Evaluation of Chelating Agents for Iron Sulfide FeS Scale Removal

Raja Ramanathan and Hisham Nasr-El-Din, Texas A&M University

Abstract

Scaling of well tubulars can become a very expensive problem because of well deliverability and integrity issues such as reduced production rates and damage to well tubulars. Alternative chemicals such as chelating agents are necessary to dissolve iron sulfide scales because of the the conventional HCl treatment is corrosive and toxic. However, chelating agents have been scarcely studied for iron sulfide dissolution. This paper investigates Ethylenediaminetetraacetic acid (EDTA), Diethylenetriaminepentaacteic acid (DTPA), and N-(2-Hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid (HEDTA) for its iron sulfide (FeS) dissolution capacity and kinetics at 150°F.

Chelating agents are expensive chemicals and must be investigated to determine the optimum concentration, pH, and treatment time at 150°F. 0.1g of iron sulfide composed of mainly troilite was used as the scale. 10 cm³ of EDTA, DTPA, and HEDTA solutions were prepared at different concentrations ranging from 0.05 to 0.4 mol/L using deionized water with a resistivity of 18.2 MΩ-cm. The pH of the dissolvers were dependent on the concentration and the degree of neutralization. The ligands were deprotonated at higher pH using sodium hydroxide or potassium hydroxide. A comparative study of the chelating agents with a low pH (3-5), moderate pH (5-9), and high pH (10-14) determined the optimum pH for the scale treatment. The sampling time of the dissolution process set at 1, 2, 4, 8, 20, 30, and 72 hours determined the kinetics of the scale dissolution process and helped optimize the treatment time. The iron concentration in the dissolver was quantified using an Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

Two calculated parameters, dissolution capacity and dissolver consumption, determined the effectiveness of the chelating agent in dissolving iron sulfide. From the bottle tests at 150°F, lower pH solutions were more effective. 100% of the iron from iron sulfide was complexed by 0.3 mol/L K_2-DTPA after 20 hours of soaking. 0.2 mol/L Na_2-EDTA and 0.3 mol/L K-HEDTA was able to remove 69 and 96% of the initial iron present in 0.1 g of iron sulfide. The mechanism of dissolution at pH < 5 was determined to be H^+ attack with surface complexation. At alkaline conditions (pH > 10), the dissolution of the scale was negligible and was a result of solution complexation after surface hydrolysis. The order of the chelating agents in terms of dissolution capacity was DTPA > HEDTA > EDTA at all pH conditions. The kinetics study showed that the optimum treatment depended on the pH of the chelating agent. For pH < 5 dissolvers, 16-20 hours was sufficient to obtain the maximum dissolution capacity. For dissolvers with a pH greater than 10, the

dissolution continued for more than 72 hours and was minimal. Increasing the concentration of the chelating agent aided the solubility of the scale at pH < 5 only. A SEM study showed the changes in the morphology of the iron sulfide particles after dissolution with low and high pH solutions of the chelating agent.

The role of chelating agents in iron sulfide dissolution has not been thoroughly investigated. There is no study that reports the optimum treatment time. The role of pH of the dissolver also needs more attention. This paper fills these gaps in literature and provides the optimum dissolver composition and treatment time for field operations.

Introduction

During the course of production from a well, scaling problems often come up due to excessive water production, leading to lower well deliverability, and well tubular damage. This may happen in wells producing from conventional or unconventional resources, and is often diagnosed through surface monitoring or downhole diagnosis via production logging, or well testing (Quintero et al. 2017, Khan et al. 2017, Hamza et al. 2015).

The use of alternative chemicals to remove oilfield scales is necessary because of the problems associated with using HCl. Chelating agents is stable at high temperature conditions, does not reprecipitate the scale, is corrosion friendly, and is non-toxic. Untill now, chelating agents have been used to solve sulfate scales such as barite and calcium sulfate. Iron sulfide scales have very low solubility, precipitating much easier than other scales (Martell et. al 1996). Iron sulfides can be of various forms depending on the pH, pressure, temperature, and aging time. Hafiz et al. (2017) showed that the iron sulfide scale remains as troilite (FeS) at high temperatures.

Iron reprecipitation is a major issue associated with HCl treatment of iron sulfide scales. These problems can be solved by using alternative dissolvers that effectively dissolves iron sulfide, have a low corrosion rate, produce less H_2S, be stable at high temperature conditions, and does not reprecipitate iron or sulfur.

Organic acids such as formic acid, maleic acid, citric acid, and lactic acid were tested to dissolve iron sulfide at 150°F and 1,000 psi, but the dissolution capacity did not exceed that of Na_2-EDTA (Ramanathan and Nasr-El-Din 2019). THPS and a novel chemistry was evaluated and optimized to dissolve marcasite, pyrite, pyrrhotite, and troilite at 122°F (Wylde et al. 2016, Patel et al. 2019). They found THPS to be effective in dissolving all the polymorphs except pyrrhotite ($Fe_{1-x}S$). 50 wt% THPS was found to have a corrosivity of 0.05 and 0.1 lbm/ft^2 at 122 and 212°F (Mahmoud et al. 2018), which is beyond the acceptable standards. Polyaminocarboxylic acids have high stability constants with metal ions, preventing reprecipitation. Wells that are shut in for scale treatment can cost millions of dollars in production revenue for the operator. Therefore, optimizing the treatment time is essential for chelating agents to be economically effective. The concentration and volume of the chelating agent to dissolve the scale is important. Optimizing the molar ratio of the chelating agent to the iron sulfide can lead to improved economics as well. High temperature conditions render HCl to be expensive because of the additional cost of corrosion inhibitors, intensifiers, and hydrogen sulfide scavengers. Chelating agents have high temperature stability and does not require any additional additives to be effective at temperatures up to 350°F (Sokhanvarian et al. 2012).

Chemistry of Polyaminocarboxylic Acid

Chelating agents with one or more nitrogen atoms and two or more carboxyl groups are termed as polyaminocarboxylic acids. They are negatively charged organic molecules, which work by forming coordination bonds with the metal ions, creating a ring like complex. Stability of such complexes are commonly found to be high and depends on the type of metal ion, pH, concentration, system pressure, and temperature (Almubarak et al. 2017a). EDTA, DTPA, and HEDTA have been used in food, biomedical, soil, waste water, and oil industry to dissolve metal carbonates, sulfates, and sulfides. EDTA is a hexadentate chelating agent capable of using 6 ligands to capture the metal atom. Similarly DTPA is an octadentate

chelating agent having 8 locations that can donate electrons to the metal atom. HEDTA's structure is similar to EDTA except one carboxyl group is replaced with a hydroxyl group, making it more soluble at pH<5 conditions (Frenier 2001). The chemical structure of chelating agents have multiple locations where deprotonation can occur by reducing its pH. Different species of a chelating agent are formed by deprotonation and for a chelant having 4 ligands like EDTA, the deprotonation equations can be written as (Spencer 1958):

$$H_4Y \rightleftharpoons H_3Y^- + H^+, \tag{1}$$

$$H_3Y^- \rightleftharpoons H_2Y^{2-} + H^+, \tag{2}$$

$$H_2Y^{2-} \rightleftharpoons HY^{2-} + H^+, \tag{3}$$

$$HY^{3-} \rightleftharpoons Y^{4-} + H^+, \tag{4}$$

where H_mY^{m-n} is the chelating agent with m hydrogen atoms from the carboxylic acid groups. The pKa values for EDTA, HEDTA, and DTPA are given in Table 1. Fig. 1 presents the distribution of the ionic species of EDTA and DTPA with pH at 25°C. For example, at pH 4.4, EDTA mainly exists as H_2Y^{2-}. DTPA is in the form of H_2Y^{-3} at pH 6.4. Each species of the chelating agent is unique in its way to form a complex with the metal ions. Chelating agents are known to adsorb on the solid surfaces and destabilize the crystal structure of the mineral (Chang and Matijević 1983). The metal ion gets removed from the mineral surface and forms a complex in the interface between the solid and the bulk solution. Therefore, the effectiveness of the chelating agent depends on (a) diffusion of the active ligands from the bulk, (b) surface adsorption, (c) surface reaction, (d) complex desorption, and (e) complex diffusion into the bulk solution. The rate limiting step is dependent on the chemistry of the chelating agent. The type of mineral, dissolver concentration, dissolver pH, chemical impurity, and system temperature are some of the factors which govern this process. Literature has limited application of chelating agent to dissolve iron sulfide, and does not investigate its dissolution mechanism.

Table 1—pKa values of the chelating agents used (Chang and Matijević 1983).

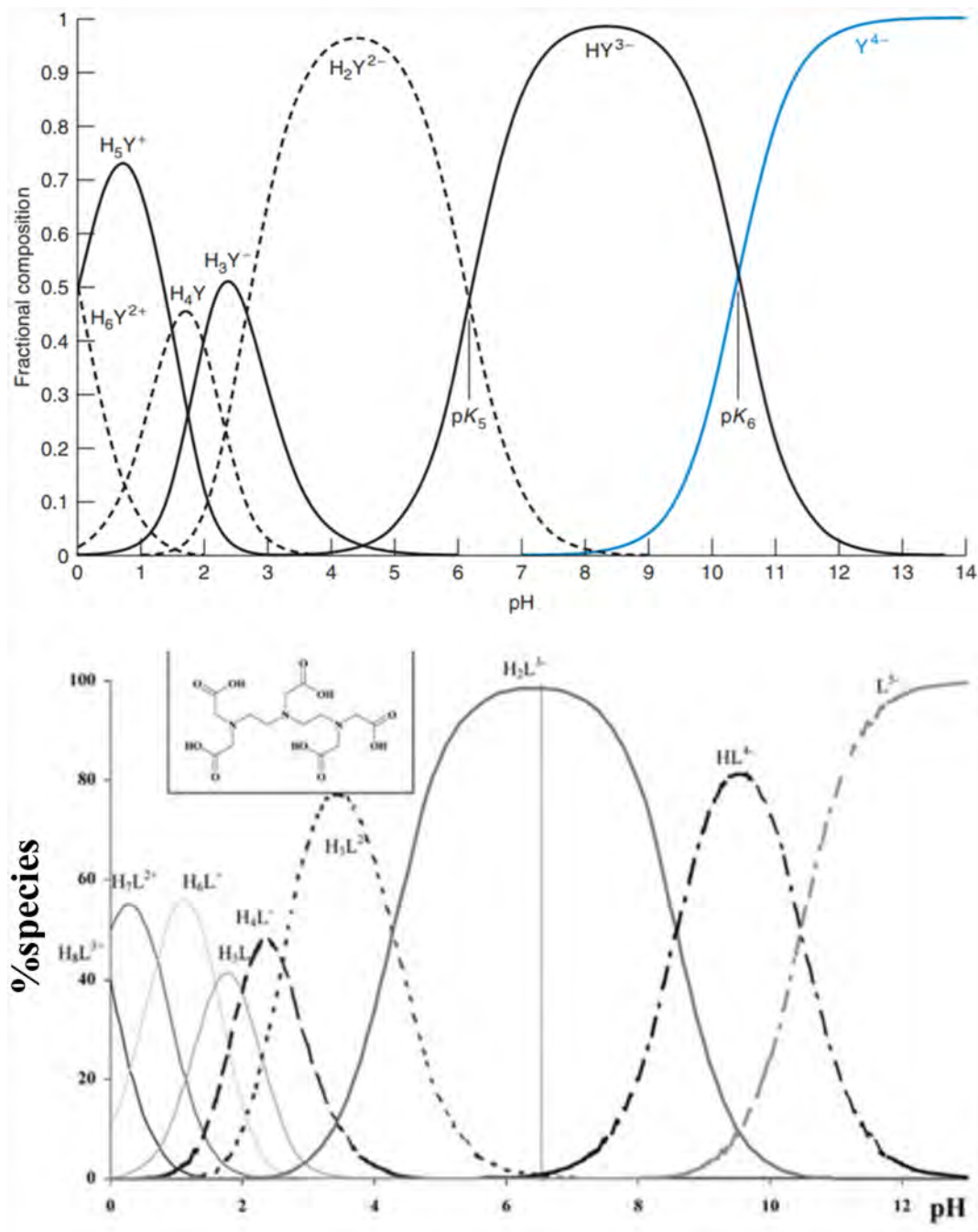| pKa	EDTA	DTPA	HEDTA
a1	1.99	2.14	2.8
a2	2.67	2.38	5.6
a3	6.16	4.26	10.3
a4	10.37	8.60	-
a5	-	10.53	-

Figure 1—Speciation diagrams for: (a) EDTA (Harris 2007) and (b) DTPA (Moulin et al. 2003).

Literature Review

Almubarak et al. (2017b) and Kamal et al. (2018) provide literature reviews of chelating agents that are used to enhance the productivity of oil/gas wells. The study of the interactions of the scale with chelating agents is complicated by the physical and chemical properties of the solid and the ligand solution. Surface defects, surface area, surface charge, solution pH, solution concentration, and the presence of other cations/anions in solution are some parameters that can alter the solid-liquid reaction. The pressure and temperature are external factors that also play a key role in the dissolution. Perry et al. (2005) noted the application of ligand promoted dissolution for calcite minerals in petroleum wells, boilers, and heater tubes. Chelating agents have been used to treat other types of scales such as barite (Geri et al. 2017) and calcium sulfate (LePage et al. 2011).

The role of HEDTA, EDTA, and DTPA to dissolve alkaline earth deposits were investigated by Frenier (2001). He introduced solvent formulations based on hydroxyaminocarboxylic acids because of its unique ability to be soluble at pH < 4. Low pH (< 5) chelating agents were found to dissolve more calcite than its high pH (> 7) counterpart at 72, 150, and 190°F. Torres et al. (1989) and Chang and Matijević (1983) discussed the mechanisms of metal hydrous oxides dissolution with chelating agents. In-depth investigations of the kinetics of ligand adsorption and surface dissolution led them to make suggestions about the mechanisms of the ligand-solid interactions at different pH levels and temperatures. The authors observed similar dissolution behavior (increase of dissolution at early time followed by plateau) with time at pH 3-11, however the quantities of hematite dissolved using excess EDTA, HEDTA, and DTPA were different. This difference in the quantity of hematite dissolved at different pH increased as the temperature increased. The acidic form of EDTA is known to chelate calcium ions from calcium carbonate through H^+ attack and free calcium ion sequestering (Fredd and Fogler 1996). Calcite dissolution kinetics was observed to be dependent on the H^+ concentration. The authors defined two mechanisms to dissolve calcite: surface complexation and solution complexation. The surface complexation is related to the chelation of the metal ion through surface adsorption and destabilization of the bond between the calcium and carbonate ions. Solution complexation is the free metal ion chelation from the solution. The metal ions are released into the solution because of hydrolysis on the scale surface. The pH of the dissolver was crucial in determining the dissolution mechanism. The increase in protonation of the chelating agent led to higher rate of dissolution. Putnis et al. (1995) studied the effect of concentration, temperature, and scale surface area by conducting kinetic dissolution tests with barium sulfate using DTPA. The reaction rate was observed to be controlled by desorption of the Ba-DTPA complex from the solid surface. They also found that the efficiency of the solvent in dissolving the barium sulfate is inversely related to the solvent concentration. Atomic force microscopy of the barite particles after dissolution with DTPA indicated trapezoidal pits (Wang et al. 1999). The authors also concluded that one DTPA molecule could bind to two or three Ba^{2+} cations exposed on the scale surface. Dunn and Yen (1999) investigated surface pitting phenomenon on the barite scale when soaked in DTPA. The fundamental study of the interaction of iron sulfide (FeS) with chelating agents has not yet been reported. Limited work has been done to investigate the changes in surface morphology due to dissolution of iron sulfide by chelating agents.

There is a gap in literature involving the study of dissolving iron sulfide (FeS) with different kinds of chelating agents. Due to the aforementioned advantages of using polyaminocarboxylic acids over conventional HCl treatment, they must be investigated in detail. The concentration, pH, scale treatment time are important factors in deciding the optimum treatment for iron sulfide scales in well tubulars, pipelines, or boilers. This paper focuses on three kinds of polyaminocarboxylic acids namely EDTA, HEDTA, and DTPA to dissolve iron sulfide (FeS) at 150°F. The objectives of this paper are to:

1. Evaluate the effect of pH, concentration, treatment time, and type of chelating agent on the solubility of the iron sulfide scale at 150°F.
2. Interpret the mechanism of scale dissolution from the dissolution tests.
3. Study the morphology of the iron sulfide scale before and after treatment with the chelating agents.

These objectives were met by conducting bottle tests and analyzing the results using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS). This paper describes the materials and experimental procedure before presenting the results and discussion of the bottle tests.

Materials

Dissolvers.
Table 2 lists of polyaminocarboxylic acids used, their pH range, and concentration range. Their chemical structure is presented in Fig. 2. The fully protonated form of the chelating agents were purchased and used. The pH was increased by adding sodium hydroxide or potassium hydroxide. Different concentrations of the chemicals were prepared using deionized water with a resistivity of 18.2 MΩ-cm.

Table 2—List of dissolvers used, their concentration range, and pH.

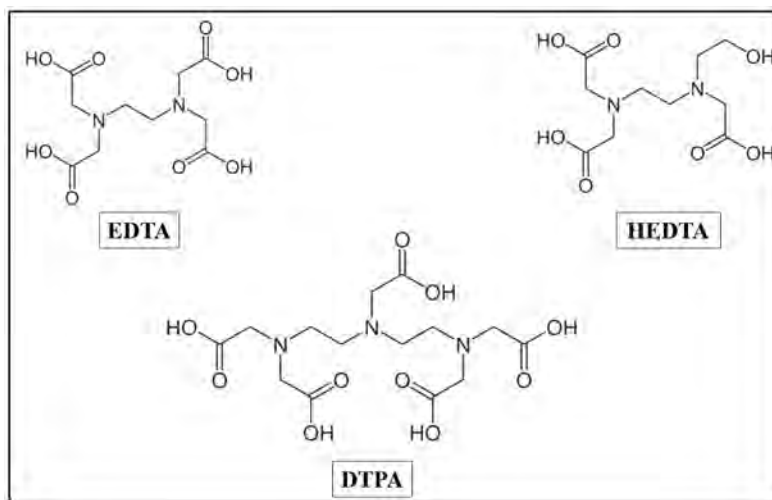| Dissolver	Concentration (mol/L)	pH
Na_2-EDTA	0.05 – 0.2	4.4
Na_3-EDTA	0.1 – 0.4	5.1 – 8.3
Na_4-EDTA	0.1 – 0.4	10.1 – 10.7
K-HEDTA	0.05 – 0.3	3.7 - 4
K_2-HEDTA	0.1 – 0.4	6.2 – 6.7
K_3-HEDTA	0.1 – 0.3	11.2 – 11.5
K_2-DTPA	0.1 – 0.3	3.4 – 3.6
K_3-DTPA	0.1 – 0.3	5.9 – 6.6
K_5-DTPA	0.1 – 0.3	11.5 – 11.7

Figure 2—Chemical structures of EDTA, HEDTA, and DTPA.

Iron Sulfide Scale.
Reagent grade iron sulfide purchased from Sigma Aldrich (CAS No. 1317-37-9) were crushed and used as the scale. The iron sulfide was crushed into a powder using an agate mortar and pestle. Sieving the iron sulfide to a size between 75 and 150 μm helped control the surface area of the scale used for the tests. X-ray Diffraction (XRD) analysis of the particles indicated troilite (75%), pyrrhotite (6%), elemental iron (14%), and remaining maghemite (5%) (Fig. 3). Troilite is in the form of stoichiometric FeS, pyrrhotite is $Fe_{1-x}S$ $(0 < x < 0.125)$, and maghemite is Fe_2O_3.
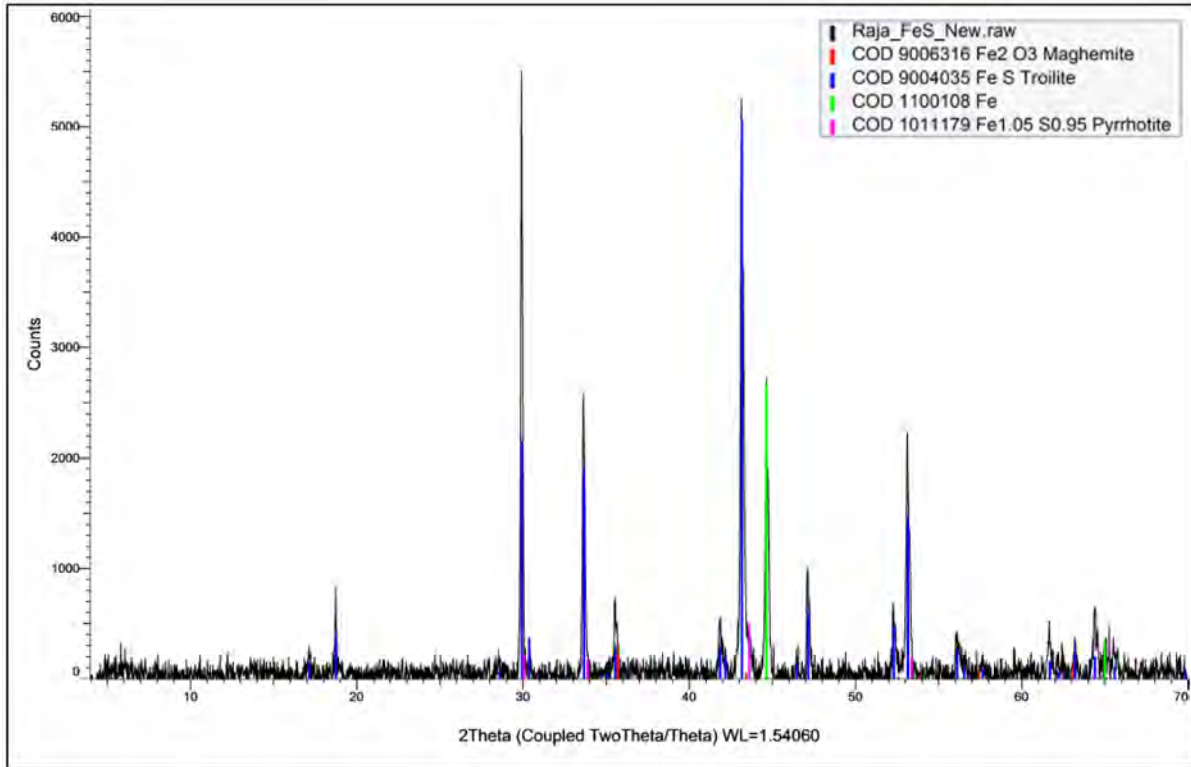
Figure 3—XRD pattern of the iron sulfide scale.

Experimental Tests and Procedures

Solubility Test.
10 cm³ of the prepared dissolver was added to a Pyrex culture tube containing 0.1 g of the iron sulfide scale. The tests were conducted in a static mode. The Pyrex tube has Teflon-lined screw caps that provided an excellent seal and prevented any fluid loss at 150°F. The culture tube was kept in a conventional oven and 0.05 cm³ of the supernatant fluid was withdrawn for sampling at 1, 4, 8, 20, 30, 48, and 72 hours. The fluid was diluted to 10 cm³ and was analyzed for iron concentration using ICP-OES. The remaining solids were filtered with a 1-5 μm filter paper. The solids were rinsed thoroughly with isopropanol and dried at 212°F for 12 hours. SEM analysis was done on the dried solids. The pH of the dissolver was measured before the test. Two parameters were calculated based on the measurements made: (1) dissolving capacity (C/C_o) and (2) dissolver consumption. The dissolving capacity is defined as the ratio of the concentration of iron (ppm) in the spent dissolver to the concentration of iron (ppm) at 100% dissolution using 20 wt% HCl. It is given by Eq. 4:

$$\frac{C}{C_o} = \frac{Concentration\ of\ Fe\ in\ the\ spent\ dissolver\ (ppm)}{Concentration\ of\ Fe\ in\ the\ initial\ iron\ sulfide\ (ppm)}, \tag{4}$$

The dissolver consumption is a measure of the dissolver needed (in mol/L) to achieve maximum dissolution of the iron sulfide scale. It is calculated by the ratio of maximum concentration of iron chelated to the concentration of chelating agent. Eq. 5 presents the dissolver consumption as:

$$Dissolver\ consumption = \frac{Molarity\ of\ Fe\ in\ the\ dissolver\ (M)}{Molarity\ of\ the\ dissolver\ (M)}, \tag{5}$$

Results and Discussion

The study of the effect of the dissolver's pH and concentration on the solubility of the iron sulfide scale determined the nature of the chemical interactions between various species of the chelating agent and the scale. The optimum treatment time for scale dissolution was inferred from the dissolution test results. SEM study demonstrated the mechanism of scale dissolution.

Effect of pH.
The speciation of chelating agents varies with pH. As the pH increases, the ligands get deprotonated. The species of DTPA, HEDTA, and EDTA at acidic conditions of pH<5 consisted of K_2-DTPA, K-HEDTA, and Na_2-EDTA, respectively. Table 2 shows the type of species of the chelating agents used at various pH conditions. Fig. 4 shows a bar chart between the dissolved iron from iron sulfide as a function of pH after 72 hours of dissolution at 150°F. The iron sulfide solubility is the highest at pH<5 for EDTA, HEDTA, and DTPA. The low pH values ranged from 3.5 to 4.4, moderate pH from 6.3 to 8.2, and high pH values of greater than 10. The results in Fig. 4 show that the dissolution of iron sulfide is strongly dependent on the pH of the chelating agent. At 0.2 mol/L and pH < 5, DTPA, HEDTA, and EDTA show iron concentrations of 6.3, 5.2, and 4.4 g/L, respectively. The solubility dropped to 2.3, 1.5, and 1.5 g/L at moderate pH and 0.17, 0.12, 0.16 g/L at high pH conditions for DTPA, HEDTA, and EDTA, respectively. The higher concentration of H^+ ions in the acidic ligand dissolvers is crucial in promoting dissolution. The H^+ ions can react with the sulfur atoms in the iron sulfide and produce hydrogen sulfide. The reactions associated with the acidic dissolution of iron sulfide using Na_2-EDTA, for example are as follows:

$$H_2L^{2-} + FeS \rightarrow FeSH_2^{2+} + L^{4-} \tag{6}$$

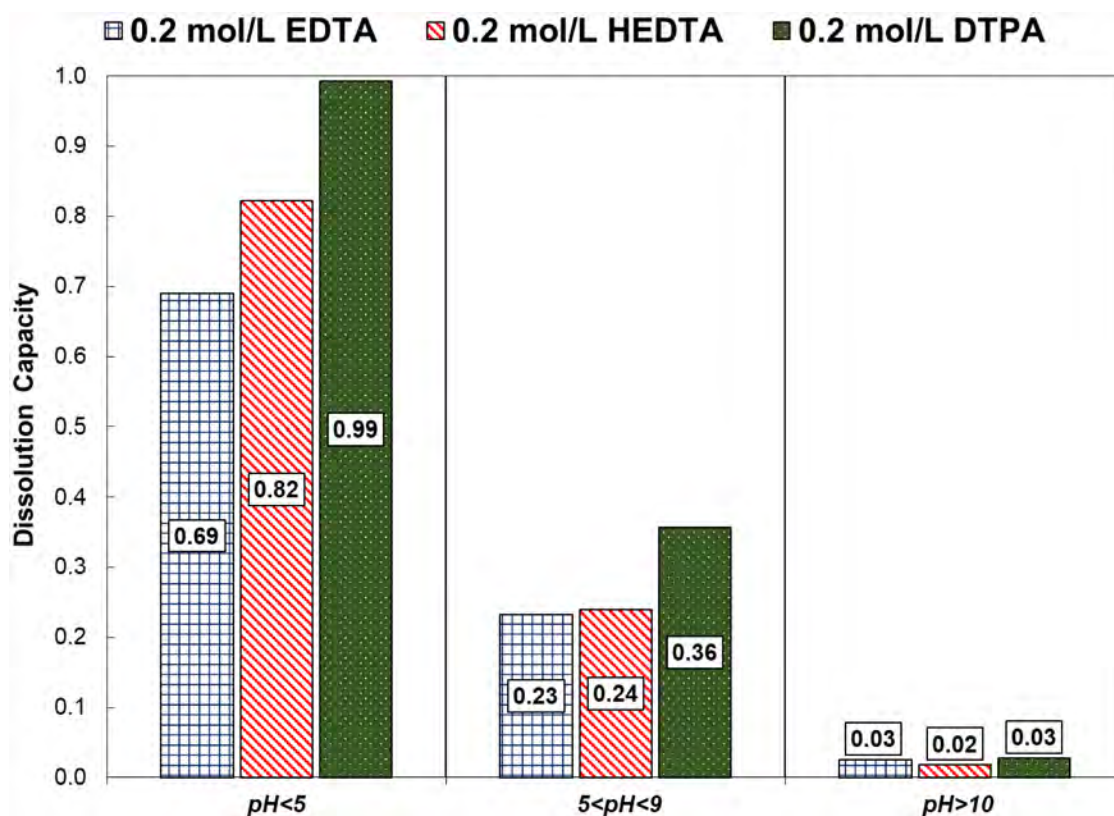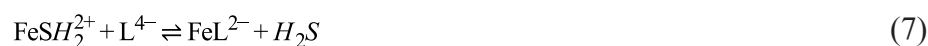$$FeSH_2^{2+} + L^{4-} \rightleftharpoons FeL^{2-} + H_2S \tag{7}$$

Figure 4—Effect of pH on the iron sulfide dissolution capacity after 72 hours of soaking.

The Fe^{2+} in Eq. 6 is sequestered by the ligand. The stability constant of Eq. 7 is high and prevents the reprecipitation of the iron sulfide. The $FeSH_2^{2+}$ is unstable and the bond between Fe and S breaks, resulting in Fe^{2+} and H_2S. The Fe^{2+} gets chelated by the chelating agent in the solution. The H_2S will be in the solution phase at high pressure conditions, increasing the corrosion of tubulars. The dissolution continues in the forward direction until the concentration of H^+ ions is reduced to 0. As Chang and Matijević (1983) noted in the case of iron oxides, chelation can occur by surface complexation as well. The chelating agent adsorbs on the surface of the scale at the iron lattice site and creates a charge imbalance leading to removal of Fe^{2+} ion from the surface of the iron sulfide.

At moderate and high pH conditions, the H^+ concentration is low and does not play a major role in the dissolution of the scale. The adsorption of the ligands on the surface of the iron sulfide and the surface reaction to remove the Fe^{2+} ion may be the rate limiting step at pH > 5. The negative charge contributed by the chelating agent must be higher than the sulfur atom in order to break the bond. This can be assisted by the weakening of bond strength by increasing the temperature. However, at 150°F, the rate of dissolution is very slow and does not complete even after 72 hours. The dissolution of the scale occurs primarily as a result of solution complexation, where the hydrolysis of the iron sulfide leads to Fe^{2+} release to the solution and subsequently chelated.

Effect of Dissolver Concentration.
The concentration of the fully dissolved iron from the 0.1 g iron sulfide powder in 10 cm^3 solution is 0.11 mol/L. It requires a 1:1 molar ratio of the chelating agent to the iron for complete sequestration of Fe^{2+} ions. This study shows the effect of concentration of the ligand on the iron sulfide solubility. At pH < 5, chelating agents have limited solubility in water. EDTA at pH < 5 was evaluated to dissolve iron sulfide at 0.05, 0.1, and 0.2 mol/L. Concentrations of greater than 0.25 mol/L EDTA could not be prepared at pH < 5. Similarly, DTPA and HEDTA were evaluated for its iron sulfide dissolution at 0.05, 0.1, 0.2, and 0.3 mol/L for pH < 5. The chelating agents were studied to dissolve iron sulfide at 0.1, 0.2, 0.3, and 0.4 mol/L and pH > 5 as well.

In acidic conditions (pH < 5), the solubility of iron sulfide increased with the increase in concentration (Fig. 5). Even though there is an increase in the solubility at higher concentrations, the increase in solubility dimishes at every step increase in concentration. For example, when the concentration was changed from 0.05 to 0.1 mol/L K-HEDTA, the incremental dissolution was 81%. However, when the concentration changed from 0.1 to 0.2 mol/L, the incremental dissolution was 48%. Similarly, there was a 17% improvement in dissolution for 0.3 mol/L when compared to 0.2 mol/L K-HEDTA. This shows that there is excess chelating agent in high concentration solutions. There could be steric hindrance effects in the interface between the solids and the bulk solution, limiting the activity of the chelating agent and preventing further dissolution. The trend was similar for Na_2-EDTA and K_2-DTPA as well.
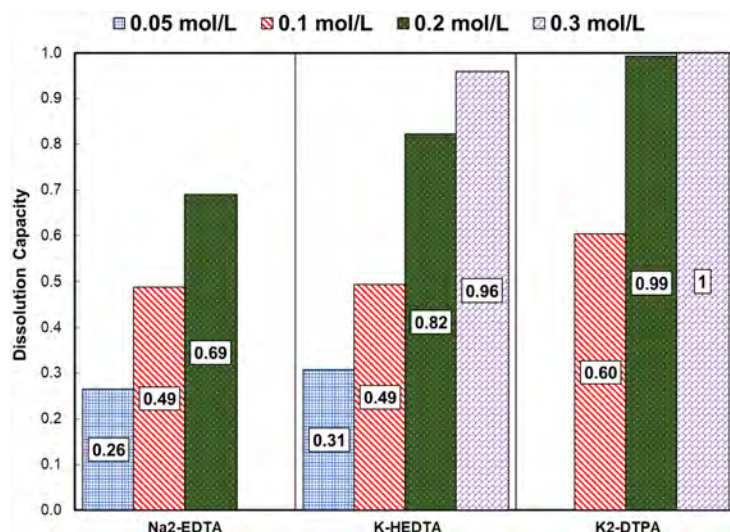
Figure 5—Effect of concentration on the iron sulfide dissolution at pH < 5 after 72 hours of soaking.

For chelating solutions at 5 < pH < 9, the incremental solubility with higher concentration solutions was minimal (Fig. 6). At 0.05 mol/L Na_3-EDTA, the iron dissolved from iron sulfide was noted to be 0.95 g/L. It increased to 1.65 g/L for 0.1 mol/L Na_3-EDTA. However, for 0.4 mol/L Na_3-EDTA, the dissolution did not improve and the final iron concentration in the dissolver was measured to be 1.62 g/L. This showed that increasing the concentration beyond a 1:1 molar ratio of iron sulfide to the neutral/alkaline chelating agent (pH > 5) does not yield additional dissolution. This is due to the mechanism of dissolution of iron sulfide by solution complexation at moderate and high pH conditions. There is no significant activity at the surface of the scale. The dissolution of iron sulfide occurs as a result of surface activity as well as solution complexation at pH < 5. Thus, it can be concluded that the solubility of iron sulfide is dependent on the concentration only at pH < 5. From this study, a molar ratio of 3:1 K_2-DTPA:FeS at pH = 3.6 sequesters 100% of the available iron. 69% of the available iron from the iron sulfide is dissolved in a 2:1 molar ratio of Na_2-EDTA and scale. This investigation found the maximum dissolution of iron sulfide is at the maximum possible concentration of the chelating agent at pH < 5 conditions.
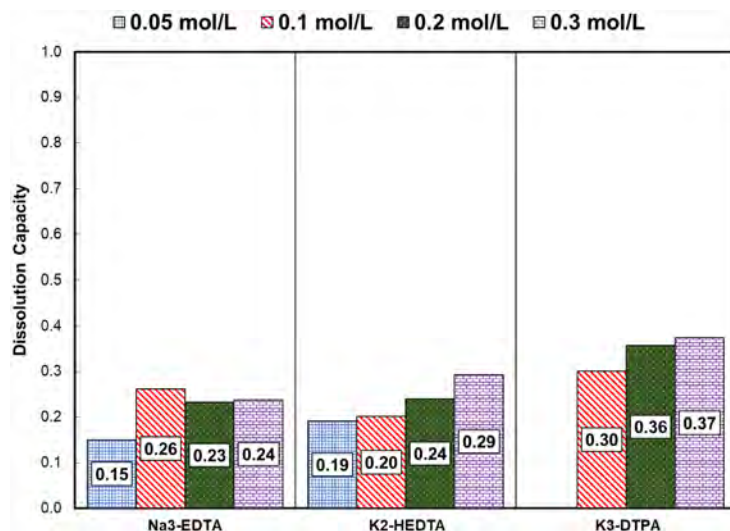

Figure 6—Effect of concentration on the iron sulfide dissolution at pH between 5 and 9 after 72 hours of soaking.

The dissolver consumption as a function of dissolver concentration is plotted in Fig. 7 for the acidic chelating agents. The dissolver consumption reduces as the concentration increases. For K_2-DTPA, the

dissolver consumption reduces from 0.68 to 0.41 when its concentration increases from 0.1 to 0.3 mol/L. Similarly, the dissolver consumption reduces as the ligand concentration increases for K-HEDTA and Na_2-EDTA. The reduction in the dissolver consumption can be explained by the restriction of incremental dissolution at the solid-liquid interface as a result of excess chelating agent. The low dissolver consumption at high concentration can yield bad economics for the treatment. Thus, it is important to consider treating the scale at lower concentrations and refreshing the solution after obtaining maximum dissolution.
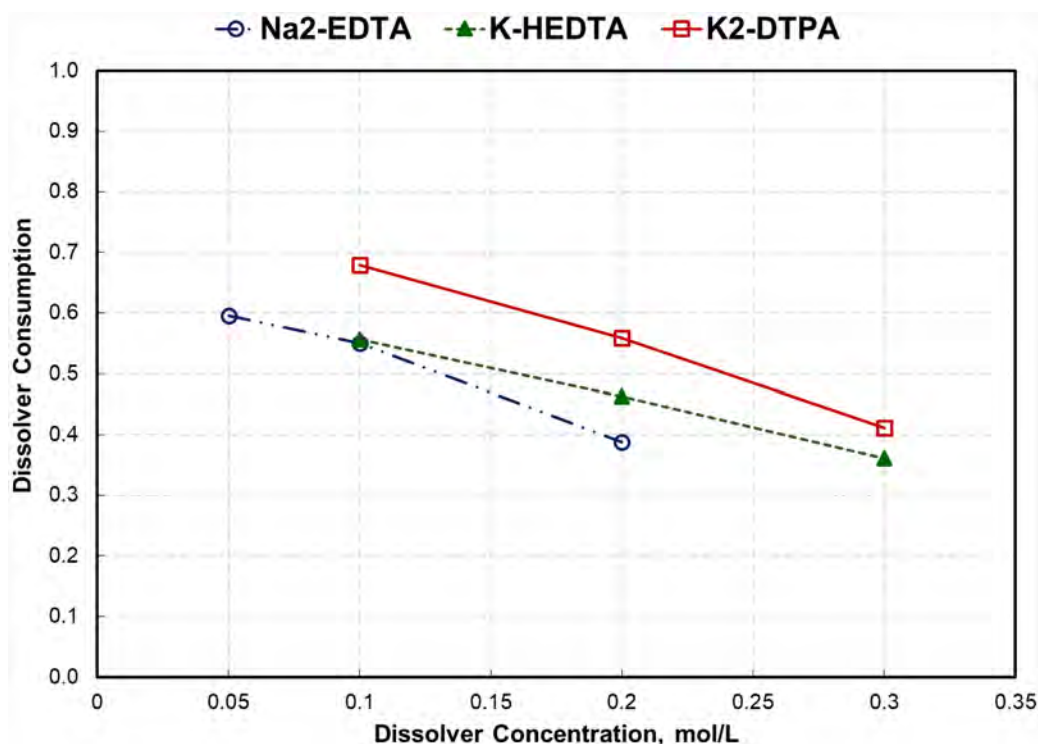

Figure 7—Dissolver consumption as a function of dissolver concentration for acidic chelating solutions (pH < 5) after 72 hours of soaking.

Effect of Treatment Time.

The dissolution rate depends on the pH of the chelating agent. This paper investigated the dissolution of iron sulfide scale for a period of 72 hours. Supernatant samples of 0.05 ml were taken at 1, 4, 8, 20, 30, 48, and 72 hours. ICP analysis determined the iron concentration in the dissolver solutions. Optimization of treatment time is crucial for scale dissolution to make it economical in the field. The treatment is discontinued when the incremental dissolution over time is minimal. In the field, this could mean removing the spent dissolver after the optimized treatment time and replacing it with new solution for continued treatment. Figs. 8, 9, and 10 present a semi-log plot for the iron concentration in the spent dissolver vs time. These results demonstrate that at pH < 5, the solubility of iron sulfide scale reaches the maximum within 16-20 hours and there is no further significant increase in the dissolution after 20 hours. It was observed that higher concentration solutions reach their peak faster than low concentration dissolvers. The dissolution rate may be reduced significantly due to the consumption of H^+ ions in the solution. There is limited interaction of the dissolver with the scale solids when H^+ is consumed from the chelating agent. The surface of the iron sulfide changes to a more sulfur rich layer, which inhibits further dissolution as well. This was observed from the SEM study, which w ill be addressed in the following sections. At 150°F, the bond strength of iron sulfide is still strong and doesn't allow the chelating agent to destabilize it. An increase in the temperature may lead to bond cleavage and subsequent chelation of the iron.
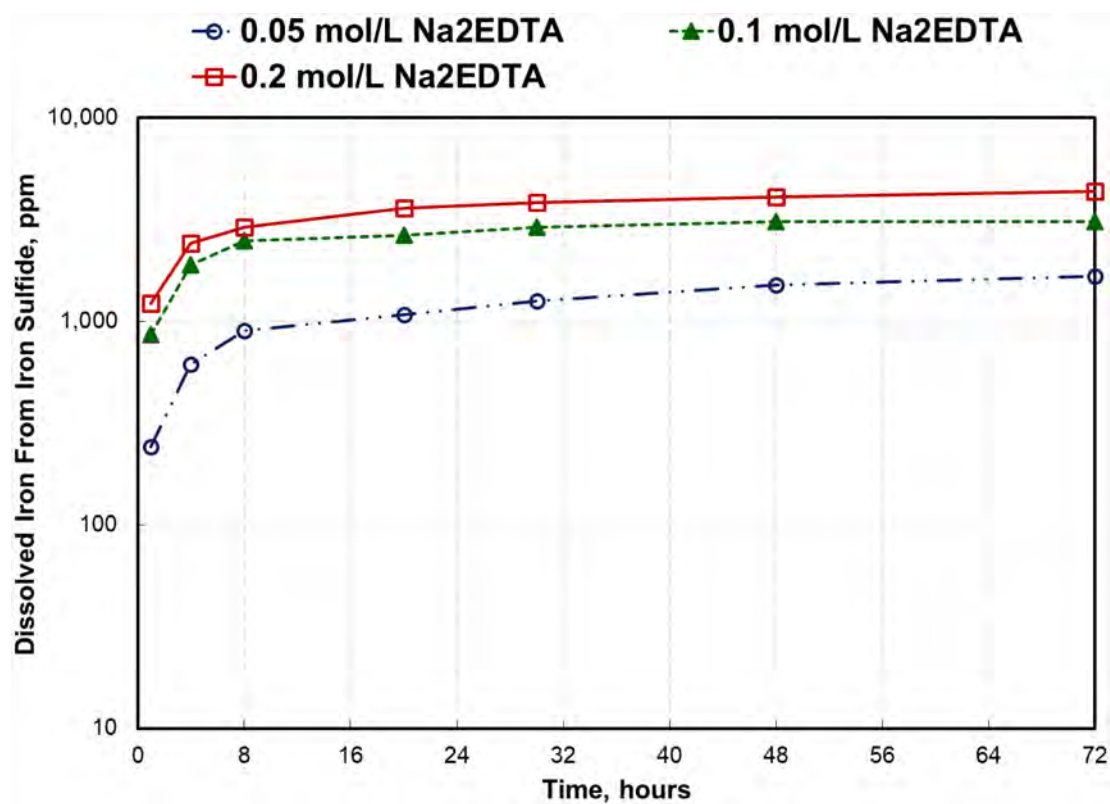
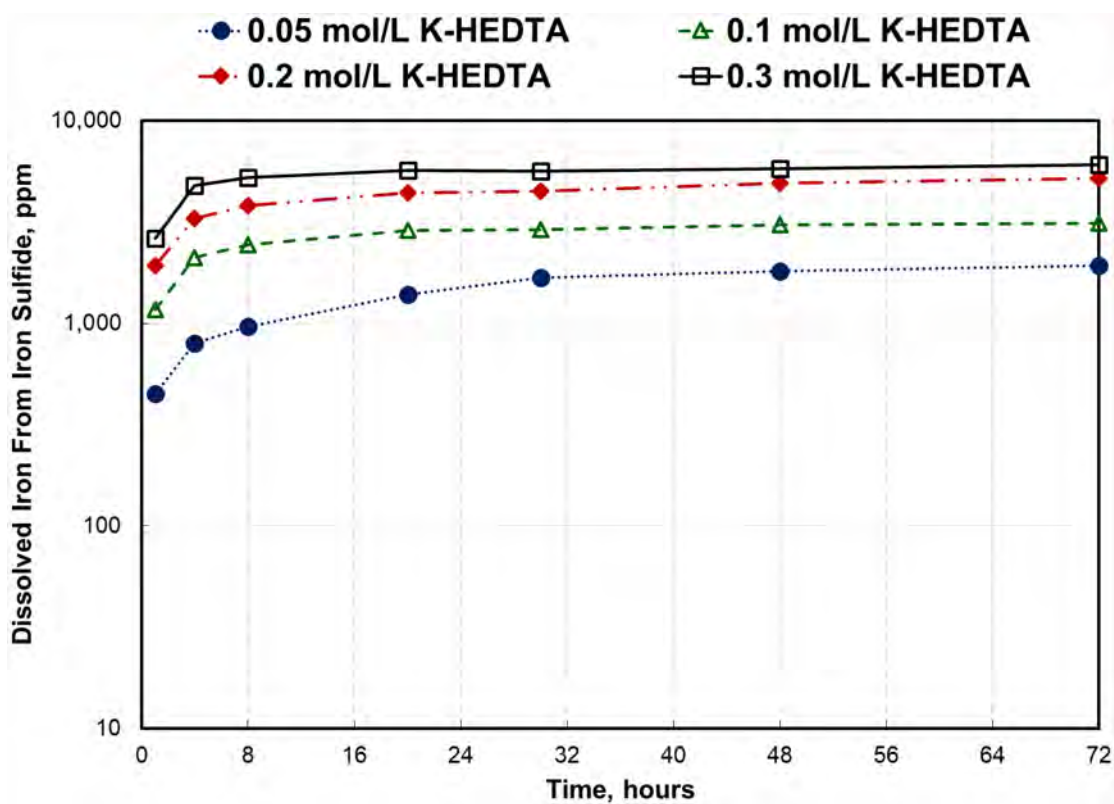**Figure 8—Iron sulfide dissolution as a function of time for Na$_2$-EDTA at 150°F.**

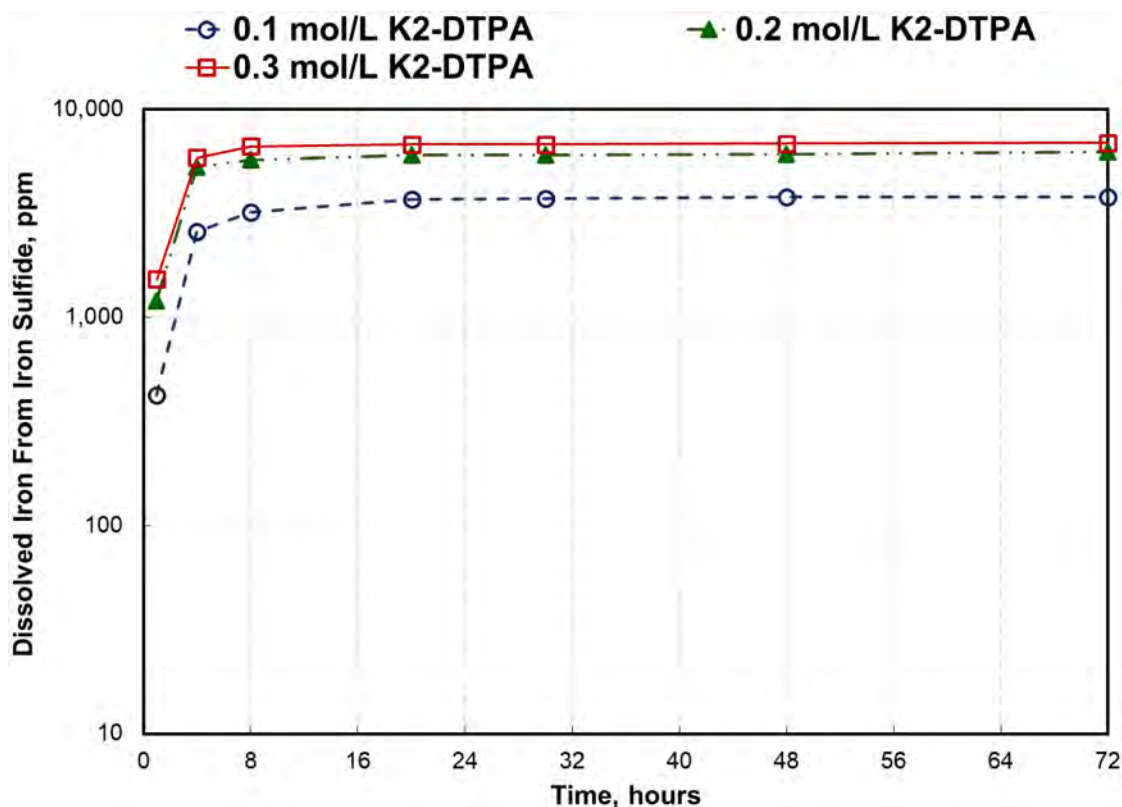**Figure 9—Iron sulfide dissolution vs time for K-HEDTA at 150°F.**

Figure 10—Iron sulfide dissolution vs time for K$_2$-DTPA at 150°F.

It was observed that the dissolution did not flatten out for higher pH dissolvers (Fig. 11). The iron concentration in the spent dissolver continued to increase throughout the 72 hours of the experiment. Since the H$^+$ concentration is low at higher pH conditions, the mechanism of dissolution is primarily solution complexation. Aljeban et al. (2018) reported similar findings of the nature of dissolving iron sulfide using an alkaline chelating solution developed by Chen et al. (2017). They noticed that, at 250°F, the pyrrhotite chips continued to be dissolved in the alkaline chelating dissolver until 24 hours (maximum time tested), whereas an acidic chelating dissolver achieved maximum dissolution at 4 hours. Surface adsorption of the chelating agent contributes very little to the dissolution of iron sulfide at 150°F. Surface defects can cause the Fe^{2+} to be released from the solid and consequently getting chelated by the dissolver. Fig. 12 compares the dissolution as a fraction of the maximum dissolution vs time for low and high pH solutions of DTPA. While designing a field treatment for iron sulfide dissolution, the treatment time must be strongly considered and optimized. This paper demonstrates that 20 hours is the optimum treatment time for the dissolution of the iron sulfide scale by EDTA, HEDTA, and DTPA at pH < 5.
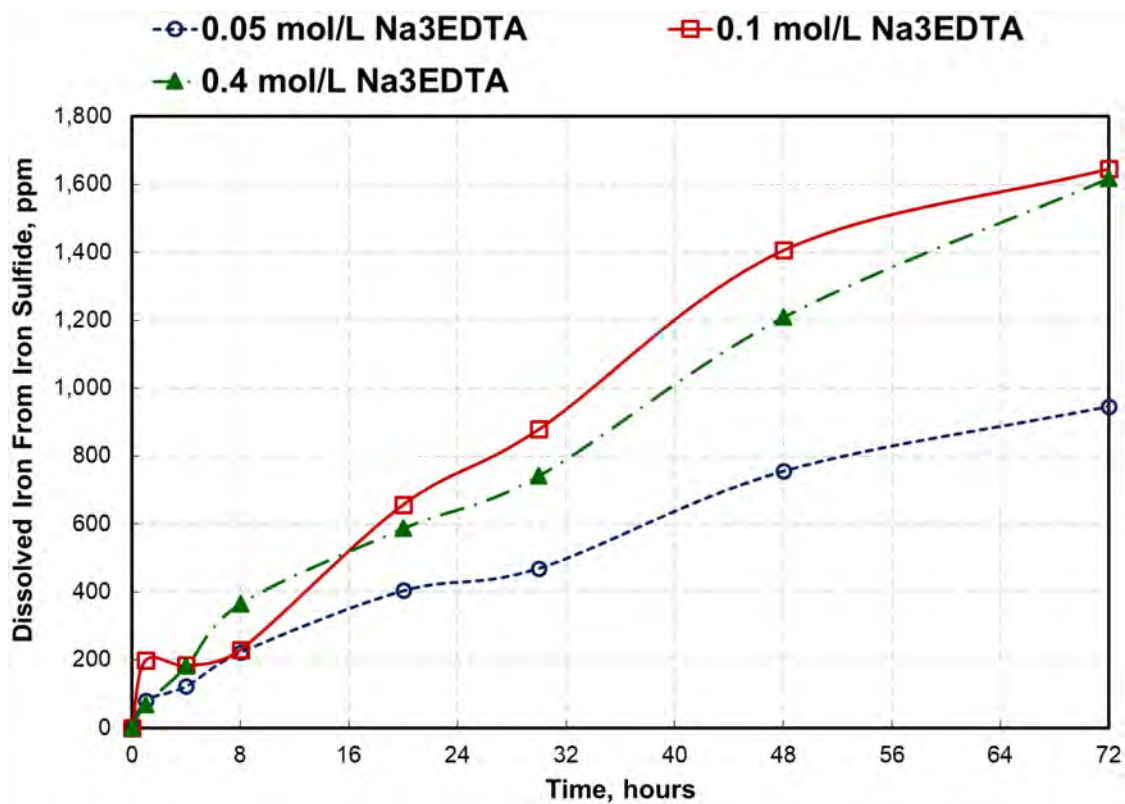
Figure 11—Dissolution of iron sulfide as a function of time at pH between 5 and 9 of EDTA and 150°F.
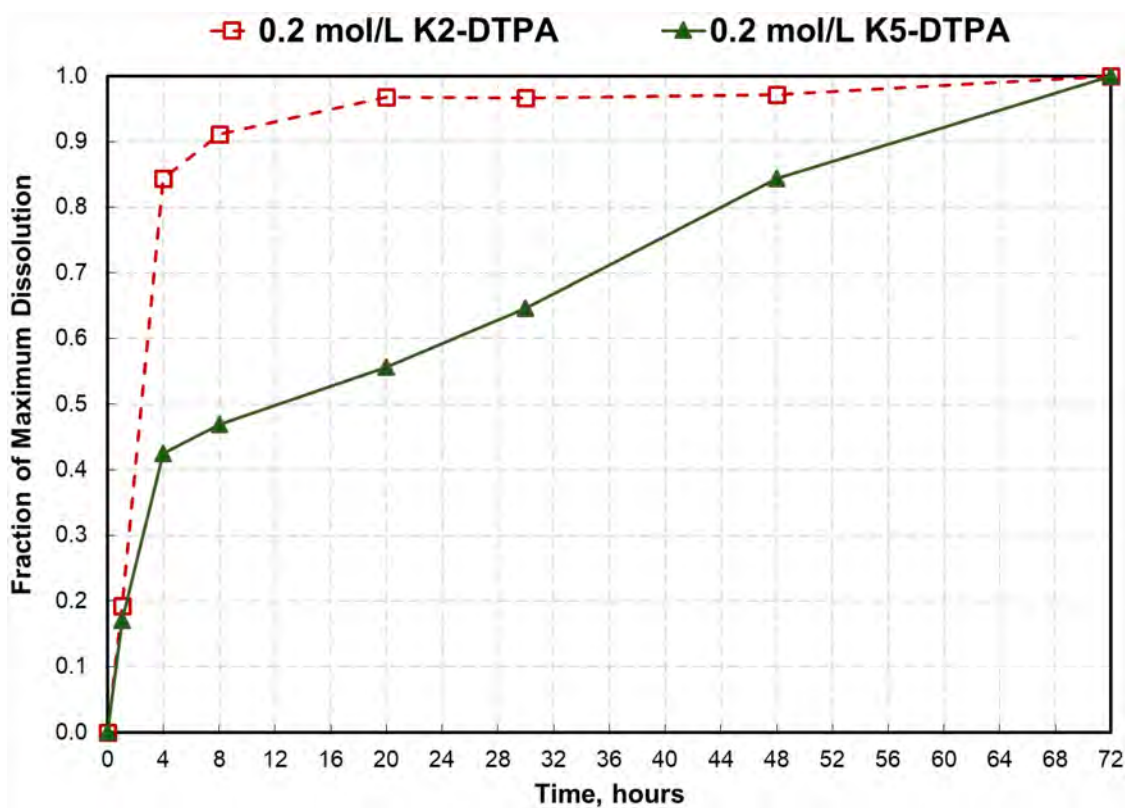

Figure 12—Comparison of fractional dissolution as a function of time for pH<5 (K_2-DTPA) and pH>10 (K_5-DTPA) DTPA solution and 150°F.

Effect of Type of Chelating Agent at pH < 5.

The three chelating agents studied in this paper belong to the same class: Polyaminocarboxylic acids. The difference in the activity to dissolve iron sulfide is due to the difference in the number of active ligands in each dissolver. HEDTA has 2 nitrogen atoms, 3 carboxylic groups, and 1 hydroxyl group. The number of active ligands in this case is 5. The presence of the hydroxyl group enhances its solubility in water at pH<5, and hence a concentration of 0.3 mol/L K-HEDTA can be prepared at pH = 3.7. EDTA has 2 nitrogen atoms and 4 carboxylic groups, making it a hexadentate ligand. DTPA has 3 nitrogen groups and 5 carboxylic groups and it termed as octadentate ligand. DTPA has the highest stability for most metal ions amongst the three polyaminocarboxylic acids studied here. Fig. 1 demonstrates the difference in the dissolution of iron sulfide by the three chelating agents at acidic conditions (pH < 5). DTPA is the best dissolver for iron sulfide, followed by HEDTA, and lastly EDTA. The iron dissolved from iron sulfide was measured to be 6.3 g/L in the case of 0.2 mol/L K_2-DTPA, 5.2 g/L at 0.2 mol/L K-HEDTA, and 4.4 g/L at 0.2 mol/L Na_2-EDTA. The trend of the scale dissolution is consistent with the pH level of the dissolver. 0.2 mol/L K_2-DTPA has the lowest pH, followed by 0.2 mol/L K-HEDTA, and Na_2-EDTA has the highest pH. Even though the stability constant of EDTA is higher than HEDTA for Fe^{2+}/Fe^{3+} ions, these tests show that surface kinetics plays an important role as well. A similar observation was made by Frenier (2001). There was a difference i n the dissolver color after reaction with the iron sulfide scale. The dissolver is initially colorless. For K_2-DTPA and Na_2-EDTA, the dissolver color changes to yellow, whereas for K-HEDTA the color changes to red (Fig. 13). The authors recommend using K_2-DTPA instead of Na_2-EDTA and K-HEDTA to dissolve the iron sulfide scale.
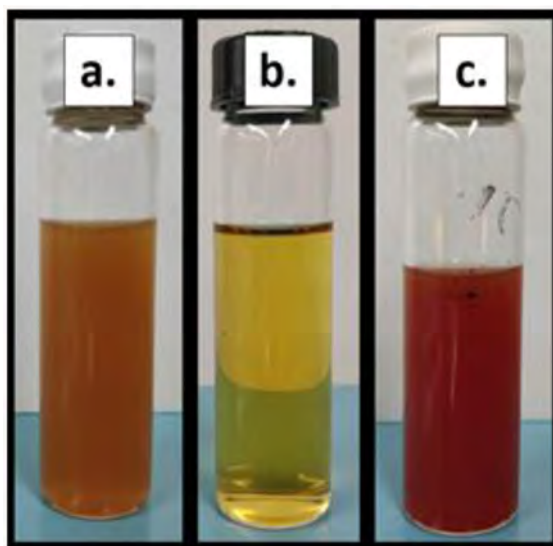

Figure 13—(a) Na₂-EDTA (b) K₂-DTPA (c) K-HEDTA solutions after 72 hours of reactions with iron sulfide.

Effect of the Chelating Agent at pH > 5.

At 150°F, the dissolution of iron sulfide by EDTA, HEDTA, and DTPA is minimal. The dissolution occurs as a result of solution complexation, where iron from the iron sulfide is released into the solution and chelated by the ligands. The release of iron happens due to hydrolysis at the surface of the iron sulfide. At 150°F, the release of iron is very slow and minimal, hence the low dissolution capacities. At pH between 5 and 9, a 0.2 mol/L solution of Na_3-EDTA, K_2-HEDTA, and K_3-DTPA showed 23, 24, and 36% dissolution capacity, respectively, after 72 hours of soaking. At pH>10, Na_4-EDTA, K_3-HEDTA, and K_5-DTPA dissolves 3, 2, 2% of the iron from the iron sulfide scale, respectively. This shows that the chelating agents are not effective in dissolving the FeS scale at 150°F.

Mechanism of Iron Sulfide Dissolution.

As discussed previously, the mechanism of the dissolution of iron sulfide depends on the dissolver pH. The selection of the dissolver concentration and the scale treatment time is also dependent on the pH. At pH < 5, the mechanism of iron sulfide dissolution is dominated by the attack of H^+ ions on the surface of the scale. The H^+ ions reacts with the scale to produce H_2S and free Fe^{2+} ions. The Fe^{2+} ions are chelated by the ligands. The process continues until either (a) the H^+ concentration is reduced to 0 or (b) the iron on the surface is completely removed exposing a layer of sulfur. For alkaline solutions (pH > 10), the mechanism of dissolving iron sulfide is through solution complexation. The hydrolysis of the iron sulfide results in free Fe^{2+} in solution, which is chelated by the ligands. The hydrolysis of iron sulfide in the dissolver is the rate limiting step and at 150°F, it is minimal for all the chelating agents and hence yielding low dissolution.

The role of H^+ ions in the dissolution of the iron sulfide scale was studied using scanning electron microscopy. The undissolved iron sulfide after the reaction with the chelating agent was filtered with a 1-5 μm filter paper, washed with isopropanol, and dried at 105°C for 12 hours under nitrogen atmosphere. The dried iron sulfide particles was studied under a SEM to observe its morphology. Fig. 14 demonstrates an iron sulfide particle before and after reaction with K_2-DTPA. The images show pits and pores on the surface. This is indicative of H^+ attack on the particle (Fig 14b). There are smooth surfaces as well as porous surfaces on the particle. An energy dispersive X-ray spectroscopy (EDS) on the smooth surfaces reveals mainly sulfur (97%) and very low iron content (3%). The porous surfaces show both iron (37%) and sulfur (63%). The elemental analysis of the pitting area shows higher concentration of sulfur (84%) than the porous surface. This shows that the layer of iron sulfide is attacked by the H^+ ions, releasing the iron from the surface. A layer of sulfur is present underneath the top layer and is exposed after the H^+ concentration is reduced to near 0. This confirms the H^+ attack to be the main mechanism of dissolution at pH < 5.
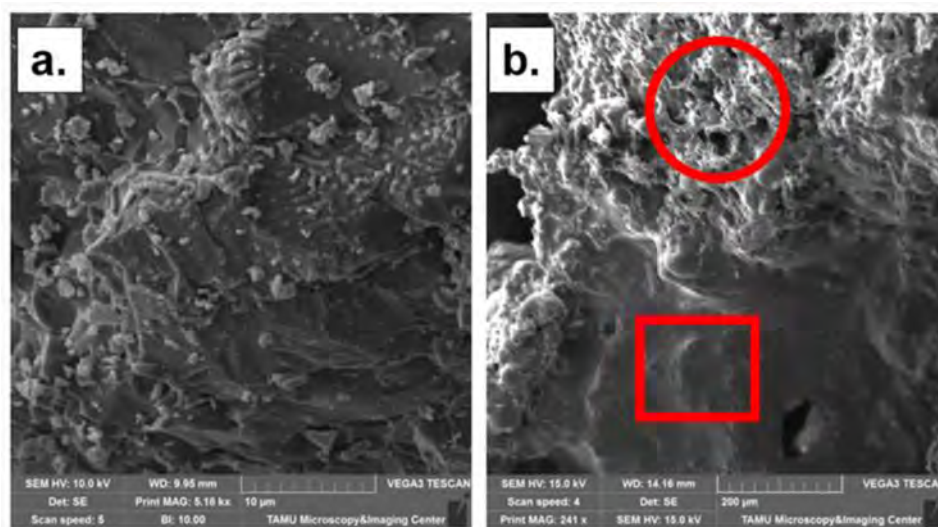

Figure 14—SEM image: (a) original iron sulfide particles having continuous non porous structure and (b) undissolved iron sulfide particles after dissolution with 0.3 mol/L K$_2$-DTPA (pH 3.6) at 150°F, showing smooth (red box) and porous (red circle) structures.

Fig. 15 presents a SEM image of an undissolved iron sulfide particle after reaction with tetrasodium EDTA (pH = 10.2). The particle does not have any pitting on the surface. This proves that the main mechanism of iron sulfide dissolution at pH > 10 is solution complexation.
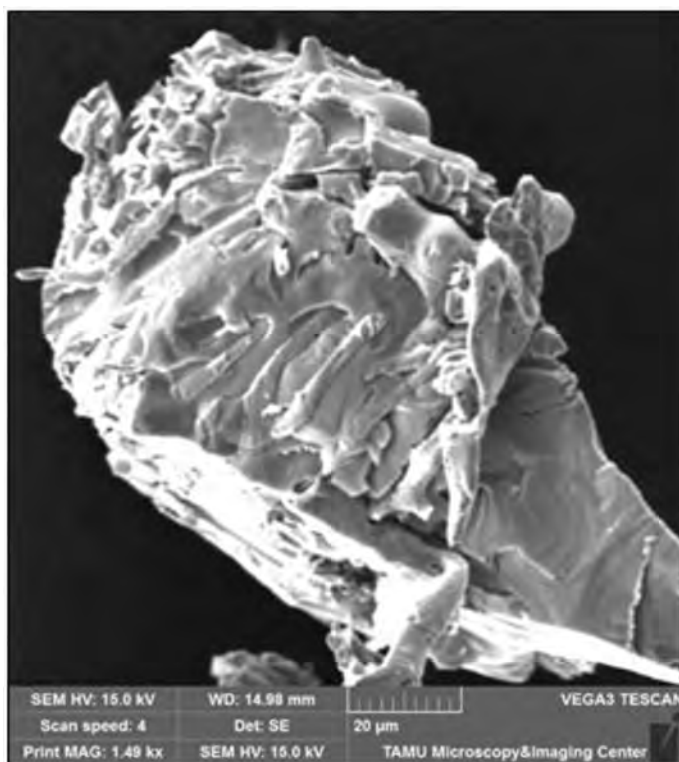
Figure 15—SEM image of undissolved iron sulfide particles after reaction with 0.3 mol/L Na$_4$-EDTA (pH 10.2) showing smooth surfaces, indicating no surface activity.

Conclusions

Alternative iron sulfide scale dissolvers are required to replace the corrosive and toxic use of conventional HCl field treatment. There is limited understanding of iron sulfide scale (FeS) dissolution by chelating agents. The dissolver pH, chelant concentration, and treatment time are parameters that have not been investigated in detail for FeS dissolution in literature. The addition of synergists to the chelating agents in order to enhance the iron sulfide solubility has not been extensively studied. To address these gaps in literature, the present work evaluated EDTA, HEDTA, and DTPA at pH of 3-12 and concentration of 0.05-0.4 mol/L to dissolve FeS at 150°F and a soaking time of 72 hours. The authors present the following conclusions:

1. At all pH levels, the maximum iron sulfide solubility was achieved by DTPA followed by HEDTA and EDTA.
2. Iron sulfide scale dissolution was maximum at pH < 5. 99% of the iron from iron sulfide was dissolved by 0.2 mol/L K$_2$-DTPA with a pH 3.5.
3. At pH > 5, the FeS dissolution capacity did not exceed 36%.
4. Increasing the chelating agent concentration improved the solubility of the scale only at pH < 5.
5. The optimal treatment time for all the three chelating agents at pH < 5 were determined to be 16-20 hours. Beyond 20 hours, there is minimal increase in the solubility of iron sulfide scale at 150°F.
6. 0.2 mol/L solutions of potassium iodide, potassium formate, potassium chloride, and potassium citrate enhanced 0.2 mol/L Na$_2$-EDTA's dissolution capacity by 37.7, 33.3, 14.4, and 4.3%, respectively, after 72 hours.
7. The mechanism of dissolution by the acidic ligands at pH < 5 were postulated to be mainly H$^+$ attack with surface complexation. At 150°F and alkaline medium (pH > 10), hydrolysis of the scale yielded Fe^{2+} ions that are complexed by the dissolver through solution complexation mechanism.

Based on this investigation, the authors recommend the use of 0.2 mol/L DTPA with a pH < 5 at 150°F to obtain maximum solubility of iron sulfide scale. The treatment time must not exceed 20 hours and the dissolver must be refreshed to ensure continued dissolution of the scale. The present work also provides valuable experimental data for future modeling and simulation studies.

Acronyms

EDTA	=	ethylenediaminetetraacetic acid
DTPA	=	diethylenetriaminepentaacetic acid
HEDTA	=	N-(2-Hydroxyethyl)ethylenediamine-N, N', N'-triacetic acid
XRD	=	X-ray diffraction
ICP-OES	=	inductively coupled plasma optical emission spectroscopy
SEM/EDS	=	scanning electron microscopy/energy dispersive spectroscopy

References

Aljeban, N., Chen, T., and Balharth, S. 2018. Kinetics Study of Iron Sulfide Scale Dissolution. Presented at the Abu Dhabi International Petroleum Exhibition and Conference, Abu Dhabi, UAE, 12-15 November. SPE-192675-MS. https://doi.org/10.2118/192675-MS.

Almubarak, T., Ng, J. H., and Nasr-El-Din, H. A. 2017a. Oilfield Scale Removal by Chelating Agents: An Aminopolycarboxylic Acids Review. Presented at the SPE Western Regional Meeting, Bakersfield, California, 23-27 April. SPE-185636-MS. https://doi.org/10.2118/185636-MS.

Almubarak, T., Ng, J. H., and Nasr-El-Din, H. A. 2017b. Chelating Agents in Productivity Enhancement: A Review. Presented at the SPE Oklahoma City Oil and Gas Symposium, Oklahoma City, Oklahoma, 27-31 March. SPE-185097-MS. https://doi.org/10.2118/185097-MS.

Chang, H. C. and Matijević, E. 1983. Interactions of Metal Hydrous Oxides with Chelating Agents: IV. Dissolution of Hematite. *J. Colloid and Interface Science* **92** (2): 479-488. https://doi.org/10.1016/0021-9797(83)90169-8.

Chen, T., Wang, Q., Chang, F., et al. 2017. Multi-Functional and Non-Acidic Iron Sulfide Scale Dissolver for Downhole Applications. Presented at the Abu Dhabi International Petroleum Exhibition & Conference, Abu Dhabi, UAE, 13-16 November. SPE-188924-MS. https://doi.org/10.2118/188924-MS.

Dunn, K. and Yen, T. F. 1999. Dissolution of Barium Sulfate Scale Deposits by Chelating Agents. *Environmental Science & Technology* **33** (16): 2821-2824. https://doi.org/10.1021/es980968j.

Fredd, C. N. and Fogler, H. S. 1996. Alternative Stimulation Fluids and their Impact on Carbonate Acidizing. Presented at the SPE Formation Damage Control Symposium, Lafayette, Louisiana, 14-15 February. SPE-31074-MS. https://doi.org/10.2118/31074-MS.

Frenier, W. W. 2001. Novel Scale Removers Are Developed for Dissolving Alkaline Earth Deposits. Presented at the SPE International Symposium on Oilfield Chemistry, Houston, Texas, 13-16 February. SPE-65027-MS. https://doi.org/10.2118/65027-MS.

Geri, B., Salem, B., Mahmoud, M. A., et al. 2017. Evaluation of Barium Sulfate (Barite) Solubility Using Different Chelating Agents at a High Temperature. *J. Petroleum Science and Technology* **7** (1): 42-56. https://doi.org/10.22078/jpst.2017.707

Harris, C. 2007. Quantitative Chemical Analysis, seventh edition. China Lake, California: Craig Bleyer.

Hafiz, T., Hoegerl, M., AlSuwaij, A., et al. 2017. Synthetic Iron Sulfide Scale and Polymeric Scale Dissolvers. Presented at the SPE Middle East Oil & Gas Show and Conference, Manama, Kingdom of Bahrain, 6-9 March. SPE-183954-MS. https://doi.org/10.2118/183954-MS.

Hamza, F., Staib, E., Cottle, E., and Quintero, L. 2015. Application of Pulsed Neutron Logging to Enhance Production from Mature Fields. Presented at the 22nd Annual India Oil and Gas Review Summit and International Exhibition, Mumbai, India, 19-10 September.

LePage, J., Wolf, C. D., Bemelaar, J., et al. 2011. An Environmentally Friendly Stimulation Fluid for High-Temperature Applications. *SPE J.* **16** (01): 104 - 110. SPE-121709-PA. https://doi.org/10.2118/121709-PA.

Mahmoud, M., Hussein, I. A., Sultan, A. et al. 2018. Development of Efficient Formulation for the Removal of Iron Sulphide Scale in Sour Production Wells. *The Canadian J. Chemical Engineering* **96** (12): 2526-2533. https://doi.org/10.1002/cjce.23241.

Martell, A. E., Motekaitis, R. J., Chen, D. et al. 1996. Selection of new Fe(III)/Fe(II) Chelating Agents as Catalysts for the Oxidation of Hydrogen Sulfide to Sulfur by air. *Canadian J. Chemistry* **74** (10): 1872-1879. https://doi.org/10.1139/v96-210.

Moulin, C., Amekraz, B., Steiner, V. et al. 2003. Speciation Studies on DTPA Using the Complementary Nature of Electrospray Ionization Mass Spectrometry and Time-resolved Laser-induced Fluorescence. *Applied Spectroscopy* **57** (9): 1151-1161. https://doi.org/10.1366/00037020360696026.

Kamal, M. S., Hussein, I., Mahmoud, M. et al. 2018. Oilfield Scale Formation and Chemical Removal: A Review. *J. Petroleum Sci. and Eng.* **171**: 127-139. https://doi.org/10.1016/j.petrol.2018.07.037.

Khan, W., Azari, M., Hamza, F. et al. 2017. Case Study: Multirate Multizone Production Logging and Testing Provides Real-Time Reservoir Insight for Stimulation Treatment Optimization in Deepwater GOM. Presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA, 9-11 October. SPE-187407-MS. https://doi.org/10.2118/187407-MS.

Patel, D.R., Ramanathan, R., and Nasr-El-Din, H.A. 2019. Optimization and Thermal Stability of the THPS and NH4Cl Blend to Dissolve Iron Sulfide (FeS) Scale at HPHT Conditions. Presented at the Abu Dhabi International Petroleum Exhibition & Conference, 11-14 November, Abu Dhabi, UAE. SPE-197632-MS.

Perry IV, T. D., Duckworth, O. W., Kendall, T. A. et al. 2005. Chelating Ligand Alters the Microscopic Mechanism of Mineral Dissolution. *J. American Chemical Society* **127** (16): 5744-5745. https://doi.org/10.1021/ja042737k.

Putnis, A., Putnis, C., and Paul, J. 1995. The Efficiency of a DTPA-Based Solvent in the Dissolution of Barium Sulfate Scale Deposits. Presented at the SPE International Symposium on Oilfield Chemistry, San Antonio, Texas, 14-17 February. SPE-29094-MS. https://doi.org/10.2118/29094-MS.

Quintero, L., Azari, M., and Hamza, F. 2017. Dynamics of Multiphase Flow Regimes in Toe-Up and Toe-Down Horizontal Wells. Presented at the 23rd Formation Evaluation Symposium of Japan, Chiba, Japan, 11-12 October. SPWLA-JFES-2017-M.

Ramanathan, R. and Nasr-El-Din, H. 2019. Improving the Dissolution of Iron Sulfide by Blending Chelating Agents and its Synergists. Presented at the SPE Middle East Oil and Gas Show and Conference, Manama, Bahrain, 18-21 March. SPE-195128-MS. https://doi.org/10.2118/195128-MS.

Sokhanvarian, K., Nasr-El-Din, H. A., Wang, G., et al. 2012. Thermal Stability of Various Chelates That are Used in the Oilfield and Potential Damage due to Their Decomposition Products. Presented at the SPE International Production and Operations Conference & Exhibition, Doha, Qatar, 14-16 May. SPE-157426-MS. https://doi.org/10.2118/157426-MS.

Spencer, C. 1958. The Chemistry of Ethylenediamine Tetra-acetic Acid in Sea Water. *J. Marine Biological Association of the United Kingdom* **37** (1): 127-144. https://doi.org/10.1017/S0025315400014880.

Torres, R., Blesa, M. A. and Matijević, E. 1989. Interactions of Metal Hydrous Oxides with Chelating Agents: VIII. Dissolution of Hematite. *J. Colloid and Interface Science* **131** (2): 567-579. https://doi.org/10.1016/0021-9797(89)90199-9.

Wang, K. S., Resch, R., Dunn, K. et al. 1999. Dissolution of the Barite (001) Surface by the Chelating Agent DTPA as Studied with Non-Contact Atomic Force Microscopy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **160** (3): 217-227. https://doi.org/10.1016/S0927-7757(99)00183-1.

Wylde, J. J., Okocha, C., Smith, R., et al. 2016. Dissolution of Sulfide Scale: A Step Change with a Novel, High Performance, Non-Mineral Acid Chemical. Presented at the SPE International Oilfield Scale Conference and Exhibition, Aberdeen, Scotland, UK, 11-12 May. SPE-179880-MS. https://doi.org/10.2118/179880-MS.