

Means and consequence of pH control for the qualification of OCTG sour service grades

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ABSTRACT

Many Oil & Gas fields are sour with H₂S partial pressures above 0.05 psi. For such situations, it is critical to employ OCTG qualified for sour service, resistant to SSC. As corrosion processes in acidic environments with dissolved H₂S make the testing solution to drift, some standardized test solutions are highly buffered with the acid-base couple acetic acid / acetate. Another method for limiting the pH drift consists by frequent additions of strong acid during the test. The objective of this work is to compare NACE TM0177 Solution B, EFC 16 solution with and without pH adjustment and HLP solution. Thermodynamic calculations for predicting the saturation pH, hydrogen permeation tests, corrosion rates and fine characterizations of iron sulfide scales were performed for being correlated to SSC test results and for understanding the impact on the hydrogen uptake and the protectiveness of corrosion products.

Key words: SSC, OCTG, NACE TM0177 Method A, pH drift

INTRODUCTION

Enhanced metallurgies must be selected for OCTG for preventing catastrophic failures due to SSC in sour gas and oil wells. According to the Annex B of the NACE MR0175/ISO 15156-2 document,¹ a material is identified as SSC resistant when it has a threshold stress higher than 80% AYS with uniaxial tensile test in the sour brine NACE TM0177 Solution A saturated by 1 bar H₂S.² Since a couple of decades, the increase of the mechanical properties of OCTG was motivated to access hydrocarbons in deeper reservoirs. For example, 125 ksi SMYS materials resistant to SSC were developed but for limited range of range of pH and P_{H₂S}, so-called fit-for-purpose (FFP) environments.³⁻⁵ NACE TM0177 Solution A, as defined in the 70's, is acknowledged as a very severe sour Quality Control (QC)

condition. Consequently, the pH drift during the corrosion test and resulting from corrosion processes is not a matter of concern. On the contrary, for materials qualified in FFP environments, it is important to keep constant the sour severity level by limiting the pH drift as much as possible. Several strategies are employed to fulfill that objective; either by increasing the buffer capacity of the test solution, which is predominantly done thanks to the acid-base couple acetic acid/acetate,⁶ or by the regular addition of a strong acid during the test duration.⁷ Up to now, few information is available on the impact of pH control and more globally of the test solution composition on SSC. Even though regions of environmental severity for SSC in NACE MR0175 / ISO 15156-2 are defined only through pH and P_{H_2S} , it is now well established that the gas composition modifies the risk of SSC occurrence by affecting H_2S gas fugacity and consequently aqueous H_2S activity. This fact has motivated the addition of a technical circular inside ISO 15156 document.⁸ Some works provided evidences that the composition of the solution itself is susceptible to impact directly the risk of SSC on low alloyed steels. Case et al. observed an increase of the threshold stress intensity factor on C110 when increasing salt concentration, which impacts the aqueous H_2S activity and also likely adsorbed H_2S coverage on steel surface.⁹ Duvall Deffo Ayagou and co-authors investigated the influence of the acetic acid / acetate buffering on the corrosion rate and the hydrogen uptake of X65 linepipe.¹⁰ Corrosion rates markedly increase with the buffer capacity of the test solution and hydrogen permeation fluxes as well.

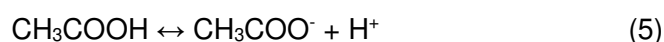
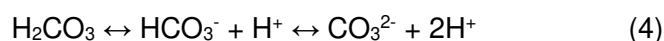
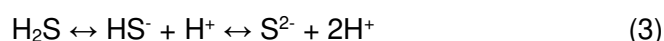
In the following, a thermodynamics study of the corrosion processes and associated chemical reactions have been investigated. This work highlights mechanisms behind the pH drift and provides a comparison of different test solutions focusing on the impact of their buffer capacities. This study is completed by experimental data of pH drifts, corrosion rates and hydrogen permeation fluxes on selected sour environments. It points out the solution buffer capacity effect on the solution corrosiveness.

Basics on solution chemistry

When exposed to an acidic brine solution saturated by sour gas, the generalized corrosion process involves two half-cell reactions (Eq. 1 and Eq.2):

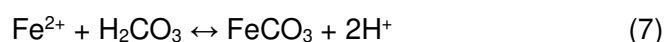
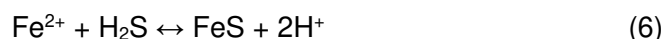


Proton is coming from the free acidity (pH) or from acid-base reactions, which corresponds to the buffer capacity of the solution (Eq. 3 to Eq. 5):



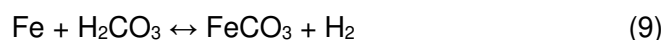
It leads that the cathodic activity is responsible of the pH drift to higher values during the corrosion test. Based on literature results, direct reduction of H_2S can occur;¹¹ on the contrary for H_2CO_3 and CH_3COOH that enhanced the corrosion rate only via a buffer effect.^{12,13}

Precipitation of corrosion products comes in a second step when the limit of solubility is reached (Eq. 6 and Eq. 7).



It is crucial to notice that the precipitation releases acidity. This controls the observation of a plateau for the pH value after some days of exposure.¹⁴ Indeed, at the corrosion steady-state which corresponds to

a combination of balance equations (Eq. 8 and Eq. 9), solution pH does not evolve anymore because of the saturation by the corrosion products in a given steel surface over a volume of solution ratio.



EXPERIMENTAL PROCEDURE

Material and sour environments

Four sour environments have been considered for experiments as summarized in Table 1 below: NACE TM0177 Solution B (i.e. leading to a target pH of 3.5), Solution B modified at pH 4.5 by reducing the initial content in acetic acid, EFC 16 Solution A and B at starting pH 3.5 and 4.5 respectively. Solutions were saturated at atmospheric pressure with 0.1 bar H_2S balanced by CO_2 . Exposure tests were performed on a C125 type low alloyed steel pipe for OCTG applications.

Table 1: Denomination and composition of test solutions.

Test solution	Denomination	NaCl	CH_3COONa	Acidification
NACE TM0177 Solution B	B-3.5	5% wt.	0.41% wt.	2.5% wt. CH_3COOH (target pH 3.5)
NACE Solution B mod. – pH 4.5	B-4.5			CH_3COOH to reach pH 4.5
EFC 16 – pH 3.5	EFC16-3.5	50 g/L	0.4 g/L	HCl to reach pH 3.5
EFC 16 – pH 4.5	EFC16-4.5			HCl to reach pH 4.5

Thermodynamic calculations

OLI Studio© software version 9.6.3 from OLI Sytems was used for doing thermodynamic calculations of the aqueous phase. MSE-SRK model was used. It calculates the chemical potentials in the aqueous phase by the combination of the Helgeson-Kirkham-Flowers (HKF) equation of state for standard-state properties and the MSE activity coefficient model for solution nonideality. The Soave-Redlich-Kwong (SRK) equation of state applied to the gas phase. The corrosion was simulated by the addition of $\text{Fe}(\text{OH})_2$ iron oxide, meaning Fe^{2+} cations released by the anodic reaction (Eq. 1) and OH^- species by the cathodic reaction, which is strictly similar to a consumption of acidity (Eq. 2). By this way, it is not necessary to consider any hypothesis on the reaction pathway, on which species released the proton: acid-base reactions are activated during the calculations for reaching the equilibrium. Additional H_2S and CO_2 species are introduced into the system for compensating their consumption by the corrosion processes (acid-base reactions, corrosion products formation), keeping the appropriate partial pressure of H_2S and CO_2 at the final equilibrium. Solid phases included in OLI are pyrrhotite FeS and siderite FeCO_3 only. For the simulation of the buffer capacity of test solutions, $\text{Na}(\text{OH})$ replaced $\text{Fe}(\text{OH})_2$ and the same process was employed. All calculations were done at the atmospheric pressure. Solutions investigated were those of Table 1 plus NACE TM0177 Solution A (so-called A thereafter) and the solution proposed by High Strength Line Pipe (HLP) committee of the Iron and Steel Institute of Japan (ISIJ) (so-called HLP thereafter), which contains 5% wt. NaCl, 5% wt. acetic acid and 0.8% wt. sodium acetate and presents an initial pH equal at 3.5. This latter solution has been introduced for comparative purpose because it is much more buffered than all the others.

Weight loss procedure

Weight loss samples consisted in 10 x 10 x 45 mm steel samples, mechanically polished up to 1200 SiC grit paper. After being degreased with ethanol in an ultrasonic bath and rinsed with acetone, six samples were hung to a glass bar in the test vessel thermostated at 24°C +/- 3°C, exposing all faces with the test solution. After a deaeration of the glass vessel with Argon, the test solution was introduced. The solution volume on exposed steel surface ratio was equal to 30 mL/cm². Then the solution was saturated at atmospheric pressure with 10% H₂S balanced with CO₂ and a continuous flow rate was preserved throughout the test duration for keeping the saturation level. After a duration of 7, 14, 21 or 30 days, the vessel was deaerated with Argon and the samples were taken out and dried in air. Five samples were pickled in a solution composed of 18.5% HCl solution inhibited with 7 g/L Hexamethylenetetramine, then weighted. The weight values were compared to the measurements done before the test for the determination of the average corrosion rate. The last sample was vacuum sealed in a low temperature resin and cut for a transverse micrographic examination of corrosion products with a scanning electron microscope (SEM). Before the observation, the sample is mirror polished using SiC paper and alumina powder, dried with ethanol and a conductive nanometric carbon layer was deposited on the surface.

Permeation procedure

The electrochemical permeation experiments were based on the Devanathan and Stachursky apparatus¹⁵ composed of two glass cells separated by a steel membrane. 500 mL of solution were introduced in each cells made of a double wall for water circulation allowing a tight control of the temperature at 24°C. A 3 mm thick membrane was sampled in the pipe and was mechanically polished up to 1200 SiC grit paper, then rinsed with acetone. A palladium coating was deposited on the desorption side for enhancing hydrogen oxidation.¹⁶ Palladium deposition was performed using a cathodic current of 2 mA/cm² for 90 s in a 28% ammoniac solution containing 5 g/L of dissolved PdCl₂ salt. The membrane is then installed between the charging cell and the desorption cell further deaerated with Argon. The desorption cell was filled with deaerated 0.1 mol/L NaOH and the membrane is polarized anodically at 300 mV/SCE on the coated side (detection side). Once reaching a passivation current below 2 µA/cm², the charging cell is filled with the charging solution and a flow of 10% H₂S in CO₂ at atmospheric pressure is introduced. Sour gas flow in the charging cell and argon flow in the detection cells are maintained until the end of the test, which lasted 30 days. The anodic current recorded in the detection cell, i.e. the permeation current, corresponds to the oxidation of hydrogen.

At regular intervals, linear polarization measurements were performed at the charging side of the membrane for the determination of the direct corrosion rates from polarization resistance (R_p) values. Potentiodynamic curves at 10 mV/min sweep rate were obtained from E_{OC} - 15mV to E_{OC} + 15mV where E_{OC} is the open circuit potential. For each set of points, the polarization resistance R_p was determined by linear regression near the open circuit potential using Ohm's law. R_p was corrected from the resistance of electrolyte R_e, giving the corrosion polarization resistance R_{corr} = R_p - R_e. R_e was determined from Electrochemical Impedance Spectroscopy (EIS) where a sinusoidal potential signal of 10 mV amplitude on a frequency range 50 Hz to 1 mHz was applied. The monitored current was averaged over 3 measurements for each frequency. The electrolyte resistance R_e was defined as the real component at the highest frequency (50Hz). Finally, the corrosion rate i_{corr} was calculated using the Stern-Geary formula (Eq. 10).

$$i_{corr} = \frac{B}{R_{corr}} \quad (10)$$

where $B = \frac{b_A \cdot b_C}{\ln(10) \cdot (b_A + b_C)}$ is the Stern-Geary coefficient calculated from the anodic and cathodic Tafel slopes (b_A & b_C). B was equal to 0.0174 V with b_A equal to 0.06 V and b_C equal to 0.12 V.

RESULTS

Environmental parameters controlling pH drift and value of the saturation pH in laboratory corrosion tests

To highlight the different buffer capacity of selected solutions, Figure 1 plots evolution of the pH with the addition of Na(OH). HLP presents the highest buffer capacity, meaning the highest resistance to the evolution of its pH, whereas EFC 16 presents the lowest buffer capacity. Approximately 20 times more caustic soda is required for reaching a pH 6 with HLP solution than with EFC 16.

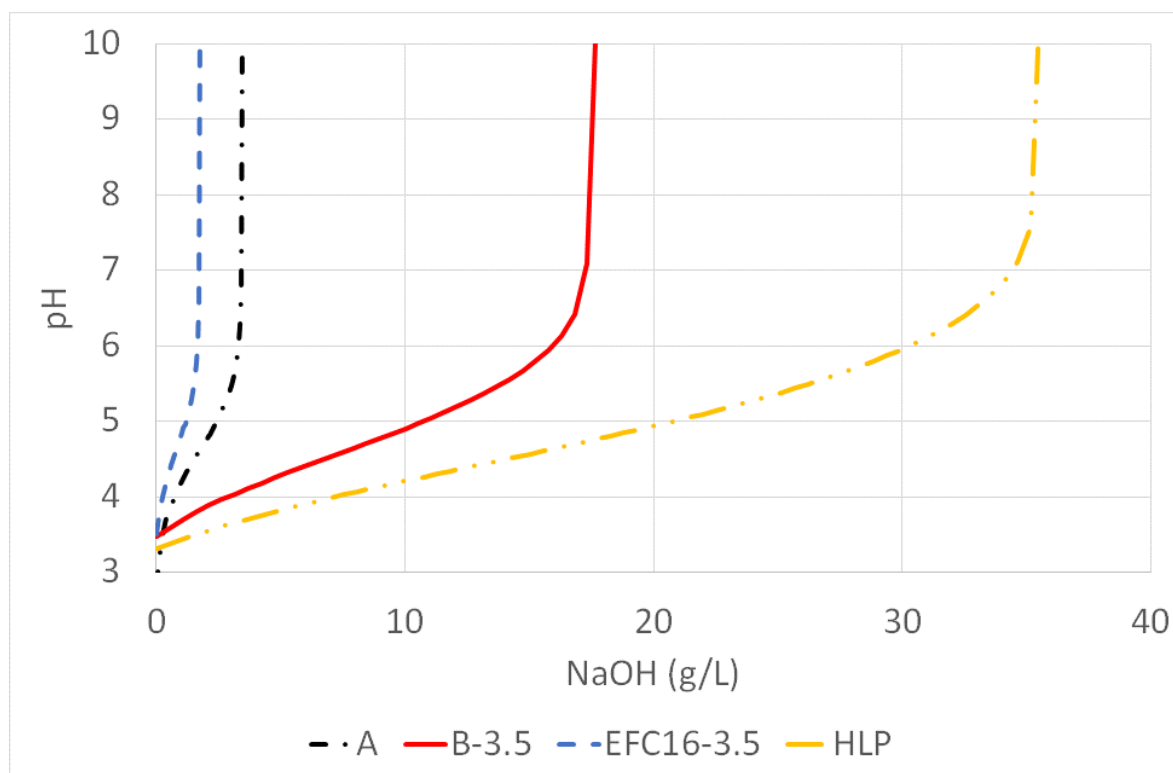


Figure 1: Thermodynamic calculations of the evolution of the pH with the addition of Na(OH) in the test solutions saturated with 0.03 bar H₂S in CO₂, highlighting their different buffer capacities.

Evolution of pH during the corrosion of iron exposed to selected brine saturated with 1 bar H₂S or 0.03 bar H₂S in CO₂ is simulated in Figure 2. As a trend, solution pH increases from the initial value by addition of iron oxide up to a plateau, above which it is not possible to go beyond. It is worth to note that initial pH calculated by OLI slightly underestimates expectations, e.g. pH 3.3 has been calculated for HLP solution instead of 3.5. Nevertheless, it has been chosen to preserve the composition of solution as described in standards. The plateau is reached once the first solid phase is formed which was FeS. No FeCO₃ solid phase was formed for all configurations. Final pH ranking is: A < HLP < B-3.5 < EFC16-3.5 for 1 bar H₂S and HLP < B-3.5 < A < EFC16-3.5 for 0.03 bar H₂S in CO₂. Final pH depends on solution composition and gas phase composition. It decreases when increasing H₂S partial pressure.

Figure 3 shows the evolution of Fe²⁺ concentration in test solutions with the addition of iron oxide. Starting from zero, the concentration increases up to a maximum value. The plateau is reached for the same Fe(OH)₂ addition than for the saturation pH and also once the first solid phase is formed. The saturation value of [Fe²⁺] is higher when the saturation pH is lower. Moreover, the saturation value of [Fe²⁺] increased when decreasing the partial pressure of H₂S.