5	0.0060 max	Bal.
The Alloy	0.008	0.08	0.10	21.7	57.3	5.9	<0.0004	0.004	0.043	0.01	0.45	0.80	4.8	0.0029	8.8

Table 2: Mechanical properties of the material

Tensile Properties at mid-radius and Longitudinal Direction at 68 °F (20 °C)				Hardness Grain Size		M.R. and Transverse (C-L) Direction at -76 °F (-60 °C)	Lateral Expansion (inches)	Shear (%)
Y.S. at 0.2% (ksi)	UTS (ksi)	%El (4D)	%RA	HRC	Average	CVN Impact Values (ft.lb)		
130	162	39	54	36-38	2-3	75, 77, 76	0.031, 0.033, 0.033	100, 100, 100

Test Specimens

Compact tension (CT) test specimens were extracted from a mid-radius (or T/4, where T is the thickness) location and in an L-R orientation with the notch direction running from the inner to the outer surface. The CT specimens used for FT and crack growth rate (CGR) tests are illustrated in Figures 1 and 2.

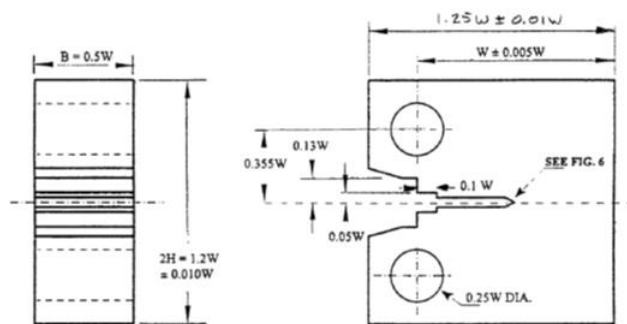


Figure 1: FT test specimen geometry in accordance with ASTM⁽³⁾ E1820.⁹

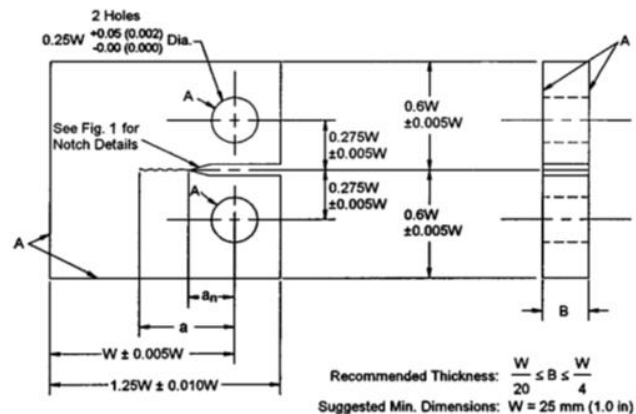


Figure 2: FCGR and SCGR test specimen in accordance with ASTM E647.¹⁰

The dimensions and properties of the specimens used for FT testing to determine the J-R curve (hereafter, JCT) and those of the specimens used for the CGR studies are given in Table 3.

⁽³⁾ ASTM, 100 Barr Harbor Dr., PO Box C700, West Conshohocken, PA 19428-2959, USA

Table 3: Dimensions and precracking conditions of the FT and CGR test specimens

Specimen	W (mm)	B (mm)	a _{notch} (mm)	a/W _{final}	Side Groove (%)	Precracking Parameters			
JCT	25.4	12.7	12.7	0.55	5	Δa (mm)	K_{max} (MPa $\sqrt{m}$)	R	f (Hz)
CT	50.8	25.4	16.51	0.35	5	1.27	27.5	0.2	0.3

Precracking was performed using a servo-hydraulic test machine with the parameters given in Table 3. After precracking, the specimens were side grooved to avoid crack branching and out-of-plane crack growth, especially at lower frequencies.

Test Environment

The actual field chemistry for which this research work was carried out is given in Table 4.

Table 4: Actual field chemistry

Parameter	Cl ⁻ (mg/L)	CO ₂ (mol%)	Partial Pressure CO ₂ (psi)	Partial Pressure (fugacity) H ₂ S (psia)	pH	T (°C [°F])	Dissolved Oxygen
Value	240,000	1.14	171	0.4	4.2	204 (400)	< 10 ppb

Due to the precipitation of sodium chloride (NaCl) when exceeds its solubility limit, the required amount of chloride could not be obtained solely from NaCl. OLI⁽⁴⁾ Stream Analyzer was used to simulate the field condition with high chloride concentrations to determine the corresponding water chemistry as well as the acid gases composition to be used. The test solution formulation and the gas bottle composition based on the material balance of the test solution are given in Table 5.

Table 5: Solution chemistry and acid-gas composition used for testing

Test Solution Formulation - Water Chemistry		mg/L (fill to 1 L at 25 °C)
NaCl		106,631
KCl		91,525
Na[C ₂ H ₃ O ₂]		60
CaCl ₂ .2H ₂ O		268,856
MgCl ₂ .2H ₂ O		3,013
B(OH) ₃		250
NaOH		77.6
HCl		0.00
Gas-Cylinder Composition Based on the Material Balance Above		
Gas		mol%
N ₂		60.75
CO ₂		39.17
H ₂ S		0.08

The test solution was deaerated with high-purity nitrogen gas in a preconditioning vessel and transferred to the autoclave under nitrogen blanket. The autoclave was filled to approximately 70% of its total volume. Then the test solution was purged with N₂ for two hours, after which a 60-psia head pressure of N₂ was applied. The autoclave was closed and heated to 204 °C (400 °F), and after the temperature was stabilized, the test gas mixture given in Table 5 was used to charge the autoclave to a total pressure of 500 psia (3.45 MPa). The final pH of the test solution was estimated to be 4.2 at the test temperature of 204 °C (400 °F). The partial pressure of H₂S in the sour environment was 0.4 (2.76 kPa)-psia fugacity.

⁽⁴⁾ OLI Systems, 2 Gatehall Dr., Suite 1D, Parsippany, NJ 07054, USA

Test Vessel

Experiments were performed in a 4-L autoclave made of UNS N10276 (Alloy C-276) and mounted in a load frame. The vessel was heated with a heating mantle that controlled by a proportional integral derivative system. The temperature was controlled and maintained at $204\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ ($400\text{ }^{\circ}\text{F} \pm 1.8\text{ }^{\circ}\text{F}$). To avoid galvanic coupling, the CT specimens were loaded into the load train and electrically isolated using ceramic coated pins and Alloy C276 clevises. Figure 3 illustrates the test vessel and test setup.

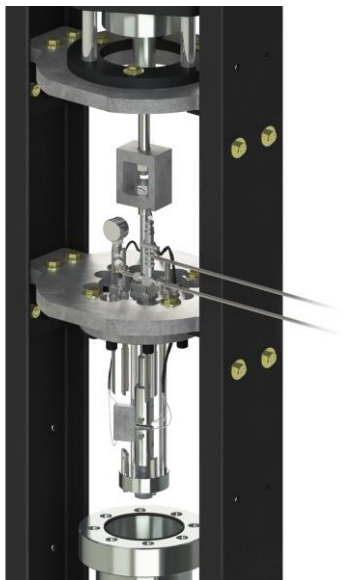


Figure 3: Schematic illustration of FT and FCGR test vessel and test setup.

Crack Length Measurements

Crack lengths were measured by reversing direct current potential drop (DCPD). DCPD measurements were performed using platinum wires of 1 mm for the current and 0.5 mm for the potential drop measurements. The wires were heat shrunk in polytetrafluoroethylene and spot welded to the sample. The spot-weld location was epoxy coated to prevent galvanic coupling between the platinum wires and the sample.

A 4-A current was applied to the sample and reversed approximately every second to minimize thermal junction effects. The absolute values of the measured potentials associated with the reversing current were averaged to obtain a single data point. Typically, anywhere from 100 to 1,000 data points were averaged to create a single datum. A reference sample that was nominally identical to the test sample was exposed to the same conditions. The signals from the reference sample were used to correct for temperature fluctuations in the cell and drift in the voltage signals over time. The measured signals from the sample were normalized with the signals from the reference sample and converted to a crack length on the basis of the Johnson equation.¹¹ All tests were performed under K control. The measured crack length was used to estimate the load required to maintain the desired K level. Load adjustments were made for K control tests when the K value deviated from the target value by more than 0.1%. No changes were made to the load for any apparent decrease in crack length.

Under constant K conditions, attempts were made to measure the CGR over extended periods of time (hundreds of hours) to ensure a representative behavior. In general, wherever practical, crack extension on the order of 50 μm was measured, which is approximately 10 times the resolution of the DCPD system. This is typical of the increments that have been measured when measuring CGRs in the 10^{-7} to mid- 10^{-8} mm/s range.¹²⁻¹⁴ When CGRs are in the low to mid- 10^{-9} mm/s range, a crack-extension measurement of 50 μm is often impractical.^{13,14} It is important to note that with low CGRs of 10^{-8} to 10^{-9} mm/s, variations in the CGR are often associated with small pockets of crack extension. Typically, at these low rates, a total crack extension of approximately 12.5 to 25 μm has been measured. The important aspect of measurements of CGRs at the low end is to demonstrate that very slow and stable crack extension is possible under constant K conditions.