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Evaluation of pH stability and localized corrosion influence of various buffer solutions for simulated well condition

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Abstract

In order to evaluate the material corrosion susceptibility under oil and gas field conditions, it is necessary to simulate the well environment in a corrosion laboratory test. Among all parameters that influence the corrosion test, the pH solution stability has a large effect on localized corrosion and consequently on sulfide stress corrosion cracking (SSC) material susceptibility. The bulk solution pH variation and local acidification could be, a certain extent, prevented using buffered solutions. However there are a few problems concerning the buffer solution such as the capability to keep targeting pH throughout test duration (buffer power) and if the system could simulate the behavior of actual field conditions. The objective of the present work is to estimate the buffer capacity of some buffering systems and evaluate their influence on localized corrosion in Super Martensitic Stainless Steel (SMSS) by means of electrochemical tests. The results showed that higher amount of acetate give higher buffering capacity and better localized corrosion resistance. In the condition studied of pH 4.5 the exclusive use of bicarbonate in test solutions is not recommended due the unrealistic low buffer capacity (compared to field conditions) that leads to higher localized corrosion susceptibility of the SMSS.

Keywords: acetic acid, sodium acetate, buffering solution, pH stability, localized corrosion.

Introduction

Under corroding conditions, metal surface pH elevation or depression in nascent pits may occur in the static conditions that the most of the laboratory tests are conducted. The solution pH stability (bulk solution and local acidification) during corrosion test is important because it influences the passive film stability. The pH variation could be prevented, in a certain extent, by the use of buffer solution (1, 2, 3).

Buffers systems consist of an acid-base pair (conjugate acid-base). In the case of acetate/acetic system the excess of the H⁺ react with the conjugate base whether from the parent acid or sodium acetate, to drive the equilibrium back. The ability of the buffer system to resist changes in pH by either absorbing or desorbing H⁺ and OH⁻ is defined as buffer capacity (4, 5).

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Although the standards recommendation, different buffering procedures are used to conducted SSC tests. Some buffering systems used for evaluating SSC of martensitic and supermartensitic stainless steel have included (6-10).

- 4 g/L sodium acetate + hydrochloric acid;
- 4 g/L sodium acetate + acetic acid;
- 0.4 g/L sodium acetate +acetic acid;
- 0.4 g/L sodium acetate + hydrochloric acid;
- 0.5% wt acetic acid + sodium acetate;
- Bicarbonate (NaHCO₃).

The corrosion resistance of 13Cr and Super 13Cr martensitic stainless steels are considered to be influenced by the composition of the buffer solution, even at the same pH. The choice of buffering system could influence on: solution pH stability, alloy passivation and pitting corrosion susceptibility (1, 2). If a not proper buffer solution is used, the protons released from the hydrolysis reaction of the metallic ions could decrease locally the pH and the passive film could become unstable. That is, if the pH falls to a value near of the material depassivation pH (pH_d), pitting (or crevice) corrosion will initiate. Different buffering system at same pH could show different test results due the difference of buffer capacity.

The objective of the present work is to estimate the buffer capacity of some buffering systems capacity to maintain the bulk solution pH and evaluate their influence on localized corrosion by means of electrochemical tests of step potential.

Methodology

The material used in this study is 13% chromium super martensitic stainless steels (SMSS) - 13Cr5Ni2Mo. The chemical composition is given in Table 1.

Table 1 - Chemical Composition (%wt) – Super 13Cr martensitic stainless steel.

%	C	Si	Mn	P	S	Cr	Mo	Ni
Min.	-	0.10	0.30	-	-	11.50	1.50	5.50
Max.	0.03	0.50	0.70	0.025	0.010	13.50	2.50	6.50

The Step Potential electrochemical technique was used to obtain pitting potential for SMSS under various buffer solutions conditions. The tests were carried out at LNDC (Coppe - UFRJ) corrosion laboratory using a GAMRY[®] potentiostat model Reference 600 in a conventional three electrode system: SMSS alloy was used as the working electrode, a Hastelloy as the reference electrode and a two graphite bars were used as the counter electrode. All of the measurements were performed at room temperature in a deaerated solution with 200 g/L NaCl, 7% H₂S at pH of 4.5, in different buffer systems, as described in Table 2.

Table 2- Buffer solution test conditions - Step Potential test.

Test Condition	Buffer System
1	4 g/L Sodium Acetate + Acetic Acid
2	0.4 g/L Sodium Acetate + Acetic Acid
3	0.4 g/L Sodium Acetate + HCl*
4	Sodium Bicarbonate (112.5 ppm de HCO_3^-)
5	Sodium Bicarbonate (112.5 ppm de HCO_3^-) + Acetic Acid

*HCl - Hydrochloric Acid

The corrosion potential (E_{corr}) was monitored during 3600 s, and subsequently the system was anodically polarized in steps of 10 mV (vs Hastelloy electrode) every 30 min until a current of 1 mA was attained. At each step the current variation was recorded as a function of time until the current increase exponentially. The potential level at which the current density is equivalent to 0.1 mA/cm^2 was defined as the pitting potential – E_{pit} . After the electrochemical pitting corrosion test the sample surface was examined to confirm the presence of pit attack. An area of the specimen exposed to the corrosion environment was 5.0 cm^2 and the surfaces exposed to the electrolyte were sequentially grinded with silicon carbide paper up to 600 mesh. The tests were carried out in duplicate for each condition.

The pH stability of various buffer solutions in room pressure and temperature were estimated by addition of HCl to quantify the inhibitive effect on pH change. The measurements were conducted at LNDC (Coppe – UFRJ) corrosion laboratory in a deaerated solution with 200 g/L NaCl, 7% H_2S at pH of 4.5. The buffer systems used were the same applied in the electrochemical tests. The data were plotted on pH shift – HCl (μl) volume graph.

In order to confirm that the buffer capacity is directly linked to the acetate content in the solution, acetates species (CH_3COO^-) coming from sodium acetate or acetic acid, in the solution were calculated using OLI[®] Analyzer 9.5.

Results and Discussion

In Figure 1 is shown the pH stability of various buffer solutions in the room pressure and temperature estimated by addition of HCl (μl) performed in the solution containing 200 g/L NaCl, 7% H_2S at pH of 4.5.

The results obtained by the buffer capacity tests confirmed that the buffer solution composition could affect the solution pH stability. In the solution with 4g/L of sodium acetate + acetic acid the pH slightly decreased with the addition of the acid solution (HCl), this condition presented the highest pH stability. However for the buffer solution with bicarbonate the pH rapidly changed with small amount of acid added.

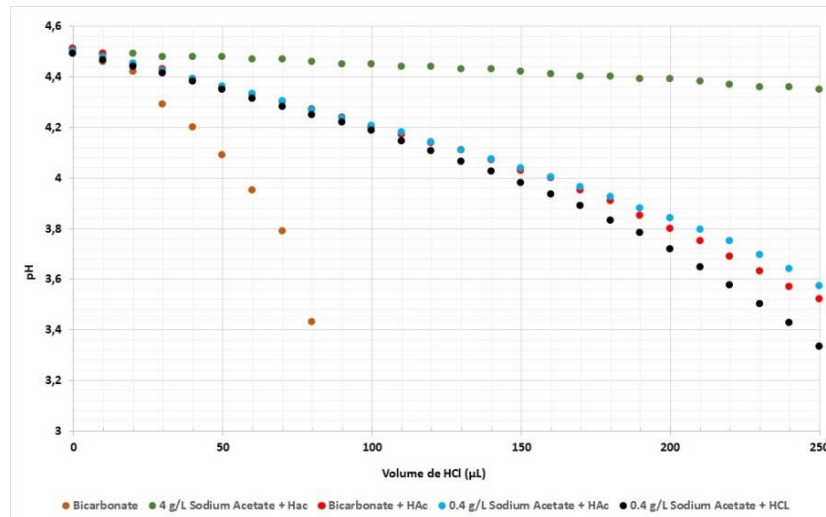


Figure 1 - pH stability measurement of different buffer solutions.

For the acetate + acetic acid buffer system it was observed that the solution with 4g/L of sodium acetate showed highest pH stability followed by the solution with 0.4 g/L acidified with acetic acid. The same tendency was obtained by Sagara et al. In the study the authors found, by simulation and laboratory measurements, that the pH slightly decreased by adding $[H^+]$ in the buffer system of 4g/L of sodium acetate + acetic acid. This condition showed higher buffer capacity than the condition with 0.4g/L of sodium acetate (11).

The condition with 0.4 g/L of sodium acetate and acidified with hydrochloric acid (HCl) presented lower pH stability than the system acidified by acetic acid. Ishiguro and Fujimura conducted a similar study. The authors simulated the buffer capacity of various buffer systems, including the NACE TM 177 Solution C – 0.4g/L of sodium acetate + HCl and a solution that they identified as *modified* Solution C - 0.4g/L of sodium acetate + acetic acid (8). In their study, for pH around 3.4-3.5, the NACE TM 177 Solution C (8) acidified with acetic acid showed higher stability than the solution with HCl. (12). Meng et al demonstrated in their study for 15Cr martensitic stainless steel that the acetic /acetate buffer solution has strong buffer capacity and was effective in preventing pH drift during 30-days of sulfide stress corrosion cracking (9). Mizuno et al. showed that the pH shift of the buffer solution with acetic acid was lower than conventional buffer solution with HCl, in the conditions studied, due to high concentration of acetic acid and sodium acetate (13).

In Figure 2 is presented the pitting potential (E_{pit}) obtained from the step potential electrochemical tests performed in the solution containing 200 g/L NaCl, 7% H_2S at pH of 4.5 in various buffer solutions.

From the results could be observed that the sample tested in buffer system with 4g/L of sodium acetate + acetic acid obtained the highest pitting potential, whilst the sample tested with bicarbonate showed the lowest pitting potential. No significant difference was observed in the pitting corrosion potential between the conditions with 0.4 g/L of sodium acetate acidified with HCl and with acetic acid.

Meng et al. studied the susceptibility of UNS42500 steel in a solution buffered with acetic acid/acetate and with bicarbonate by means of cyclic polarization curves. It was shown that in the buffer system with acetate the material presented a higher pitting and repassivation potential than the material tested in the bicarbonate solution (9).

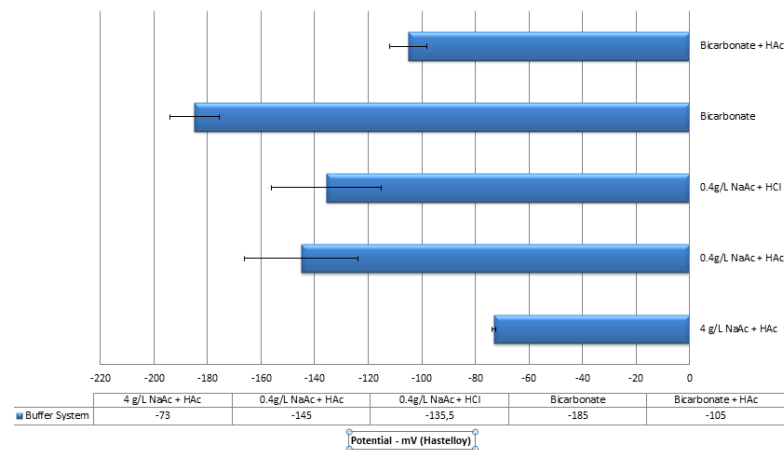


Figure 2 – Pitting Potential obtained from step potential test results for SMSS in various buffer systems – HAC: Acetic Acid.

Under corroding conditions, metal surface pH elevation or depression in nascent pits may occur in the static conditions that the most of the laboratory tests are conducted. The bulk and local pH are variables that influenced the initiation of localized corrosion in SMSS. The protons released from the hydrolysis reaction of the metallic ions, decrease the pH and the passive film could become unstable if the locally pH falls to a value near of the material depassivation pH (pH_d) permitting that the pitting (or crevice) corrosion will initiate (1-3, 14). In a buffered solution the pH is naturally stabilized by binding or releasing hydrogen ions in response to pH changes when corrosion proceeds. The pH tends to stay constant microscopically and macroscopically and near of the target pH defined for the test – avoiding the occurrence of localized corrosion.

In this context the results obtained in the electrochemical tests confirmed that the solution buffer capacity could affect the localized (pitting) corrosion susceptibility. The buffer system with 4g/L sodium acetate + acetic acid has higher pH stability and also presented the highest pitting potential.

In a buffered solution the hydrogen ions (H^+) generated by the corrosion process is consumed through the buffering reaction in accordance with the Le Châtelier's law. The equation is shifted leftward and pH remains constant. In the case of acetate/acetic system the excess of the H^+ react with the conjugate base (CH_3COONa - sodium acetate) whether from the parent acid or sodium acetate, to drive the equilibrium to the left. The net result is a new equilibrium composition that has a lower $[CH_3COONa]$ than before. In a buffer solution where the concentration of acetic acid and sodium acetate are higher the pH is more stabilized. Because either acetic acid or acetate is used for buffering reaction when pH varies by corrosion reaction, a pair of buffer solution with higher concentration of acetate and acidified with acetic will presented more pH stability than a pair with reduced acetate concentration and acidified with HCl (12, 13, 15).

In the Figure 3 (a) is presented the titration curve, obtained from the literature, for the buffer system acetate + acetic acid and in the Figure 3 (b) for bicarbonate system.

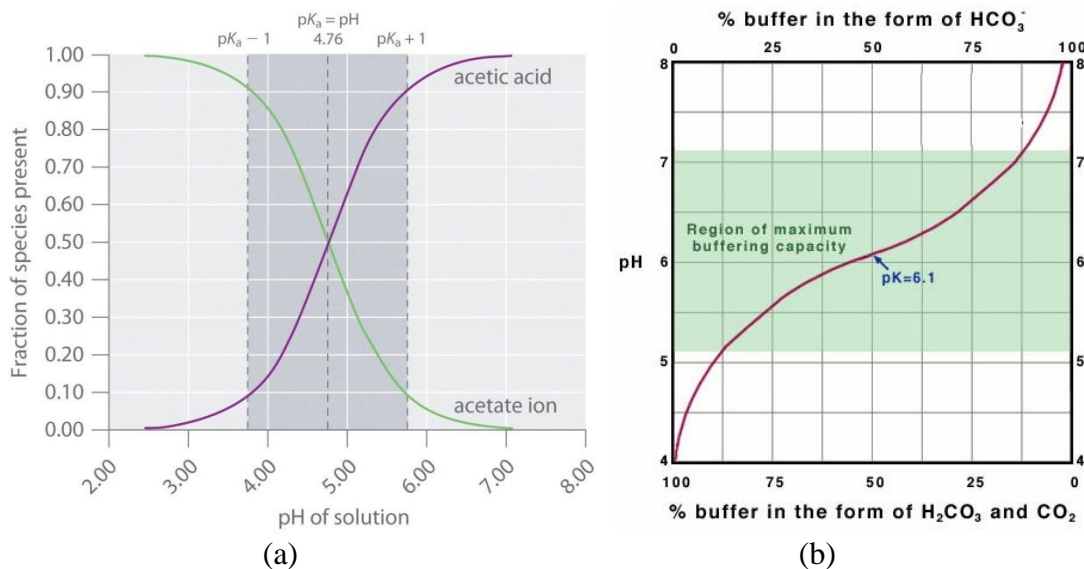


Figure 3 - Titration curves. (a) acetic acid; (b) bicarbonate. The boxes indicated the regions of the maximum buffering capacity (16, 17).

The ability of a substance to maintain the pH of such solutions (high buffer capacity) is more effective when the pKa and pH are close. pH may be estimated from pKa and concentrations by the Henderson-Hasselbach equation (Equation 1) (16).

$$\text{pH} = \text{pKa} + \log \frac{[\text{Base}]}{[\text{Acid}]} \quad \text{Equation 1}$$

From the Figure 3 it could be observed that the buffer solution of acetic acid + acetate has the predominant buffering capacity in pKa around 4.76 ± 1 while for the bicarbonate this region is in pKa of 6.1 ± 1 . The pH used in this study is 4.5 and is closed to pKa value of the system acetic + acetate, as already pointed; the buffer capacity is maximized when the target pH is within one unit of pKa. Although the bicarbonate salts are presented in the oil and gas field conditions it is considered as a weaker buffer in pH less than 5 (10, 15).

In the

Table 3 is presented the acetate specimens (CH_3COO^-) in equilibrium in aqueous solution obtained from OLI[®] simulation for buffer systems studied. A chart with concentration comparison is shown in Figure 4.

Table 3 – Acetic specimens in aqueous concentration (ppm) obtained from OLI[®] simulation.

Buffer System	CH_3COO^- (ppm)
4 g/L Sodium Acetate + Acetic Acid	1261
0.4 g/L Sodium Acetate + Acetic Acid	138
0.4 g/L Sodium Acetate + HCl*	49.2
Sodium Bicarbonate (112.5 ppm de HCO_3^-)	0
Sodium Bicarbonate (112.5 ppm de HCO_3^-) + Acetic Acid	35

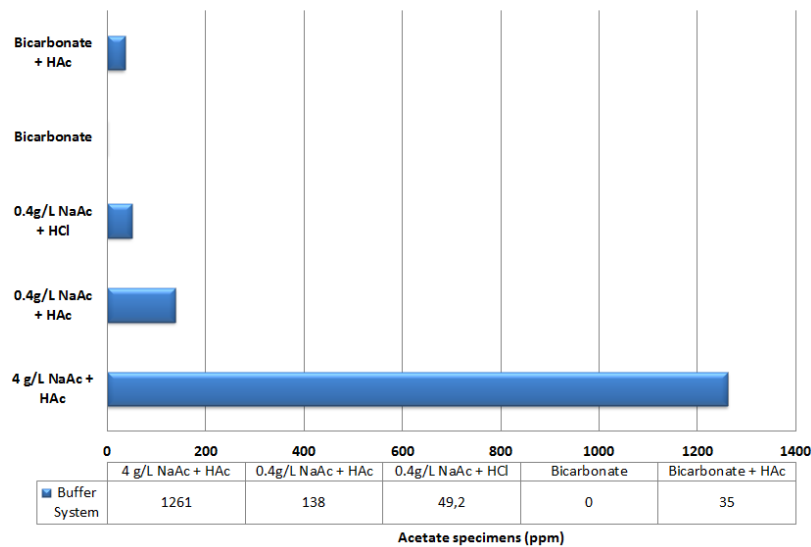


Figure 4 - Acetate specimens in aqueous solution (ppm) simulated by OLI® in different buffer system.

Simulation results are in accordance with others results found in the literature: a pair of buffer solution with higher concentration of acetate and acidified with acetic will presented more pH stability and lower localized corrosion susceptibility than a pair with reduced acetate concentration (12, 13, 15, 16).

As could be observed, the condition with the best performance in the electrochemical test and highest pH stability (4g/L of sodium acetate) presented the highest concentration of acetate specimens and the condition with the worst behavior in localized corrosion tests and lowest pH stability (bicarbonate) do not have acetate species in aqueous solution. Although no significant difference was observed in the pitting corrosion potential between the conditions with 0.4 g/L of sodium acetate acidified with HCl and with acetic acid, for the solution with HCl it was obtained lower acetate aqueous solution concentration than the system acidified with acetic acid. The results found for the condition with 0.4 g/L of sodium acetate acidified with acetic acid and HCl contributed with the affirmative that a system with highest concentration of acetate will present higher pH stability.

The exactly role of the influence of acetate specimens in the localized corrosion susceptibility is not well understood. Amaya and Ueda (1) suggested in their study using ^{13}Cr SS in a test solution with pH 3.5 that the passive film stability could be affected, not only due the pH stability but due the kind of oxide layer. The excess of acetate specimens in the solution could permit the formation of CH_3COO^- complex ion with iron (Fe) and chromium (Cr) ions that is a porous oxide layer, allowed the breaking of the passive layer.

Another concern about buffer solution is how can simulate the field condition behavior. In the oil and gas field a high pressure of CO_2 and bicarbonate buffer system is presented and the SSC tests are not carried out at a high pressure but in a 1 bar pressure condition. Sagara, et al. comparing in their study the pH behavior in a high pressure CO_2 condition and in 1 bar pressure and established a suitable buffer system in terms of buffer capacity. The authors recommended that the buffer system used in laboratory tests at 1 bar should have the equivalent buffer capacity as the field condition at high pressure condition (11). The same recommendation was done by Ishiguro and Fujimura, buffer system for laboratory test should simulate high pressure of CO_2 , environment in a real oil and gas field. The pH stability in test

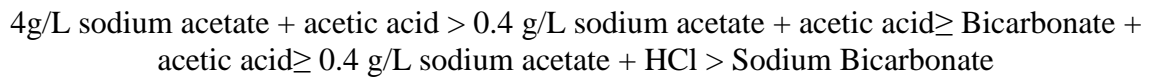
solution should accurately reflect the environment in oil and gas well or the SSC resistance may be evaluated too conservatively (12).

Buffer test solution for stainless steel to be used in SSC laboratory test evaluation should be discussed in terms of buffering stability, oxide layer formation and also in terms of field representativeness.

Conclusions

The buffer capacity and the buffer solution effect in the localized corrosion were studied. The following results were obtained:

1- The buffer solution could affect the bulk pH stability. The buffer with 4g/L of sodium acetate presented the higher capacity to keep the target pH and the bicarbonate the lowest. The following order of buffering stability was obtained:



2- The results suggested that the solution buffer capacity could affect the localized (pitting) corrosion susceptibility. For the 13Cr5Ni2Mo material, the highest pitting potential is obtained with the buffer system with 4g/L sodium acetate + acetic acid that has higher pH stability

3- A pair of acetate/acetic buffer solution presented more pH stability than a pair acetate/HCl, when pKa is closed to the target pH around 4.5.

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