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Corrosion Rates of Stainless Steel and Low Alloy Steels in Harsh and Corrosive Environments for Subsea Application

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ABSTRACT

Corrosion assessments based on available data or modelling are necessary for end-user material selection, yet there is limited data to specific well conditions. For subsea landing strings, various alloys are used, and due to the chemistry and corrosivity variation from one field to another, a study was conducted to investigate the corrosion performance of four specific alloys for the application.

Experiments were performed in a high-pressure, high-temperature (HPHT) autoclave and corrosion rate was measured using weight loss (WL) method and rotating cage autoclave with WL coupons. After each experiment and WL measurements, the coupons were studied for pitting corrosion using profilometry scans.

Four alloys, UNS⁽¹⁾ K21590 (F22), UNS G41400 (4140), UNS G86300 (8630) and UNS S17400 (17-4PH), were evaluated in HPHT autoclaves for corrosion under three different environment conditions

⁽¹⁾ Unified Numbering System for Metals and Alloys (UNS). UNS numbers are listed in Metals & Alloys in the Unified Numbering System, 10th ed. (Warrendale, PA: SAE International and West Conshohocken, PA: ASTM International, 2004).

varying in temperature (60°C and 150°C), H₂S and CO₂ partial pressures, and shear stress in HPHT autoclaves. The comparison showed that the corrosion rate for all the studied alloys increased as partial pressures of the acid gases increased and temperature decreased. Between the three low alloy steels studied in this work, UNS G41400 performed worst, especially at a lower temperature. As expected, alloy UNS S17400 showed the best performance and the lowest corrosion rates. Profilometry studies showed no evidence of localized corrosion and pitting in all four alloys.

Key words: Low Alloy Steels, Stainless Steel, Weight Loss Corrosion Rate Measurement, Rotation Cage Autoclave

INTRODUCTION

Subsea well-intervention jobs such as coil tubing, wireline, chemical injection, completions, well cleanout, fishing, milling, flowback, etc. are temporary and can last anywhere between one to four weeks on a particular well. During flowback, there are no corrosion inhibitors introduced in the bore and the bore wetted parts are directly exposed to bore fluids. During this time, the bore wetted metal parts are most susceptible to corrosion. Materials that make the bulk of the subsea well-intervention equipment are low alloy steels such as UNS K21590, UNS G41400, UNS G86300, and stainless steels such as UNS S17400 alloys. These materials are often exposed to wellbore fluids and seawater. Wellbore fluids in contact with the materials are oil and/or gas accompanied with water, acid gases such as H₂S and CO₂, elemental sulphur, various salts and organic acids. Depending on the field environmental condition, the exposed materials are subject to various types of corrosion (general or uniform, pitting, crevice, etc.) and environmentally assisted cracking (EAC) in the wellbore corrosive environments. The integrity of this equipment is important for the application and an understanding of the materials behavior and an accurate prediction of the materials' performance become crucial. Chemicals injected during well-intervention generally have corrosion inhibitors in them to aid prolonging the life of metal parts. Reviewing the literature and information in the public domain didn't provide an adequate answer leading to experimental work. The effect of well flowback during intervention on exposed metal parts is studied as it represents the worst-case scenario for corrosion rates.

Studies over the past five decades classify the influencing factors on corrosion of carbon and low alloy steels into three different categories: metallurgical, environmental, and physical factors.

Chemical composition, heat treatment, and microstructure as the metallurgical factors play significant roles in the corrosion of steel in H₂S and CO₂ containing environments. There is a beneficial effect of chromium and molybdenum addition to the steel.^{1,2,3,4} Kermani et al. developed an optimal metallurgy of carbon and low alloy steels for both downhole and pipelines by the addition of microalloying elements such as titanium, vanadium, molybdenum, copper, and chromium.^{5,6} Adding a small amount of chromium (0.5 to 3 wt. pct.) can enhance corrosion resistance of low alloy steels due to formation of a stable protective chromium oxide film in CO₂-containing environments.⁵⁻⁸ Moreover, studies by Mishra et al. showed that the addition of chromium and molybdenum to mild steel greatly reduced the corrosion rate by direct protection of alloy and preventing the formation of Fe₃C. In addition, the corrosion rate also increased with an increase in carbon content.³ Kermani and coworkers developed^{5,6} novel carbon and low alloy steels with superior resistance to CO₂ corrosion while tolerating H₂S corrosion for applications in the Region 2 of NACE⁽²⁾ MR0175. The underlying philosophies of Kermani's work were 1) to lower carbon content and add carbide-forming alloying elements to ensure keeping chromium and molybdenum in solid solution 2) to accomplish the desired properties by the addition of microalloying elements and

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thermomechanical treatments. The strong carbide-forming elements such as niobium, vanadium, and titanium preferentially combine with the carbon in steel, leaving chromium and molybdenum un-combined and dissolved in the ferrite to improve its corrosion resistance. Moreover, the presence of silicon can lead to the formation of bainite under normalized condition. According to this extensive study, an amount of 2-3 wt. pct. chromium was considered crucial to achieve the anticipated corrosion resistance improvement. Therefore, chromium is helpful above a certain level, below which it is detrimental to the anodic reaction on bare steel. These studies lead to the definition of optimum steel composition to meet the properties such as weldability, strength, and corrosion resistance which are required in the oil and gas industry.^{1,5,6}

Mishra et al.³ studies on tempered martensite steels showed that when increasing tempering temperature in the ranges where cementite starts to precipitate and coarsen, corrosion rate decreased. This decrease was attributed to the decrease in surface area of cementite as a result of coarsening. According to this observation, the cementite/ferrite interfacial area decreases as the tempering temperature increases. Apparently, in controlling the corrosion rate, the cementite/ferrite interfacial area seems to play an important role.

Environmental parameters that influence the corrosivity of the wellbore fluid are water chemistry, temperature, pH, presence of acetic acid (HAc), and the partial pressure of CO₂ and H₂S. The effects of pH⁹, presence of low molecular weight acids¹⁰⁻¹³, such as acetic acid, were not evaluated in this paper. The most detrimental effect of H₂S in oil and gas industry is sulphide stress cracking (SSC) of high strength steels. H₂S can either decrease CO₂ (sweet) corrosion rate by forming a more protective scale or it can increase the corrosion rate by promoting anodic dissolution through sulfide adsorption thus lowering the pH. At H₂S/CO₂ ratio greater than 1/500, iron sulphide (FeS or FeS₂) forms thus requiring sour service considerations per NACE MR0175 to be applied.¹

Other than metallurgical and environmental factors, physical factors are also important in CO₂ corrosion of carbon and low alloy steels by affecting the interface between the environment and steel surface as well as hydrodynamics of the system. CO₂ corrosion occurs when water is present in the system, and it wets the steel surface (which is called water wetting). The intensity of CO₂ corrosion attack increases with the time during which the water phase is in contact with the steel surface. Therefore, the water content (water cut) is an important factor. To appropriately consider the impact of water content on overall corrosion properties, other factors such as oil/water ratio, flow rate and flow regime, surface condition (roughness, cleanliness), water drop out, and water shedding due to flow profile alteration (bends, tees, welds) should be considered.¹ It has been reported that crude oil can have positive and negative effects on corrosion performance.

Crude oil can alter compaction, composition, and morphology of corrosion products and, therefore, can undermine protective iron carbonate film formations. This phenomenon accelerates localized corrosion.^{1,14} Alternatively, crude oil provides a barrier to water accessing the surface of steel as long as it resides on the steel surface.¹⁵

The presence or absence of a protective film can impact the effects of flow and erosion. Normally at low pH in condensed water, a protective scale does not form. Therefore, turbulent flow with higher wall-shear stress increases the transport of species (ions) at the steel surface, leading to an increase in the rate of corrosion. In contrast, at high pH conditions in which protective iron carbonate is formed or in case of presence of inhibitor film on the metal surface, these scales are a source of corrosion prevention. Removing these scales lead to an increase in corrosion rate. In a multiphase flow system, it is important

to characterize the flow pattern because flow patterns affect water wetting and consequently, the corrosion rate.⁷

Review of literature and publications did not prove sufficient to understand or predict the corrosion behavior of the materials in question in the expected service conditions. The purpose of the experiment presented in this paper was to test the corrosion performance of exposed metal parts to understand the effect of well flowback during intervention. The parameters tested represent worst-case scenario.

EXPERIMENTAL PROCEDURE

The corrosion performance of the alloys was assessed using HPHT autoclaves constructed of UNS N10276 following standard test methods. The performance test procedure was based on ASTM⁽³⁾ G184¹⁶, with the coupon cleaning procedure based on ASTM G1¹⁷. The bulk fluid homogeneity was accomplished through the rotational speed of the cage assembly. The temperature of the fluid in the autoclave was sensed by a thermocouple probe, held by a UNS N10276 sleeve, and an electronic controller was used to maintain temperature and stir rate throughout the experiment. Corrosion rates were calculated from coupon weight loss measurements (Equation 1).

$$\text{Corrosion Rate (mpy)} = \frac{W \times 3.45 \times 10^6}{A \times T \times D} \quad (1)$$

Where,

W = mass loss, grams (g)

A = initial exposed area of coupon (cm²)

T = exposure time (hours)

D = density of metal coupon (g/cm³)

The test fluids were purged with carbon dioxide for two hours. Prewedged coupons were mounted in the autoclave and immersed into the test fluid. The autoclave was then assembled and purged with nitrogen for one hour to remove any oxygen ingress that occurred due to the fluid transfer process. The vessel was then charged with the desired gas composition. Shear stress was calculated on operational parameters including temperature, pressure, flowrates, and tubing diameter. At the end of the test, the coupons were removed, cleaned using Super Clarke's solution (10 g L N,N-dibutylthiourea diluted in 1L of 18.5% HCl), reweighed, and the corrosion rate calculated. A representative section of the coupons was scanned using a profilometer to assess localized corrosion, if present. The parameters for the profilometry analysis were 2,000 Hz acquisition rate, a 300 µm optical pen, and an area of 2 mm x 2 mm.

The test environment chemistries representative of the fields' conditions are summarized in Table 1.

Table 1
Autoclave Test Conditions

Parameter	Condition 1	Condition 2	Condition 3
Temperature (°C)	150	60	150
ppCO ₂ (psi)	960	1,566	1,566
ppH ₂ S (psi)	0.3	12	12

⁽³⁾ ASTM International (ASTM), 100 Barr Harbor Dr, West Conshohocken, PA 19428-2959