Strategies for corrosion inhibition of slurry pipelines prior to commissioning

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Abstract

A practice used to prevent corrosion in buried slurry pipelines is the hibernation of pipelines with an aqueous solution containing corrosion inhibitors before beginning the mining operation. The aim of this work is to evaluate the corrosion resistance of API 5L X70 steel used in the slurry pipelines in hibernation solution containing sodium sulphite, sodium hydroxide and glutaraldehyde in a synthetic river water. The electrochemical techniques used are the Tafel analysis and electrochemical impedance spectroscopy. The synergistic effect of the components of hibernation solution on the corrosion resistance of the API 5L X70 steel was evaluated. A lower corrosion resistance was obtained for the API steel in aqueous solution of sodium sulphite, and in solution of sodium sulphite with glutaraldehyde. The hibernation solution was efficient in inhibiting steel corrosion but the highest corrosion inhibition efficiency was obtained with the glutaraldehyde aqueous solution.

Keywords: Mining; Corrosion; Hibernation Solution; API steel; Electrochemical Impedance Spectroscopy.

1. Introduction

A slurry pipeline is used in mining to transport mineral concentrate from a mineral processing plant near a mine. A practice used to prevent corrosion in buried slurry pipelines is the hibernation of pipelines with an aqueous solution, usually of river water, containing corrosion inhibitors and biocides, before beginning the mining operation. Another alternative to prevent steel corrosion inside the mining pipelines before the start of operation of mining activities is filling the pipes with nitrogen, which is a solution environmentally friendly but economically unfeasible.

The slurry pipeline studied in this work is 525 km long, and will transport iron ore from Minas Gerais to Rio de Janeiro, in Brazil. It is estimated that the reserves of iron ore contain 2 billion tons of ore with a high iron concentration (68.50 wt-%.).The pipeline used is made of carbon steel, with specification API 5L X70, and was externally coated with extruded polyethylene triple layer. The thickness of the tube used varies from 0.01 m to 0.023 m, with a diameter of 0.66 m.Several works have been developed on corrosion and inhibition protection by the American Petroleum Institute (API) steel in acid media including sour service, and in neutral and alkaline environments containing chlorides, carbonate and carbon dioxide (Hernández-Espejel *et al.*, 2010; Eliyan *et al*., 2012;Meresht *et al*., 2012). Studies of corrosion of API steel exposed to hibernation solution of river water containing inhibitors and biocides were not found in literature, according to our knowledge.

In this work, the hibernation solution proposed contains glutaraldehyde, sodium hydroxide, and sodium sulphite in river water. Among the non-oxidizing biocides available are formaldehyde, glutaraldehyde, isothiazolones, and quaternary ammonium compounds (Wen *et al*., 2009).Substances which promote the increase of the solution pH, such as sodium hydroxide, and substances which are oxygen scavengers, such as hydrazine, are also considered to be biocides, even if this is not the main function of these substances. Glutaraldehyde acts as an inhibitor and a biocide, and is capable of reacting chemically with the cell membrane proteins killing off microorganisms rapidly from a minimum concentration of active biocide (Liu *et al*., 2012). Glutaraldehyde was more effective as a biocide when associated with techniques such as ultrasound (Pound *et al*., 2005) or with compounds such as ethylene diaminedisuccinate, EDDS [$C_{10}H_{16}N_2O_8$], and methanol (CH_4O) against souring and microbiologically influenced corrosion (MIC) caused by sulphate-reducing bacteria (SRB) (Xu *et al*.,2012).Corrosion inhibitors commonly used, which sequestrate oxygen from environments are hydrazine and sodium sulphite (Gouda and Sayed, 1973).The reaction between sodium sulphite and oxygen is:

$$2\,Na_2SO_3 + O_2 \rightarrow 2\,Na_2SO_4 \qquad (1)$$

This reaction is slow at low temperatures and pH values below 4.0 or above 9.0.

The corrosion resistance of API X70 steel used in the pipelines exposed to the hibernation solution containing sodium sulphite, sodium hydroxide and glutaraldehyde was evaluated. The pipe will be exposed to the hibernation solution for a period of two years before the commencement of the mining operations. According to our knowledge, this research which is associated to a real application in mining industry is an unpublished work, not found in literature. The study of the inhibition effect on API steel corrosion of the each component of the hibernation solution and the synergistic effect of combinations of the solution components using direct current (DC) and alternate current (AC) techniques was not found in literature and contributes to elucidate the mechanisms of inhibition of API steel corrosion. The electrochemical techniques used are polarization curves with Tafel analysis and electrochemical impedance spectroscopy.

2. Materials and methods

Samples of API 5L X70 steel with a surface area of 6.25cm^2 were used. The API X70 steel was supplied by a steel industry and contains 0.07wt-% of carbon and 1.58 wt-% of manganese, 0.013wt-% of phosphorous and 0.001wt-% of sulphur. Steel samples were analyzed after having been grounded with emery papers 120 and 220 grit.

The pH and conductivity values of the seven electrolytes studied are shown in Table 1. The chemical characterization of the synthetic river water (R) is shown in Table 2.

Electrolytes used	Abbreviations	*pH*	Conductivity (μS.cm-1)
River water	R	6	251 (28.4°C)
River water and glutaraldehyde	G	5	261 (28.4°C)
River water and sodium sulphite	S	5.5	547 (28.3°C)
River water and sodium hydroxide	N	12	10200 (28.3°C)
River water, sodium sulphite and glutaraldehyde	S + G	5.5	494 (28.3°C)
River water, sodium hydroxide and sodium sulphite	N + S	12	10200 (28.3°C)
River water, sodium hydroxide and glutaraldehyde	N + G	12	9870 (28.3°C)
River water, sodium hydroxide, sodium sulphite and glutaraldehyde	N + S + G	12	10200 (28.3°C)

Table 1
pH and conductivity of the electrolytes used in electrochemical testing.

Table 2
Chemical parameters
of synthetic river water.

Chemical parameters	Values (mg/kg)
SO_4^{2-}	50
Cl^-	50
SiO_2	4
Dissolved solids	332
Total hardness	230
Calcium hardness	210
CO_3^{2-} and HCO_3^-	180

The chemical composition of the river water was provided by the mining company. The content of sodium hydroxide (N) was 2.0 $g.L^{-1}$, sodium sulphite (S) concentration was 0.150 $g.L^{-1}$, and 0.070 $mg.L^{-1}$ of glutaraldehyde (G) was used. The formulation of the solution hibernation was provided by the mining company.

The Tafel analysis was performed with ±250 mV(AgCl/Cl^-) polarization in relation to the open circuit potential, and with a scan rate of 0.167 $mV.s^{-1}$. The electrochemical impedance spectroscopy was performed by using potential amplitude of 10mV(AgCl/Cl^-) and a frequency range of 100 kHz to 1mHz. The potentiostat used was a Princeton VersaStat, with the reference electrode of silver/silver chloride and the counter electrode of platinum. The EIS results were analyzed by using the ZSim Echem Software. Electrochemical tests are performed in triplicate.

3. Results

The polarization curves obtained using the Tafel analysis for polished steel samples are shown in Figure 1. The electrochemical parameters, obtained using the Tafel extrapolation, are shown in Table 3 for steel samples. The API 5L X70 steel in the solution of glutaraldehyde showed the highest corrosion potential and the lowest corrosion current density. The API 5L X70 steel in the hibernation solution showed a higher corrosion resistance than the steel in river water. Higher values of corrosion current density were obtained for the API steel in aqueous solution of sodium sulphite, and in solution of sodium sulphite with glutaraldehyde.

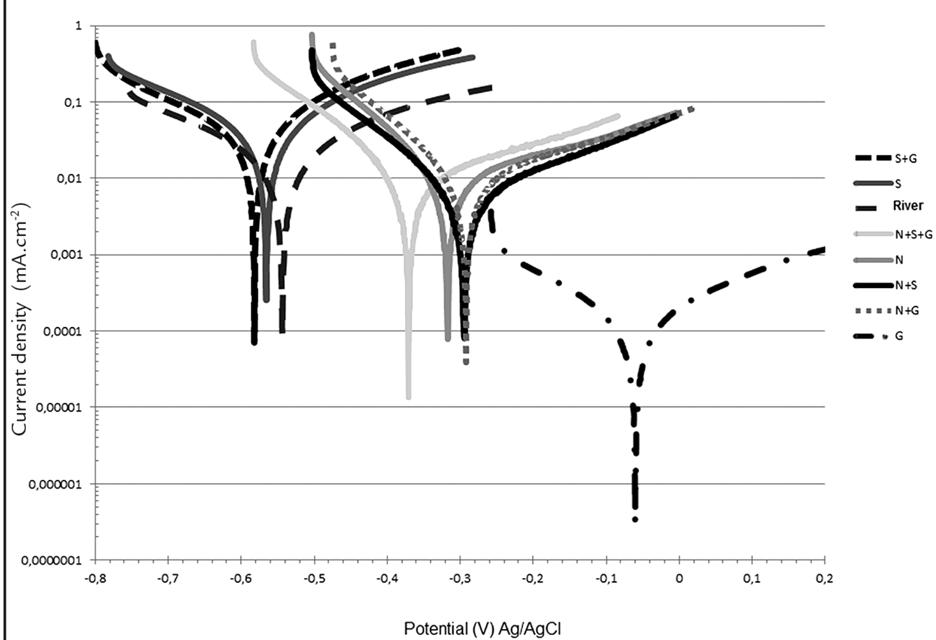

Figure 1
Polarization curves of polished API X 70 steel samples obtained using Tafel analysis.

Electrolyte	Ecorr/ mV(AgCl/Cl⁻)	icorr/ mA.m^{-2}	βa/ mV.decade^{-1} (AgCl/Cl⁻)	βc/ mV.decade^{-1} (AgCl/Cl⁻)	Rp/ kΩ.cm^2
G	-61±9	0.40±0.05	253±8	-353±45	1611±96 (Tafel) 1620±269 (EIS)*
N+G	-291±11	18.5±0.9	133±5	-382±49	23.2±1.0 (Tafel) 25.8±0.6 (EIS)*
N+S	-294±13	11.8±0.6	145±8	-320±32	36.7±2.6 (Tafel) 35.0±2.8 (EIS)*
N	-314±15	19.2±0.9	127±4	-438±61	22.3±1.8 (Tafel) 14.0±2.8 (EIS)*
N+S+G	-370±17	19.9±0.4	146±6	-438±56	23.9±1.4 (Tafel) 24.3±3.8 (EIS)*
River water	-543±20	76.1±10.6	439±13	-409±45	12.1±0.7 (Tafel) 12.7±0.7 (EIS)*
S	-565±13	145.8±17.4	439±11	-409±43	6.3±0.6 (Tafel) 5.0±0.6 (EIS)*
S+G	-581±15	135.1±21.6	433±17	-340±34	6.1±0.2 (Tafel) 4.6±0.6 (EIS)*

* Impedance values obtained at 30 mHz

Table 3
Electrochemical parameters of polished API X70 steel in electrolytes studied obtained using Tafel analysis and electrochemical impedance spectroscopy.

The Bode diagrams of phase angle (a) and impedance modulus (b) versus frequency for the API X 70 steel in all electrolytes are shown in Figure 2 (a). A maximum peak is identified between 1 and 10 Hz for the solutions of N+S+G, N+S, N+G, N and G. The maximum peak was shifted for lower frequencies for the steel in aqueous solutions of river water (R), sodium sulphite solution (S), and glutaraldehyde and sodium sulphite solution (S+G).

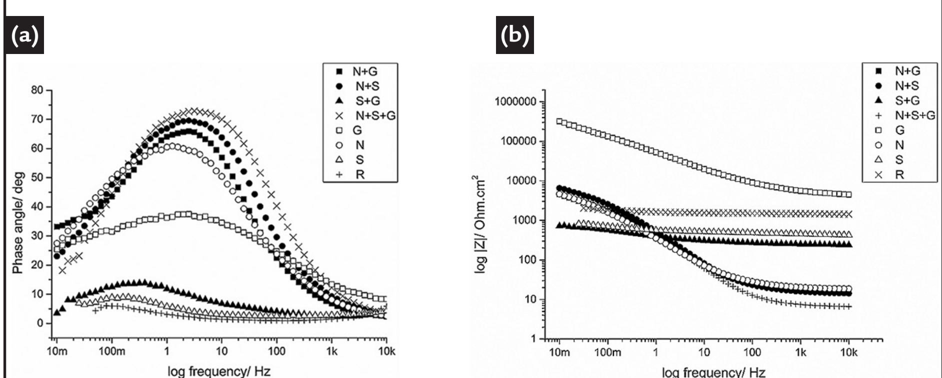

Figure 2
Bode diagram of phase angle (a) and impedance modulus (b) versus logarithm of frequency for the API 5L X 70 steel in river water (R), river water with sodium hydroxide (N), sodium sulphite (S), and glutaraldehyde (G); and aqueous solutions of (N+G), (N+S), (S+G) and (N+S+G).

Bode diagrams indicated one time constant for the API steel in all electrolytes, indicating a corrosive process on the surface of electrode. The impedance modulus at 30 mHz was shown in Table 3 for the API 5L X70 steel in each electrolyte studied (Silva *et al.*, 2006).

The Bode diagram of impedance modulus versus logarithm of frequency and the Nyquist diagram (Figure 3) indicated the highest corrosion resistance of API steel in solution of glutaraldehyde. The API steel showed an intermediate corrosion resistance in solutions containing sodium hydroxide: N, N+G, N+S, and N+S+G.

The Nyquist diagram (Figure 3) and Bode diagrams (Figure 2) showed a lower corrosion resistance of API steel in electrolytes of sodium sulphite, sodium sulphite and glutaraldehyde, and in river water. The impedance values for the API steel in river water, solution of sodium sulphite, and in sodium sulphite plus glutaraldehyde were lower than in electrolytes containing sodium hydroxide or containing only glutaraldehyde. The Bode diagram of phase angle showed lower values of phase angle at the maximum peak for the API steel in electrolytes of river water, sodium sulphite, and sodium sulphite plus glutaraldehyde, indicating a lower corrosion resistance of the API steel in these media.

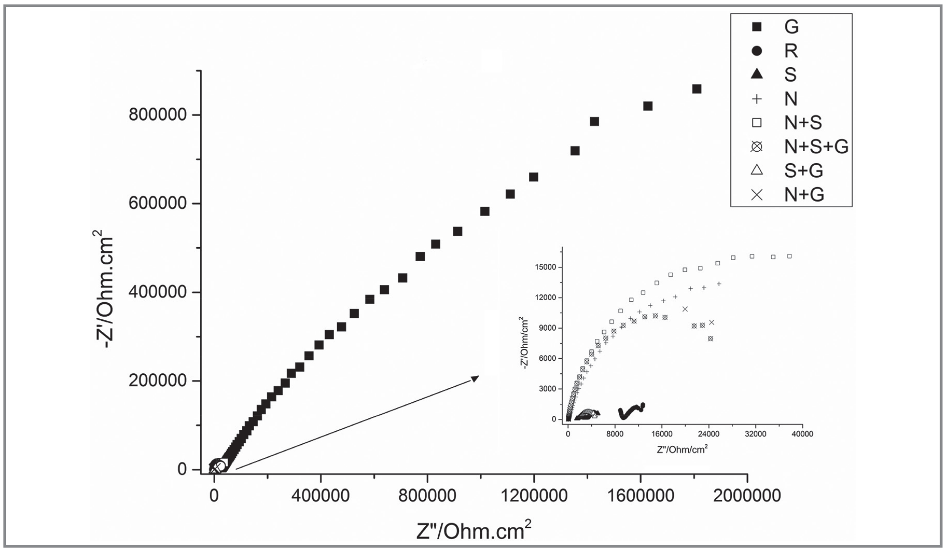

Figure 3
Nyquist diagram of API 5L X70 steel surface in aqueous solution of river water with sodium hydroxide (N), sodium sulphite (S), and glutaraldehyde (G); and aqueous solutions of (N+G), (N+S), (S+G) and (N+S+G).

The polarization resistance values obtained using Tafel analysis and electrochemical impedance spectroscopy (EIS) are of the same order of magnitude (Table 3). According to the Tafel and EIS results, the highest polarization resistance was obtained for the API steel in aqueous solution of glutaraldehyde. Lower values of polarization resistance were obtained for the steel in aqueous solution of sodium sulphite and sodium sulphite with glutaraldehyde.

The API steel in the hibernation solution (N+S+G) showed a polarization resistance three times the resistance of API X70 steel in river water. However, it is important to emphasize that the API steel in an aqueous solution of glutaraldehyde showed a charge transfer resistance two orders of magnitude higher than in hibernation solution which is proposed by the mining company.

4. Discussion

The API 5L X70 steel showed the highest corrosion potential, the highest polarization resistance, and the lowest corrosion current in the glutaraldehyde aqueous solution (Table 3). The glutaraldehyde ($C_5H_8O_2$) has two unsaturated C=O end-groups and hydrolyses in water and produces hydrates which adopt several structures including cyclic structures (Zhou *et al*., 2014). It is well known that glutaraldehyde acts as a cross linker (Campos *et al*., 2013) and the hydrolyzed glutaraldehyde has additional hydroxyl groups and can interact with FeOOH molecules to produce a protective layer.

The Kramers-Kroning (K-K) relationships were applied to check the validity of experimental results. Any system that satisfies the a priori conditions of linearity, stability, and causality must satisfy the K-K relationships. A good agreement between the experimental and transformed impedance data for both real and imaginary components validates the EIS data (Zheng *et al*., 2014).

Analyzing Bode diagrams, one time constant is identified for the corrosive process of the API steel in all solutions.

According to Pourbaix diagrams for iron-water system at 25°C, the iron passivates in alkaline media, above pH 9 (McCafferty, 2010). The addition of sodium hydroxide to the river water improved the corrosion resistance of the API X70 steel in these environments (Table 3, Figure 2 and Figure 3).

The API steel in solution of sodium hydroxide and glutaraldehyde showed a polarization resistance of 25.8kΩ.cm², lower than the polarization resistance of steel in media of aqueous solution of glutaraldehyde. Monomeric glutaraldehyde can polymerize by an aldol condensation reaction which produces alpha, beta-unsaturated polyglutaraldehyde (Rembaum *et al*., 1978).This reaction usually occurs in alkaline pH values and can occur in the media containing sodium hydroxide and glutaraldehyde of pH 12 (Rembaum *et al*., 1978). The polyglutaraldehyde can contribute to form a protective layer on the steel surface, and literature reported that the reaction of polyglutaraldehyde with hydrophilic low molecular weight molecules such as iron hydroxide was found to be faster than that of the monomer (Ortega-Toledo *et al*., 2011). In media containing glutaraldehyde and sodium hydroxide, the glutaraldehyde can react with the hydroxyl group of the iron hydroxide to form a protective layer, but also can react with the hydroxyl groups of the sodium hydroxide present in the aqueous solution. As there is a competition for hydroxyl ions that can react with both ferrous ions forming iron hydroxide or with glutaraldehyde, sodium hydroxide and glutaraldehyde compete for adsorption on steel surface.

The highest value of corrosion current density and the lowest value of polarization resistance of API X70 steel were obtained in media containing sulphite. The pH of solutions containing sulphite (S) was 5.5. The corrosion inhibition of steel in a closed system containing sodium sulphite at room temperature has been established (Gouda and Sayed, 1973). Steady-state potential as well as weight loss measurements indicated that sodium sulphite did not only remove O_2 from the solution but also brought cathodic protection providing another anodic reaction of sulphur oxidation which competes with the iron oxidation. It was also found that sodium sulphite could tolerate the presence of Cl^-, SO_4^{2-} and S^{2-} (Gouda and Sayed, 1973). Sodium sulphite is a scavenger of oxygen and inhibits the cathodic reaction of oxygen reduction. However, it also inhibits the formation of iron oxide/hydroxide on the steel surface, which may partially be a barrier to dissolution of iron. Furthermore, in the acidic medium of sulphite, the cathodic reaction of hydrogen reduction can occur. In river water solution containing sodium sulphite and glutaraldehyde, the polarization resistance was lower than the polarization resistance of steel in medium containing only glutaraldehyde(G) due to the reaction between glutaraldehyde and sodium sulphite. The sodium sulphite reacts with glutaraldehyde producing sodium hydroxide and glutaraldehyde-bisulphite, increasing pH but inhibiting the interaction of glutaraldehyde and the layer of iron oxide/hydroxide (Zhou *et al*., 2014).

5. Conclusions

The highest corrosion resistance of polished API 5L X70 steel was observed when the steel was immersed in the solution of glutaraldehyde in the river water. The API 5L X70 steel showed the highest corrosion potential and polarization resistance and the lowest corrosion current in this medium. An aqueous solution of glutaraldehyde as a biocide and corrosion inhibitor showed the highest efficiency as a hibernation solution of API 5L X70 pipelines.

The lowest corrosion resistance of polished API 5L X70 steel was obtained in media containing sulphite.

The polished API 5L X70 steel in hibernation solution (N+S+G) showed a polarization resistance three times the resistance of API 5L X70 steel in river water, which demonstrated the efficiency of the hibernation solution proposed. However, it is important to emphasize that the API steel in an aqueous solution of glutaraldehyde showed a charge transfer resistance two orders of magnitude higher than in hibernation solution which is proposed by the mining company.

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