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Development of Efficient Formulation for the Removal of Iron Sulfide Scale in Sour Production Wells

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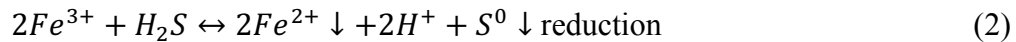*Corresponding Author: ihussein@qu.edu.qa

Abstract

Iron sulfide scale is common in sour oil and gas production wells, which exists in different forms. Iron sulfide hard scales are difficult to remove with acids, requiring the mechanical intervention or replacement of the production tubing. An environmentally friendly formulation with a high pH is proposed for the removal of both soft and hard iron sulfide scale from oil and gas wells. The formulation consists of DTPA (Di-ethylene Tri-amine Penta Acetic acid) in addition to K_2CO_3 as a catalyst. High-pressure high temperature solubility experiments were performed under both static and dynamic conditions in the temperature range 70 to 150 ${}^{\circ}$C and a constant pressure of 500 psi. Several combinations of the catalyst and DTPA chelating agent were used to optimize the catalyst/DTPA ratio to achieve maximum scale solubility. Field scale samples were collected and analyzed using XRD. The scale removal efficiency of the proposed formulation outperforms that of the current formulations used in the oil industry, with the added advantage of not releasing H_2S. The optimum DTPA concentration is 20 wt % and the optimum catalyst concentration is 9 wt % which provide a solubility of 90 % of the field scale. In addition, the ecotox profile of the proposed formulation is better than that of the currently used formulations because toxic corrosion inhibitors are not used. The maximum reported corrosion rate for the new formulation is 0.036 kg/m^2, which is well below the acceptable limit (<0.227 kg/m^2).

Keywords: Iron Sulfide Scale, chelating agent, catalyst, corrosion, hydrogen sulfide free formulation.

INTRODUCTION

During the production stage, wellbore fluids such as gas, oil, steam, and hot water are typically produced in the wellbore and scale can form in the wellbore subterranean formation and/or on the associated equipment. Formation of iron sulfide scale in producer, injection, and supply wells due to the presence of hydrogen sulfide and iron causes many operational problems in the oil and gas industry. [1-4] Iron sulfide compounds form a type of scale, which have the physical appearance of amorphous solid particles, and they are capable of absorbing water and oil. Iron sulfide scale is a significant problem in the oil and gas industry and its deposits have an adverse impact on the production operations. For instance, the presence of iron sulfide scale near the wellbore can degrade the productivity of a production well [5] and lead to a loss of performance and injectivity of water supply and injection wells, respectively. [4; 6-8] Even though soft iron sulfide scales can be removed easily using HCl acid, the process generates H_2S.

The sources of hydrogen sulfide are sulfate reducing bacteria (SRB), thermo-chemical sulfur reduction, thermal decomposition of organic sulfur compounds, acid treatment of deep sour wells, and hydrolysis of metal sulfides [1; 9]. Iron is present in formation brine, well tubular and downhole due to corrosion processes [8]. The chemical reactions (1) and (2) are the main reactions associated with iron sulfide formation[10].

$$Fe^{2+} + H_2S \leftrightarrow FeS \downarrow + 2H^+ \text{ above pH 2} \tag{1}$$

$$2Fe^{3+} + H_2S \leftrightarrow 2Fe^{2+} \downarrow + 2H^+ + S^0 \downarrow \text{reduction} \tag{2}$$

Iron is typically present in 2^+ and 3^+ oxidation states. Typically, iron is present in the 3^+ oxidation state under equilibrium conditions in surface facilities. However, at normal reservoir conditions iron is present in the 2^+ oxidation state. Analysis of field samples indicates that the ratio of iron (II) to iron (III) is generally 5 to 1.[11] However, the ratio can vary depending on the type of well or formation [10; 12; 13]. However, acids cannot remove hard iron sulfide scales. **Fig** shows typical deposits of iron sulfide scale.

Unlike the other scales, carbonate or sulfate scales, there are several forms of iron sulfide scale, with FeS and FeS_2 being the common types [7; 12]. The ratio of iron to sulfur in the iron sulfide scale decreases as the location of the scale gets closer to the wellhead. The scale type depends on the temperature and the age of the iron sulfide scale, which can exist in different forms with varying sulfur to iron ratios. The scale can be pyrrhotite (Fe_7S_8), troilite (FeS), marcasite (FeS_2), pyrite (FeS_2), greigite (Fe_2S_4) and/or mackninawite (Fe_9S_8). [7; 12]. Considering the varying chemical and physical conditions under which iron sulfide scales can be formed, several types of scales can be found in a given section of a wellbore or a pipeline. The scale with a low solubility (mostly pyrite FeS_2) exists at shallower depths and the soluble scale such as FeS exists at deeper locations. Thus, a single treatment cannot be designed for a given well.

Acids, such as HCl, are used to chemically remove iron sulfide scale. [14] HCl is the most effective dissolver of scale; it is very corrosive to mild steel, especially at high concentration and high temperature. Wang et al. used a range of formulations to remove iron sulfide scales with different compositions. [15] The scale samples used contained

pyrrhotite (Fe$_{1-x}$S), mackinawite (FeS), pyrite (FeS$_2$,) marcasite (FeS$_2$), calcite, siderite, and anhydrite. Tetrakis hydroxymethyl phosphonium sulfate (THPS) used was in the range of 15 to 75 wt % for soaking for a time ranging from 1 to 24 h. The effect of ammonium chloride salt on the scale dissolution process was investigated, and found that 50 wt % THPS yielded the highest removal efficiency. [15] Although the addition of ammonium chloride enhances the solubility of scale due to the production of HCl, the corrosion rate is increased at 85ºC/185ºF. Acid dissolution generates a large amount of H$_2$S gas, which can be a serious threat to the well integrity and increases operational hazards at surface facilities [3]. Dissolved iron sulfide scale can plug formations near the wellbore leading to a decrease in well productivity.

Several attempts have been made to remove iron sulfide scale in oil and gas wells [2; 7; 15]. Methods used so far have several major shortcomings, including the high corrosion rate of the formulations used, low solubility of hard scales such as pyrite, and the incompatibility of the formulations with the formation rock and fluids. The iron sulfide present downhole under high pressure- high temperature (HPHT) conditions is mainly pyrrhotite, pyrite, marcasite and mackninawite.

In summary, the previous formulations use HCl and they are expensive and release H$_2$S. Therefore, there is a need for a formulation is non-corrosive to equipment, low cost, and does not damage the formations or the environment. The limitations of the current formulations used for FeS scale removal have motivated our research group to search for alternatives. The objectives of the current study are the following: (i) introduce new formulations for removing iron sulfide scale based on the DTPA chelating agent and potassium carbonate as a catalyst; (ii) evaluate the thermal stability of the proposed formulations; (iii) identify the optimum DTPA and catalyst concentrations that yield maximum scale solubility; (iv) determine the corrosion of coupons made of tubing material at high temperature in the presence of the new formulation; and (v) study the compatibility of the proposed formulations with carbonate rocks from gas wells, using coreflooding experiments.
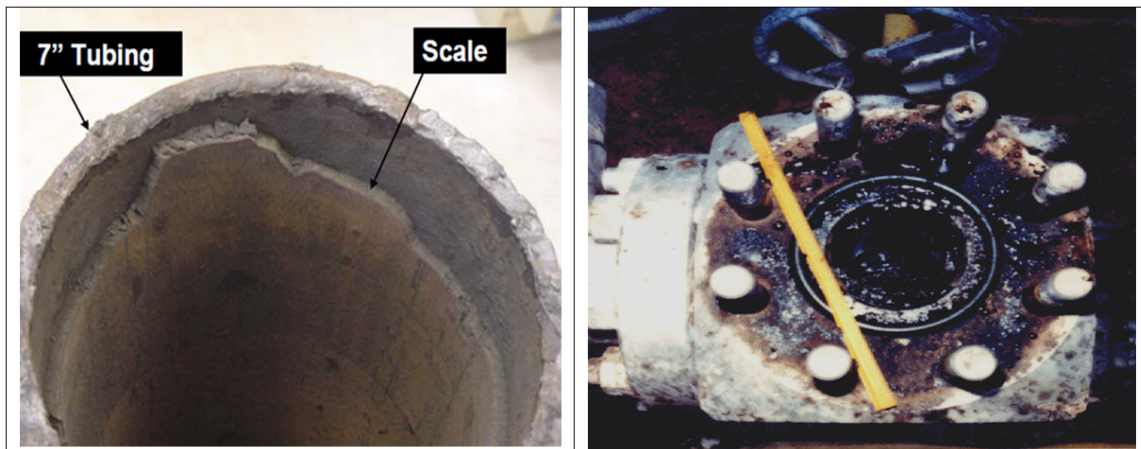

Figure 1—Typical iron sulfide scales in casing pipelines [7].

MATERIALS AND EXPERIMENTS

Materials

Iron sulfide scale samples were collected from two field locations. The samples are collected using bailer sampler. The scale was collected from the tubing at 366 m (1200 ft) depth from one well for sample 1 (S1) and at 305 m (1000 ft) depth for sample 2 (S2) from another well. Composition of S1 and S2 determined by XRD are listed in **Table 1**. Initially, a concentration of 40 wt % of DTPA chelating agent was used in this study, which was then diluted to the desired concentration with de-ionized water. Potassium carbonate at different concentrations was used as a catalyst. The carbonate core samples evaluated by the coreflooding experiments contain 95 % calcite and 5 % dolomite. The core samples used are 1.5 inch in diameter and 3 inches in length with an average porosity of 16 % and a permeability of 60 md.

Table 1—XRD Analysis of the Scale Samples Collected from the Field

Sample 1 (S1)		Sample 2 (S2)	
Mineral	**wt%**	**Mineral**	**Wt %**
Pyrrhotite (Fe_7S_8)	48	Pyrrhotite (Fe_7S_8)	50
Pyrite (FeS_2)	39	Pyrite (FeS_2)	25
Siderite (Fe_2CO_3)	13	Siderite (Fe_2CO_3)	5
		Calcite ($CaCO_3$)	20

Experiments

The selection of the conditions and procedures in this part is based on standard practice in the literature.[16] However, for the solubility measurement field practice for scale solubility (48 hours maximum) is used. Each experiment is repeated for three times, and average values are reported and the differences are within 5%.

Scale solubility experiments

The scale solubility experiments were conducted using a HPHT cell under static conditions (in the field the scale removers are injected and allowed to soak the scale in the tubing). The ratio of scale weight to the removal fluid volume is a crucial parameter that should be investigated. Published studies do not report the practical ratio that should be injected to remove scale. In this study, the pore hole volume (PHV), which is the ratio of fluid volume required to remove the scale to the volume of the production casing/tubing, is used as a measure of removal efficiency. If PHV is low, the removal efficiency will be more efficient since the amount of injected fluid would be smaller. However, in addition to this ratio,

other factors such as the composition of the formulation and the cost of material influence the cost of the treatment.

Thermal stability experiments

The thermal stability of the optimized formulation that yielded the highest scale solubility was tested for thermal stability at a temperature of 150°C for 48 hours using an HPHT see-through autoclave cell.

Corrosion experiments

Several corrosion tests were also conducted using the fluid that displayed the highest solubility. Coupons fabricated from casing materials were used in the corrosion tests. The corrosion tests were conducted for the optimum formulation of DTPA/catalyst as well as for HCl at different temperatures. HCl is used here for comparison purposes as it is currently used in the oil industry for the removal of this type of scale. The corrosion experiments were performed using an autoclave cell at 10340 kPa (1500 psi) in the presence of a mixture gases (10 % H_2S + 10 % CO_2 + 80 % N_2). Three sets of experiments were conducted at three temperatures, namely, 70 °C, 120 °C, and 150 °C. The corrosion experiments were performed using coupons fabricated from casing/tubing material collected from the field. In these experiments, 20 wt % DTPA and 20 wt % DTPA plus 3, 6, and 9 wt % K_2CO_3 at pH 11, and 15 and 20 wt % HCl, both containing 3 vol % of a corrosion inhibitor (CI), were employed.

Coreflooding experiments

The coreflooding setup used in this study consists of one backpressure regulator at the outlet of the core holder. The required confining pressure was applied on the core using an Isco pump. The pressure drop was measured using a high accuracy (accuracy = 0.01 psi) pressure transducers with a range of 0 to 10340 kPa (1500 psi). The experiments were performed at room temperature and 150 °C. The core was first saturated with brine and then the pore volume was calculated. The core was first loaded into the core holder at an overburden pressure of 3447 kPa (500 psi) higher than the inlet pressure. Then, the core is saturated with injection water until a constant brine permeability is reached. During the coreflooding experiments, a backpressure of 6895 kPa (1000 psi) was applied to the core. Six pore volumes of the optimum formulation were injected into the core.

RESULTS AND DISCUSSION

Determination of the Optimum Volume Required for Removing Scale

The volume of the tubing or casing restricts the volume of the fluid required for removing scale from a downhole casing/tubing. The ratio of scale weight to fluid volume used in the laboratory should match the one to be used in the field. The dimensionless parameter PHV defined earlier is used to determine the optimum ratio required. If the PHV of the fluid is

0.4, this means that 40% of the tubing volume of removal fluid is required to remove the iron sulfide scale from a section of the tubing.

Assuming a length of L and a diameter of D_{tubing} of a cylindrical tubing section with the inner surface coated by a uniform scale layer of thickness t_{scale}, the weight of scale, W_{scale}, is given by Equation 3.

$$W_{scale} = (V_{scale})(\rho_{scale}) = \frac{\pi}{4} L \left[D_{tubing}^2 - \left(D_{tubing} - 2t_{scale} \right)^2 \right] (\rho_{scale}) \qquad (3)$$

where V_{scale} is the scale volume and ρ_{scale} is the scale density. The pore volume of fluid that can be injected to remove scale is determined as follows:

$$V_{pore} = \frac{\pi}{4} L \left[\left(D_{tubing} - 2t_{scale} \right)^2 \right] \qquad (4)$$

where; V_{pore} is the volume of the pore. Dividing Equation 3 by Equation 4 will provide the dissolving capacity of the fluid, which is defined as the weight of the scale removed by unit pore volume. The higher this number the better the removal efficiency. The dissolving power of the treatment fluid is expressed as follows:

$$Dissolving\ Capacity = \frac{W_{scale}}{V_{pore}} = \frac{\left[D_{tubing}^2 - \left(D_{tubing} - 2t_{scale} \right)^2 \right] (\rho_{scale})}{\left[\left(D_{tubing} - 2t_{scale} \right)^2 \right]} \qquad (5)$$

The solubility experiments show that 45 g of scale can be dissolved with 1 L of the new formulation. Therefore, the required PHV is calculated as follows:

$$PHV = \frac{Wscale/Vpore}{\frac{Wscale}{Volume\ of\ treatment\ fluid}(fluid\ dissolving\ capacity)} = \frac{Dissolving\ Capacity}{45} \qquad (6)$$

The fluid volume required to remove the scale can be determined based on the scale thickness using the equations described earlier. **Figure 2** shows the variation of the required volume of the proposed formulation as a function of the scale thickness. The average density of the two field scale samples is 4.5 g/cm³. For a tubing section with a length of 7 in (17.8 cm) and a scale thickness of 5 mm the required PHV is 5.5. This means that the production tubing or casing should be filled with a volume equivalent to five and a half times its volume to remove the scale. In addition, the scale must be soaked for 24 h for its dissolution. The practical problems posed by these conditions are solved by pumping one PHV of fluid for 24 h and replacing it with an equal volume of fresh fluid every 24 h for 5.5 days. Current techniques in the industry do not take the dissolving capacity of a fluid into consideration and only pump one PHV for 24 h. The treatment volume for a given scale thickness can be determined using **Figure 2**, and the required time can be computed considering that one PHV should soak the scale for one day and the total time is equal to the number of PHVs.
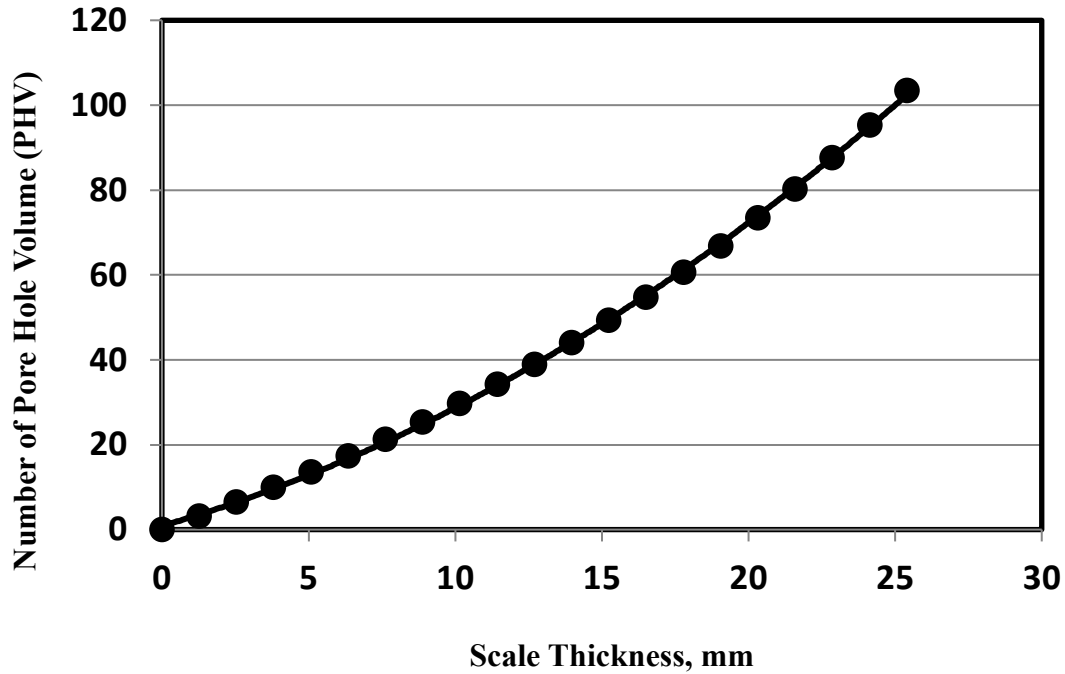
Figure 2—The variation of fluid volume required to remove the iron sulfide scale with its thickness.

Scale Solubility

The concentration of both the chelating agent and the catalyst were optimized to yield the highest scale solubility. Scale sample 1 (S1) was used for the optimization process because it contains more hard scale (insoluble). Several solubility experiments were conducted using 2 g of the field scale sample in 20 mL of DTPA solution with different concentrations. As graphically depicted in **Figure 3**, the optimum concentration of DTPA which provides the highest scale solubility is 20 wt %. Increasing the concentration beyond this value has a negative effect, most likely due to the loading of DTPA with cations, which retards scale dissolution. Loading DTPA with ferric ions increases the viscosity and reduces the diffusion coefficient of DTPA, which in turn decreases the reaction rate. Similar results were obtained by [17; 18].
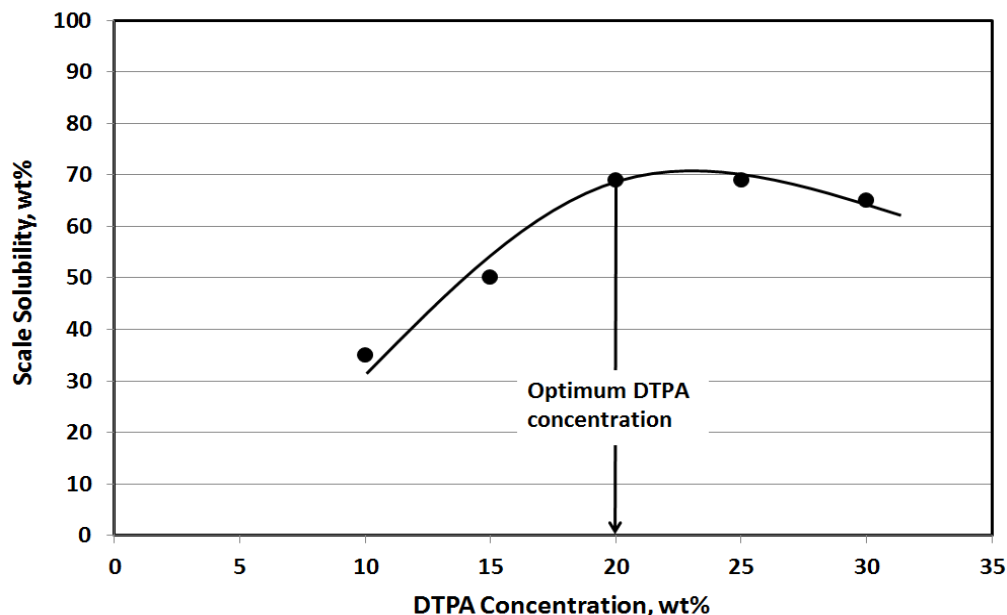
Figure 3—Variation of the scale solubility with the concentration of DTPA, at a pH of 11, a temperature of 120°C, and a soaking time of 24 h.

Next the optimum catalyst (K_2CO_3) concentration in 20 wt % DTPA under the same conditions used for the optimization of the DTPA concentration was determined. **Figure 4** shows the effect of catalyst concentration on scale solubility, indicating that the optimum concentration is 9 wt %. The optimum composition of the proposed scale removal formulation is 20 wt % DTPA containing 9 wt % K_2CO_3. The solubility of the hard scale sample (S1) is 78% at 120 °C. Further solubility experiments were performed using the optimized formulation and the results were compared with those obtained for HCl based formulations under the same conditions of temperature and soaking time. **Figure 5** shows the scale solubility of 20 wt % HCl with 3 vol % CI, 15 wt % HCl with 3 vol % CI, and 20 wt % DTPA with 9 wt % K_2CO_3. The 20 wt % HCl with 3 vol % CI yielded the highest scale solubility of 85%, while 78% of the scale is removed by the proposed formulation. The 20 wt % HCl formulation is not recommended in the field because it will cause severe corrosion of the well tubulars, which will be discussed further in the section on corrosion. The solubility in the formulation with 15 wt % HCl is lower compared to the new formulation. and Also the corrosion rate of 15 wt % HCl is very high even with the presence of corrosion inhibitors. Corrosion inhibitors are expensive and they may also retard the reaction rate. The same testing was performed on scale Sample 2 (S2). This sample has more soluble scales and contains only 25 wt % hard scale (pyrite), and HCl is very effective in dissolving scales at both 15 and 20 wt % at 120 °C (**Figure 6**). The solubility of scale in the proposed formulation is also high at 85 %.
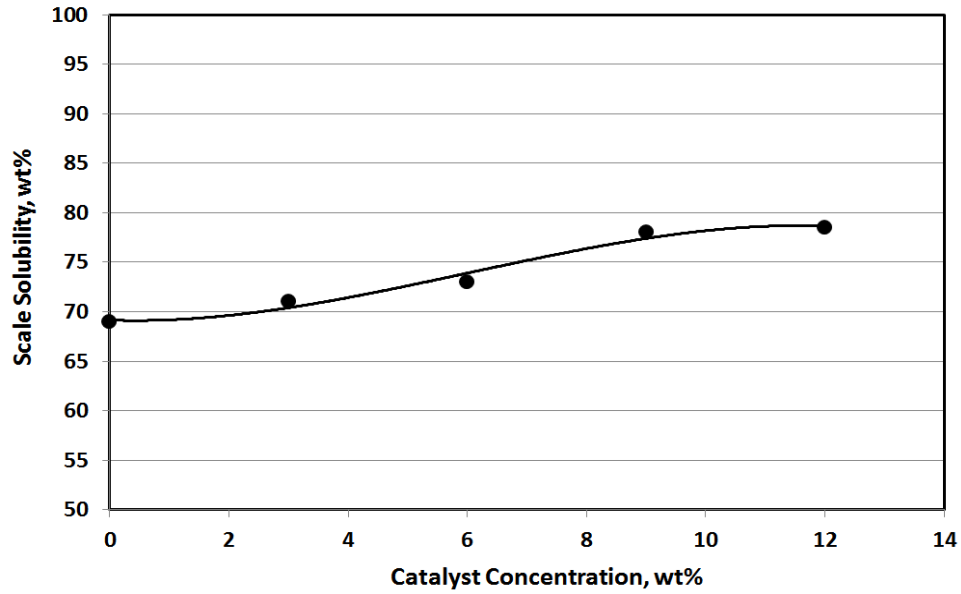
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Figure 4—Variation of the scale solubility with the concentration of the catalyst, at a pH of 11, a temperature of 120 °C, and a soaking time of 24 h, for Scale Sample 1 (S1).
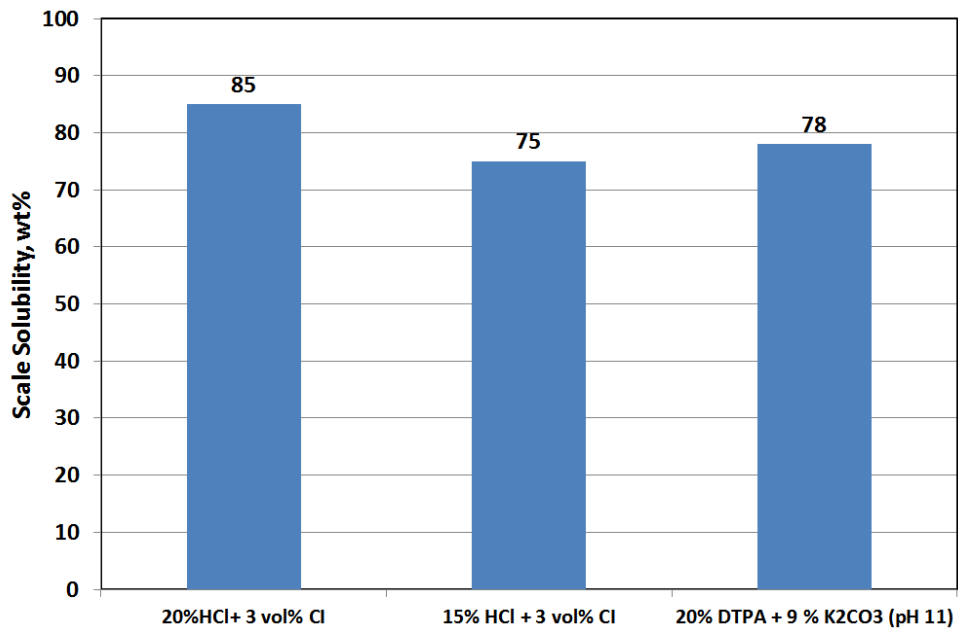

Figure 5—Scale solubility in the three formulations, at a temperature of 120°C and a soaking time of 24 h for scale Sample 1 (S1).
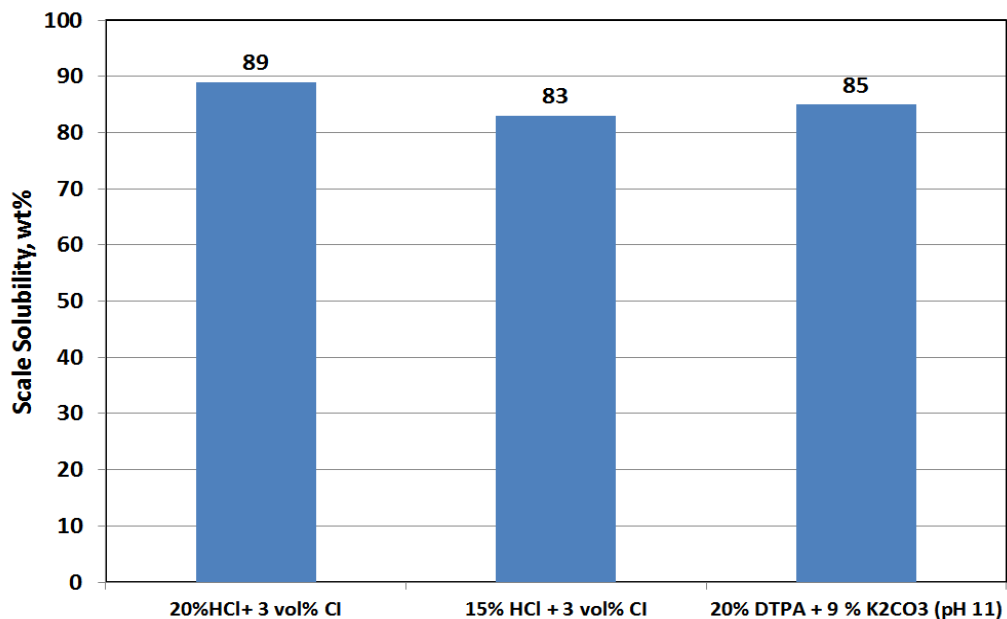
Figure 6—Scale solubility in different solutions, a temperature of 120ºC and a soaking time of 24 h for scale Sample 2 (S2).

Effect of temperature on scale solubility

For scale removal, first the thermodynamics of the reaction should be favorable or the Gibbs free energy, $\Delta G \ll 0$ or Keq> 1000 (ΔG= -RT ln Keq, Keq is the equilibrium constant). Otherwise, a lot of chelating agent is needed to drive the scaling reaction to completion. Then, the kinetics (reaction rate) at the given temperature range should be high enough in order to make it work. The effect of temperature on the solubility of the two scale samples was evaluated. The solubility of the optimum formulation of 20 wt % DTPA with 9 wt % K_2CO_3 was examined at temperatures of 70, 120, and 150 ºC and at a pressure of 500 psi. The experiments were conducted under static conditions. **Figure 7** shows that the temperature has a strong effect on the solubility of scale, which increases significantly, when the temperature is increased. Most likely the increase of the dissolution and solubility of iron sulfide with temperature due to the increase of the reaction rate of DTPA at higher temperatures. The chelating ability of DTPA increases with increasing temperature. [17] studied the kinetics of the reaction of different chelating agents with calcite, in the form of carbonate rocks, and showed that increasing the temperature from 93 ºC (200 ºF) to 149 ºC (300 ºF) doubled the reaction rate. Among several commercially available chelating agents, DTPA has the highest stability constant with ferric ions. The stability constant measures the ligand strength (chelate agent with metal ion) and is considered to be stable ligand if it is higher than 8. **Table 2** shows the stability constant of common chelating agents used in the oil and gas industry with some ions existing in rock minerals and scales. The higher the stability constant with metal ions the higher the chelation, which in turn increases the reaction rate [17]. Sample S2 contains more soluble minerals, such as calcite and soft iron sulfide scale (FeS), therefore, its solubility is higher than that of sample S1.

Table 2—Stability constants for the chelating agents EDTA, HEDTA, and DTPA (Mahmoud et al. 2011)

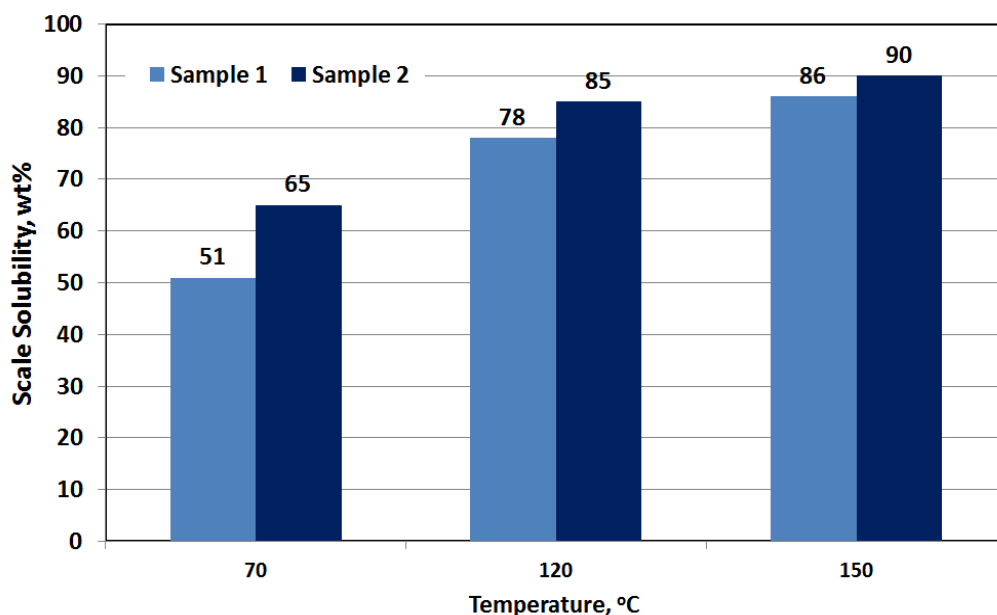|	Log (Stability Constant)		
Chelating Agent	**Ca^{2+}**	**Fe^{3+}**	**Mg^{2+}**
HEDTA	8.4	19.8	7.00
EDTA	10.7	25	8.83
DTPA	10.9	28.0	9.30

Figure 7—Effect of temperature on the solubility scale for two field scale samples with 20 wt % DTPA containing 9 wt % K_2CO_3.

Thermal Stability of the New Formulation

Thermal stability of the proposed formulation, with and without mixing with the scale sample, was studied at 150 °C and 500 psi. The formulation selected, 20 wt % DTPA with 9 wt % K_2CO_3, is stable for 48 h at 150 °C and 500 psi and did not show any incompatibility or precipitation. Under the same conditions of pressure, temperature, and aging time, the selected formulation is stable when mixed with both scale samples S1 and S2.

Results of the Corrosion Experiments

The corrosion experiments were conducted using casing/tubing coupons that are used in the field, which were exposed to several formulations at different temperatures and 1500 psi. As most of the gas wells produce H_2S and CO_2 10% of each was added to the mixtures during the corrosion tests. The corrosion tests were conducted for 6 h at 70, 120, and 150 ^oC.

Results of corrosion experiments at 70^oC

Figure 8 shows the results of the corrosion tests conducted for 6 h using three formulations at 70 ^oC and 10340 kPa (1500 psi). The industry standard for the corrosion rate is set to be a maximum of 0.227 kg/m^2 (0.05 lbm/ft^2). Any fluid should have a corrosion rate less than this value to avoid corrosion of the well tubulars [19]. The formulation containing 20 wt % HCl and 3 vol % of CI is very corrosive, ruling it out for scale removal. Even though the formulation containing 15 wt % HCl and 3 vol% CI meets the industry standard the corrosion rate is very close to the upper limit (0.227 kg/m^2 or 0.05 lbm/ft^2). The proposed formulation is CI-free and is much less corrosive than the standard formulations containing HCl. The corrosion rate of the proposed formulation (20 wt % DTPA with 9 wt % K_2CO_3) is 0.014 kg/m^2 (0.000 3 lbm/ft^2) and thus, is gentle on the well tubulars and do not require a CI. The proposed formulation can remove iron sulfide scale effectively without releasing H_2S. **Figure 9** shows photographs of the casing coupons before and after the corrosion tests. They show that HCl causes pitting to the coupon, while the proposed formulation does not. Formulations based on HCl are not suitable for the removal of iron sulfide scale both due to the high corrosion rate and the hazards associated with the generation of H_2S during treatment.
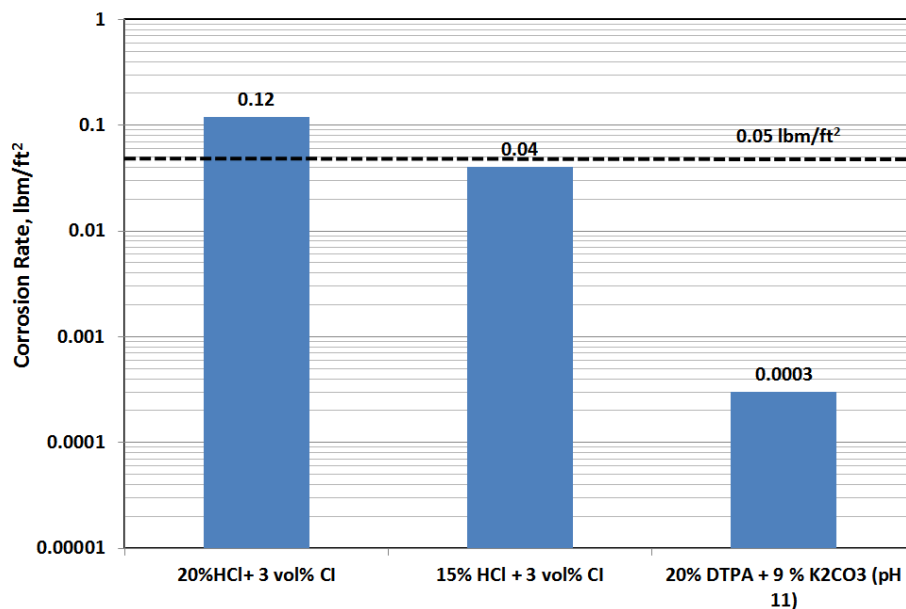

Figure 8—Corrosion rate of the evaluated formulations with casing coupons obtained from the field at 70 ^oC and 10340 kPa (1500 psi).
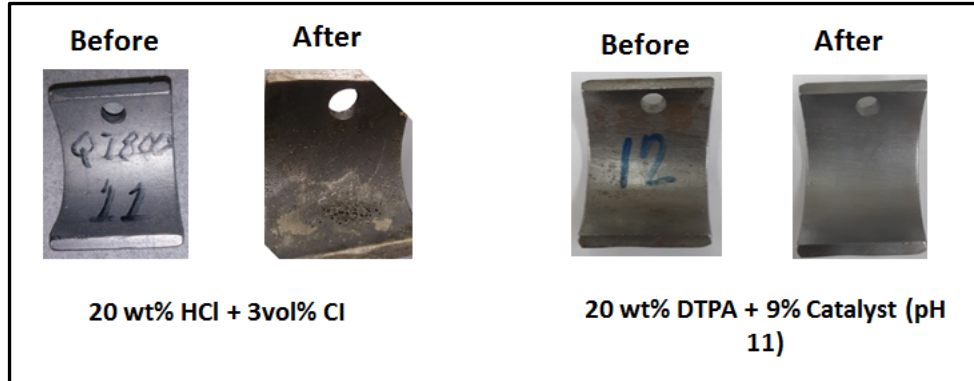
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Figure 9—Photographs for the casing coupons before and after the corrosion tests at 70 °C and 10340 kPa (1500 psi).

Results of corrosion experiments at 120°C

Figure 10 shows the results of the corrosion experiments for the three formulations at 120 °C and 10340 kPa (1500 psi) following 6 h of aging. At this temperature, both formulations based on HCl are corrosive and adding CI does not help. The two formulations with 20 wt % HCl containing 3 vol % CI and the 15 wt % HCl containing 3 vol % CI exceed the allowable corrosion rate limit of 0.227 kg/m^2 (0.05 lbm/ft^2). The corrosion rate for the proposed formulation (20 wt % DTPA with 9 wt % K_2CO_3) is 0.019 kg/m^2 (0.0004 lbm/ft^2), which is far below the allowable limit. This indicates that the proposed formulation can be used safely at this high temperature to remove iron sulfide scale formed in oil and gas wells.

Results of the corrosion experiments at 150°C

Figure 11 shows the results of the corrosion experiments for the three formulations conducted at 150 °C and 10340 kPa (1500 psi) for 6 h. At this temperature the corrosion rate of the proposed formulation remains the same as that at 120 °C. The results confirm that the proposed formulation can be used for the removal of iron sulfide scale without causing corrosion to the well tubulars. Also, corrosion inhibitors are not required when the formulation based on the DTPA chelating agent at high pH is required. The formulation with 20 wt % of HCl is very corrosive at 150 °C, with the corrosion rate reaching 1.362 kg/m^2 (0.3 lbm/ft^2). Based on the corrosion rates at all temperatures, the formulations based on HCl are not recommended for the removal of iron sulfide scale from gas production wells due to the high corrosion rate associated with this acid.
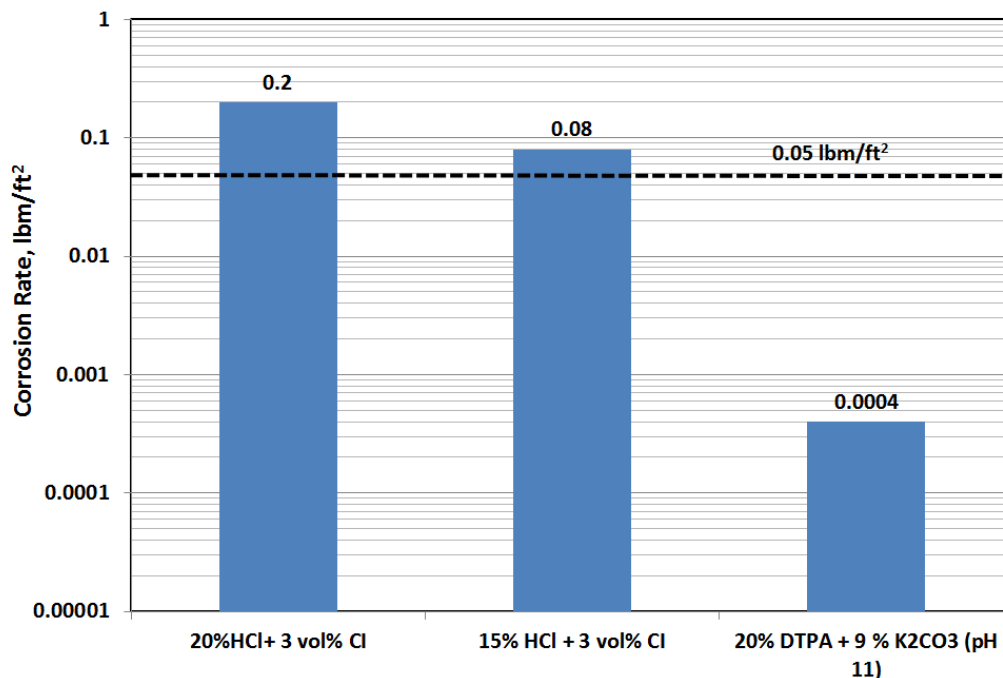
Figure 10—Corrosion rate for the formulation evaluated using casing coupons obtained from the field at 120 °C and 10340 kPa (1500 psi).
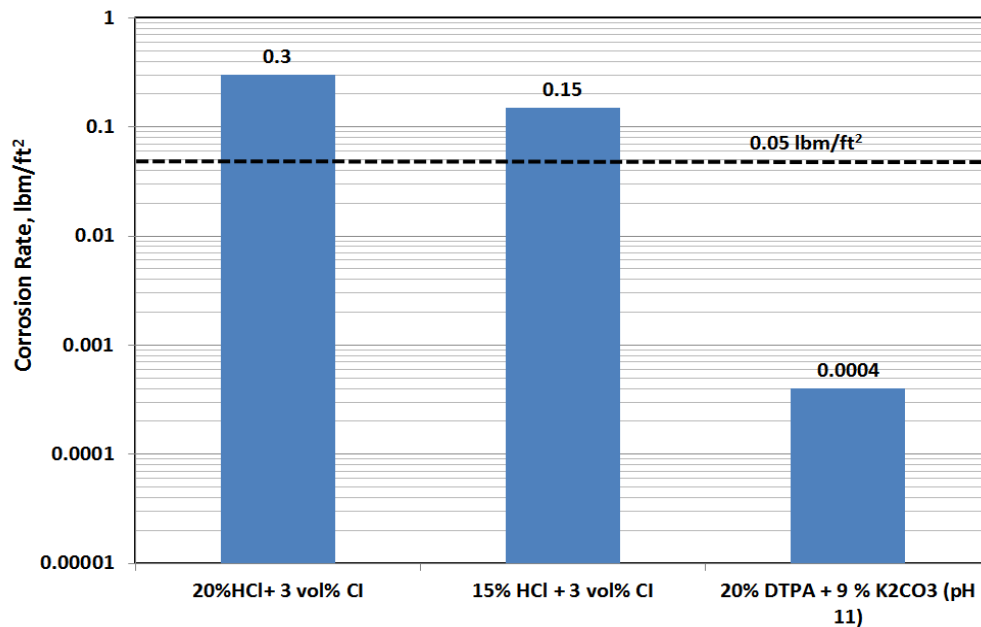

Figure 11—Corrosion rate for formulations evaluated using casing coupons obtained from the field at 150 °C and 10340 kPa (1500 psi).

Coreflooding Experiments Results

The scale removal fluids are used to soak wells and they will be in contact with formations for long periods of time. Therefore, potential formation damage due to fluid invasion or interaction with the reservoir rock must be evaluated. The coreflooding experiments were performed at 150 °C and a back pressure of 6895 kPa (1000 psi). Six pore volumes were injected through the carbonate cores and the effluent samples were collected for analysis. The injected formulation was mixed first with iron sulfide scale samples (S1 and S2) and allowed to stand for 48 h and then filtered using 5 micron filter paper. The ferric concentration in the filtrate is 15,000 and 12,000 ppm for the filtrates from samples S1 and S2, respectively.

Two coreflooding experiments were performed. The first one using the proposed formulation with 18,000 ppm ferric concentration and the second with a concentration of 10,000 ppm ferric ions. The first coreflooding experiment was performed at 1 cc/min injection rate and a core with a porosity of 16% and a permeability of 62 md. The permeability increased to 93 md after injecting six pore volumes, indicating that the risk of formation damage during scale removal using the proposed formulation is minimal. The ferric ion concentration in the effluent analysis remained at 15,000 ppm, which means precipitation does not take place inside the core and DTPA can hold the ferric ions during scale dissolution. The second coreflooding experiment was performed using a carbonate core with a porosity of 15.5 % and permeability of 58 md. The fluid with 10,000 ppm ferric was injected and the permeability increased from 58 to 86 md and the ferric concentration in the effluent remained the same as that of the injected one. Coreflooding experiments confirmed that the proposed formulation will not cause any formation damage during scale removal.

Comparison between THPS and the Proposed Formulation

Wang et al. (2015) recommended the use of 50 wt % THPS to remove iron sulfide scale. They found that the THPS formulation can remove iron sulfide scale effectively, but it has a high corrosion rate. The solubility of the two samples of iron sulfide scale evaluated in this study was determined using 50 wt % THPS at pH 4.2. The solubility of scale in the THPS formulation to the results obtained with the formulation proposed in this study.

Figure 12 shows the results of the solubility tests performed with samples S1 and S2 in 50 wt % THPS at pH 4.2 and 20 wt % DTPA with 9 wt % K_2CO_3 at 120 °C. The scale solubility is THPS 2% higher than that obtained with the proposed formulation for sample S1. For sample S2, THPS provided a 13% lower solubility, which is likely due to the presence of calcite in S2 (20 wt %). THPS contains a sulfate group (SO_4^{2-}) which can react with calcium to produce calcium sulfate that will precipitate, retarding the THPS reaction. Based on these results, THPS is not recommended to remove scale that contains calcite. In addition, THPS is highly corrosive to the well tubulars as shown in **Figure 13**. The

formulation based on THPS is very corrosive compared to the proposed DTPA formulation even at low temperatures. Thus, the formulation based on THPS cannot be used for the removal of iron sulfide scale.
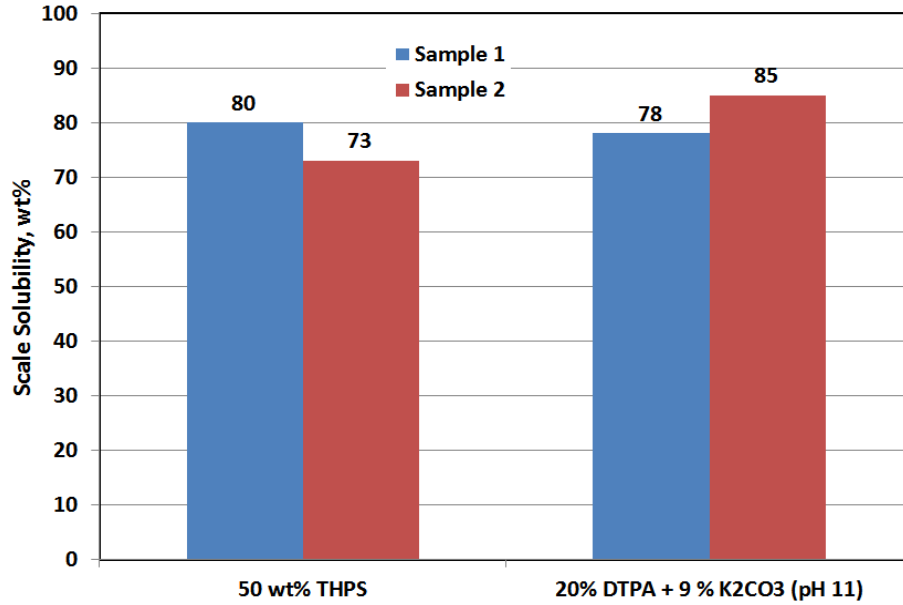

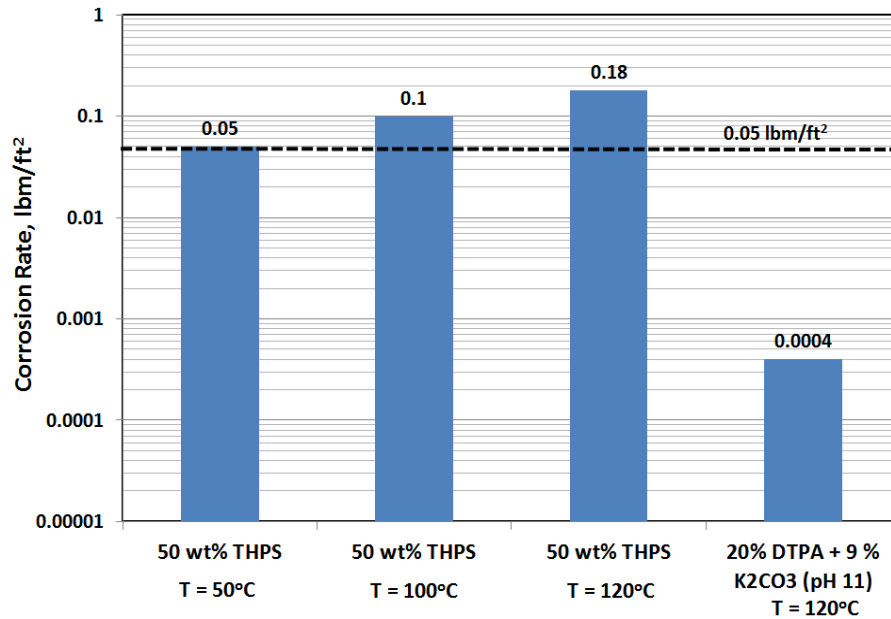**Figure 12**—Solubility of the two iron sulfide scale samples at 120 °C.

Figure 13—Corrosion rate of formulations based on THPS and the proposed formulation at different temperatures.

The formulation based on THPS loaded with the iron dissolved from the iron sulfide scale from sample S1 (with a ferric ion concentration of 16,000 ppm) was used in one coreflooding experiment. The same coreflooding procedure described in section 3.5 was

followed here. Six pore volumes were injected at 150 °C and a back pressure of 1500 psi. Carbonate cores with the same lithology with a porosity of 15% and a permeability of 60 md were used. The core permeability after the injection of the THPS formulation is 23 md. The core lost 60% of its original permeability, likely due to the precipitation of calcium sulfate. Therefore, if THPS comes into contact with the formation during iron sulfide removal, it will cause formation damage in addition to tubular corrosion.

The cost of one gallon of HCl (15 wt%) + 3 vol% corrosion inhibitors + 3 vol% corrosion inhibitor intensifier is ~ \$33. On the other hand, DTPA liquid is expensive and costs around \$15/gal. However, in this study it is prepared from powder using KOH base, which costs \$3/gallon. The cost of combined DTPA and K_2CO_3 is \$3.1/gallon. For the current formulation, there is no need for adding corrosion inhibitors because the developed formulation is non-corrosive compared to HCl. The overall cost is much less than that of HCl since at such temperatures, expensive corrosion inhibitor and the intensifier are added. This in addition to the cost of treating H_2S produced because of using HCl. The developed formulation is noncorrosive and does not release H_2S.

CONCLUSIONS

A new formulation is proposed for the removal of iron sulfide scale from sour gas wells. This formulation is based on the DTPA chelating agent and potassium carbonate as a catalyst. The developed formulation is noncorrosive and less expensive that the current HCl formulations that release H_2S. Several solubility, stability, corrosion, and coreflooding experiments were performed. The following are the main conclusions of this study:

1. The optimum formulation based on scale solubility is 20 wt % DTPA with 9 wt % K_2CO_3 at a pH of 11.
2. The proposed formulation can dissolve different types of iron sulfide scale effectively without generating H_2S.
3. The proposed formulation is gentle to the well tubulars and the formation because it has a very low corrosion rate, with the added benefit of not having to use corrosion inhibitors. In addition, the formulation does not cause any damage to the core, and even enhanced the permeability.
4. Compared to the formulations developed earlier, such as THPS, the proposed formulation is more effective in terms of iron sulfide solubility, with a very low potential to cause corrosion and formation damage.
5. The optimum DTPA concentration is found to be 20 wt % and the optimum catalyst concentration is 9 wt %. The developed formulation was able to dissolve 90% of the field scale without using any corrosion inhibitors.
6. The developed environment friendly formulation can be used in offshore operations.
7. The maximum reported corrosion rate for the new formulation is 0.036 kg/m^2 (0.008 lbm/ft^2), which is well below the acceptable limit (<0.227 kg/m^2 or < 0.05 lbm/ft^2).

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