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CHEMICAL REMOVAL OF IRON SULFIDE DEPOSIT IN PIPES FROM OIL AND SOUR GAS PRODUCTION

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ABSTRACT

Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) present in oil and natural gas cause mild steel corrosion, potentially resulting in formation of corrosion product layers on the internal surfaces of tubulars. In field experiences relating to the research reported herein, this has led to restrictions on the flow of water produced from a three-phase horizontal separator. This paper demonstrates a specific case of chemical removal of relatively hard, dark, and adherent heterogeneous deposits on the internal surface of the pipe. The phases involved in this process are iron sulfide, iron oxides and calcium carbonate existing as scales/corrosion products. To evaluate their dissolution, laboratory tests were conducted using hydrochloric acid (HCl) with additions of chlorine in the form of calcium hypochlorite [$Ca(ClO)_2$]. Appropriate safety measures were taken employed, considering hazards associated with chlorine and toxicity of hydrogen sulfide. The treatment regime had 87 % effectiveness for scale removal in combination with propargyl alcohol (2-propyn-1-ol) as a corrosion inhibitor.

Keywords: *chemical removal, iron sulfide, calcium hypochlorite, corrosion inhibitor, scale, propargyl alcohol.*

INTRODUCTION

Inspection and maintenance at the onshore oil and gas treatment plant revealed adherent deposits on the tube internals in the three-phase horizontal separators causing a reduction of productivity as shown in the scale of a horizontal separator tube exposed in Fig. 1. This plant is fed continuously by 22 oil wells and has operated uninterrupted for 20 months, with some emergency shutdowns. It is important to note that the oil/water ratios of each well are quite varied. The formation waters from these wells are composed of 30 % sodium chloride (NaCl) with calcium ion (Ca^{2+}) concentration ranging from 400 to 1320 parts per million (ppm), magnesium ion (Mg^{2+}) concentration varying from 120 to 630 ppm and potassium (K^+) from 50 to 120 ppm. Considering the existence of carbon dioxide (CO_2) in the wells that feed the oil and gas treatment plant, it is likely that the existence of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) in the formation water can generate calcium carbonate-based scale according to the following reactions [1 - 3];

$$Ca^{2+} + 2HCO_3^- \rightarrow Ca(HCO_3)_2 \tag{1}$$

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O \tag{2}$$

The presence of other constituents in the formation water, such as alkaline earth ions (like barium and strontium, Ba^{2+} and Sr^{2+}, respectively), bicarbonate (HCO_3^-) and sulfate (SO_4^{2-}) ions, and suspended solids, will be reported as they can contribute, directly or indirectly, to the formation of deposits.

The most common cations are sodium, potassium, calcium, and magnesium. The Ba^{2+} and Sr^{2+} ions can form barium sulfate ($BaSO_4$) and strontium sulfate ($SrSO_4$), respectively. However, the sum of their concentrations is less than 10 ppm, meaning the formations of precipitates are irrelevant. However, suspended solid concentrations of over 1000 ppm were also found. Suspended solids are those which do not dissolve in water and can be removed or separated by filtration. Chemical analysis revealed the presence of mud, clay, silt, iron oxides, sulfides, and hydroxides.

Considering the relationship between the occurrence of the deposits and the corrosiveness of this formation water, it can be said that H_2S (from 10 to 150 ppm) and CO_2 concentrations (from 50 to 300 ppm) were random and discontinuous, depending on the characteristics of the production wells that feed the oil and gas treatment plant. Generally, the concentrations of hydrogen sulfide found in natural sour gas and crude oil vary from 10 ppm to 100000 ppm, depending directly on the petroleum and gas and the geological diversities of the reservoir rock [4 - 8].

However, sulfide is most common in the presence of ferrous ions (Fe^{2+}). The formation of dispersed iron sulfide (FeS) particles can be explained through the corrosion associated with H_2S may be defined as the total, partial, superficial or structural deterioration of carbon steel caused by chemical or electrochemical attack, associated or not with mechanical process [9].

Chemical corrosion associated with H_2S is a process that corresponds to an attack by anhydrous H_2S (without the presence of water) directly on carbon steel and without the transfer of electrons, with base in the reaction:

$$Fe + H_2S\ (g) \rightarrow FeS + H_2 \tag{3}$$

Electrochemical corrosion associated with H_2S solution is a spontaneous process that may occur when the metal or alloy is in direct contact with an electrolyte, where the anodic and cathodic reactions occur simultaneously. In this case, the electrolyte is an H_2S solution in water, which breaks up through the following reactions:

$$H_2S\ (g) + H_2O \rightarrow H_2S\ (aq) \tag{4}$$

$$H_2S\ (aq) \rightarrow H^+ + HS^- \tag{5}$$

$$HS^- \rightarrow H^+ + S^{2-} \tag{6}$$

$$HS^- + OH^- \rightarrow H_2O + S^{2-} \tag{7}$$

The transfer of the electrons from the anodic region to its cathodic counterpart takes place through a metal conductor, with a diffusion of anions and cations in the solution completing the electrical circuit. The mechanism representing carbon steel (Fe) electrochemical corrosion in aqueous solutions containing hydrogen sulfide in acid pH or neutral/alkaline is presented:

$$Fe - 2e^- \rightarrow Fe^{2+}\ \text{(anodic reaction)} \tag{8}$$

$$2\,H^+ + 2e^- \rightarrow H_2 \text{ and } 2H_2O + 2e^- \rightarrow$$
$$\rightarrow H_2 + OH^-\ \text{(cathodic reactions)} \tag{9}$$

The concentrations of $[Fe^{2+}]$ and $[S^{2-}]$ produced in the solution reach the solubility product value and consequently form ferrous sulfide through the following reaction [10, 11]:

$$[Fe^{2+}] + [\,S^{2-}] \rightarrow FeS \tag{10}$$

The precipitation of FeS particles can also be explained by the reaction of soluble ferrous ions (Fe^{2+}) present in the reservoir waters with the high levels of hydrogen sulfide. The reaction kinetics experiments performed with variations in H_2S concentration, pressure, temperature, Fe^{2+} concentrations, and carbon steel samples show the various forms of iron sulfides that can be formed from formation waters or from corrosion of carbon steel. The forms of sulfides shown are: mackinawite ($Fe_{1+x}S$) where ($0< x < 0.30$), troilite (FeS), pyrrhotite ($Fe_{1-x}S$) where ($x = 0$ to 0.2), greigite (Fe_3S_4), and pyrite (FeS_2). Generally, the most common forms that occur in oil well scale, with occurrence of H_2S, are mackinawite, troilite, and pyrrhotite [12 - 16].

H_2S is an unpleasant smelling, extremely toxic, colorless gas that is denser than air. These concentrations prompt concern due to the toxic effects of hydrogen sulfide on human beings, as well as its corrosivity when in contact with materials and equipment, which usually results in deterioration or fractures of steel tubes or equipment with catastrophic consequences [9, 16 - 18].

The operational and occupational point of view is a large industrial apprehension and it is important to alert attention to the conditions of safety in relation to hydrogen sulfide. Due to its toxicity, hydrogen sulfide irritates the eyes and/or affects the nervous and respiratory systems. Depending on its concentration, it can kill a human being in a matter of minutes. Thus, should an accident occur that involves a hydrogen sulfide leak, the consequences may reach massive proportions: endangering human lives, threatening the integrity of industrial assets, and jeopardizing the environment [12, 19 - 22].

The present work aims to investigate the formation of the scale that occurred in the tube of the horizontal separator (shown in Fig. 1), propose a process to remove this incrustation using hydrochloric acid (HCl) with additions of chlorine (Cl_2) in the form of calcium hypochlorite [$Ca(OCl)_2$], and preserve the surface of the carbon steel pipe using corrosion inhibitor (propargyl alcohol). It is observed that the scale is about 22 mm thick, hard, compact, rough, and adherent to the metal surface. The scale occurring in the horizontal separator tubes causes restrictions of 40 % to 75 % in the formation water flow, consequently causing loss of productivity in the oil treatment process.

EXPERIMENTAL

Chemical analyses

To identify the constituents of the scale presented in Fig. 1, five samples were removed: one near the surface of the carbon steel, two in the central part, and two in the peripheral part. The crystalline chemical species were determined by X-ray diffraction (XRD) with a D8-Bruker diffractometer (Cu Kα X-ray tube), Ni-filter, 0.02 step, 0.2 s and a position sensitive detector. The analysis of the elements was done by X-ray fluorescence spectrometry (XRF), and the concentrations of carbonate (CO_3^{2-}), chloride (Cl^-), sulfide (S^{2-}) and H_2S were determined by volumetric methods. The hydrogen sulfide gas analyzer was used to determine the leakage of H_2S from the dissolution with a H_2S-780 Southland Sensing (Portable Hydrogen Sulfide Analyzer).

The 15 wt. % hydrochloric acid solution used in the tests was prepared using 37 wt. % concentrated high pure hydrochloric acid. The additions of calcium hypochlorite and propargyl alcohol (2-propyn-1-ol) in hydrochloric acid solution are with 99 % and 99.5 % purity, respectively.

Dissolution of samples of scale

Nine samples, each weighing about 2 g, were taken from the central part of the scale (Fig. 2), crushed, and homogenized, in order to use three samples in each test. The test consists of placing the samples in a glass bottle and adding 200 mL of 15 wt. % hydrochloric acid (HCl) solution and 0.5 wt.% of calcium hypochlorite [$Ca(ClO)_2$]. The experiment was repeated using 1.0 wt. % and 2.0 wt. % of calcium hypochlorite. The testing time was 4 hours and the temperature was maintained at 60°C. The corrosive solution was agitated with a magnetic bar.

Fig. 1. Horizontal separator tube scale.

Fig. 2. Scale sample removed from the horizontal separator tube.

For safety, the experiment was conducted in the fume hood of the laboratory considering the toxicity of hydrogen sulfide. Process efficiency of removal (RE %) was calculated using the expression:

$$\text{Removal Efficiency} = \text{RE\%} = \frac{W_1 - W_2}{W_1} \, . \, 100$$

where W_1 is the initial mass and W_2 is the final mass. The final mass is calculated after the removal process. A piece of filter paper was weighed and the resulting solution was filtered. The leftover precipitate was washed with distilled water, acetone, and anhydrous ethanol. The filter paper was placed in the oven for 1 hour at 120°C. Finally, after cooling to room temperature, the final mass (W_2) was determined by discounting the weight of the filter paper.

Gravimetric test (mass loss) of coupons of carbon steel

The material evaluated in this study was a carbon steel AISI 1020 (0.21 % carbon, 0.32 % Mn, 0.35 % Si, 0.011 % S, and 0.009 % P, with the reminder consisting of iron) used in the confection of the coupons. The coupons used in the gravimetric tests (weight loss) had the following dimensions: 31.8 mm outside diameter, 7.5 mm internal diameter, and 2.0 mm thickness.

The metal surfaces were prepared with sandpaper, ranging from grade 100 to grade 600. After using sandpaper, the surfaces were cleaned with acetone and ethanol and dried with hot air. The weights of the test coupons were recorded, up to fourth decimal places, using a digital electronic balance.

The test is made by placing the three coupons of carbon steel in a 500 mL glass bottle and adding 200 mL of the solution of 15 wt. % of HCl and 0.5 wt. % of calcium hypochlorite and additions of 500 mg L^{-1} and 1000 mg L^{-1} of propargyl alcohol (2-propyn-1-ol) as corrosion inhibitor.

The testing time was 1 hour and the temperature was maintained at 60°C. The experiment was repeated two more times, using 1.0 wt. % and 2.0 wt. % of calcium hypochlorite. The corrosive solution was agitated with a magnetic bar. Upon completion of the test, the system shuts down and the coupons are quickly removed from the corrosive medium then washed with water and alcohol and dried with hot air. The coupons are then weighed again to the nearest 0.0001 g. In all tests, 2 g of the scale was added, in order to represent the condition of the carbon steel with the adherent scale [23].

The corrosion rate (CR) and the efficiency of each corrosion inhibitor (IE %) were defined by the following expressions:

$$\text{Corrosion rate} = \text{CR} = \frac{W_1 - W_2}{S\,.\,t}\ , \text{mg.cm}^{-2}.\text{h}^{-1}$$

$$\text{Efficiency} = \text{IE}\ \% = \frac{W_1 - W_2}{W_1}\ .\ 100$$

where W_1 and W_2 are the weight loss in the absence and presence of inhibitor, S is the area in cm^2, and t is the exposure time in hours.

RESULTS AND DISCUSSION

Dissolution of samples of scale

The XRF analysis of samples removed near the surface of the carbon steel shows the high elemental Fe content, on the order of 55 % while in the central part and 33 % in the peripheral part. Similarly, the sulfur (S) and calcium (Ca) contents are less than 5 %, meaning that the crystallographic species determined by XRD show low pyrrhotite ($Fe_{1-x}S$), pyrite (FeS_2), and akaganeite (β-FeOOH) contents. Thus, it can be considered that the iron content is represented by amorphous forms of iron oxide or hydroxide (FeO, $Fe(OH)_2$, $Fe(OH)_3$, Fe_3O_4, Fe_2O_3, or FeOOH). Although it has not been detected by the XRD it is very likely that there are significant amounts of Fe_3C residues from carbon steel pipes [24, 25].

These compounds can be attributed to the corrosive action of formation water on carbon steel as the reactions show [26]:

$$\text{Anodic reaction: } Fe - 2e^- \rightarrow Fe^{2+} \quad (11)$$

$$\text{Cathodic reacion: } 2H_2O + 2e^- \rightarrow H_2 + OH^- \quad (12)$$

$$Fe^{2+} + 2\,OH^- \rightarrow Fe(OH)_2 \quad (13)$$

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2\,Fe(OH)_3 \quad (14)$$

$$Fe(OH)_3 \rightarrow FeOOH + H_2O \quad (15)$$

In the medium samples removed from the central and peripheral parts, the semi-quantitative XRD analysis showed the following chemical composition: 32.5 wt. % calcite ($CaCO_3$), 21 wt. % pyrrhotite ($Fe_{1-x}S$), 8 wt.% pyrite (FeS_2), 18 wt. % siderite ($FeCO_3$), 13 wt. % akaganeite (β-FeOOH), and 6 wt. % dolomite ($CaMg(CO_3)_2$). In these samples, the wet chemistry chloride content was 5 %, likely in the form of sodium chloride, ferrous chloride ($FeCl_2$) or ferrous chloride hydroxide [$Fe_2(OH)_3Cl$].

The formation of calcite and dolomite in the internal scale of the tubes can be clarified by the presence of Ca^{2+} ions and Mg^{2+} ions in the formation water (connate water) based on the following reactions [1 - 3]:

$$Ca^{2+} + 2\,HCO_3^- \rightarrow Ca(HCO_3)_2 \quad (16)$$

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O \tag{17}$$

$$Ca^{2+} + Mg^{2+} + 2\,CO_3^{2-} \rightarrow CaMg(CO_3)_2 \tag{18}$$

The presence of iron sulfide in the scales may be due to H_2S attack on the production tubing of the various oil wells that feed the treatment plant; such particles (iron sulfides) can detach from the tubing and be dragged along the scale formation. Fe^{2+} ions, also present in the formation water, can react with sulfides to form iron sulfides. The occurrence of pyrrhotite ($Fe_{1-x}S$) and pyrite (FeS_2) determined by XRD analysis of the scales is supported in the various studies cited [13 - 16].

The existence of ferrous carbonate (siderite), determined by XRD analysis of the scales, can be explained by the reaction of ferrous ions with carbonate ions in the presence of CO_2 [27].

Table 1 shows the results of scale removal efficiency using 200 mL of a 15 wt. % HCl solution and additions in each experiment of 0.5 wt. %, 1.0 wt. %, and 2.0 wt. % of calcium hypochlorite, respectively. The testing time was set at 4 hours and the temperature of 60ºC. The scale used in the tests consists of 32.5 wt. % calcite ($CaCO_3$), 21 wt. % pyrrhotite ($Fe_{1-x}S$), 8 wt. % pyrite (FeS_2), 18 wt. % siderite ($FeCO_3$), 13 wt. % akaganeite (β-FeOOH), and 6 wt. % dolomite ($CaMg(CO_3)_2$).

Hydrochloric acid when reacting with scale may result in the following reactions:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \tag{19}$$

$$CaMg(CO_3)_2 + 4HCl \rightarrow \\ \rightarrow CaCl_2 + MgCl_2 + 2CO_2 + 2H_2O \tag{20}$$

$$FeCO_3 + 2HCl \rightarrow FeCl_2 + CO_2 + H_2O \tag{21}$$

$$FeOOH + 3\,HCl \rightarrow FeCl_3 + 2\,H_2O \tag{22}$$

$$FeS_2 + 2HCl \rightarrow FeCl_2 + H_2S + S \tag{23}$$

$$Ca(ClO)_2 + 2HCl \rightarrow FeCl_2 + 2\,HClO \tag{24}$$

It can be stated that increasing HCl concentration favors increased dissolution of carbonates and akaganeite (β-FeOOH). Similarly, at temperatures higher than 60°C, increasing HCl concentration favors greater dissolution of iron sulfide. For example, with 5 wt. % HCl the dissolution efficiency is 19.2 wt. % while with 20 wt. % HCl the dissolution is 100 % [27].

Table 1. Results of scale removal efficiency.

Scale dissolver concentration	Removal efficiency, %
15 wt. % HCl solution and 0.5 wt. % of calcium hypochlorite [$Ca(ClO)_2$].	86.4
15 wt. % HCl solution and 1.0 wt. % of calcium hypochlorite [$Ca(ClO)_2$].	87.1
15 wt. % HCl solution and 2.0 wt. % of calcium hypochlorite [$Ca(ClO)_2$].	87.2

The two oxidants present, ferric ions (Fe^{3+}) and calcium hypochlorite $Ca(ClO)_2$ can oxidize the sulfides (S^{2-}) or H_2S to form sulfur according to the following reactions:

$$Fe^{3+} + S^{2-} \rightarrow S + Fe^{2+} \tag{25}$$

$$Ca(ClO)_2 + 2\,H_2S \rightarrow CaCl_2 + 2\,S + 2\,H_2O \tag{26}$$

In the tests performed, it is valid to admit that not all sulfide and H_2S were oxidized to sulfur; this means that there was little evolution of H_2S generated in the acid attack. Thus, all tests performed were done in a hood with exhaustion. In industrial cleaning, it is advisable to install a vent to burn the H_2S with a pilot flame or a container containing concentrated sodium hypochlorite solution.

In HCl injection processes in reservoir rock, the precipitation and/or deposition of elemental sulfur can cause damage; however, in chemical pipe cleaning, elemental sulfur is insoluble in HCl and can be removed using a specific organic solvent [28].

Gravimetric test (mass loss) of coupons of carbon steel

The gravimetric test results of the addition of 500 mg L^{-1} and 1000 mg L^{-1} of propargyl alcohol (corrosion inhibitor) in the acid dissolving solution containing 15 wt. % HCl and calcium hypochlorite at 60°C is presented in Table 2 refer to the average of three steel carbon coupons.

Table 2. Test results of mass loss of carbon steel coupons in the acid dissolving solution containing 15 wt. % HCl, calcium hypochlorite, and propargyl alcohol at 60°C.

Propargyl alcohol, mgL^{-1}	Calcium hypochlorite [$Ca(ClO)_2$], wt. %	Corrosion rate, $mg.cm^{-2}.h^{-1}$	Efficiency, (%)
0	0	25.32	-
500	0	0.48	98.10
1000	0	0.35	98.60
500	0.5	0.87	96.56
500	1.0	2.12	91.62
500	2.0	2.93	88.41
1000	0.5	0.75	97.03
1000	1.0	1.98	92.17
1000	2.0	2.32	90.90

The gravimetric test results of the addition of 500 mg L^{-1} and 1000 mg L^{-1} of propargyl alcohol (corrosion inhibitor) in the acid dissolving solution containing 15 wt. % HCl and calcium hypochlorite at 60°C are presented in Table 2 as the average of three steel carbon coupons. The results of mass loss assays showed that the addition of propargyl alcohol (2-propyn-1-ol) in 15 wt. % HCl provided excellent protection to the carbon steel with an efficiency superior of 98 %.

The referenced literature showed that propargyl alcohol (2-propyn-1-ol) based corrosion inhibitors showed excellent performance in protecting carbon steel in hydrochloric acid solutions at all concentration and temperature combinations [29 - 32].

There are theories that point out that the good adsorption capacity of propargyl alcohol molecules by carbon steel is linked to their π-electrons, which interact with metal surfaces and, consequently, form triple bonds, $HC \equiv C-CH-OH$ [33].

Other theories show that the propargyl alcohol molecules polymerize on the substrate and form a film and/or an adsorbed coating preventing the corrosive action of the acidic medium [34, 35].

However, as the calcium hypochlorite content in the acid solution increases, there is a decrease in efficiency to 88 %; although this efficiency can still be considered very good in terms of corrosion protection.

Finally, out of caution and considering the high toxicity of H_2S and also, to a lesser degree, the toxicity of propargyl alcohol, the laboratory tests should be performed in a fume hood.

CONCLUSIONS

The 22 oil wells, with differentiated oil/water flow rates, salt concentrations, and H_2S/CO_2 concentrations, that fed the horizontal separators for 20 months produced heterogeneous scales in the pipes and consequently reduced the production capacity of the treatment plant. Based on the laboratory tests the following conclusions can be made:

- The scale samples taken near the internal surface of the carbon steel revealed that they are composed of iron oxides and iron hydroxides from electrochemical reactions arising from contact between the high salinity water and the carbon steel surface;
- The samples taken from the central and peripheral are hard and adherent to the internal surfaces of the pipes. On average, they consisted of 35 wt. % calcite ($CaCO_3$), 21 wt. % pyrrhotite ($Fe_{1-x}S$), 8 wt. % pyrite (FeS_2), 18 wt. % siderite ($FeCO_3$), 13 wt. % akaganeite (β-FeOOH), 6 wt. % dolomite ($CaMg(CO_3)_2$), and the rest in the form of sodium or ferrous chloride or ferrous chloride hydroxide ($Fe_2(OH)_3Cl$);
- The acid solution with 15 wt. % HCl and additions of chlorine (Cl_2) or calcium hypochlorite [$Ca(ClO)_2$] has become an excellent removing agent with 87 % yield;
- Propargyl alcohol (2-propyn-1-ol) is an effective corrosion inhibitor for reducing the corrosion rate of carbon steel in hydrochloric acid and solutions with efficiency up to 98 %;
- The addition of chlorine or calcium hypochlorite favored the disintegration of H_2S into sulfur by avoiding or somewhat reducing the intense release

of this toxic gas during the acid removal process;

- However, as the calcium hypochlorite content increases in the acid solution, there is a decrease in efficiency to 88 %; although this efficiency can still be considered very good in terms of corrosion protection.

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