CORROSION OF STAINLESS STEELS EXPOSED TO SEAWATER CONTAINING SULFATE-REDUCING BACTERIA

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Abstract. Sulfate-reducing bacteria (SRB) play significant role in the corrosion of stainless steels exposed to marine environment in several industrial plants especially in the extraction and processing oil and gas industry. Sulfate reduction by bacterial species results in the production of sulfide and, depending of the pH, hydrogen sulfide, which can significantly enhances the corrosion of several types of steels. In the present study, samples of two types of stainless steel, namely the austenitic AISI type 304 and the superduplex UMS S32750, were immersed in seawater containing Desulfovibrio vulgaris ssp vulgaris DP4 collected from Brazilian oil fields and identified by sequencing aps reductase gene. The samples were examined using optical microscopy, the aqueous solution was chemically characterized, and the corrosivity of the sterile medium was evaluated using electrochemical tests. The results obtained indicated that the superduplex stainless steel present a higher resistance to corrosion in a severe media containing chlorides and SRB compared to common austenitic stainless steel AISI type 304.

Keywords: corrosion; sulfate-reducing bacteria; stainless steels; hydrogen sulfide

1. INTRODUCTION

Sulfate-reducing bacteria (SRB) such as Desulfovibrio, Desulfotomaculum and Desulfobulbus are microorganisms responsible for localized corrosion on passive materials like stainless steels causing unexpected failure of materials (Sunde et al., 1990; Nilsen et al., 1996). Sulfate-reducing bacteria can grow in anaerobic environments and in biofilms utilizing organic and inorganic carbon sources (Okabe et al., 1992; Kjellerup et al., 2005).

Suggested mechanisms of corrosion in anaerobic environment by SRB are mainly concerned with the effect of sulfide ion produced, by dissimilatory reduction of sulfate, bacterial metabolic activity and products from its oxidation and reduction (Videla et al., 1992).

Superduplex stainless steels can offer an economical combination of strength and corrosion resistance which are an attractive option for applications services where common austenitic stainless steel would fail with chloride pitting and stress corrosion cracking (Shimodaira et al., 1977; Scott et al., 1991; Werner et al., 1998; Raman et al., 2005; Senatore et al., 2007). Due the fact that these steels are emerging as a replacement for austenitic stainless steels in aggressive environments such as in oil industry, there is a pressing needing to evaluate their performance.

The main objective of this work was to evaluate if a commonly used austenitic stainless steel AISI 304 and a highly alloyed stainless steels UMS S32750 (SAF 2507, Sandvik Steel) are susceptible to corrosion when exposed to a severe media containing...
chlorides and sulfate-reducing bacteria. Anodic and cathodic polarization characteristics of the specimens and microscopic images were used to assess the existence of corrosion of the stainless steels under anaerobic conditions suitable for SRB growth.

2. MATERIALS AND METHODS

2.1. Materials
A tube of SAF 2507 superduplex stainless steel provided by Sandvik Steel and a plate of AISI type 304 stainless steel were employed for this study without further treatment.

2.2. Specimen preparation
AISI type 304 stainless steel coupons with an area between 3.1 and 3.5 cm² and SAF 2507 superduplex stainless steel with area between 11.4 and 12.6 cm² were cut. For the electrochemical studies, samples were cut, imbedded in a mold of non-conducting epoxy resin and progressively on silicon carbide paper until 300 microns. Electrical connection was done by a copper wire soldered with lead-tin alloy on the specimens. After polishing the coupons were rinsed with distilled water and degreased using acetone. For the biocorrosion studies, the coupons were also sterilized in an autoclave at 121°C for 30 minutes.

2.3. Bacteria and culture media
The Desulfovibrio vulgaris ssp vulgaris DP4 was isolated from oil fields from the state of Bahia (Brazil). The sterile culture medium was made by combining in one liter of filtered seawater (PTFE-filter, pore size 0.22 µm, Sartorius, Germany) with: 1.9 g of Bacto agar, 1.0 g yeast extract, 0.1 g ascorbic acid (C₆H₇O₆), 4.0 mL of 0.025% resarzurine solution (C₁₂H₁₀NNaO₃), 0.0129 g sodium thioglycolate (C₂H₃NaO₂S), 4.0 mL of 0.5% sodium lactate solution, 4.1 g sodium acetate (CH₃COONa), and 14.7 g sodium citrate (Na₃C₆H₅O₇·2H₂O). The initial measured pH of the medium was 6.8. The solution was homogenized by agitation and later sterilized at 121°C for 30 min.

Cell densities in aqueous samples were 2.0x10⁹ m/L determined by the most probable number method using modified Postage's medium. Standard sterile techniques were followed for inoculations and all glassware was soap-washed and rinsed with distilled water prior to use. All experiments were conducted in a temperature-controlled anaerobic chamber (Bactron III, Shellab, Sheldon Manufacturing, Inc.) at 38±1°C.

2.4. Medium and test conditions
A volume of 25 mL of the test sterile culture medium was taken and transferred to autoclaved glass tubes (Pyrex, 15x200 mm). For the biocorrosion experiments, the tubes were inoculated with 1 mL of SRB culture using a pipette with a sterile tip. The entire setup was kept in an anaerobic vacuum chamber (Bactron III, Shellab, Sheldon Manufacturing, Inc.) to prevent any ingestion of oxygen into the medium during the test period.

The AISI type 304 stainless steel and SAF 2507 superduplex samples previously washed with water and acetone, weighted and sterilized at 121°C for 30 min were placed in separated tubes in contact with the sterile culture medium containing the SRB for 15 days. The temperature during the exposure studies was kept at 38±1°C. After the 15 days of experiments, the coupons were removed, washed, degreased, and dried to evaluate the final weight.

2.5. Sulfide estimation
Sulfide level in the medium was estimated at 15 days of experimental period. The analyses were carried out using a spectrophotometer Victor 3 Perkin Elmer. The anaerobic tubes were opened inside the anaerobic chamber by lifting the removable cap vertically up. The required amount of sample was taken for the studies using a pipette with a sterile tip. After collecting the sample the tubes were closed. Standard method was used for the sulfide estimation. Sulfide was estimated in soluble form after complexing with a zinc acetate solution. The color developed by the addition of sample with amine-sulfuric acid reagent and ferric chloride solution was compared with a
control prepared by addition of sample with sulfuric acid and ferric chloride solution. Methylene blue solution was added to the control tube until the color matches with that developed in the sample tube.

2.6. Metals determination
The major trace metals in the tubes contained the coupons in contact with the sterile culture medium and in contact with the culture medium containing the SRB were determined. The samples were analyzed for chromium, iron, cupper, cobalt and nickel by a Varian flame atomic absorption spectrometer. All measurements were carried using deuterium background correction. Metal hollow-cathode lamps were used as line source. A conventional burner for air and acetylene flame was used and the signals were measured using the integrated absorbance mode.

2.7. Microscopic studies
Optical images were undertaken with the specimens exposed to sterile medium as well as medium containing SRB (after removing the biofilm) under freely corroding conditions using a Bausch & Lomb W.F Stereo with an ocular of 10x and a zoom of 3x and the incident-light microscope EPITYP 2 from Carl Zeiss with oculars of 8x, 10x, 12x, and 16x and objectives of 6.3x, 12.5x, 25x and 50x. Prior to the microscopic imaging the coupons were rinsed in sterile distilled water, degreased and dried, and in some case treated to biofilm cleanup.

2.8. Electrochemical studies
The electrochemical behavior of the samples of AISI 304 and SAF 2507 stainless steels submitted the sterile culture medium prepared with seawater, above described, was evaluated through linear polarizations. A sample of SAF 2507 was also used in the potentiostatic experiment. These samples were cut with areas of 1.245 and 4.067 cm², mounted in polyester resin and polished with a 300 µm sandpaper. The electrochemical sample preparation and experiments were performed at the Department of Materials Science and Technology of the Polytechnic School of the Federal University of Bahia. The electrochemical experiments were carried out at room temperature by a three-electrode cell assembly of 250 mL and a potentiostat/galvanostat EG&G (model 273) connected to a computer by a GPIB card and controlled by the software M352 version 2.3.

The samples were placed as work electrode, a graphite bar was used as counter-electrode, and a silver-silver chloride electrode as a reference. The electrolyte cell was placed on a heating plate with magnetic agitation that was adjusted to maintain a temperature between 28 and 41°C and an agitation just enough to assure homogeneity of the aqueous solution. In the linear polarization the potential range was from -0.6 to 1.6 V. The potentiostatic experiments were performed using the pitting potential value obtained from the experiments of linear polarization (1.164 V for the SAF 2507). The parameters related to the resistance of corrosion, specifically the polarization resistance (R_p), the corrosion currant density (I_corr) and the potential of corrosion (E(I=0)), were obtained using the analytical module of analysis the software M352.

3. RESULTS AND DISCUSSION
The linear polarization curves obtained for AISI type 304 and SAF 2507 immersed in sterile culture medium at 41°C are shown in Figure 1. Passivation is observed, due to the presence of the reagents that compose the sterile culture medium and the sulfate of the seawater used. One remarks that the pitting potential for the AISI type 304 stainless steel is lower than the case of chloride media, which indicates the aggressiveness of seawater medium. The electrochemical parameters shown in Table 1 demonstrate that current density of corrosion in the sterile culture medium is also very small for SAF 2507 and important for AISI type 304. The corrosion potential indicates the inverse order. The great resistance of polarization of SAF2507 also demonstrates the relatively inert character of this material in the sterile culture medium. Figure 2 shows to the potentiostatic curve for SAF 2507 in seawater and sterile culture medium, described in the experimental
Figure 1. Linear polarization behavior of AISI type 304 and SAF 2507 super duplex stainless steels in sterile culture medium at 41°C.

Table 1. Electrochemical parameters for stainless steels immersed in sterile culture medium at 41°C.

<table>
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<tr>
<th></th>
<th>AISI 304</th>
<th>SAF 2507</th>
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<tbody>
<tr>
<td>(I_{\text{corr}})</td>
<td>70.08 (\mu\text{A/cm}^2)</td>
<td>361 nA/cm(^2)</td>
</tr>
<tr>
<td>(E (I=0))</td>
<td>-292.2 mV</td>
<td>-217.5 mV</td>
</tr>
<tr>
<td>(R_p)</td>
<td>16.49 kΩ</td>
<td>107.2 kΩ</td>
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Figure 2. Potentiostatic curves of 2507 duplex stainless steel in sterile culture medium at 41°C and at the pitting potential (1.164 V).
procedure section at 41°C in the potential of pits equal to 1.164 V. The potentiostatic curve was found to decrease at early stages and later return to go up what it characterizes the formation of pits, as expected.

The rate of corrosion for the stainless steels in 15-day-old sterile culture medium and the culture medium containing the SRB at 38°C in anaerobic conditions were calculated by determining the initial and final weight of the specimens after the 15 days of exposure. The corrosion experiments indicated for a relatively short period of time that the AISI type 304 exposed to the sterile culture medium showed a mass consumption rate of 6.1 µm/year and a consumption rate of 10.0 µm/year in the presence of the SRB.

The results of the rates of corrosion for the SAF 2507 on the other hand, seem to indicate a less important attack, being both values of the same order of magnitude equal to 3.5 µm/year in sterile culture medium and 3.3 µm/year in culture medium containing the SRB. The activity of the SRB was evaluated during the experiments by measuring the levels of sulfide presented in Table 2. One remark higher values in the presence of SRB, which confirm the activity of the bacteria. Note that the pH in the experiment changed from 6.8 to about 9.0 which indicates a net production of OH⁻ ions in the process.

Analyses using atomic absorption were used to assess the concentration of the metal compounds that could be generated by the corrosion due to the constituents of the medium such as the chloride and due to the SRB-induced corrosion mechanisms. These compounds were mainly chromium, copper, cobalt, nickel and iron. The results are summarized in Table 3. Very low metals concentration for the SAF 2507 was observed in comparison to the AISI type 304 for both medium used. The low iron content in the case of culture medium with SRB is due to the formation of iron sulfides by this bacteria and the precipitation of ferrous hydroxide due the pH increasing. The chromium solution content seems indicate some corrosion activity, especially in the presence of the SRB.

After the contact of the samples with the SRB culture as well as the sterile culture medium optical microscopic images were taken to investigate the presence of corrosion. After removing the SRB-biofilm micropits were

<table>
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<th>Medium</th>
<th>Sample</th>
<th>[S⁻] / (mg/L)</th>
</tr>
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<tbody>
<tr>
<td>Sterile culture</td>
<td>AISI 304</td>
<td>3.4</td>
</tr>
<tr>
<td>Sterile culture</td>
<td>SAF 2507</td>
<td>1.7</td>
</tr>
<tr>
<td>Culture + SRB</td>
<td>AISI 304</td>
<td>29.6</td>
</tr>
<tr>
<td>Culture + SRB</td>
<td>SAF 2507</td>
<td>65.7</td>
</tr>
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Table 2. Solution sulphide content for 15-day-old immersed stainless steels samples.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Sample</th>
<th>Cr / (mg/L)</th>
<th>Cu / (mg/L)</th>
<th>Fe / (mg/L)</th>
<th>Co / (mg/L)</th>
<th>Ni / (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sterile culture</td>
<td>AISI 304</td>
<td>6.2</td>
<td>0.45</td>
<td>3.9</td>
<td>0.68</td>
<td>1.2</td>
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<tr>
<td>Culture + SRB</td>
<td>AISI 304</td>
<td>8.9</td>
<td>0.07</td>
<td>0.62</td>
<td>0.12</td>
<td>0.29</td>
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<tr>
<td>Sterile culture</td>
<td>SAF 2507</td>
<td>9.1</td>
<td>0.00</td>
<td>9.5</td>
<td>0.25</td>
<td>0.56</td>
</tr>
<tr>
<td>Culture + SRB</td>
<td>SAF 2507</td>
<td>20.3</td>
<td>0.00</td>
<td>1.1</td>
<td>0.57</td>
<td>0.00</td>
</tr>
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</table>

Table 3. Solution metal content for 15-day-old immersed stainless steels samples.
observed in specimens of AISI type 304. Also local areas of black colored surface film were observed. Figures 3, 4a and 4b show images from optical microscope of the samples of AISI type 304 after the immersion experiments in the sterile medium and in the culture medium with SRB. On remarks in the first case the important formation of pits and in the second case a more general corrosion or crevice corrosion after removing the biofilm.
For the specimens of SAF 2507 not much deterioration was observed on the surface exposed to the sterile culture medium as well as in the culture medium containing the SRB. Figures 5 and 6 show images from optical microscope of the samples of SAF 2507 after the immersion experiments in the sterile medium and in the culture medium with SRB. On remarks in the first case that the sample is free of pits and in the second case after removing the biofilm there is some small roughness in the surface.

4. CONCLUSION
This work presents results of corrosion experiments of AISI type 304 and SAF 2507 superduplex stainless steels exposed to sterile culture medium containing seawater and sulfate-reducing bacteria. Contrasting the electrochemical results and microscopic images for AISI type 304 and SAF 2507 stainless steel one remarks that the superduplex is very resistance to the corrosion in aggressive environments. In spite of the fact that no mechanical data are still available, the results presented in this study indicate that superduplex stainless steels may be an option for use in medium containing aggressive compounds such as chloride, hydrogen sulfide and sulfate-reducing bacteria.

ACKNOWLEDGEMENTS
Funding for this research was provided by Fundação de Amparo a Pesquisa do Estado da Bahia (FAPESB), Financiadora de Estudos e Projetos (FINEP), Conselho National de Desenvolvimento Científico e Tecnológico (CNPq), and the PETROBRAS. We would like to thank A.S. de Carvalho for helping in the chemical analysis of sulfide and in the preparations of the media for the biocorrosion experiments.

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