

Study of Buffer Solution Influence on Super-Martensitic Stainless Steel Localized Corrosion and Passive Layer Stability

Luciana I. L. Lima
Vallourec Competence Center
Rio de Janeiro, Brazil

Ilson Palmieri Baptista
Petrobras – CENPES
Rio de Janeiro, Brazil

Bruno Diehl
Petrobras – CENPES
Rio de Janeiro, Brazil

Arthur Gonçalves
National Institute of Technology
Rio de Janeiro, Brazil

Fabiana Magalhães Teixeira Mendes
National Institute of Technology
Rio de Janeiro, Brazil

Javier Alejandro Carreno Velasco
National Institute of Technology
Rio de Janeiro, Brazil

Walter Souza
National Institute of Technology
Rio de Janeiro, Brazil

Cécile Millet
Vallourec Research Center France
Aulnoye Aymeries, France

Marília Lima
Vallourec Research Center
Belo Horizonte, Brazil

ABSTRACT

In order to evaluate OCTG material susceptibility to corrosion in sour service various buffering systems are suggested by standards to simulate the actual field conditions under atmospheric pressure. This could influence the stability and performance of the passivated stainless steel surface. The effect of different buffer systems on passive layer stability was investigated in 4g/L and 0.4g/L sodium acetate, and high-pressure CO₂ (25 bar_a). The localized corrosion behavior and semiconductor properties of the passive films were analyzed by using electrochemical techniques such as linear sweep polarization and Mott–Schottky approach, respectively. The surface chemical composition and qualitative analysis of the corrosion products were studied by means of X-ray photoelectron spectroscopy. The experimental results have shown that 13Cr Super Martensitic Stainless Steel exposed to 4 g/L CH₃COONa + CH₃COOH solution have similar corrosion behavior as those exposed to high pCO₂ solution (field condition), which is more related to the enhancement of solution buffer capacity than to the difference of passive layer composition.

Key words: buffer solution, high pressure CO₂, sodium acetate, acetic acid, localized corrosion, passive film, Mott–Schottky, semiconductor properties, super martensitic stainless steel, XPS.

INTRODUCTION

In order to evaluate the OCTG (Oil Country Tubular Goods) materials corrosion susceptibility in oil and gas production, various buffering systems are suggested by standards¹⁻³ to simulate the actual field conditions under atmospheric pressure in a corrosion laboratory test. Among all parameters that influence the corrosion test, the pH solution stability has an effect on localized corrosion and consequently on Sulfide Stress Corrosion (SSC) material susceptibility.

Solution pH close to the metallic surface may vary under static corrosive conditions that most of the laboratory tests are conducted. The solution pH stability (bulk and pitting local acidification) during corrosion tests affects the passive film and pitting propagation and it is influenced by the buffer solution used⁴⁻⁶. Sulphide Stress Cracking (SSC) tests are normally performed at 1 bar with a buffered solution. Different non-standardized buffering systems are sometimes used in SSC tests^{7,8}, but there are some issues concerning the choice of buffer solution.

Buffer systems consist of an acid-base pair (conjugate acid-base). In the case of acetate/acetic acid the excess of protons (H^+) reacts with the conjugate base whether from the parent acid or sodium acetate, to re-establish equilibrium. The ability of the buffer system to resist changes in pH by either absorbing or desorbing H^+ and OH^- is defined as its buffer capacity, and could influence the test results. On the other hand, if a buffer solution is not used, the protons released from the hydrolysis reaction of the metallic ions can decrease locally the pH and the passive film become unstable. That is, if the pH falls to a value near of the material depassivation pH (pH_d) localized corrosion initiates.⁸⁻¹⁰

It is intended that the buffer system used in the corrosion tests should simulate the environment field conditions. When the partial pressure of CO_2 (pCO_2) and the bicarbonate content are high enough in the field, the buffer capacity of standardized solutions for corrosion tests in 13Cr Super Martensitic Stainless Steel (SMSS) at atmospheric pressure might not represent well service conditions. The pH stability in the test solution should accurately reflect the environment during service otherwise the corrosion and SSC resistance of the material may be evaluated too conservatively.

Passive films formed on stainless steels are well known for acting as a diffusion barrier limiting the transport of species and charge at the metal/electrolyte interface, thus reducing metal anodic dissolution. However, this film changes with the surrounding environment, it can grow or dissolve, and may absorb/adsorb anions depending upon the chemical speciation of the environment. On the other hand, electrochemical and semiconductor properties of passive films developed might be affected by the type of buffer systems used during testing. Some authors have stated that the electronic properties of passive layers, as flat band potential and doping density, directly affect localized corrosion susceptibility. A high doping density and a more negative flat band potential were typical for a less stable passive film.¹¹⁻¹⁵

A high acetate content test solution at atmospheric pressure might be more representative of high pCO_2 field conditions regarding buffer capacity, but less representative in terms of acetate influence on the resulting passive layer. A tradeoff between these two effects should be considered when selecting the most suitable solution in a way that the tests are not either too conservative or non-conservative.

This paper presents a study of the effect of different buffer systems on passive layer formation and corrosion resistance of SMSS. The localized corrosion behavior and semiconductor properties of the passive films were analyzed by using electrochemical techniques such as anodic potentiodynamic polarization and Mott-Schottky approach, respectively. The surface chemical composition and qualitative analysis of the corrosion products was studied by means of X-ray photoelectron spectroscopy (XPS). Finally, the results are used to explain differences in localized corrosion performance within the passive films obtained in the studied buffer systems.

EXPERIMENTAL PROCEDURE

Investigated Material

All test specimens were extracted from SMSS industrial tubing. Chemical composition is given in Table 1 and is compliant with 13Cr-5Ni-2Mo, UNS S41426 stainless steel for OCTG. Prior to the experiments, the specimens were grinded up to 600 grit with silicon carbide paper, rinsed with distilled water, degreased in acetone, and then dried with a blow dryer.

Table 1
Chemical Composition (%mass) –13Cr Super Martensitic Stainless Steel.

C	Si	Mn	P	S	Cr	Mo	Ni
0.01	0.30	0.40	0.02	0.002	11.80	2.0	5.70

Buffer Solution Test Conditions

The experiments at 1 bar were designed to represent a more representative buffer condition of a specific field with 25 bar CO₂ and 0.4 g/L of sodium acetate at a pH of 4.5 and sodium chloride (NaCl) content of 200 g/L.

Table 2 presents the chemical composition of the buffer solutions used in the tests, which were deaerated with nitrogen gas (N₂) and saturated with a H₂S/CO₂ gas mixture. After saturation step, the H₂S/CO₂ gas mixture was continuously bubbled through the solution until end of the experiment. The rate of bubbling reflects previous experience ensuring saturation throughout the experiment. Two H₂S/CO₂ gas mixtures were used during the tests: 7% H₂S at 1 bar_a and 0.33% H₂S in 25 bar_a of total pressure in order to obtain the same estimated H₂S fugacity (70 mbar). The pH and fH₂S was estimated by simulation using aqueous model of OLI Studio[†] (v. 9.5.2) and previous experience to adjust high pressure pH.

Table 2
Buffer Solution Test Conditions – 200g/L NaCl, pH 4.5, fH₂S: 70 mbar H₂S, 25°C.

Buffer Solution	Pressure	Acetic Acid (CH ₃ COOH)	Sodium Acetate (CH ₃ COONa)	Sodium Bicarbonate (NaHCO ₃)
Low Acetate (LNaAc)	1bar _a	Yes*	0.4 g/L	-
Higher Acetate (HNaAc)		Yes*	4 g/L	-
High Pressure (HP)	25 bar _a of CO ₂	No	0.4 g/L	2.250 g/L

* Acetic acid (CH₃COOH) was used to lead pH to 4.5 reached after sour gas saturation.

Buffer solution pH stability – laboratory measurement and simulation

In order to evaluate the pH stability of various buffer solutions at room pressure and temperature experimental tests were conducted in the buffer solutions described in Table 2 adding 112 ppm of sodium bicarbonate without sodium acetate. To compare with the stability in corrosive environment of a high pCO₂ oil well, simulations were carried out using the same software and model applied to estimate

buffer solution pH and fH_2S . The pH of the solution was measured and simulated while a solution of 1M hydrochloric acid (HCl) was added into each solution to quantify its buffer effect on pH change (buffer capacity). Then, the pH shift was plotted against the concentration of HCl (mg/L).

Electrochemical Measurements and Setup

The influence of buffer solutions on passive film of SMSS was analyzed by means of electrochemical measurements. An AUTOLAB[†] potentiostat was utilized for all the electrochemical experiments and two kinds of electrochemical cells were used in this study: Tests in standard conditions were carried out in a conventional three electrode glass cell using SMSS as the working electrode, a large surface platinum grid as counter electrode, and a rod of UNS N10276 as pseudo-reference electrode (PRE). The same configuration was used for testing at high pressure, but in an autoclave manufactured using UNS N10276 (CORTEST[†] Inc.). The potential difference between the PRE and SHE (Standard Hydrogen Electrode) was 0.177V at sea water solution without H_2S .

Polarization curves were carried out potentiodynamically in the range of -200 mV to 300 mV vs. UNS N10276 pseudo-reference electrode starting from open circuit potential (OCP), stabilized for 1h, in the positive direction at a scan rate of 0.17 mV/s.

The capacitance values to estimate the semiconducting properties of the passive films were obtained by the Mott–Schottky (MS) analysis, after exposing the work electrode to the test condition by 12 hours in order to guarantee a good interaction between sour environment and oxides film. Thus, the AC impedance was measured by applying amplitude of 0.01 V at a frequency of 1.0 kHz, in the range of 0.2 V beginning from OCP. The stepwise potential rate was 20 mV/s.

The capacitance (C) of the thin passive films measured with applied potentials can be expressed as C^{-2} versus E (potential) by Mott–Schottky plots. Assuming that the capacitance, of the Helmholtz layer is fairly enough, compared with that of the space charge layer, the linear relation between C^{-2} and potential can be expressed by the following Mott–Schottky equation:

$$\frac{1}{C_{sc}^2} = \pm \frac{2}{\epsilon \epsilon_0 e N} \left(E - E_{fb} - \frac{kT}{e} \right) \quad (1)$$

Where ϵ is the dielectric constant of passive film, considered here as 12^{16} , ϵ_0 is the vacuum permittivity constant ($8.854 \times 10^{-14} \text{ F} \cdot \text{cm}^{-1}$), e is the elementary charge ($1.062 \times 10^{-19} \text{ C}$), E_{fb} is the flat-band potential, k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J} \cdot \text{T}^{-1}$) and T is the absolute temperature.^{16,17} N is the donor number (for n-type semiconductor - N_D) or acceptor densities number (for p-type semiconductor - N_A) and could be determined from the slop of C^{-2} versus E plots. For a p-type semiconductor the Mott–Schottky plot should be linear with negative slope. For n-type semiconductor a positive slop is expected.

Surface Analysis - X-ray photoelectron spectroscopy (XPS)

To evaluate the effect of buffer solution on the surface of passive film composition X-ray photoelectron spectroscopy (XPS) was performed. Prior the analysis the specimens were immersed in the various buffer solutions for 14 days. The XPS spectra were recorded in a UHV chamber with a PHOIBOS[†] 150 electron analyzer and sample surfaces were irradiated with Al radiation (1.4 KeV). The energy scale was calibrated so as to fix the C1s line. An analysis of the peaks on the measured curves was conducted via the commercial software Casa XPS 2.3.17.