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The influence of *Desulfovibrio vulgaris* on the efficiency of imidazoline as a corrosion inhibitor on low-carbon steel in seawater

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ABSTRACT

The action of *Desulfovibrio vulgaris* (Dv) during a corrosion process has been reported in literature, but the influence of imidazoline in the formation of biofilms is not clear, as well as the effect of bacteria on the efficiency of the corrosion inhibitors. The aim of this work is to determine the behavior of bacteria in the presence of imidazoline. Therefore, the growth of Dv, isolated and characterized from a morphological point of view, was monitored during 21 days, during which synthetic seawater was used as the culture medium, according to the ASTM D665-98 standard. Electrochemical noise (EN) was employed to establish the corrosion type generated by the microorganism on an AISI 1018 steel cylinder. The attack was observed using scanning electron microscopy (SEM). In order to evaluate the efficiency of the corrosion inhibitor, Tafel extrapolation was used; the optimum concentration of the inhibitor was used in the presence of sulphate-reducing bacteria (SRB). In general, two forms of corrosion were observed: localized corrosion (in the LAG phase) and mixed corrosion (in the LOG phase).

1. Introduction

Sulphate-reducing bacteria (SRB) are a group of anaerobic Gram-negative microorganisms that conduct dissimilatory sulphate reduction [1]. However, active cultures can also be isolated from sites where bacteria are exposed to O_2 [2–4]. Since the SRB show considerable adaptability to extreme conditions, they are widespread in various ordinary environments. These microorganisms can coexist in naturally occurring biofilms with a wide bacterial community including fermentative bacteria, often forming synergistic communities (consortia) that are capable of affecting electrochemical processes through co-operative metabolism [5].

The biocorrosion process may be detected by a combination of observations: corrosion morphology, presence of microbial slime masses, presence of hydrogen sulphide and ferrous or ferric hydroxide as observed in anaerobic systems [6]. This process is of considerable concern because the sulphate-reducing activity of bacteria is thought to be responsible for >75% of the corrosion in productive oil wells and for >50% of the failures in buried pipelines [7].

In order to avoid failures due to the corrosion of these systems, corrosion inhibitors are employed. Corrosion inhibitors are organic or inorganic chemical substances which, when added at low concentrations, are capable of preventing or controlling corrosion in 80–90% in most cases.

In closed systems, inhibitors are one of the more frequent methods employed, since they do not alter the environment's physical and chemical properties [8].

Corrosion inhibitors based on organic compounds contain nitrogen, oxygen and sulphur atoms, as well as multiple bonds in the molecules, and have good adsorption properties [9]. Corrosion inhibition efficiency by means of organic compounds is related to their adsorption properties. The adsorption depends on the metal's nature and surface, on the type of corrosive medium and on the inhibitor's chemical structure [9].

Studies have reported that the adsorption of organic inhibitors depends mainly on some properties of the molecules, related to their functional groups, on the possible steric effects and on the electronic density of donor atoms [10–12]; adsorption is also supposed to depend on the possible interaction between the inhibitor's p-orbitals and the surface atoms' d-orbitals [13,14], which induce to a greater adsorption of the inhibitor's molecules into the carbon steel surface [12,15], leading to the formation of a corrosion protecting film.

Different derivatives from imidazoline are employed as steel corrosion inhibitors, especially in the oil industry. Recently, many studies have been undertaken, using computational tools and electrochemical techniques, to understand how the corrosion inhibitor works, and so a better understanding of corrosion inhibitors and their mechanisms can now be achieved [16–18]. Ramachandran et al. [8], Wang et al. [18], and Cruz et al. [19,20] have published

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papers concerning the molecular structure of imidazoline as a corrosion inhibitor. In these papers, authors implied some key questions regarding the structure–performance relationships of the imidazolines, the role of the hydrocarbon chain relative to the imidazoline head group in film formation, the thickness of the imidazoline film, the stability of the imidazoline film, and imidazoline's solution composition and hydrolysis.

The SRB *Desulfovibrio vulgaris* is a hydrogenotropic microorganism isolated from an oil field separator in the Gulf of Mexico, which had undergone biocorrosive damage. Imidazoline is currently employed to minimize the damages caused by corrosion in the systems where *D. vulgaris* is present.

2. Materials and methods

2.1. Materials

AISI 1018 mild steel coupons were employed, which had a percent composition of Mn 0.76, Ni 0.069, Al 0.005, Cr 0.0698, Cu 0.3122, Si 0.159, S 0.02, P 0.03 and C 0.207, the rest being Fe. The surfaces were metallographically polished according to ASTM A262 and degreased with acetone, washed with distilled water and sterilized with ethanol before exposure to the experimental media.

2.2. Test organisms and medium

D. vulgaris was previously maintained in a Posgate medium [5]. Then it was conditioned in deaerated seawater at 33 °C during 15 days till bacterial growth was observed.

Artificial seawater was used according to the ASTM D665-98 standard. The cellular count was carried out using the Neubauer camera adapted to a microscope.

2.3. Test probes

The steel probes used in the electrochemical tests were built by embedding three cylindrical specimens into resin epoxy. The exposed area of each electrode was 0.7854 cm^2. These probes had a three-electrode arrangement, two of which acted as working electrodes, and the other one was the reference electrode. The surface preparation of the steel probes was carried out using Nos. 240, 320, 400 and 600 sand papers.

Finally, the samples were polished with a thick cloth using 1- and 0.3-mm particle size alumina, and a soft cloth with 0.05-mm alumina. The probes were rinsed with water, and dried off with dry air. The surface was sterilized by immersion in a solution of 70% ethanol during 1 h, and finally dried with dry air before each test.

2.4. Growth curve

D. vulgaris growth curve and the control were plotted simultaneously for 21 days at 33 °C. Two corrosion cells were utilized and adapted in order to control, inoculate and monitor the experiments. 800 mL of artificial seawater were added to each flask and then sterilized in an autoclave during 15 min at 120 °C; after that, the electrolytes were deaerated with UN1066 nitrogen.

The sterilized test probes were introduced to the dearated systems with and without bacteria. One of the flasks was inoculated with 1 mL of *D. vulgaris* containing 12,000 bacteria/mL. The growth curve of the *D. vulgaris* with the corrosion inhibitor was carried out in two ways: by adding the corrosion inhibitor to the system before inoculating the bacteria and by adding the corrosion inhibitor after inoculating the microorganisms.

2.5. Polarization curves

Potentiodynamic polarization curves were generated by using a Potentiostat Gill ACM Instrument. Polarization curves were recorded from −300 to 800 mV vs. corrosion potential (E_{corr}) with a sweep rate of 60 mV/min. All experiments were performed in a three-electrode electrochemical cell containing 800 mL of artificial seawater at 33 °C. A Pt electrode and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively.

Polarization studies were carried out in a flask containing various concentrations of imidazoline (5, 20, 50, 100, and 200 ppm). Each Tafel slope was obtained by the 120 mV criteria applied to each polarization curve.

2.6. Electrochemical noise in the presence of imidazoline and D. vulgaris

Electrochemical noise (EN) tests were performed simultaneously with the growth curve, with and without imidazoline as an inhibitor corrosion agent, by using test probes with three nominally identical steel electrodes exposed to the electrolyte with and without bacteria, registering the spontaneous fluctuations of the potential and current due to corrosion reactions.

2.7. Microscopic examination

The attack caused by the *D. vulgaris* was examined using a scanning electron microscope (SEM).

3. Results

3.1. Metallographic analysis

A photograph of steel microstructure is shown in Fig. 1. Perlitic and ferritic phases can be distinguished in Fig. 1, as well as small cavities (pores) that are due to the material's production process. The uniformity of the grain size (from 14 to 22 μm) in the whole surface shows that the steel employed was normalized.

3.2. Growth curve

The results of the growth curve are shown in Fig. 2.

In Fig. 2, four typical phases of the bacteria growth can be appreciated. The LAG or adaptation phase is very lingering, taking almost 156 h; the LOG or exponential phase lasted 76 h, the microbial growth speed was 14,276 bacteria/min. The steady phase was observed between 228 and 420 h, with a mean velocity of about 2094 bacteria/min. The death phase starts approximately after 432 h with a decreasing speed of 32,500 bacteria/min.

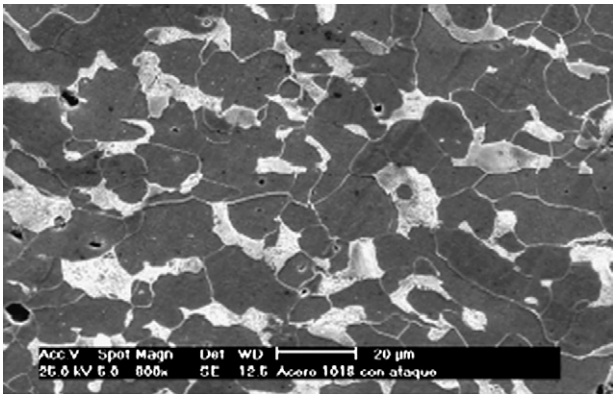

Fig. 1. SEM micrograph of steel AISI 1018 (600×).