Abstract. Halogenated salt (HS)-acetylenic compound (AC) mixtures were tested as corrosion inhibitors of 13Cr and 22Cr stainless steel and N80 and P110 carbon steel when exposed to 15 wt.% HCl solutions, at 50°C, 80°C and 100°C. The best corrosion inhibition efficiency is obtained when the concentration of both AC and HS is 1.5 wt. %, which indicates the use of all tested steels in oil well stimulation operated at 50°C and the use of 13Cr, N80 and P110 steels in oil well processing temperatures up to 100°C.

Keywords: oil well stimulation; carbon steels; corrosion inhibitors; acetylenic compound; halide salt

1. INTRODUCTION

Oil well stimulation, usually done with hot solutions of hydrochloric acid, may induce severe corrosion attack on production tubing, downhole tools and casing. In general, organic compounds are more effective than inorganic compounds when used as corrosion inhibitors to protect steel in acidic media. However, although organic corrosion inhibitors have revealed sufficient effectiveness protection of low alloy steel tubing during oil well stimulation operations, they have not provided satisfactory results for high chromium stainless steel (Walker, 1985).

A literature review on high-temperature acid corrosion inhibitors revealed that effective corrosion inhibitors used in oil well acidization phenomena include acetylenic alcohols, quaternary ammonium salts, aldehydes, amines and inhibitor aids (Liu et al., 2004; Emranuzzaman et al., 2004; Oliveira et al., 2002; Quraishi and Jamal, 2001; Jayaperumal et al., 2000; Trabanelli et al., 1988; Mack, 1985).

Corrosion-resistant alloys, such as 13Cr and 22Cr stainless steel, have proven to be more susceptible to corrosive attack of hydrochloric acid used in acidization stimulation operations at temperatures above 65°C than low alloy steels (Walker, 1986), and the same occurs when using hydrofluoric acid (Morgenthaler, 1997; Trabanelli, 1998).

Aiming the development of new inhibitor compositions for materials used in oil well stimulation, corrosion tests were performed with 13Cr, 22Cr, N80 and P110 steels, in order to evaluate the temperature dependence of the corrosion, when exposed to 15 wt.% aqueous hydrochloric acid solutions, using acetylenic compound (AC) / halogenated salt (HS) mixtures as corrosion inhibitors, in different proportions. The use of the former was based on the fact that acetylenic compounds are good corrosion inhibitors in both acidic media and high temperature (Rozenfeld, 1981), and the latter, due to the fact that halide ions, when combined with a variety of organic compounds, present synergistic effects (Neemla et al., 1992), which may result in effective and better...
anticorrosive action as observed with some of the tested mixtures.

2. MATERIALS AND METHODS

The corrosion tests were carried out at 50°C, 80°C and 100°C, in fresh 15 wt.% HCl aqueous solutions, by adding halogenated salt (HS) / acetylenic compound (AC) mixtures, in order to have the following final weight contents: 0.2 wt.% HS+ 0.2 wt.% AC; 0.2 wt.% HS + 1.5 wt.% AC; 1.5 wt.% HS+ 0.2 wt.% AC and 1.5 wt.% HS + 1.5 wt.% AC. The hydrochloric acid solution was prepared from reagent-grade concentrated acid and bidistilled water. The chemical compounds are pro-analysis products purchased from SIGMA-ALDRICH Co.

Rectangular specimens with dimensions of 2 cm x 0.8 cm x 0.5 cm, whose compositions are shown in Table 1, were mechanically polished on wet SiC paper (grade 400), ultrasonically degreased in acetone and dried with hot air before use. The specimens were then weighed to the 10^-4 g and immersed in the acid solution with the selected inhibitor composition, giving a volume to surface ratio equivalent to 83 ml/cm². The tests were performed in coated TEFLEX™ stainless steel cylinders, assembled in a roller oven for 5 hours at 50°C, 80°C and 100°C. At the end of this period, the specimens were cleaned, dried and reweighed. The data were calculated from corrosion rate equations in accordance with the ASTM G1-30 method [ASTM, 2004]. Three specimens of each type of steel were used to

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
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</thead>
<tbody>
<tr>
<td>P-110</td>
<td>0.13</td>
<td>0.67</td>
<td>0.001</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N-80</td>
<td>0.028</td>
<td>1.48</td>
<td>0.015</td>
<td>0.015</td>
<td>0.17</td>
<td>-</td>
<td>-</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>13Cr</td>
<td>0.19</td>
<td>0.5</td>
<td>0.013</td>
<td>0.001</td>
<td>0.15</td>
<td>0.008</td>
<td>0.191</td>
<td>13.72</td>
<td>0.001</td>
</tr>
<tr>
<td>22Cr</td>
<td>0.024</td>
<td>1.16</td>
<td>0.027</td>
<td>0.003</td>
<td>0.63</td>
<td>0.075</td>
<td>4.84</td>
<td>23.91</td>
<td>3.02</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition of the steels (wt.%).

<table>
<thead>
<tr>
<th>Mixture (wt.%)</th>
<th>13Cr</th>
<th>22Cr</th>
<th>N80</th>
<th>P110</th>
</tr>
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<tbody>
<tr>
<td>HS AC</td>
<td>50°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>12.9±0.8</td>
<td>12.1±0.4</td>
<td>4.4±0.1</td>
<td>4.2±1.5</td>
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<tr>
<td>0.2</td>
<td>7.2±1.0</td>
<td>6.9±0.7</td>
<td>1.8±0.1</td>
<td>2±0.1</td>
</tr>
<tr>
<td>1.5</td>
<td>7.2±0.1</td>
<td>6.4±0.4</td>
<td>4.3±0.5</td>
<td>4.2±0.1</td>
</tr>
<tr>
<td>1.5</td>
<td>3.5±0.4</td>
<td>3.3±0.2</td>
<td>2.1±0.2</td>
<td>2±0.1</td>
</tr>
<tr>
<td>Blank</td>
<td>93.3±3.7</td>
<td>110.7±10</td>
<td>32.1±5.7</td>
<td>58.6±10</td>
</tr>
<tr>
<td>HS AC</td>
<td>80°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>25.0±0.4</td>
<td>352±33</td>
<td>368.2±24</td>
<td>16.2±0.4</td>
</tr>
<tr>
<td>0.2</td>
<td>4.9±0.2</td>
<td>143±21.3</td>
<td>4.1±0.6</td>
<td>4.4±0.3</td>
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<td>1.5</td>
<td>3.4±0.1</td>
<td>83.8±2.3</td>
<td>1.9±0.5</td>
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<tr>
<td>1.5</td>
<td>3.9±0.2</td>
<td>74.6±2.1</td>
<td>18±0.4</td>
<td>2.3±0.2</td>
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<tr>
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<td>1,216.6±22.9</td>
<td>1,204.7±15.4</td>
<td>807.4±29.4</td>
<td>415±11.9</td>
</tr>
<tr>
<td>HS AC</td>
<td>100°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>67.5±1.5</td>
<td>1120±67</td>
<td>284.3±6.1</td>
<td>57.7±2.5</td>
</tr>
<tr>
<td>0.2</td>
<td>3.5</td>
<td>530.1±10</td>
<td>0.6±0.1</td>
<td>2.7±0.2</td>
</tr>
<tr>
<td>1.5</td>
<td>18.3±4.0</td>
<td>403.4±3.0</td>
<td>9.4±0.4</td>
<td>12.3±4.2</td>
</tr>
<tr>
<td>1.5</td>
<td>1.4±0.1</td>
<td>294.4±11</td>
<td>1.5±0.4</td>
<td>2.4±0.3</td>
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<tr>
<td>Blank</td>
<td>1,878.9±55.8</td>
<td>1,822.6±44.4</td>
<td>1,052±65</td>
<td>761±56.8</td>
</tr>
</tbody>
</table>

Table 2. Average corrosion rates (CRa) of 13Cr, 22Cr, N80 and P110 steels at 50°C, 80°C and 100°C (values in mm/y).
calculate the average corrosion rate (Cr). The acceptance criterion adopted for the corrosion rate was 2.5 mm/y and 5 mm/y for pitting corrosion and general corrosion occurrence, respectively.

3. RESULTS AND DISCUSSION

Table 2 shows the average corrosion rate results (CRa) in mm/y, which were obtained from three tested specimens of each type of steel for each inhibitor composition. Corrosion rate results obtained at 50°C for the 0.2 wt.% HS + 0.2 wt.% AC mixture decreased the corrosion rates of 22Cr, N80 and P110 steels to acceptable values, that is, to less than 5 mm/y; however, this mixture was clearly less efficient in protecting 13Cr, 22Cr, N80 and P110 steels at 80°C and 100°C.

Values less than 5 mm/y were obtained when using 1.5 wt.% of both HS and AC compounds in the protection of 13Cr and 22Cr steels at 50°C. All mixtures showed inhibition effects when protecting N80 and P110 steels at this temperature. Electrochemical Impedance Spectroscopy (EIS) measurements, performed with samples of N80 steel at 50°C, using a GAMRY PCA4 750 System, in a frequency range of 0.002 Hz to 500 Hz, showed that, in these conditions, the charge-transfer resistance (Rt), calculated from the respective impedance diagrams (Nyquist), is about 70 times higher than when using 0.2% of both HS and AC, indicating that when both additive contents are equal to 1.5 wt.%, a better corrosion protective film is formed.

All results obtained at 80°C, with the exception of those obtained with the mixture 0.2 wt.% HS + 0.2 wt.% AC, indicate good protection for 13Cr, N80 and P110 steels, with corrosion rates lower than 5 mm/y. At that temperature, the best results for N80 and P110 steels, were obtained for mixtures containing 1.5 wt.% of HS. At 100°C, the 1.5 wt.% HS + 0.2 wt.% AC mixture has no sufficient inhibition effect on any the four types of steel, although significantly decreasing the corrosion rate of N80 and P110 steels, as compared to the 0.2 wt.% HS + 0.2 wt.% AC results.

The hydrochloric acid commonly used during oil well acidization operations promotes the dissolution of passivating chromium oxide film on 22 Cr steel surface. On 22 Cr steel, the ferrite phase is preferentially attacked in relation to the austenite phase (Vicentini et al., 1987). Under test conditions using the four mixtures, both 13Cr and 22Cr steels are more corroded than N80 and P110 steels. Under the experimental conditions tested, the 22Cr steel exhibited corrosion rate values higher than those presented by 13Cr, as in other published results (Valdes, 1995).

Tests performed with 0.2 wt.% HS + 1.5 wt.% AC and 1.5 wt.% HS + 1.5 wt.% AC mixtures revealed that corrosion rate values for 13Cr, N80 and P110 steels at 100°C were

![Figure 1. Temperature dependence of the average corrosion rate of 13Cr, N80 and P110 steels in 15 wt.% HCl solution with the 0.2 wt.% HS + 1.5 wt.% AC mixture.](http://www.portalabpg.org.br/bjpg)
lower than at 80°C. This behavior indicates that the mixture inhibition activity increases at 100°C. A probable reason for this fact is that acetylenic compound (AC) oligomerization reaction provides a film formation on the metal surface (Rauscher et al., 1993; Burke et al., 1987).

Since all of the corrosion rate values are within the limits allowed, it can be assumed that there is a synergistic effect between the dissociated ions of the halogenated salt and acetylenic compound (Zucchi et al., 1992; Neemla, 1992). In acidic media, the halide ions are adsorbed on the metal surface, creating oriented dipoles which change the properties of the metal surface and consequently enhance the adsorption of the organic cations on the dipoles.

In Figures 1, 2, and 3 the average corrosion rate of 13Cr, N80 and P110 steels are plotted as a function of temperature, in order to better evaluate its effect on the corrosion inhibition performance of the mixtures. Figure 1 shows that when the 0.2 wt.% HS + 1.5 wt.% AC mixture is used, as the temperature increases the corrosion rate of 13Cr steel decreases, with

![Figure 2](http://www.portalabpg.org.br/bjpg)

**Figure 2.** Temperature dependence of the average corrosion rate of 13Cr, N80 and P110 steels in 15 wt.% HCl solution with the 1.5 wt.% HS + 0.2 wt.% AC mixture.

![Figure 3](http://www.portalabpg.org.br/bjpg)

**Figure 3.** Temperature dependence of the average corrosion rate of 13Cr, N80 and P110 steels in 15 wt.% HCl solution with the 1.5 wt.% HS + 1.5 wt.% AC mixture.
a linear correlation, whilst both N80 and P110 steels present a non-linear behavior, with the highest corrosion rate value at 80°C. Besides the fact that the interface interaction effects depend on the surface material with the same inhibitor, a possible explanation for the better corrosion inhibition at 100°C than at 80°C, for all three cases and mainly for the carbon steel cases, is that AC oligomerization reaction is more enhanced at 100°C, providing a more protective film on the metal surface.

From Figure 2, it is evident that the corrosion inhibition efficiency of the 1.5 wt.% HS + 0.2 wt.% AC mixture to protect N80 and P110 steels significantly decreases at 100°C, with similar corrosion rate values. This result may be attributed to decomposition or desorption processes of the HS molecules, because of lack of acetylenic compound oligomer required to maintain, at 100°C, the stability of some HS-AC complexes, which apparently might act against corrosion at temperatures up to 80°C. Note that the corrosion rate values for these steels are decreasing from 50°C to 80°C, the same occurring in the case of 13Cr steel, whose mean corrosion rate observed at 100°C was not plotted, since it was extremely high, showing that at this temperature this mixture has no corrosion inhibition properties for any of the chromium containing steels.

Figure 4. Surface aspects of the specimens after corrosion tests at 50°C.
As shown in Figure 3, when the 1.5 wt.% HS + 1.5 wt.% AC mixture is used, 13Cr steel shows a higher corrosion rate at 80°C and a lower one at 100°C. The behavior of the corrosion rate of the carbon steels is different from 50 to 100°C. P110 steel presents practically equivalent results, which suggests a stability of the inhibition effect, and N80 steel shows a decrease of the mean corrosion rate as the temperature increases. It must be noted that for all the three types of steel, this mixture provides good corrosion inhibition for all temperatures tested, without the occurrence of pitting corrosion.

Figures 4, 5 and 6 show, respectively the photographs of the different aspects of the surfaces of the specimens, after the respective weight loss tests at 50°C, 80°C and 100°C. As can be seen at 50°C, when the lowest content of the inhibitors mixture (0.2 wt.% HS + 0.2 wt.% AC) was used, a higher sensitivity to acid attack was noticed in the case of 22Cr and 13Cr steel specimens. At 80°C, with the same content mixture conditions, all types of steels showed severe attack, as well as the 22Cr specimens for the mixtures with 0.2 wt.% of HS inhibitor. At 100°C, there is a similar behavior to what happens at 80°C, with total destruction of the specimen in the case of 22Cr steel, when the lowest content of inhibitor mixture was used. It must be pointed out that for all cases shown in Table 2, with a corrosion

Figure 5. Surface aspects of the specimens after corrosion tests at 80°C.
rate lower than 200 mpy, no pitting was noticed on the specimen surface after the corrosion test.

4. CONCLUSIONS

The acetylenic compound (AC) and halogenated salt (HS) used in this study present corrosion inhibition properties for 13Cr, 22Cr, N80 and P110 steels when these materials, which are used in oil well stimulation, are exposed to 15 wt.% HCl solutions in the temperature range from 50 to 100°C.

The best corrosion inhibition efficiency is obtained when the concentration of both AC and HS is 1.5 wt.% without pitting corrosion, which enables one to indicate the use of all tested steels in oil well stimulation operated at 50°C and the use of 13Cr, N80 and P110 steels, at well processing temperatures up to 100°C.

In certain cases, corrosion rate values obtained at 100°C were lower than at 50°C and 80°C. This fact may be due to a higher synergistic effect between AC and HS, as well as to AC oligomerization reactions being favoured at 100°C, leading to the formation of a more protective film adsorbed onto the metal surface.

Figure 6. Surface aspects of the specimens after corrosion tests at 100°C.
ACKNOWLEDGMENT

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REFERENCES