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INIBIÇÃO DE INCRUSTAÇÃO EM TUBULAÇÕES POR POLIACRILATOS

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RESUMO

Uma instalação de tratamento de minérios localizada no Quadrilátero Ferrífero (Brasil) foi estudada visando conhecer o comportamento da incrustação em tubulações de água de processo. A determinação dos melhores polímeros inibidores de incrustação foi feita por testes de eficiência dinâmica, por medições utilizando monitoramento ultrassônico e acompanhamento da variação em massa de cupons de prova introduzidos no sistema. Uma análise preliminar foi realizada para o líquido bombeado e foi possível observar uma alta correlação entre a dureza da água e a taxa de formação de incrustação. Conforme determinado pela dissolução em ácido clorídrico e espectroscopia de absorção na região do infravermelho, a escala é carbonática devido à presença de íons cálcio. Os testes de eficiência dinâmica mostraram que Polystabil VZ e Polystabil KWS (poliacrilatos) apresentaram um caráter anti-incrustante, sendo que o Polystabil KWS possui uma eficiência mais elevada. A inserção de cupons de prova forneceu resultados semelhantes em relação ao nível de eficiência. Polystabil KWS resultou em valores de incrustação dentro de parâmetros aceitáveis para as dosagens de 6 ppm. Como resultado deste estudo, a aplicação industrial do produto testado já foi adotada em uma empresa de mineração de grande porte.

PALAVRAS-CHAVE: Incrustação, Polystabil, poliacrilatos.

FOULING CONTROL OF CARBONATES IN PROCESS WATER PIPES BY THE ADDITION OF POLYACRYLATES

ABSTRACT

An industrial ore treatment facility, located in the Iron Quadrangle (Brazil), was used for the study of scale formation in pipes. Scale formation is predominantly carbonatic on iron mineral processing. The determination of the best fouling inhibitor polymer was done by dynamic efficiency tests, by fouling measurements performed by ultrasonic monitoring (using *On Guard 3S*) and by mass monitoring of carbon steel test coupons introduced into industrial pipes. A preliminary analysis was performed for the pumped liquid and it was possible to notice a high correlation between water hardness and scale formation rate. As determined by dissolution by hydrochloric acid and absorption spectroscopy in the infrared spectral region, the scale is carbonatic due to the presence of calcium ions. The dynamic efficiency tests showed that Polystabil VZ and Polystabil KWS (polyacrylates) presented an antifouling character, Polystabil KWS having higher efficiency. The insertion of fouling test coupons provided similar results regarding the efficiency level. Polystabil KWS has resulted in scale values within acceptable parameters for dosages of 6 ppm. As a result of this study, industrial application of the tested product was already adopted in a large iron ore mining company.

KEYWORDS: Fouling, Scale Formation, Polystabil, Polyacrylate.

1 INTRODUCTION

Fouling can be defined as the deposition of compounds on the surface of industrial pipes due to the presence of calcium and magnesium ions from several minerals. The precipitation is resulted from three processes which interact in same time: supersaturation, nucleation and crystal growth. The supersaturation occurs when the solubility limit of certain dissolved salt is exceeded, being strongly dependent on temperature, pH and ion concentration (Muryanto et al., 2014). Nucleation happens in the bulk of solution producing a layer on pipe surface by adsorption. The crystal growth occurs from the aggregates formed by the nucleation process, generating bigger granules and increasing scale formation (Martinod et al., 2008).

There are a few studies on scale inhibition mechanisms, especially due to complex interactions between the ions in solution. Scale inhibition is made by adsorption of reagents, nucleation of granules and changes in crystal growth as well as chemical reactions. Chemical methods consist of adding strong acids to lower the pH or adding chelating agents to complex Ca^{2+} (among others) ions. These techniques are expensive and have terrible consequences to environment (Ketrane et al., 2009). Commercial polymer-based fouling inhibitors use mechanisms such as dispersion, ion sequestration, and adequate modification of the morphometric features of precipitates and their aggregates. In line with this statement, the main probably mechanisms are the threshold effect, the crystal distortion, the pulp dispersion and chelation. Shakkthivel and Vasudevan indicate that threshold inhibition is the most appropriate method to control scale formation (Shakkthivel and Vasudevan, 2006).

Polyelectrolytes can prevent the crystal growth due to the strong chelation in their functional groups. The retardation of crystal formation results in irregular crystals and the structure distortion could cause internal fractures and avoid precipitation. Polycarboxylic acids can also chelate Ca^{+2} ions and inhibit the calcium carbonate formation also generating distortions on the crystal (Yang et al, 2001). The most common polycarboxylic are the polyacrylic acid, polymethacrylic acid and polymaleic acid.

The carboxylic acids are considered to have no influence on calcium carbonate nucleation; however, they are effective growth modifiers by competition. It can be explained by assuming a stronger affinity of the carboxylic acids for $CaCO_3$ particles than for Ca^{2+} ions in the solution. The main mechanism of inhibition is the adsorption of the carboxylic acids into the surface of calcium carbonate. Although, the degree of inhibition depends on the molecular structure and the dosage of reagents in system (Wada et al., 2001).

The performance of polyacrylates (derived from polyacrylic acid) is very studied in mineral processing as a dispersant in other operations and is becoming more common in antiscaling application. Castro discusses the use of several reagents and observed that sodium hexametaphosphate and sodium polyacrylate were the most efficient dispersants for iron ore beneficiation (Castro, 2012). These reagents are always anionic (negative charged) and inhibit the precipitation of several crystallographic phases. The main mechanism of dispersion is the charge increase in the electric double layer and it is resistant to high ionic forces (Bulatovic, 2007). Lierde (1980) presents the ionization range of polyacrylates as a function of pH and observer that polyacrylates show complete ionization at pH around 6.5. In accordance with Le Chatelier's principle, the ionic form (COO^-) is the prevalent species in the basic range, while the molecular form (COOH) is the majority in the acidic range.

One of the most common types of fouling is the formation of calcium carbonate (in various crystallographic forms) on the surface of pipes, showing also varied texture. The formation of calcium carbonate occurs by the reaction between the water present in the suspensions, the carbon dioxide (CO_2) and the calcium ions that also promote the water hardness (Fevang, 2017). Water hardness is understood as the ability to form precipitates by calcium and magnesium ions present in the pulp and its calculation is done by the relation of concentrations of components (Rice et al., 2005)

The calcium carbonate precipitates following the (simplified) equations below. Ketrane et al. (2009) presents electrochemical measurements to investigate calcium carbonate formation during scaling processes.

$$O_{2\,(dissolved)} + 2\,H_2O + 4\,e_0^- = 4\,OH^- \qquad (1)$$

$$Ca^{2+} + HCO_3^- + OH^- = CaCO_{3\,(s)} + H_2O \qquad (2)$$

The standard electrochemical potential referring to Equation 2, according to Fiorucci & Benedetti Filho (2005), is E° = 0.401 V. The rate of this reaction, however, depends on the concentration of aqueous oxygen (reactant in Equation 1), which depends on the partial pressure of oxygen and water vapor in the surrounding atmosphere (Gnaiger, 2011), and is ultimately given by Henry's law, which establishes the proportionality of the dissolved gas with its partial pressure. Thus, it follows that the equilibrium oxygen molar concentration in pure water is given by:

$$\left[\mathrm{O}_{2(aq)}\right] = K_H * p_{\mathrm{O}_2} = K_H * \left(p - p_{\mathrm{H_2O}}\right) * X_{O_2} = K_H * (p - \phi * p_{sat}) * 0.20946 \qquad (3)$$

Where: $[O_{2(aq)}]$ — concentration of dissolved oxygen [mol/L]; p_{O2} — partial pressure of oxygen in the air [Pa]; p_{H2O} — partial pressure of water in air [Pa]; p_{sat} — saturation pressure of water in the air [Pa]; f — relative humidity of air. The constant X_{O2} = 0.20946 is the oxygen molar concentration in today's Earth atmosphere. The value of Henry's constant for oxygen in pure water is K_H = 1.273 x 10^{-3} kmol/(m³.Pa) at room temperature (or 1.29 x 10^{-3} mol/(L.atm)). Naturally, due to the salting-out effect, this value should be decreased correspondingly when dealing with saline water.

Calcium carbonate crystallizes in different crystallographic forms, being calcite, aragonite and vaterite the more commons ones. Calcite is more stable, whereas aragonite and vaterite are thermodynamically unstable crystals and can be transformed into calcite (Muryanto et al., 2014). Differentiation of the crystallographic forms of calcium carbonate can be accomplished by comparing the various transmittance spectra in the infrared spectral region. Differentiation of minerals by this method is possible because the bonds among different atoms has resonance energies at different wavelengths for each mineral (Valadão & Araujo, 2007).

One of the methods of forecasting carbonate precipitation is based on the Langelier saturation index (LSI). This index provides a tendency value to form fouling. Negative values indicate that there will be no precipitation and fouling formation. On the other hand, positive values indicate the formation of calcium carbonate (Anthony et al., 2011).

$$LSI = pH - 44.25 + \left(\frac{\log_{10} TDS - 1}{10}\right) + 13.12 * \log_{10}(T + 273)) + \log_{10} Ca^{+2} + \log_{10} A) \tag{4}$$

Where: LSI — Langelier saturation index (LSI) [-]; pH — suspension pH [-]; TDS — total solids dissolved [ppm]; T — temperature [ºC]; Ca^{+2} — calcium concentration [ppm]; A — alkalinity [ppm].

This work aims to evaluate the application of Polystabil VZ and Polystabil KWS (antifouling agents from Solenis company), indicating a dosage sufficient to slow or inhibit the scale formation in the mineral industry pipes. The products of the Polystabil line act in a way to reduce scale formation in pipes. Polystabil is a scale inhibitor composed of aqueous sodium polyacrylate solution and has very good dispersive properties and excellent stability for the treatment of high hardness waters. According to the manufacturer, it can be applied as supplied or diluted in water in any ratio.

2 MATERIAL AND METHODS

Initially, a characterization of water transported in the pipe was done aiming to determine the water hardness and pH. Samples of formed scale were removed for identification of the main compounds. A comparison was made between the sample analyzed and the spectra in the infrared region. Another method used to characterize the compound formed is the reaction for 6 hours with hydrochloric acid (HCl), thus identifying the existence of carbonate base.

According to the work of Huang and Kerr (1960), the spectrum of infrared absorption of calcite is characterized by three intense peaks between the ranges of 1449.3 and 1434.7, 886.5 and 865.8, and 748.5 and 713.3 cm^{-1}; and two peaks of lower intensity: between 2551.0 and 2518.9, and between 1828.2 and 1811.6 cm^{-1} (Huang and Kerr, 1960). By comparison of spectra, it is possible to verify that the calcium hydroxides have a characteristic peak around 3600 cm^{-1}, whereas the carbonates do not show this peak. Thus, it is possible to differentiate hydroxides from calcium carbonates (Legodi et al., 2001).

Performance evaluation of inhibition can be done by dynamic tests, aiming to evaluate the scale formation by varying temperature, concentration of ions and water hardness (Rebeschini, 2010). Dynamic efficiency tests consist of a system for pumping and recirculating solutions (Figure 1) and constant pressure measurement by the liquid passage through an orifice. At each curve, the increase in pressure indicates the onset of precipitation of the crystals and ultimately resulting precipitated deposits on pipes walls. Performance is evaluated through the pressure versus time curve for each dosage of added reagent. If incrustation occurs, the pressure values are increased indicating the decrease in the effective diameter of the piping. In the present work, Polystabil KWS and Polystabil VZ were tested using dosages of 2 ppm, 4 ppm and 6 ppm.

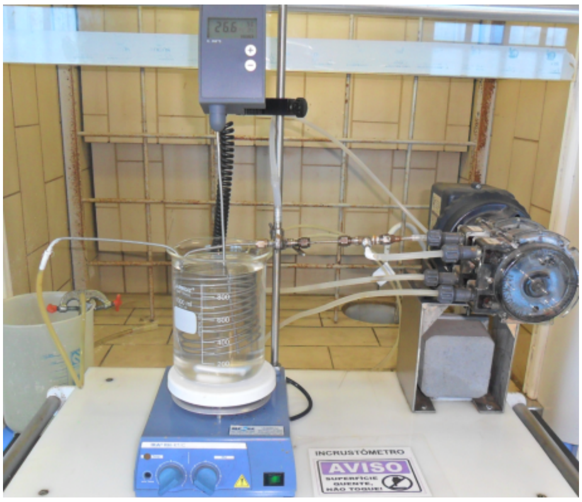

Figure 1 - Apparatus for evaluating the performance of reagents

Polystabil KWS is a low molecular mass polycarboxylate. It is non-volatile and practically inert to hydrolysis within the temperature range of its application. Polystabil KWS exhibits excellent effectiveness in stabilizing carbonate hardness even under difficult conditions, thus ensuring high cooling performance for long periods. The product's versatility allows for high flexibility. Because of its molecular mass distribution, Polystabil KWS acts not only as a scale inhibitor but also as a dispersing agent. Its scale inhibiting effect acts mainly against the substances $CaCO_3$, $CaSO_4$, silicic acid, silicic silicates and $BaSO_4$.

Polystabil VZ is a low molecular mass copolymer, phosphorus-free, non-volatile and practically stable to hydrolysis at working temperatures. Polystabil VZ inhibits the formation of scale in the evaporators, formed by the presence of hardness, typically manganese and calcium ions in the presence of oxalate, carbonate and sulfate ions. Incrustations reduce heat transfer in the evaporator stage, causing higher unit costs. The way in which Polystabil VZ works can be explained through the concept of the "threshold effect", that is, used in quantities much lower than the stoichiometric quantity calculated based on the hardness components. The threshold concentration depends on the initial hardness and the duration (retention time) in the equipment, subjected to thermal factors. Inhibition of scale formation starts in the range of 2 to 20 ppm.

Ultrasound monitoring was used to quantify material deposition on the inner walls of the pipes. The *On-Guard 3S* is an online ultrasonic from Solenis (Figure 2). An ultrasonic pulse is emitted from a probe to the ends of the pipe surface and compared to the surface absent from incrustation. The comparison between the return times for the reflected wave in both conditions provides the distance between the sensor and the pipeline wall, allowing measuring the scale thickness accurately up to 1 micrometer.

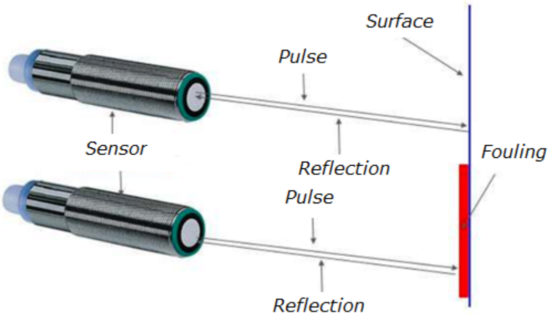

Figure 2 — Principle of operation of *On Guard 3S*

Another method of determine the thickness of scale formation in pipes is the introduction of test coupons. These coupons are made of carbon steel, numbered and with standardized measures. After a period of exposure to the physicochemical environment under study, the coupons are weighed again, being able to evaluate, the increase of the thickness due to the increase of mass by incrustation. The equation used to quantify the scale thickness is given below and the most commonly used unit to express the thickness increase rate is mm per year.

$$\varepsilon = \frac{\Delta mass}{\rho_{Caco3} * A * t} \tag{4}$$

Where: ε — thickness increase speed [m/s]; Δ_{mass} — mass variation [kg]; ρ_{CaCO_3} — specific mass of calcium carbonate (2,700 kg/m^3); A — area of the coupon (0.002118 m^2); t — exposure time [s].

3 RESULTS AND DISCUSSION

The values obtained for the process water samples analyzed were shown in the following figure.

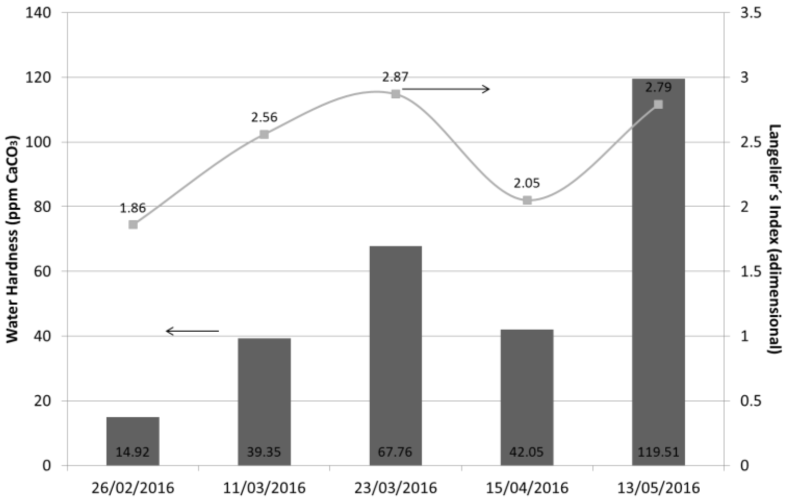

Figure 3 — Results of process water analysis

It is possible to observe that the process water has a high hardness. By Langelier´s Index (LSI), it is possible to verify that all samples have an incrustation character (LSI > 0), and a correlation can be established between the scale level and the hardness of the pulp. The complete dissolution of sample removed from the pipes by hydrochloric acid was observed, which proves that is mainly carbonatic.

The transmittance spectrum obtained in the infrared spectral region for the sample is shown in Figure 4. It is possible to observe that there is the majority formation of calcium carbonate, due to the characteristic valleys (of greater absorption). The carbonate differentiation for the hydroxides can be performed by observing the absence of a characteristic valley at 3600 cm^{-1}, showing that sample is calcium carbonate formed.

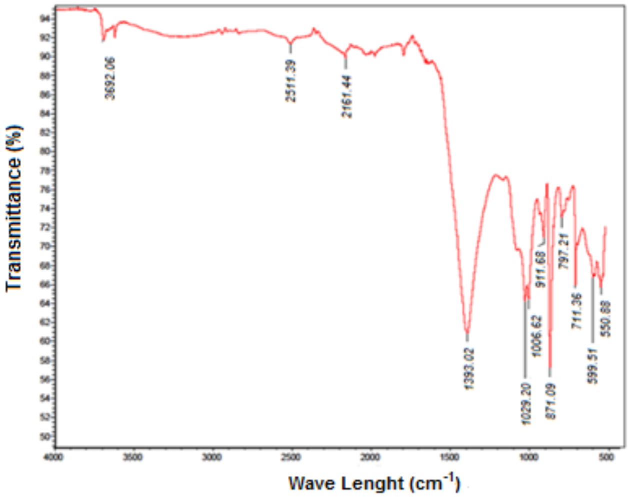

Figure 4 — Spectrum obtained for samples

It can be observed that all the analyzed products tested presented better performance to the test in the absence of reagents (black line in Figure 5), proving the antiscaling character of Polystabil. Polystabil KWS presented superior performance to the Polystabil VZ product at all analyzed dosages.

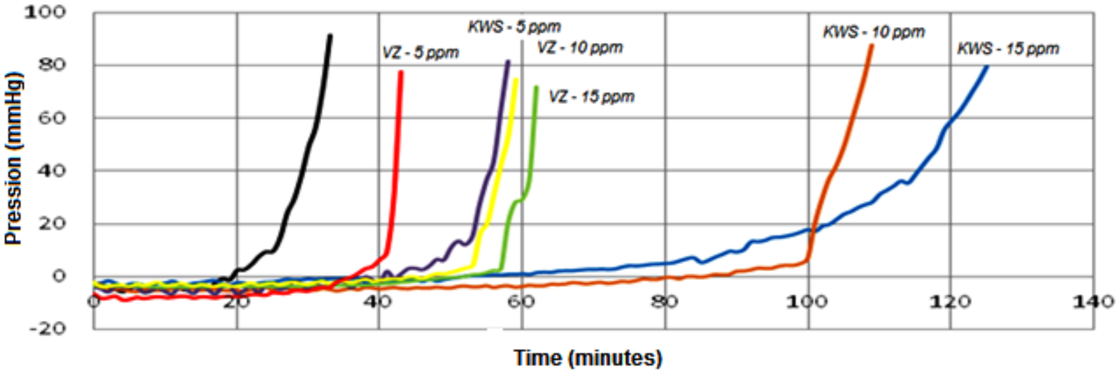

Figure 5 — Dynamic efficiency assay

The results obtained with the insertion of test coupons for each dosage of polyacrylates indicated that the addition of the Polystabil KWS reagent resulted in a decrease in fouling rate. Scale rates of less than 10 mm per year (3.171×10^{-10} m/s) are considered acceptable and such conditions were obtained for Polystabil KWS dosages between 4 and 6 ppm. For the dosage of 2 ppm reagent, it is noted from the following figure that the scale values do not reach the stated target. The Figure 6 illustrates a boxplot, showing the interquartile range and the lower and upper limits of the fouling rate values.

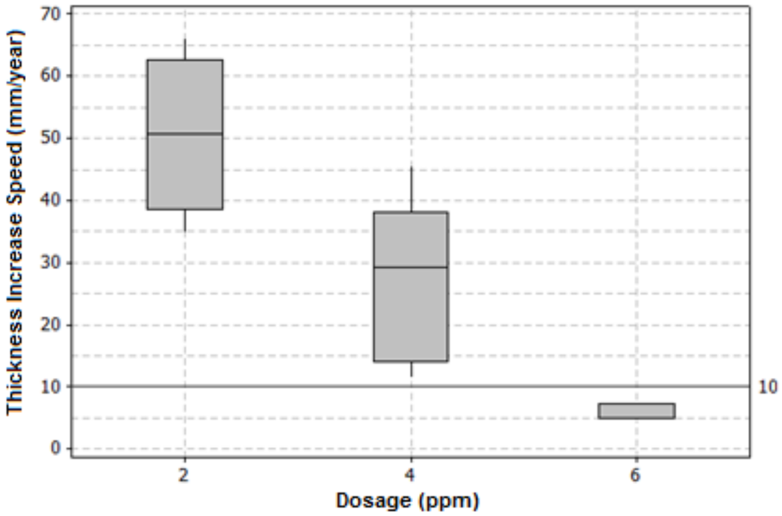

Figure 6 — Scale formation rate versus Polystabil KWS dosage.

The following figure illustrates the visual appearance of the test coupons with the respective analyzed reagent dosages. Addition of Polystabil KWS at the 6-ppm dosage caused a very low levels of scale formation, with mean values below the target established (10 mm / year). It is necessary to point out that the 6-ppm dosage is lower than the dosage of usual antifouling reagents currently used in the same processes, demonstrating the applicability of the product tested in the pumping systems.

2 ppm 4 ppm 6 ppm

Figure 7 — Photographs of coupons with respective dosages

It is important to note that the decreasing fouling values occur even in slurries with high hardness values. The hardness values increase as more reagents are added, as there is no precipitation of the calcium ions and so they are dissolved (or complexed) in the slurry.

It is also possible to observe that the average fouling rate increases to increasing hardness values. That is, the pulp that has higher concentrations of calcium and magnesium will have a greater tendency to form calcium carbonate scale in the same dosages of reagents. It is possible to see in the figure below the evolution of the scale values, hardness and dosage of reagents with the passage of time.

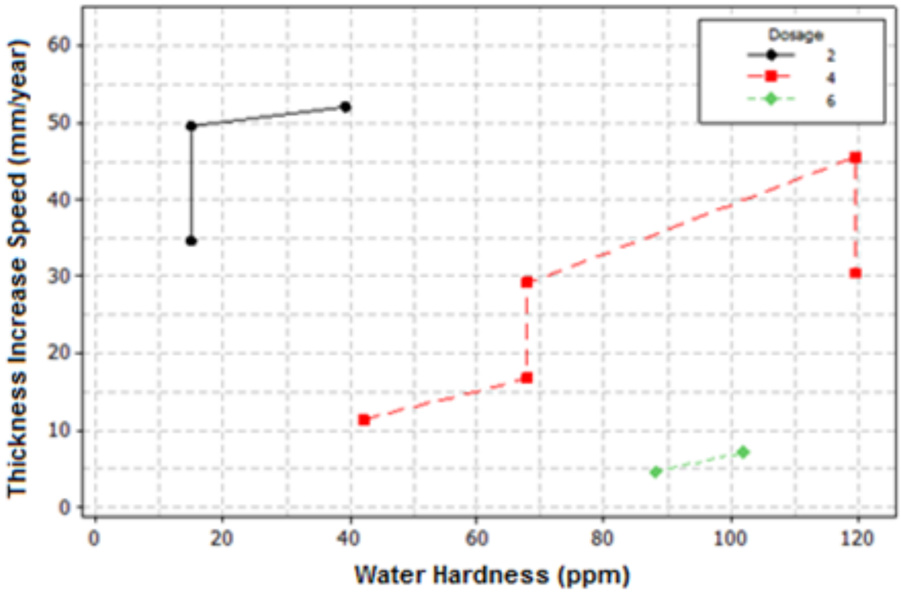

Figure 8 — Scale formation varying water hardness.

The values obtained by the *On Guard 3S* ultrasonic scale analyzer show the tendency for fouling at low reagent dosages, while the fouling tendency remains constant at high reagent dosages (test performed in July 2016). This behavior can be seen in Figure 10. It is possible to observe in the figure an abrupt decrease in the values of incrustation (May, 1st 2016). This is due to maintenance of the equipment, thus zeroing out the scale values in the measured period. However, it is possible to verify that the trend of formation of the crystals prior to the cleaning of the equipment has continued to prove the measurement efficiency of the apparatus.

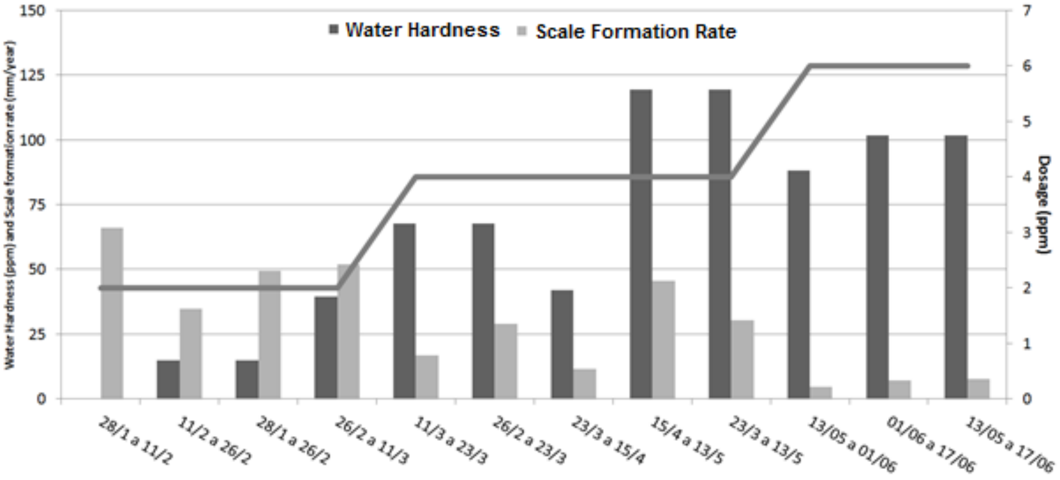

Figure 9 — Parameters obtained by coupons insertion

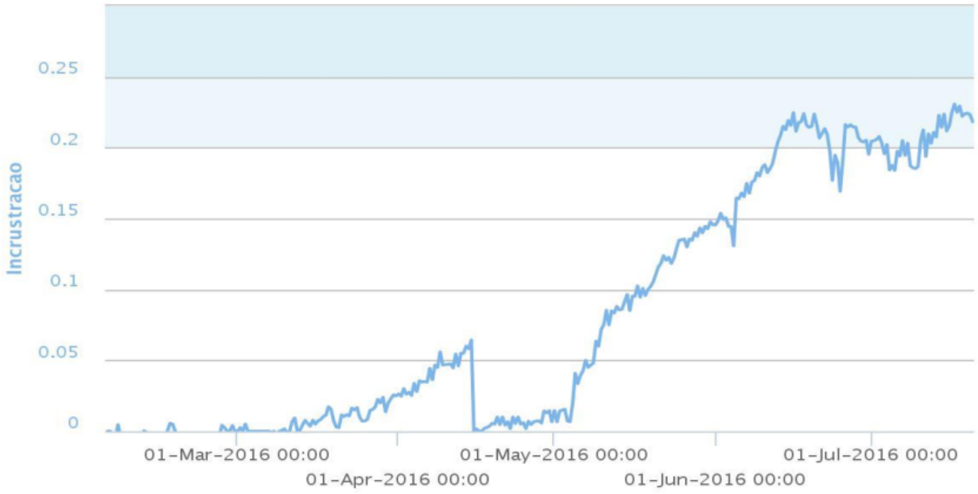

Figure 10 — Parameters obtained by the On Guard 3S equipment

4 CONCLUSION

From the initial analyzes, it is possible to identify a high correlation between the hardness of the analyzed process waters and the scale level in the pipes. The identification of the compounds formed in the pipelines of the mineral processing industry used as a study was carried out by dissolving in hydrochloric acid and analyzing the spectrum of the minerals removed. The analyzed samples consisted essentially of calcium carbonate ($CaCO_3$). Dynamic efficiency tests have shown that Solenis's antiscaling product line is efficient under the proposed conditions and Polystabil KWS had higher antiscaling character than Polystabil VZ under all analyzed dosages. The introduction of controlled mass test coupons and the analysis of data obtained by the ultrasonic scale analyzer equipment (the registered trademark *On Guard 3S*) validated the improvement obtained in the previous tests. There was reduction of scale for dosages of 2 and 4 ppm, but the target was not reached. The dosage of 6 ppm showed lower levels of fouling, allowing an adequate pumping, thus reaching the initial objectives of this work.

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