

Development of a new electrochemical methodology at carbon steel/Na₂S system for corrosion monitoring in oil refineries

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Abstract The current trend for processing more aggressive crude oils has resulted in a considerable increase of corrosion and hydrogen damage at Fluid Catalytic Cracking Units in Brazil. Therefore, it was proposed a new method for on-line and real time corrosion monitoring: evaluation of the integrity of the iron sulfide film by the voltammetric technique. This methodology would allow one to detect and inhibit the destruction of the sulfide layer by cyanide ions before a significant amount of hydrogen is generated and permeates the steel. Therefore, the lifetime of industrial equipment would be considerably improved. The feasibility of the proposed methodology was validated through bench scale tests.

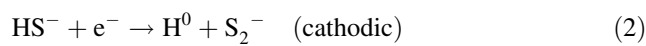
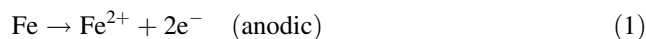
Keywords Corrosion monitoring · Cyclic voltammograms · H₂S corrosion · Cyanide · Hydrogen permeation · Iron sulfide

1 Introduction

Fluid Catalytic Cracking Light End Recovery Units have been extensively affected by stress corrosion cracking and hydrogen-related damage [1–4]. Such phenomena are

caused mainly by the presence of H₂O, H₂S, NH₃, and CN⁻ in the process flow.

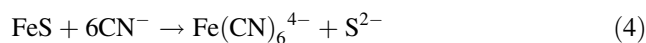
The corrosive species is the bisulfide ion, which is the most stable sulfide form in this alkaline sour environment. Thus, the corrosion of carbon steel by bisulfide occurs according to the reactions (1–3) [2, 3, 5]:



A fraction of the atomic hydrogen (H⁰) generated during reaction (2) can penetrate through the vessel wall and be retained in the crystal structure of the steel. It is well known that trapped hydrogen can cause serious damage to metal, such as embrittlement, cracking or even blistering [1, 6–8].

Otherwise, a nonstoichiometric iron sulfide (Fe_xS_y) is also produced and deposited on the steel surface during the corrosion process—reaction (3). This product acts as a physical barrier between the steel and the bulk solution, reducing the corrosion rate and the generation of hydrogen.

However, the presence of a certain amount of cyanide ion (CN⁻) destroys the sulfide film (reaction (4)), again rendering the metal surface susceptible to corrosion processes and to the generation of hydrogen [1–8].



Several techniques have been studied for monitoring corrosion and hydrogen-related damage in Fluid Catalytic Cracking Units (FCCUs), among them electrochemical impedance spectroscopy, electrochemical noise, and hydrogen probes. The measurement of hydrogen permeation has been the most commonly adopted method

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[9, 10]. However, a growing trend for processing high nitrogen content crude oils has led to increasing susceptibility to corrosion- and hydrogen-related damage in FCCUs in Brazil [10, 11]. Thus making it extremely important to develop a more effective methodology to monitor this corrosion process with a real time response. This need led to the proposal of a new on-line monitoring method [12]. The methodology consists of applying cyclic voltammetry to evaluate the integrity of a protective iron sulfide film. This corrosion monitoring approach allows the detection and control of cyanide attacks on the film in at real time, before any substantial amount of hydrogen permeates into the metallic structure. In comparison with the use of hydrogen probes, whose response depends on a certain degree of hydrogen diffusion, the use of this new method could result in significantly extending the lifetime of equipment.

The main objective of this work was to evaluate, at a laboratory level, the viability of applying this new methodology to detect cyanide attacks on sulfide films. Considering the previous factor and safety reasons, a carbon steel electrode was used and Na₂S solution to simulate the real fluid conditions. The carbon steel electrode material can be substituted by any other material of the FCCUs plant.

2 Materials and methods

2.1 Solutions

The medium used for the laboratory tests, for safety reasons, was an aqueous Na₂S 0.05 M solution prepared from analytical grade reagents (Na₂S·9H₂O) and distilled water. Before each experimental run, the solution was replaced (about 100 mL) and purged with nitrogen gas (99.996% purity) for 1 h. The solution's pH was adjusted to 9 by the addition of sulfuric acid (96%). During the experiments, N₂ was continuously injected over the electrolyte to prevent the entrance of air. Cyanide was injected into the electrolyte from an aqueous 125 g L⁻¹ potassium cyanide (KCN) solution—analytical grade reagent.

2.2 Apparatus

The electrochemical tests were performed using a Radiometer Analytical PGZ 100 (VoltaLab 10) potentiostat controlled by VoltaMaster4 software and a conventional three-compartment cell. The cell was equipped with a water jacket to control the temperature and was maintained at 25 °C by a thermoregulator coupled to a thermostat. A magnetic stirrer bar was placed at the bottom of the cell to keep the solution homogeneous.

2.3 Electrodes

The counter electrode was a spiral-shaped platinum wire and the reference electrode was silver–silver chloride (Ag/AgCl (sat. KCl)) having a potential of +0.197 V in comparison with the standard hydrogen electrode. The reference electrode had a double junction to prevent its degradation in sulfide solution due to the possible formation of silver sulfide [13]. The working electrode consisted of a carbon steel cylinder (AISI 1020) embedded in a glass tube with epoxy resin. The area exposed to the electrolyte, which was 0.255 cm², was prepared before each run. The electrode surface was polished with SiC sandpaper up to 600 grit, rinsed in distilled water, and then dried with a soft tissue.

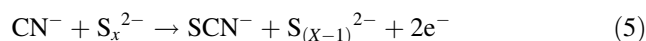
2.4 Electrochemical methodology

The steady-state condition in a FCCUs system will be reached when the carbon steel, or other constructive material, is covered by a continuous polysulfide layer. The laboratory simulation of the polysulfide layer formation was obtained by potential cycling the carbon steel electrode in a Na₂S solution.

The aim of this work was to simulate the formation of this continuous polysulfide layer over a carbon steel electrode and destroy it with cyanide injection.

Cyclic voltammograms were recorded at a sweep rate of 10 mV s⁻¹ from -1.4 V to -0.4 V (vs. Ag/AgCl). Cyanide was injected just after the voltammetric profile reached a pseudo steady state obtained after cycling. In each case, a certain amount of cyanide was added so that a resulting concentration of 1000 ppm CN⁻ in the solution was obtained.

A relatively high concentration of cyanide was used in the tests due to several parallel reactions that consume this ion. In addition to reaction (4), cyanide can react with polysulfides as in reaction (5). It also can volatilize as HCN if the pH is lowered, or it can polymerize to polycyanides [5]:



3 Results and discussion

Figure 1 illustrates the cyclic voltammogram of carbon steel in Na₂S 0.05 M without cyanide (solid lines), which was obtained at a potential range of -1.4 V to -0.4 V.

When the electrode is cycled, a progressive increase of the current densities relating to both the anodic peak (2A)—around -0.8 V—and the plateau (1A) is visible. In

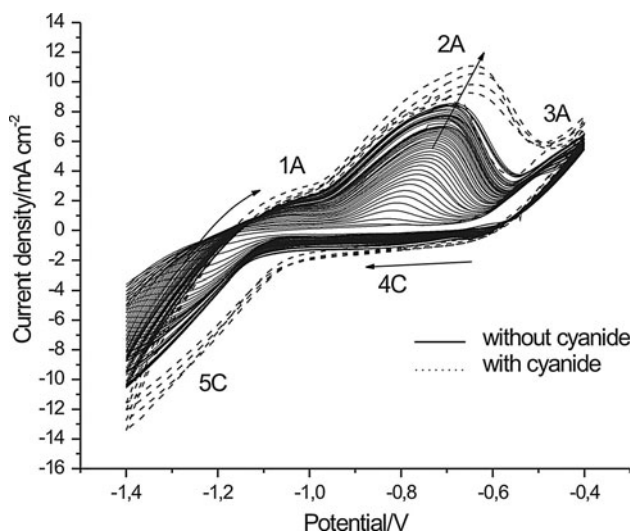


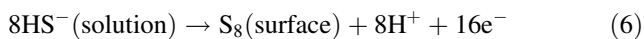
Fig. 1 Cyclic voltammograms of the carbon steel in Na₂S 0.05 M solution, from -1.4 V to -0.4 V (vs. Ag/AgCl) (56 cycles), with later addition of 1000 ppm CN⁻

addition, there is a peak potential (E_p) displacement towards more positive values.

The 1A and 2A peaks are probably related to the formation of iron sulfide and/or oxide (or hydroxide). According to Salvarezza et al. [14], there is a competitive adsorption between OH⁻ and HS⁻ ions on the electrode surface to form oxide or sulfide, respectively.

In the same potential range, Shoesmith et al. [13] observed two peaks, which they ascribed, respectively, to the formation of Fe(OH)₂ and to the subsequent production of a mixture of Fe₃O₄ and γ -Fe₂O₃. Vera et al. [15] reported that an iron sulfide film (probably, mackinawite) could be formed at potentials lower than -0.65 V (vs. SCE). The simultaneous presence of iron sulfide and oxi-hydroxide during the first anodic peak of the voltammetry was checked by Caram et al. [16].

Still in the anodic branch, a region named (3A) occurs at about -0.47 V. According to several researchers [13, 15, 17–20], this may be attributed to: (a) transformation of the FeS into Fe₂O₃ and S (elemental sulfur) on the electrode surface; (b) direct oxidation of the HS⁻ ions, also generating S on surface, as shown in the following reaction:



In the region around -0.9 V, Shoesmith et al. [20] found a broad cathodic peak, which was ascribed to the reduction of iron sulfide.

The region of rapid current increase (5C) could be associated mainly with the reduction of bisulfide ions—reaction (2).

Moreover, reactions of oxide reduction were also identified in the potential range of -1.2 to -1.4 V by other researchers [13].

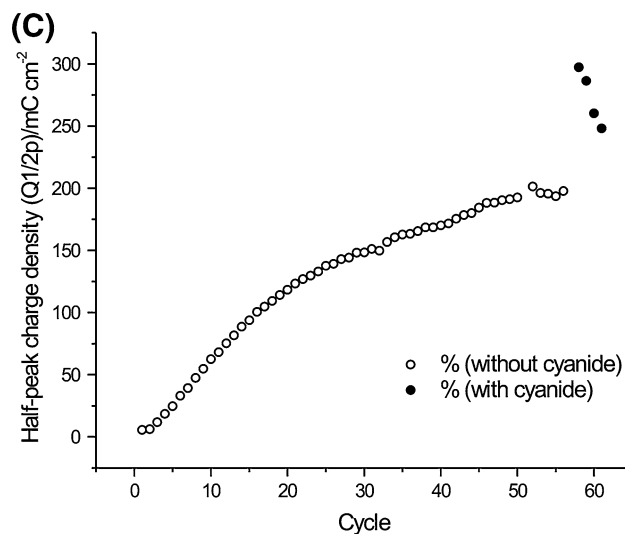
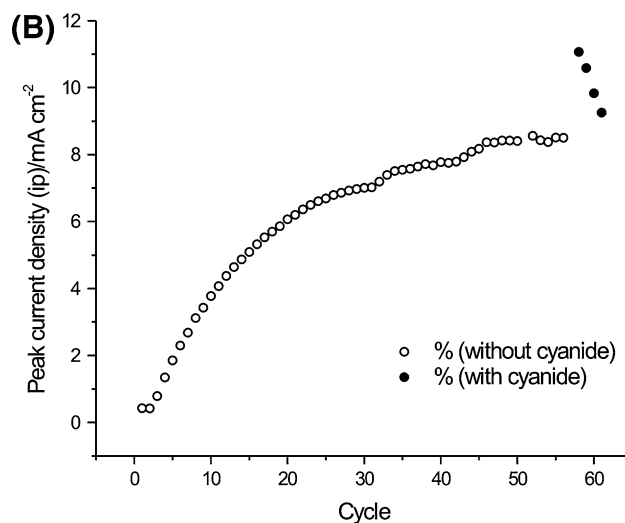
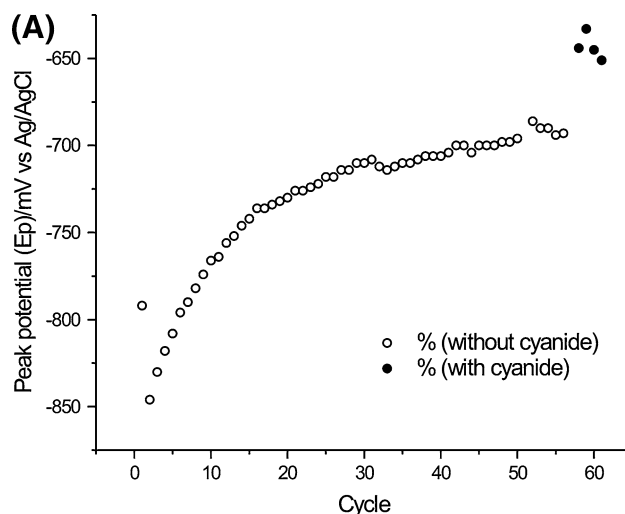


Fig. 2 a Variation of the values of peak potential (E_p), b peak current density (i_p), and c half-peak charge ($Q_{1/2p}$) density related to the peak (2A) in Fig. 1, during film stabilization (white points) and after cyanide addition (black points)

The growing behavior of the 2A peak could be related to the surface area growth caused by a Fe_xS_y film formation (reaction (3)). When the formation of the Fe_xS_y surface layer attained a steady state, the growing charge density of 2A peak became constant. This condition will be considered as a pseudo steady state one.

3.1 Addition of cyanide ion

After about 56 cycles, the voltammetric profile attained a pseudo steady state (solid lines Fig. 1) and the surface polysulfide film was considered stabilized. Cyanide was injected into the solution at this point. The dashed lines in Fig. 2 show the resulting curve after the cyanide injection.

The addition of CN^- caused significant changes in both the anodic and cathodic branches of the voltammetry. Current and charge densities relating to peak (2A) considerably increased. This behavior probably resulted from the surface growing area after partial destruction of the film previously formed on the electrode surface. Therefore, at the laboratory conditions, the film is repaired in the next potential cycle, requiring more charge in this process.

Figure 2 presents the variation of peak current density (i_p), peak potential (E_p), and half-peak charge density ($Q/2p$) with respect to peak (2A). During the stabilization process (i.e., before the cyanide injection), all the values of the parameters analyzed tended toward a plateau. After the addition of cyanide, however, abrupt changes on these parameters were detected, indicating the feasibility of detecting cyanide attack on iron sulfide by the developed methodology and corrosion monitoring in laboratory conditions. Its practical application could involve specifying a “set point”, such as “ i_p ”, “ E_p ”, or “ $Q/2p$ ”.

4 Conclusions

It was found that the addition of 1000 ppm CN^- to a 0.05 M Na_2S aqueous solution caused significant changes in the cathodic and anodic voltammetric branches during the cycling process of carbon steel. An increase of the dissolution-passivation charge and current densities was observed to occur in response to the cyanide attack on the sulfide film. According to these laboratory results, the developed methodology proved to be effective for evaluating the integrity of iron sulfide and could therefore be applied for on-line corrosion monitoring in catalytic cracking units.

The simple methodology proposed here should allow for the detection and mitigation of sulfide film destruction at real time, before the onset of significant hydrogen permeation into the steel. A long-term benefit of this technique would be the considerable enhancement of operational reliability and availability of industrial plants.

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