OPTIMIZATION AND THERMAL STABILITY OF THE THPS AND NH_4Cl BLEND TO DISSOLVE IRON SULFIDE (FeS) SCALE AT HP/HT CONDITIONS

A Thesis

by

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ABSTRACT

Iron sulfide scales of different forms exist in sour oil/gas-producing wells as well as seawater injection wells. Traditionally, they are dissolved using HCl and other inorganic acids. In the past decade, a tetrakis (hydroxymethyl) phosphonium sulfate (THPS) and ammonium chloride blend have shown potential to dissolve FeS scales. The objective of this study is to optimize the dissolver composition and treatment time for the dissolution of FeS using different concentrations of THPS and ammonium chloride at 150 and 300°F. This work also evaluates the thermal stability of the blend at 350 and 400°F using aging cells.

The optimum blend composition and treatment time at high pressure-high temperature (HP/HT) conditions is not available in the literature. The thermal stability of THPS and ammonium chloride is unknown at a temperature greater than 300°F. Bottle tests at 150°F helped optimize the THPS and ammonium chloride blend composition and treatment time. 10 cm^3 dissolver solutions prepared at concentrations of 0.1 to 1 mol/L THPS and 0.25 to 1.5 mol/L NH_4Cl were added to 0.1 g FeS. An Inductively Coupled Plasma (ICP) analysis of the supernatant solution at 1, 4, 8, 12, 24, 48, and 96 hours revealed the kinetics of the dissolution process. Thermal degradation experiments were performed in an OFITE aging cell and analyzed using Fourier-transform Infrared Spectroscopy (FTIR).

At 150°F, the blend with 0.1 mol/L THPS showed maximum FeS dissolution at 1.5 mol/L NH_4Cl. But for THPS concentration greater than 0.1 mol/L, maximum dissolution was observed at 0.5 mol/L NH_4Cl. For a 0.25 mol/L NH_4Cl, 1.0 mol/L THPS showed the maximum dissolution capacity, but for NH_4Cl concentration greater than 0.25 mol/L, maximum dissolution was observed at 0.5 mol/L THPS. Based on these results, 0.5 mol/L THPS and 0.5 mol/L NH_4Cl is the best dissolver composition. The optimal time for treatment was lower than 48 hours when THPS concentration was higher than 0.8 mol/L or NH_4Cl concentration was higher than 1.0 mol/L. The spent dissolver pH values were lower than the initial pH values, indicating the generation of acid. At 300°F, the 0.2 mol/L THPS and 0.2 mol/L NH_4Cl blend dissolved 40% more iron sulfide than at 150°F.

This work provides an investigation of the kinetics of iron sulfide dissolution using the THPS and NH_4Cl blend. This study optimizes the blend composition and treatment time, at 150 and 300°F. Thermal stability evaluation along with the dissolution study fills the gaps in the literature and provides an optimized solution for well treatment.

DEDICATION

Dedicated to my parents, sister and late grandparents

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The analyses depicted in Chapter VII were conducted in part by Raja Ramanathan and Salar Afra of the Department of Petroleum Engineering.

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NOMENCLATURE

BMPA	Bis (Hydroxymethyl) Phosphonic Acid
EDTA	Ethylenediaminetetraacetic Acid
FTIR	Fourier-transform infrared spectroscopy
HPHT	High Pressure/High Temperature
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
ppm	Parts per million
psi	Pounds per square inch
SEM / EDS	Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy
THPO	Trihydroxymethyl Phosphine Oxide
THPS	Tetrakis (Hydroxymethyl) Phosphonium Sulfate
XRD	X-Ray Diffraction

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CHAPTER I

INTRODUCTION

Scale deposition still remains a challenging problem in the oil and gas industry. This subsurface rock formations have fluids such as formation water (brine), crude oil, and associated gas. These fluids have achieved chemical equilibrium with the environment and each other over millions of years. When a new well is drilled and hydrocarbons produced, this natural equilibrium is disturbed and causes depositions of solid material consisting of organic and inorganic scales. In general, inorganic scales in oil and gas wells are formed due to either direct precipitation from the water or because of the interaction between two incompatible fluids.

Conventional scales such as carbonates and sulfates impair the production of oil and gas by forming water-oil emulsions, reducing injectivity, and damaging the surface and subsurface equipment which result in additional expenditure and lower returns. In addition, sulfide scales containing iron, zinc, and lead cations typically have a lower potential to dissolve than sulfate and carbonate scales (Przbylinski 2001). Iron sulfide is the most common type of sulfide scale. Even small amounts of iron-containing scale, often viewed as insignificant, are capable of placing large volumes of precipitate in the formation (Walker et al. 1991). The world’s biggest conventional oil reservoir field, Ghawar oilfield in Saudi Arabia has wells with 43% iron sulfide scale deposits (Chen et al. 2016). Many types of iron sulfide can be present in hydrogen sulfide (H_2S)-rich environments, which include those with stoichiometric and non-stoichiometric compounds such as amorphous FeS, mackinawite, marcasite, greigite, pyrrhotite, troilite, and pyrite (Nasr-El-Din and Al-Humaidan 2001; Nasr-El-Din et al. 2001).

Different sources of iron in oil and gas reservoirs include (Okocha 2011):

- Reservoir formation containing minerals such as pyrite and siderite reacting with connate and aquifer water to generate products with iron ions
- Corrosion by-product from the production tubulars and surface facilities

Hydrogen sulfide gas is the most common source of sulfide ions, which reacts with iron to form iron sulfide scale. H_2S gas is generated due to thermal decomposition of sulfate in the formation, sulfur-reducing bacteria (SRB), or introduction into the well as in gas lift operations (Nasr-El-Din and Al-Humaidan 2001).

Iron sulfide can cause crevice or bimetallic corrosion in the presence of water (Nasr-El-Din and Al-Humaidan 2001). The formation of FeS also stabilizes oil-water emulsions and may damage near wellbore formations (Kelland 2014).

Hydrochloric acid (HCl) is the most efficient dissolver of iron sulfide scale. It can dissolve troilite (FeS) but is inefficient in dissolving pyrite or marcasite (FeS_2). Treatment of iron sulfide with HCl produces very high concentration of hydrogen sulfide (H_2S), which is corrosive and toxic. HCl is also notorious for its corrosive behavior at high temperature. To overcome these problems created by HCl, various chemicals are being evaluated in this work for iron sulfide dissolution capabilities.

Oxidizing agents can overcome some of the problems with acid, but they can produce elemental sulfur, which is highly corrosive and causes formation damage (Gilbert et al. 2002). Acrolein is proved to be efficient in dissolving iron sulfide but it is a very difficult material to handle (Salma 2000). Hence, it is necessary to develop a new alternative iron sulfide dissolver which can overcome these issues.

One solution is tetrakis (hydroxymethyl) phosphonium sulfate (THPS). THPS is well known as a highly effective biocide for a variety of water treatment applications including oilfield (both downhole and topside), cooling systems, and paper manufacture (Gilbert et al. 2002). Conventionally, THPS research was focused on analyzing its application as a biocide for prevention and control of microorganisms that cause souring in oil and gas wells. However, studies have highlighted that tetrakis (hydroxymethyl) phosphonium sulfate dissolves iron sulfide using a chelation method (Wylde et al. 2016). It is also useful for inhibition and dispersion of iron sulfide. The efficiency of THPS to dissolve iron sulfide can be improved drastically by adding ammonium chloride (NH_4Cl) as an additive.

Even with the proof of this chemical blend to be efficient in dissolving iron-sulfide scale, laboratory studies have been insufficient in this area. The effect of concentration of THPS and ammonium chloride on the dissolution of iron sulfide has contradictory claims in the literature (Gilbert 2002; Gallup et al. 2013; Wang et al. 2015). The optimized concentration of THPS and ammonium chloride at different temperatures has not been studied. The rate of dissolution of iron sulfide in a blend of THPS and NH_4Cl at 150 and 300°F has not been discussed.

The literature lacks information about an optimized blend of THPS and ammonium chloride at HP/HT conditions. There are no thermal stability tests done at 350 and 400°F. To fill the gaps in the literature, this research has the following objectives:

1. Evaluate the effect of concentration of THPS and ammonium chloride to dissolve iron sulfide (FeS) at 150 and 300°F.
2. Optimize the treatment time for the dissolver blend. Different samples at different time intervals will be collected to optimize the treatment time of the dissolver blend and iron sulfide scale.

3. Evaluate the optimized blend for iron sulfide dissolution at 1,000 psi in anoxic conditions. The test would be conducted at 150 and 300°F.
4. Conduct thermal degradation experiments of THPS and ammonium chloride blend at 350 and 400°F.

By doing these tests, an optimal blend of THPS and NH_4Cl is provided. This recommended formulation maximizes the dissolution of iron sulfide and optimizes the downtime for production operations. This work discusses the effectiveness of the blend at 350 and 400°F.

CHAPTER II

LITERATURE REVIEW

Various factors such as the mineralogy, chemical composition, and formation of sulfide scales/minerals have been researched because of their financial and environmental impact. The term “exotic scales” is used in the oilfield for scales which do not form very often such as sulfide scales. But recently, due to increases occurrence in the oilfield, that view is changing. This literature review deals with the parameters that can influence sulfide scale deposition and removal in oil and gas wells. Many widely used treatment methods and prevention techniques for sulfide scale deposition along with recent advancements are reviewed.

Different forms of iron sulfide scales have been observed in oilfield wells. Pyrite (FeS_2), troilite (FeS), and marcasite (FeS_2) are stoichiometric iron sulfides, and pyrrhotite (Fe_7S_8), greigite (Fe_3S_4), mackinawite (Fe_9S_8), are non-stoichiometric compounds (Lee 2004). Different forms of iron sulfides have created variety of complex problems in oil and gas wells, in which different iron sulfide products have precipitated at a different location in turns requiring different treatment design. Aging of iron sulfide scale from a low sulfur mineral to a high sulfur mineral as a function of time, temperature, pressure, pH and exposure to H_2S makes the prevention and removal process more complex (Luther 1991; Nasr-El-Din and Al-Humaidan 2001). At deeper depths, wells have less exposure to H_2S gas and so iron sulfide scale deposits have an iron-to-sulfur molar ratio close to one but at a shallower depths, iron sulfide scale has more exposure to H_2S gas, causing a reduction in the iron-to-sulfur ratio and becoming harder to dissolve (Nasr-El-Din and Al-Humaidan 2001). **Table 1** shows the different crystalline structures of iron sulfide found in oil and gas wells and their solubilities in mineral acids and thermodynamic solubility (Nasr-El-Din and Al-Humaidan 2001; Ball and Frenier 1984; Harmandas et al. 1998).

	Mackinawite	Marcasite	Pyrite	Pyrrhotite	Troilite
Chemical formula	Fe_9S_8	FeS_2	FeS_2	Fe_7S_8	FeS
Crystalline structure	Tetragonal	Orthorhombic	Cubic	Monoclinic	Hexagonal
Color	Bronze	Tin-white	Pale yellow	Bronze yellow	Dark brown
Hardness	Soft	6-6.5	6-6.5	3.5-4.5	3.5-4.5
Density (g/cm^3)	4.30	4.875	5.013	4.69	4.85
Solubility in mineral acids	Fast	Slow and difficult	Slow and difficult	Moderate	Rapid and easy
Formula	$\alpha_{Fe}^{2+}\ \alpha_{S}^{2-}$	$\alpha_{Fe}^{2+}\ \alpha_{S2}^{2-}$	$\alpha_{Fe}^{2+}\ \alpha_{S2}^{2-}$	$\alpha_{Fe}^{2+}\ \alpha_{S}^{2-}$	$\alpha_{Fe}^{2+}\ \alpha_{S}^{2-}$
K_{sp}	$2.88x10^{-18}$	$8.65x10^{-26}$	$8.51x10^{-26}$	$2.70x10^{-19}$	$6.17x10^{-17}$

Table 1—Physical and thermodynamic properties of different types of iron sulfide scales.

Smith and Miller (1975) brought together information about sulfides, particularly iron sulfide. They reviewed previous research and combined it to provide crystalline structures of different polymorphs of iron sulfide (Jellinek 1968, Erd et al. 1957). They compared corrosion rates of different sulfur species and found that corrosivity of elemental sulfur is highest, followed by greigite, pyrite and hydrogen sulfide in sour wells.

Crowe (1987) explored an improved method of acidizing sour gas wells using an aqueous acidizing solution consisting of water, an acid, an iron complexing agent (e.g., EDTA), and an iron-reducing agent (e.g., erythorbic acid, ascorbic acid). This paper mentioned that the function of an iron-reducing agent is to reduce ferric (Fe^{3+}) ions in solution to ferrous (Fe^{2+}) ions at a pH of about 6 or less.

Nasr-El-Din et al. (2002) tested a specific combinations of aldehyde-based sulfide-suppression chemicals that can dissolve FeS and suppress the formation of H_2S at the same time to prevent corrosion according to industry standards. Iron ions and sulfide reactions produce iron sulfide and, if the ferric ion is present, elemental sulfur can precipitate. This research suggested Hexamethylenetetramine (HMTA) as an alternative that reacts with HCl to produce formaldehyde, which works as a hydrogen sulfide scavenger.

Walker et al. (1991) concluded that iron control methods used in sweet wells may not provide adequate iron control in sour environments. They found out that simultaneous use of a sulfide scavenger and an iron-control agent (chelating) allows acid to dissolve more iron sulfide than normally observed when either agent is used alone. This combination prevents the precipitation of elemental sulfur in many cases.

Ramanathan and Nasr-El-Din (2019) investigated the effect of organic acids such as maleic acid, formic acid, citric acid, lactic acid, disodium ethylenediaminetetraacetic acid (EDTA), and pentapotassium diethylenetriaminepentaacetic acid for the dissolution of iron sulfide-scale. They also evaluated the effect of potassium oxalate and potassium citrate as synergists for Na_2-EDTA. An improvement in the effectiveness of Na_2-EDTA as an iron-sulfide dissolver was observed when potassium citrate was added to the chelating agent.

In the past, phosphine ligands such as $P(CH_2OH)_3$ were seen as a useful precursor for the synthesis of water-soluble transition metal complexes (Ellis et al. 1992). Researchers at that time had an interest in the related phosphonium salt $[P(CH_2OH)_4]_2SO_4$ (THPS) because of its effectiveness as a biocide in oil wells, where the dissolution of iron sulfide with THPS was evidenced by a red coloration of produced water from the well.

Jeffery et al. (2000) studied a complex created by the reaction of THPS and iron sulfide in the presence of ammonium ions and derived a single-crystal X-ray structure of the complex shown in **Fig. 1**. Jeffery also explained the reduction of pH due to the liberation of the counter ion of ammonium salts as acid, as shown in **Eq. 1**.

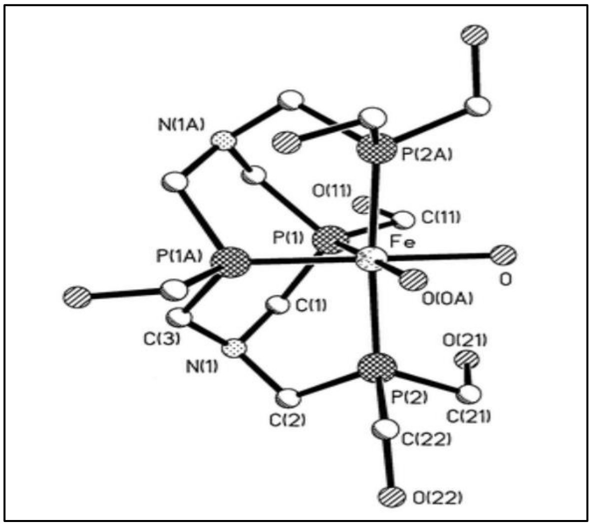


Fig. 1—Molecular structure of the cation of the complex $[Fe(H_2O)_2\{RP(CH_2N(CH_2PR_2)CH_2)_2PR\}]SO_4{\cdot}4H_2O$ (R = CH_2OH).

$$2[P(CH_2OH)_4]_2SO_4 + 2NH_4Cl + Fe^{2+} \rightarrow [Fe(H_2O)_2\{RP(CH_2N(CH_2PR_2)CH_2)_2PR\}]SO_4 \cdot 4H_2O + 2HCl \quad ....(1)$$

Gilbert et al. (2002) reviewed the chemistry behind the dissolution of iron sulfide using THPS over a wide range of conditions. They found that the ammonium ions required for efficient complexation are often present in sufficient amounts in the produced water. Experimental results showed that the dissolution of troilite and pyrite increases with an increase in THPS concentration and ammonium chloride concentration (or phosphonate concentration). However, they did not optimize the treatment.

Mattox et al. (2006) published a patent about use of THPS for iron-sulfide dissolution, where THPS concentration varied from 1 wt% to 90 wt%. Results showed a decrease in reaction time from 26 hours to 15 minutes with an increase in pH values from 2.68 to 4.96.

Zhao et al. (2008) created a mechanistic model that showed THPS degradation is a complex process and it can be affected by many factors. According to this study, THPS degradation increases with the increase of temperature and pH, and the pH effect can be decoupled with temperature. Therefore at low temperature and pH values, THPS is more stable than at high temperature and pH values. This research provided the THPS chemical structure and its major degradation (**Fig. 2)**. Here, trihydroxymethyl phosphine oxide (THPO) and bishydroxymethyl phosphonic acid (BMPA) were identified as two major breakdown products.

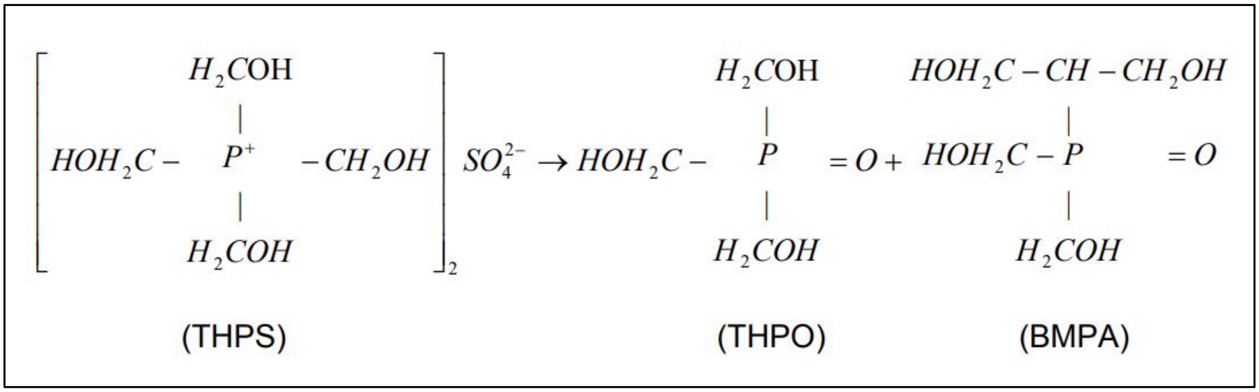


Fig. 2—Degradation of THPS into THPO and BMPA.

Trahan (2010) tried a new additive, iminodisuccinic acid (IDS), which resulted in a 95% increase in the amount of iron ions dissolved when used with a THPS and ammonium chloride formulation. The effect of pH was also analyzed and researchers found that the THPS and ammonium ion formulation is stable below a pH of a 4, whereas at a pH above 6, ammonium ions polymerize quickly, which can increase the risk of polymer deposition in the formation, obstructing oil and gas flow.

Gallup et al. (2013) investigated the efficiency of THPS to dissolve different water-soluble and water-insoluble metal sulfides (Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, and Pb^{2+}). Their results did not confirm the complexation of Fe^{2+} with THPS in the presence of ammonium ion. They observed that THP works efficiently to suppress hydrogen-sulfide gas. They concluded that THPS or THPC for FeS dissolution can also dissolve oxides and sulfides of Cu, Hg, Pb, and Zn.

Wang et al. (2015) showed that the dissolution power is not directly proportional to the THPS concentration, but it can be significantly improved by adding ammonium chloride. It is possible that the mass-transfer rate of reactants and reaction products surrounding the scale surface decreases at high THPS concentrations. Also, high THPS concentration increases viscosity, which results in an expanded diffusion boundary layer. Another observation was a decrease in pH at elevated temperature, which is a result of thermal decomposition of ammonium chloride at high temperature (**Eq. 2**).

$$NH_4Cl \xrightarrow{Heat} NH_3 + HCl \cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

Hussein and Mohamed (2017) studied THPS for dissolving zinc sulfide and lead sulfide under different conditions. They tested THPS with different additives of ammonium ions and chloride ions such as ammonium bisulfite, potassium chloride, ammonium citrate, ammonium oxalate and ammonium chloride along with sodium azide and phosphonates. The results showed that ammonium chloride is far better than any other additives. Maximum dissolution was obtained at 15 and 30% THPS concentration for zinc sulfide and lead sulfide, respectively, with 12 wt% NH_4Cl concentration.

CHAPTER III

EXPERIMENTAL STUDIES

In this chapter, different materials and instruments used are briefly introduced and explained.

Materials

Materials used for this research can be divided into dissolvers and iron sulfide scales.

Dissolvers

All chemicals used were reagent grade. Tetrakis (hydroxymethyl) phosphonium sulfate (THPS) and ammonium chloride (NH_4Cl) were used to dissolve iron sulfide. THPS (75%) was purchased from Compass Chemical and ammonium chloride ($\geq 99.5\%$) was purchased from Sigma Aldrich. Various concentrations of given dissolvers were prepared by diluting the stock solution with deionized water with a resistivity of 18.2 MΩ-m. All of the blends of dissolvers are given in **Table 2**. **Fig. 3** shows the structures of the chemicals. For high-pressure experiments carried out in an autoclave, a quaternary ammonium-based corrosion inhibitor provided by Baker Hughes was added to the dissolver blend.

Iron-Sulfide Scale

For all of the experiments, reagent grade iron-sulfide sticks acquired from Sigma Aldrich (CAS No. 1317-37-9) were pulverized using an agate mortar and pestle to prevent contamination of any other minerals. The pulverized iron-sulfide particles were sieved and sized in the range of 75 and 106 microns was used for the autoclave tests and size lower than 150 microns was used for bottle tests. The constant size of iron-sulfide particles was used to keep the surface area of the scale equal for all experiments. X-ray Diffraction (XRD) analysis of the pulverized scale indicated the presence of iron sulfide minerals such as troilite (75.21%), and pyrrhotite (6.11%) along with iron oxide mineral maghemite (4.59%) and elemental iron (14.60%). **Fig. 4** presents the XRD pattern of the minerals in the iron-sulfide sample.

DISSOLVERS

0.1 M THPS + 0.25 M NH_4Cl	0.1 M THPS + 0.5 M NH_4Cl
0.2 M THPS + 0.25 M NH_4Cl	0.2 M THPS + 0.5 M NH_4Cl
0.3 M THPS + 0.25 M NH_4Cl	0.3 M THPS + 0.5 M NH_4Cl
0.5 M THPS + 0.25 M NH_4Cl	0.5 M THPS + 0.5 M NH_4Cl
0.8 M THPS + 0.25 M NH_4Cl	0.8 M THPS + 0.5 M NH_4Cl
1.0 M THPS + 0.25 M NH_4Cl	1.0 M THPS + 0.5 M NH_4Cl
0.1 M THPS + 1.0 M NH_4Cl	0.1 M THPS + 1.5 M NH_4Cl
0.2 M THPS + 1.0 M NH_4Cl	0.2 M THPS + 1.5 M NH_4Cl
0.3 M THPS + 1.0 M NH_4Cl	0.3 M THPS + 1.5 M NH_4Cl
0.5 M THPS + 1.0 M NH_4Cl	0.5 M THPS + 1.5 M NH_4Cl
0.8 M THPS + 1.0 M NH_4Cl	0.8 M THPS + 1.5 M NH_4Cl
1.0 M THPS + 1.0 M NH_4Cl	1.0 M THPS + 1.5 M NH_4Cl

Table 2—Different blends of dissolvers for bottle test.

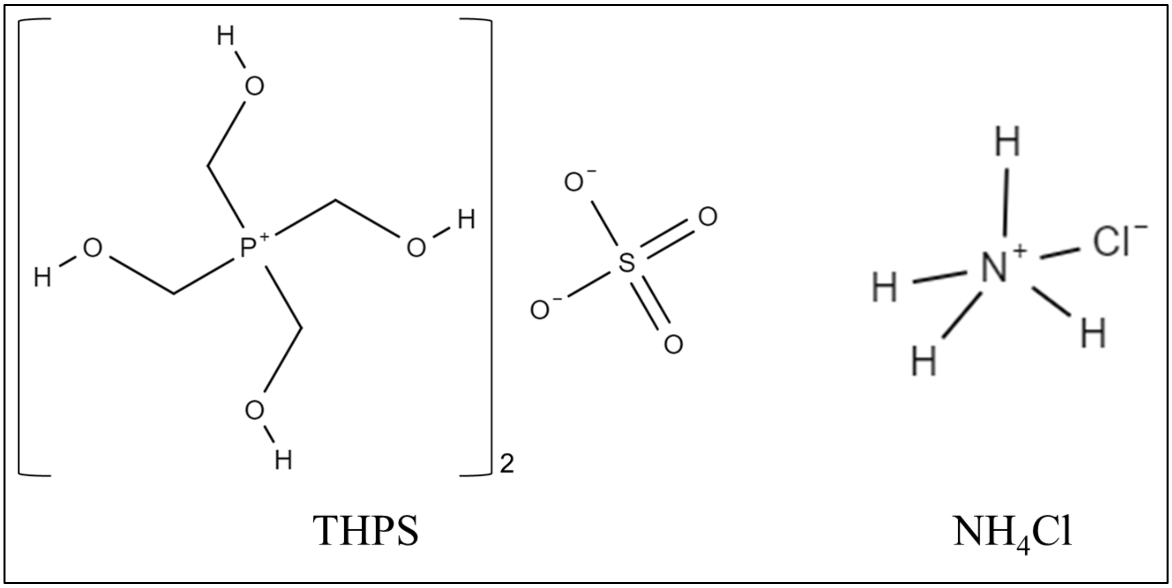


Fig. 3—Chemical structure of THPS and NH_4Cl.

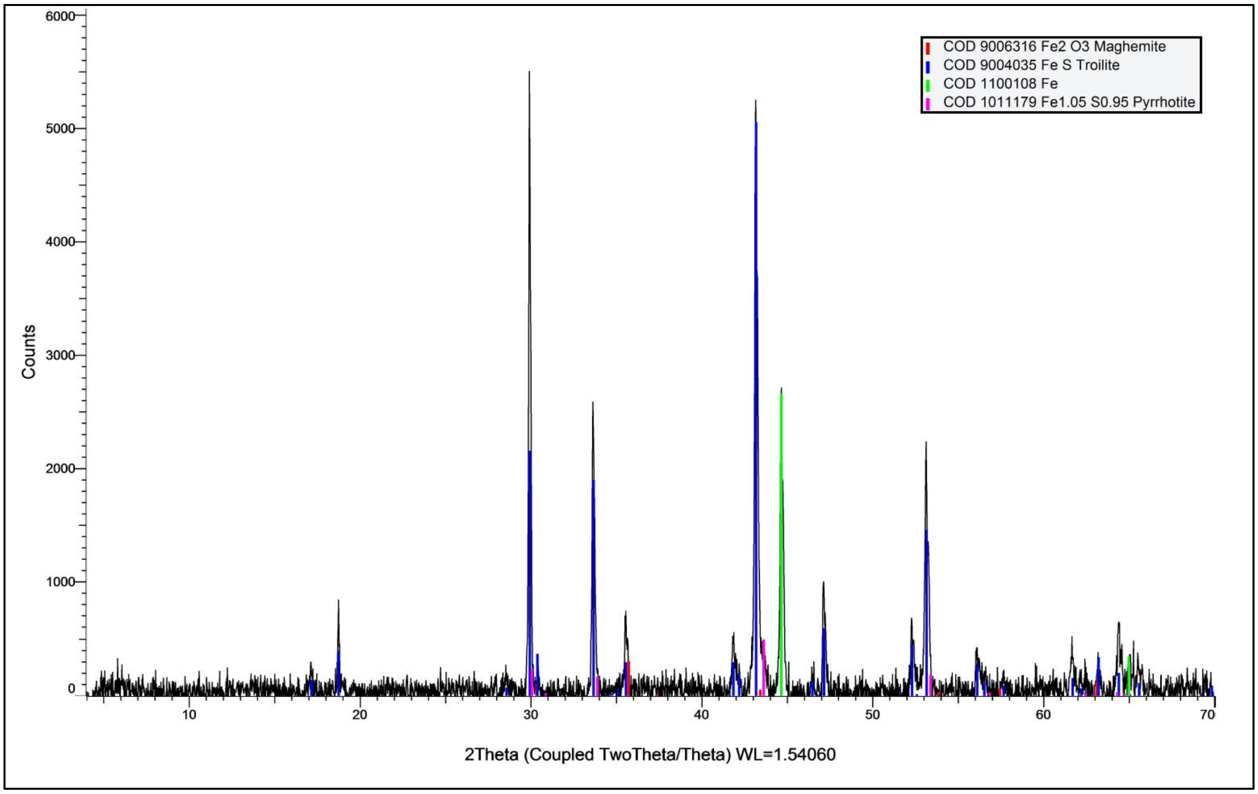


Fig. 4—XRD pattern of the iron sulfide sample.

Procedure and Equipment

Bottle tests

For bottle tests, 15 cm^3 glass tubes were used for all experiments. Each glass tube contained 0.1 g of crushed iron-sulfide sample. 10 cm^3 of the different dissolver blends were added into those glass tubes, which were then tightly sealed for the experiment to prevent loss of water-based dissolver due to boiling at high temperature. The tests were conducted at 150 and 300°F. Samples of the supernatant solutions were collected at time intervals of 1, 4, 8, 12, 24, 48, and 96 hours.

Autoclave tests

The autoclave can simulate high-pressure, high-temperature (HP/HT) well conditions. **Fig. 5** shows different parts of the autoclave setup.

For these experiments, after assembling the reactor as shown in **Fig. 6**, nitrogen was purged to create a hypoxic condition. The purging of the system was to prevent the formation of iron oxide and to simulate well conditions. The reactor was pressurized to value lower than 1000 psi considering pressure increase from gas expansion under increased temperature (Gay-Lussac law). For example, the pressure in the reactor was kept at 880 psi for an experiment at 150°F and 705 psi for an experiment at 300°F. The inside pressure of the reactor reached 1000 psi when the desired temperature value was achieved. It took about one hour to reach the desired temperature inside the autoclave reactor using a heating jacket for all of the experiments. The experiment was allowed to run for a fixed time after the desired temperature and pressure was achieved.

At the end of the experiments, a Dräger tube and an Accuro manual hand pump (**Fig. 7**) were used to measure the precise amount of H_2S evolved during the reaction at given pressure and temperature. The H_2S gas from the reactor was sampled using gas sampling bags. H_2S gas was measured multiple times to check the consistency of the result.

The reactor was allowed to cool down to room temperature using cold water. The exhaust valve was opened to release the pressure into two stages of 1.0 mol/L NaOH scrubber solutions, which can neutralize any residual H_2S using **Eq. 3**.

$$H_2S + 2NaOH \longrightarrow Na_2S + 2H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Spent dissolver was filtered through a 5 μm size filter paper to collect undissolved iron-sulfide particles. The iron concentration in the supernatant was measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

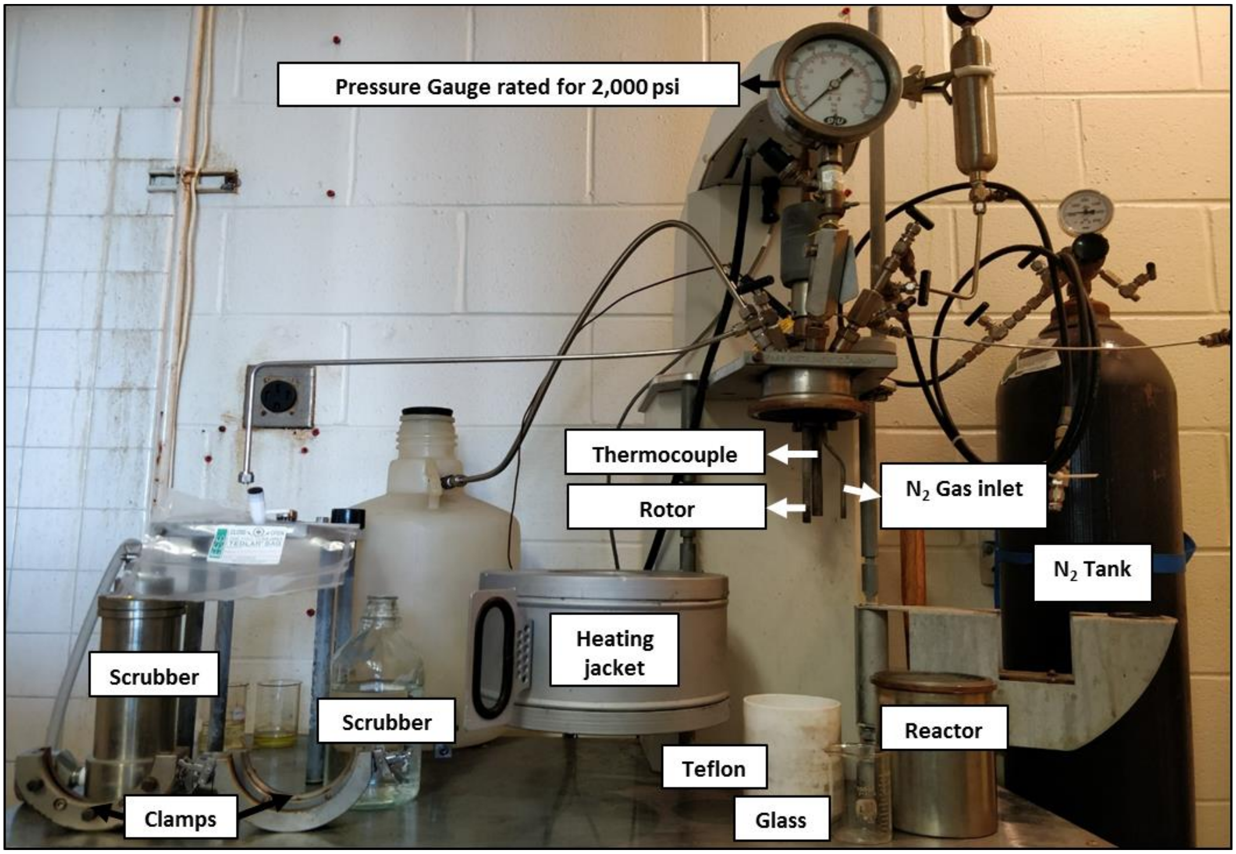


Fig. 5—Autoclave test components.

Fig. 6—Assembled autoclave reactor.

Fig. 7—Dräger tube and Accuro manual hand pump.

pH measurements

The pH of prepared dissolver and spent dissolver after the treatment with iron-sulfide scale was measured using an Oakton pH meter as shown in **Fig. 8**. The pH meter was calibrated before each use to ensure accurate readings.

Fig. 8—Oakton pH meter.

Inductively Coupled Plasma Optical Emission Spectroscopy

An Optima 7000 DV ICP-OES Spectrometer was used to analyze the supernatant for the iron element concentrations from the bottle tests and autoclave experiments. **Fig. 9** shows the setup of the ICP-OES instrument used for the analysis of supernatant.

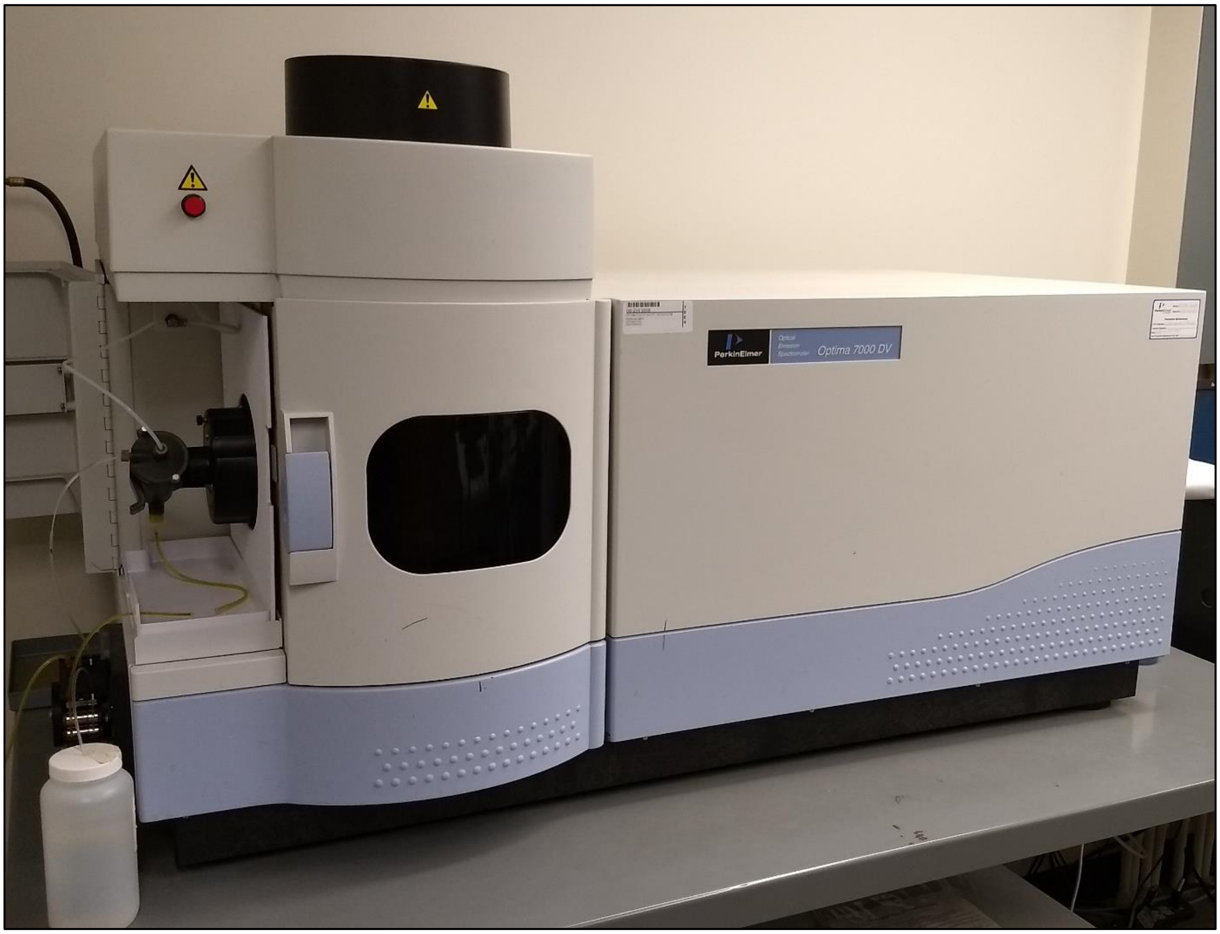


Fig. 9—Optima 7000 DV Inductively Coupled Plasma Optical Emission Spectroscopy.

Thermal degradation study

An OFITE aging cell was used to carry out the thermal degradation study. It is a pressure vessel that was designed for HPHT conditions which also prevents the evaporation of the liquid samples. The Teflon liner was filled with the dissolver and closed with the piston plug (**Fig. 10**). It was placed in the steel aging cell shown in **Fig. 11**. The aging cell was pressurized using nitrogen to 200 psi pressure to prevent boiling of the water-based dissolver at high temperatures. Once no pressure leakage was observed, the assembly was placed in a preheated oven at the desired temperature. After the desired time, it was removed from the oven and allowed to cool down. The samples were collected for pH measurement and FTIR study to determine thermal degradation.

Fig. 10—Teflon liner with T screw.

Fig. 11—OFITE aging cell.

CHAPTER IV

RESULT AND DISCUSSION

Bottle Tests

This test helped in evaluating the effectiveness of the different dissolver blends in reacting with iron-sulfide scale. After 0.1 g iron-sulfide scale was measured and added into the different glass tubes, 10 cm^3 of different dissolvers were added. Immediately, glass tubes were kept inside the preheated oven at 150°F. Starting time was noted for each tube and samples of supernatant were collected after 1, 4, 8, 12, 24, 48, and 96 hours. ICP-OES evaluated the iron concentration in the collected samples.

Effect of THPS and NH_4Cl concentration on pH values

Once all the dissolvers were prepared, the Oakton pH meter was used to measure the pH values of each dissolver. After 96 hours of treatment time, supernatants were collected and their pH values were measured to observe the change in the pH values. **Fig. 12** shows the initial pH and final pH values for all of the dissolvers. Fig. 12 shows that increasing ammonium chloride concentration reduces the initial pH and final pH values. The maximum initial pH was noted to be 3.47 in 1.0 mol/L THPS and 0.25 mol/L NH_4Cl dissolver blend, whereas minimum initial pH was noted to be 2.41 in 0.1 mol/L THPS and 1.5 mol/L NH_4Cl dissolver solution. Based on this data, it can be deduced that an increase in THPS in dissolver increases the initial pH values.

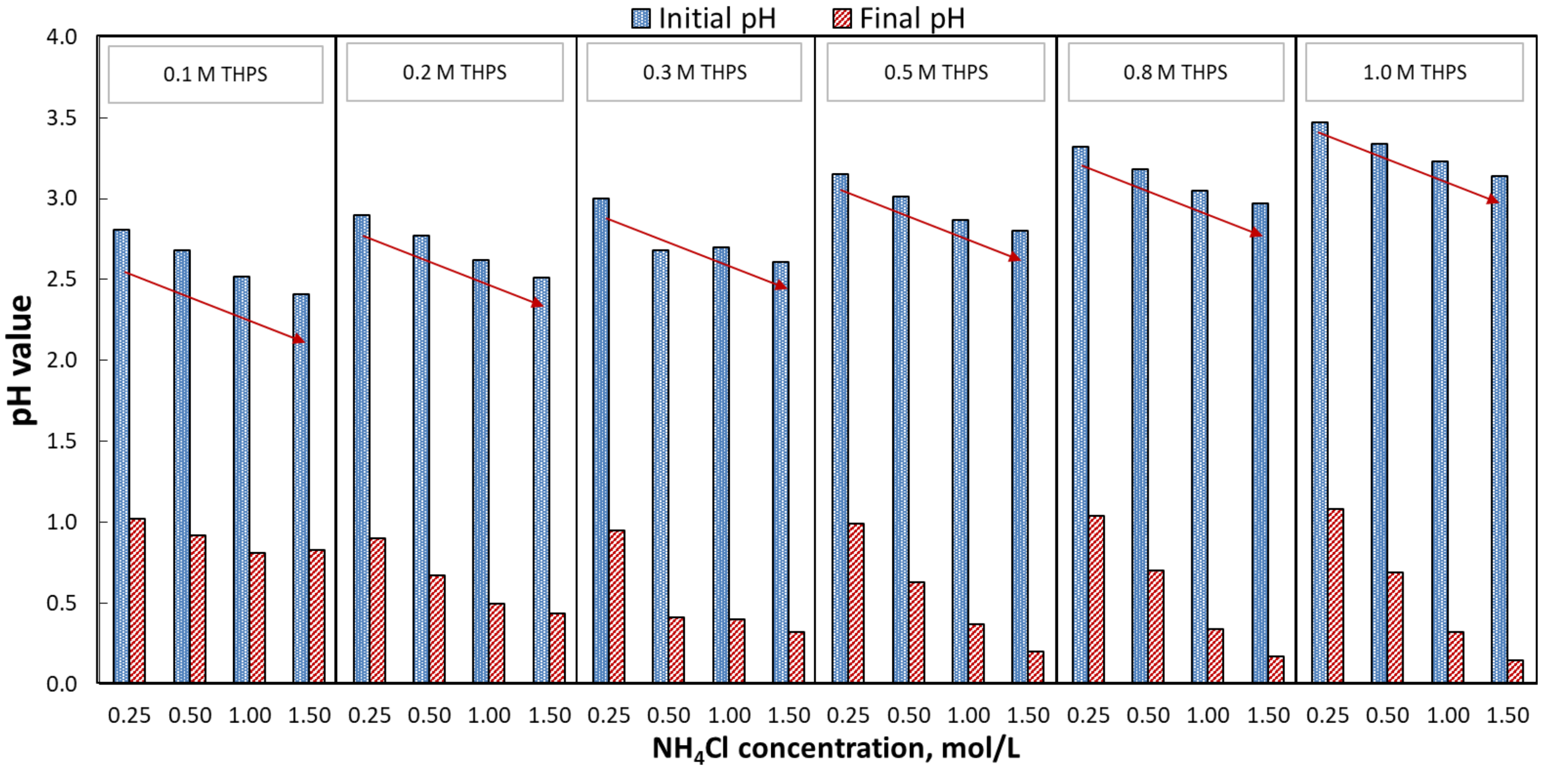
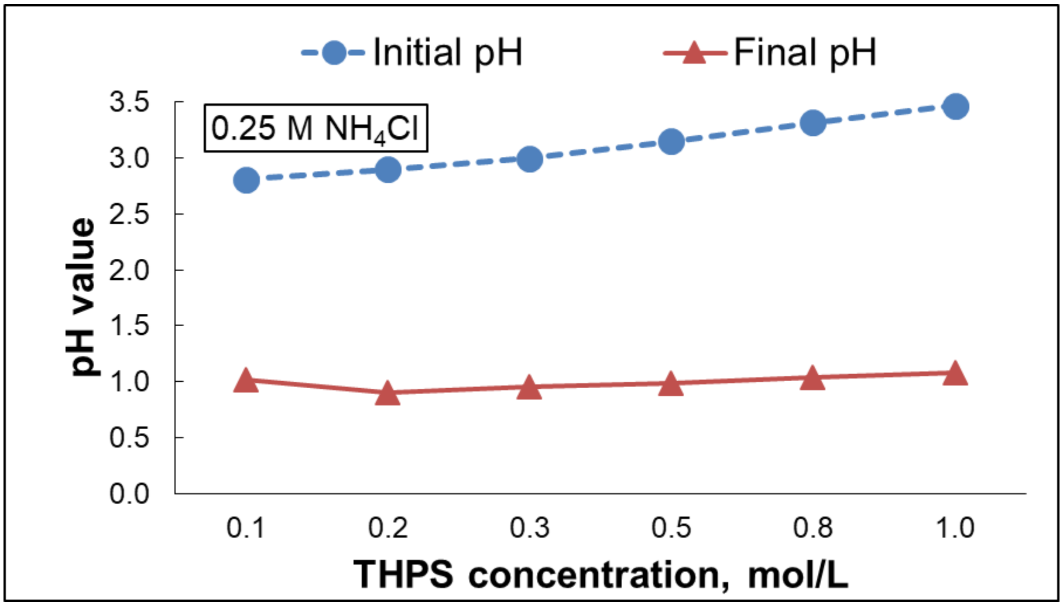
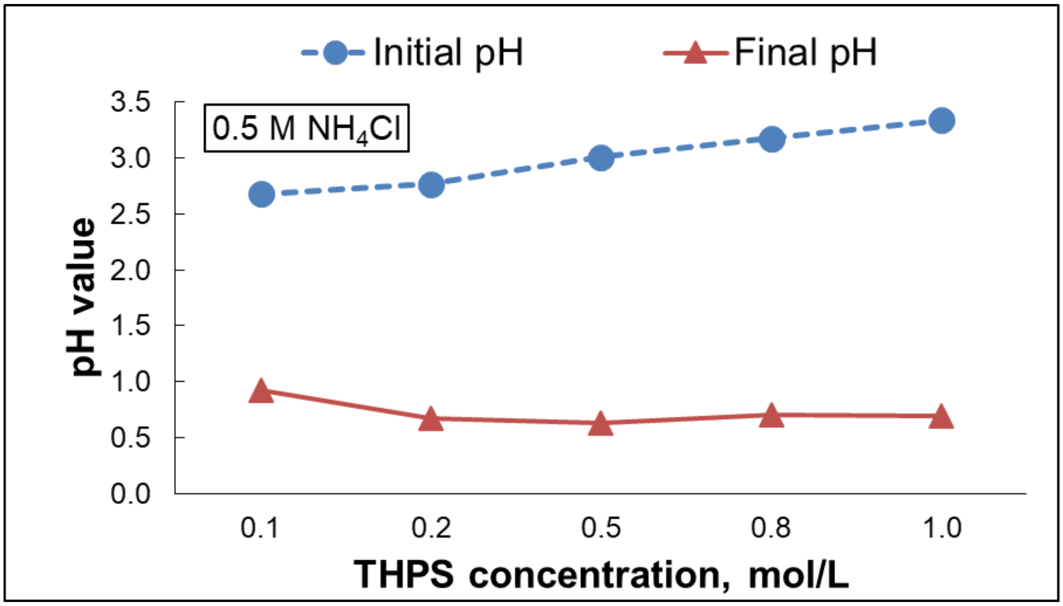


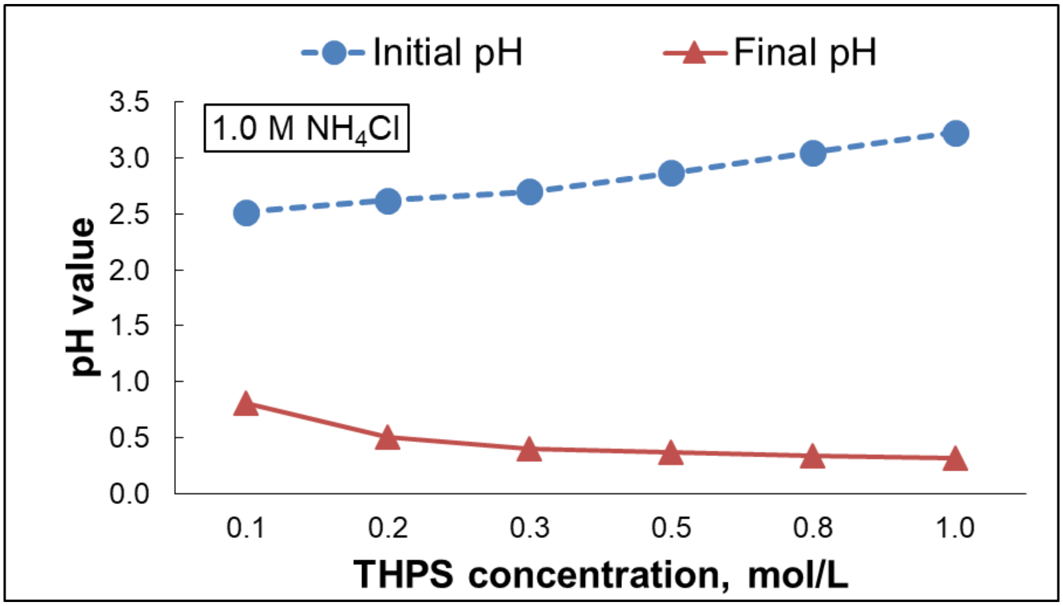
Fig. 12—pH values of each dissolver before and after the experiment.


Initial pH
Final pH
0.25 M NH_4Cl
pH value
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.2
0.3
0.5
0.8
1.0
THPS concentration, mol/L

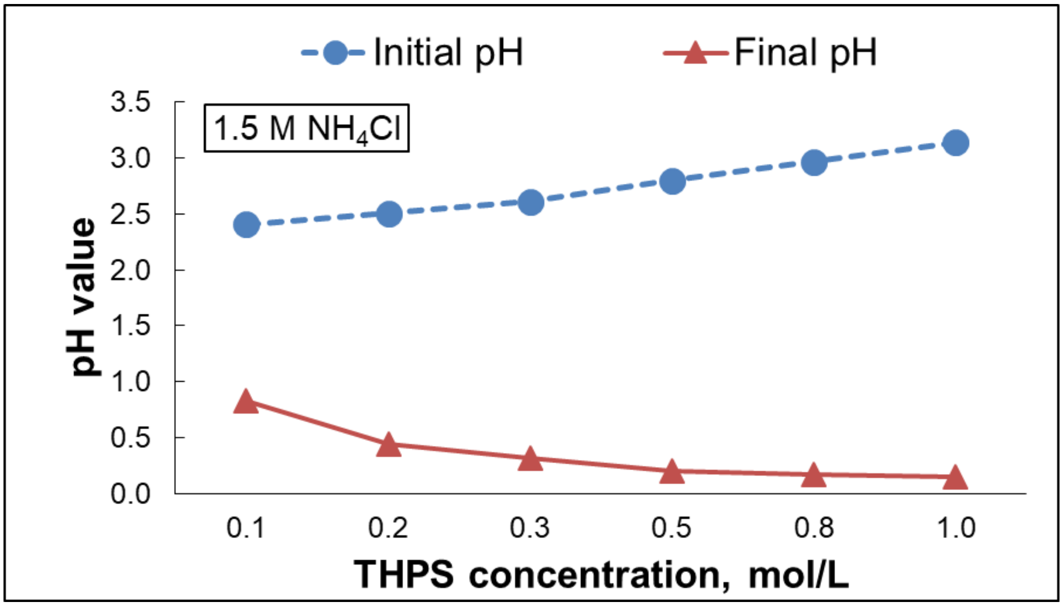
(a)


Initial pH
Final pH
0.5 M NH_4Cl
pH value
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.1
0.2
0.5
0.8
1.0
THPS concentration, mol/L

(b)



(c)



(d)

Fig. 13—Initial and final pH values as a function of THPS concentration for a constant NH_4Cl concentrations of (a) 0.25 mol/L NH_4Cl, (b) 0.5 mol/L NH_4Cl, (c) 1.0 mol/L NH_4Cl, (d) 1.5 mol/L NH_4Cl.

Fig. 13 shows a change in initial and final pH values as a function of THPS concentration for a constant ammonium chloride concentration. It can be easily observed from the curves that in all the cases, increasing THPS concertation increased the initial pH. However, the same trend is not observed in the final pH values. For 0.5 mol/L NH_4Cl concentration, final pH values were constant at 1.00 with an increase in THPS concentration, but for NH_4Cl concentrations greater than 0.5 mol/L, final pH values decreased with increase in THPS concentration. For the case of 0.5 mol/L NH_4Cl, final pH values at 0.1 and 1.0 mol/L THPS were 0.92 and 0.69, respectively. Whereas, in the case of 1.5 mol/L NH_4Cl, final values at 0.1 and 1.0 mol/L THPS were 0.83 and 0.15, respectively.

This behavior pattern can result from increased reaction at higher concentration of THPS and ammonium chloride. According to Eq. 1, two moles of THPS and ammonium chloride reacts with one mole of iron to create a complex and one mole of hydrochloric acid. Based on that formula, increasing concentration of ammonium chloride will result in increased concentration of H^+ and Cl^- ions acid, which can reduce pH values. It is possible that the complex is acidic, and that increasing the concentration of THPS and ammonium chloride also increases the concentration of complex, which reduces final pH value. During the chemical reaction, the THPS complexed the ferrous ions and the liberated acid from the dissociation of ammonium salts dissolved scale, which increases overall dissolution capacity (Jawish 2018).

Effect of THPS and NH_4Cl concentration on iron sulfide scale dissolution

The effect of THPS and NH_4Cl blend concentration on iron-sulfide solubility can be explained using the plot of iron dissolution versus THPS concentration at a constant NH_4Cl concentration. This plot can help to understand the effect of THPS concentration and NH_4Cl concentration both at the same time.

Fig. 14 shows maximum dissolution as a function of THPS concentration at a constant ammonium chloride concentration. According to Fig. 14, the concentration of iron sulfide dissolved in the blend increases with the increase in THPS concentration. At 0.1 mol/L THPS, maximum dissolution is observed to be 5,095 ppm at 1.5 mol/L NH_4Cl concentration, but for THPS concentration greater than 0.1 mol/L, maximum dissolution is observed at 0.5 mol/L NH_4Cl concentration. Overall, maximum dissolution was observed at 0.8 mol/L THPS concentration followed by 0.5 mol/L THPS concentration.

For 0.25 mol/L NH_4Cl, maximum dissolution is observed to be 6,798 ppm at 1.0 mol/L THPS concentration. For NH_4Cl concentration greater than 0.25 mol/L maximum dissolution is observed to be slightly higher than 7,700 ppm at 0.8 mol/L THPS. However, the increase in dissolution from 0.5 to 0.8 mol/L THPS is very minor ($\leq 3\%$). Except in the case of 0.25 mol/L NH_4Cl, all other dissolvers showed the maximum limit of dissolution at around 7,700 ppm for THPS concentration greater than 0.5 mol/L.

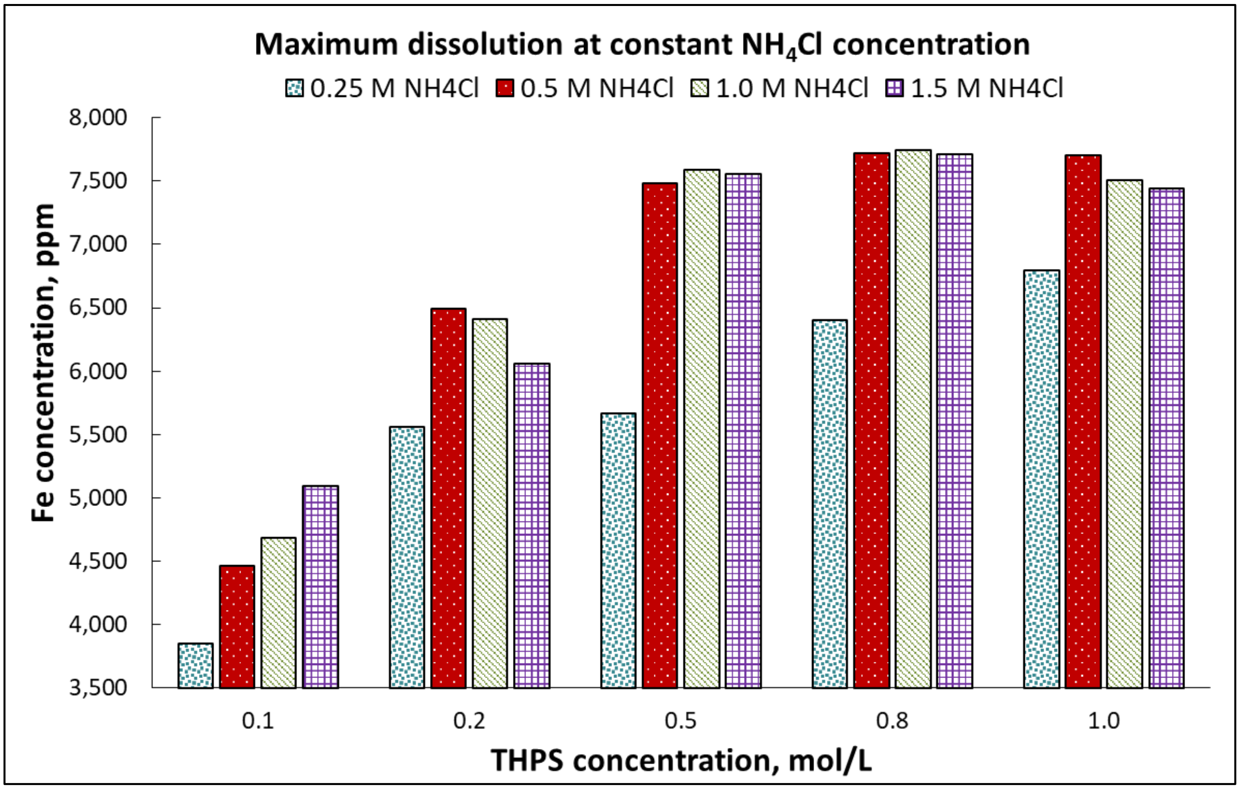


Fig. 14—Maximum dissolution at constant NH_4Cl concentration.

At 0.1 mol/L THPS concentration, minimum dissolution is observed to be 3,851 ppm at 0.25 mol/L NH_4Cl and maximum dissolution is observed to be 5,095 ppm at 1.5 mol/L implying solubility of iron sulfide increases with increase in the concentration of ammonium chloride. Similarly, at 0.25 mol/L NH_4Cl concentration, minimum dissolution is observed at 0.1 mol/L THPS and maximum dissolution is observed to be 6798 ppm at 1.0 mol/L, proving the dissolution of iron-sulfide scale increases with increases in the concentration of THPS. But at THPS concentration greater than 0.5 mol/L, the effect of NH_4Cl will not be dominant. For example, at 1.0 mol/L THPS concentration, dissolution is almost the same for NH_4Cl concentration greater than 0.5 mol/L. Likewise, at NH_4Cl concentration greater than 0.5 mol/L, increasing THPS concentration above 0.5 mol/L will not increase the solubility of iron-sulfide scale (e.g. at 1.5

mol/L NH_4Cl concentration, dissolution is almost similar for THPS concentration greater than 0.5 mol/L).

It can be inferred that using a THPS and ammonium-chloride concentration greater than 0.5 mol/L will not result in the maximum dissolution of iron-sulfide scale. Use of a high concentration of either THPS or ammonium chloride can increase the cost of the treatment, so optimization of the concentration is important. The best dissolver chemistry out of 24 dissolvers is 0.5 mol/L THPS concentration with 0.5 mol/L NH_4Cl concentration; in this case, the concentration is not extreme but the performance is good.

Effect of time on the solubility of iron sulfide

For all of the dissolvers, iron concentration in supernatant samples collected increases with passing time, but increase in the dissolution was not significant after a certain time. One such example is presented in **Fig. 15**, which plots iron concentration against time for varying ammonium chloride concentrations and a constant THPS concentration of 0.1 mol/L. After 24 hours, all of the curves plateau and an increase in the iron concentration was not significant. Similar behavior was observed with all of the dissolvers, where the curves were getting flatter after a certain time period.

To get a better idea of the optimal time for each dissolver at 150°F, a new definition of optimal time was created for this work. In this study, the optimal time of treatment was defined as the time in hours, where dissolution was greater than 85% of overall dissolution. Using this concept, optimal time was plotted as a function of THPS concentration (Fig. 15).

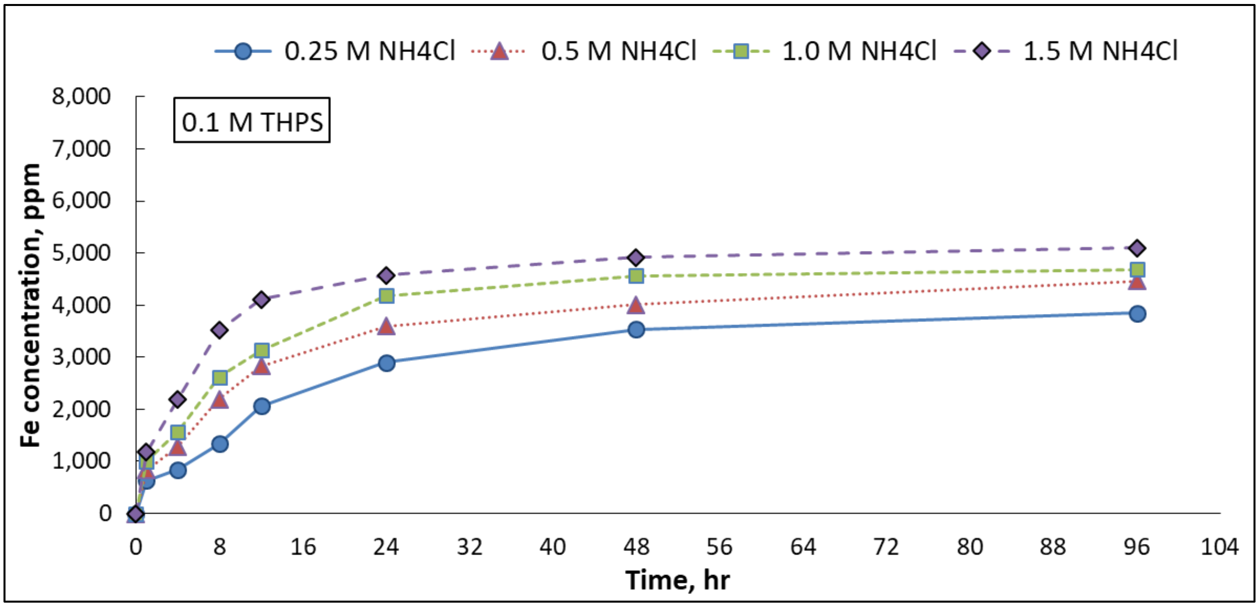


Fig. 15—Fe concentration vs time at constant THPS concentration of 0.1 mol/L.

Fig. 16 shows observed optimal time as a function of THPS concentration for a constant concentration of NH_4Cl for dissolution of iron-sulfide scale. According to the plot, all dissolvers showed faster reactions with an increase in THPS concentration. For a constant THPS concentration, the optimal time declined with an increase in NH_4Cl. For 0.1 mol/L THPS concentration, optimal time was 48 hours for 0.25 mol/L NH_4Cl, and it reduced continuously with increase in NH_4Cl concentration. Optimal time reduced to 12 hours at NH_4Cl concentration of 1.5 mol/L. Increase in THPS concentration from 0.5 mol/L to 1.0 mol/L has a significant reduction in the optimal time for dissolving FeS scale.

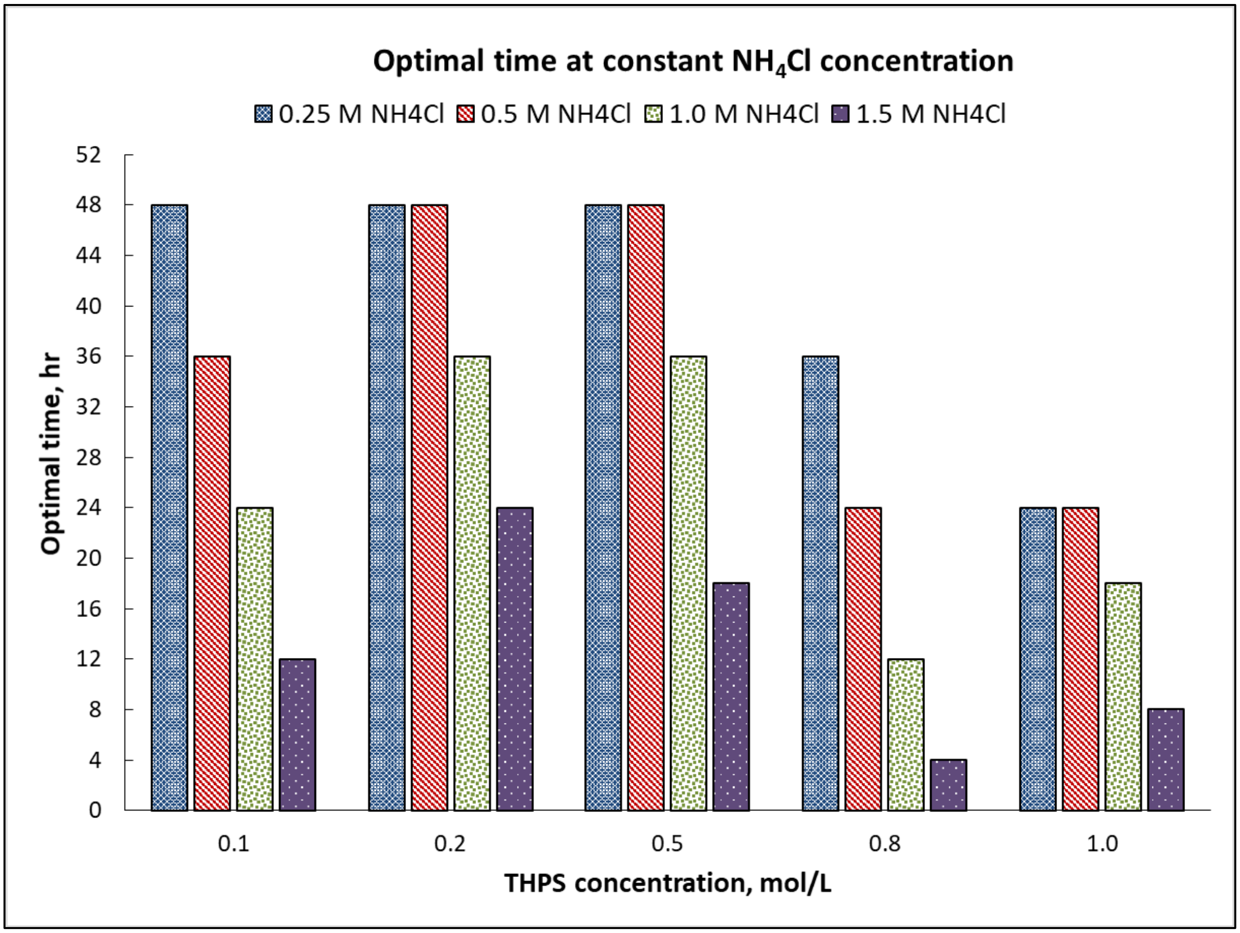


Fig. 16—Optimal time at constant NH_4Cl concentration.

The optimal time was 48 hours at 0.1 mol/L THPS for a 0.25 mol/L NH_4Cl, but it was 36 hours and 24 hours at 0.8 and 1.0 mol/L THPS concentration, respectively. **Fig. 16** shows that for a constant NH_4Cl concentration greater than 0.25 mol/L, increasing THPS concentration was not following any proper trend line; rather, overall it showed a reduction in the optimal time.

High concentrations of THPS greater than 0.5 mol/L and NH_4Cl greater than 0.5 mol/L allowed a high reaction rate and dissolved the maximum amount of iron sulfide faster than in the case of a low concentration of the THPS and NH_4Cl blend. This trend can be explained by a higher amount of active concentration of dissolver blend that can react faster with iron sulfide scale.

Keeping a high concentration of both THPS and NH_4Cl showed faster reaction rates than a high concentration of only one of them.

Effect of temperature

After all bottle test experiments were carried out at 150°F, six dissolvers were selected for a 300°F bottle-test experiment based on the analysis of the same dissolvers at 150°F. Two different ammonium chloride concentrations 0.25 and 0.5 mol/L were selected for this experiments because 0.25 mol/L was the minimum value and 0.5 mol/L was the best ammonium chloride concentration among all. Likewise, three different THPS concentrations 0.1, 0.5, and 1.0 mol/L, were selected because 0.1 and 1.0 mol/L were the extreme values and 0.5 mol/L gave the best performance among all other dissolvers for the experiments at 150°F.

Final pH values of all of the dissolver after the experiment were measured using an Oakton pH meter. **Fig. 17** shows the effect of temperature on the final pH values at 150 and 300°F. According to this plot, for all of the dissolvers, the final pH values were lower than the initial pH values irrespective of temperature or concentration of THPS and ammonium chloride.

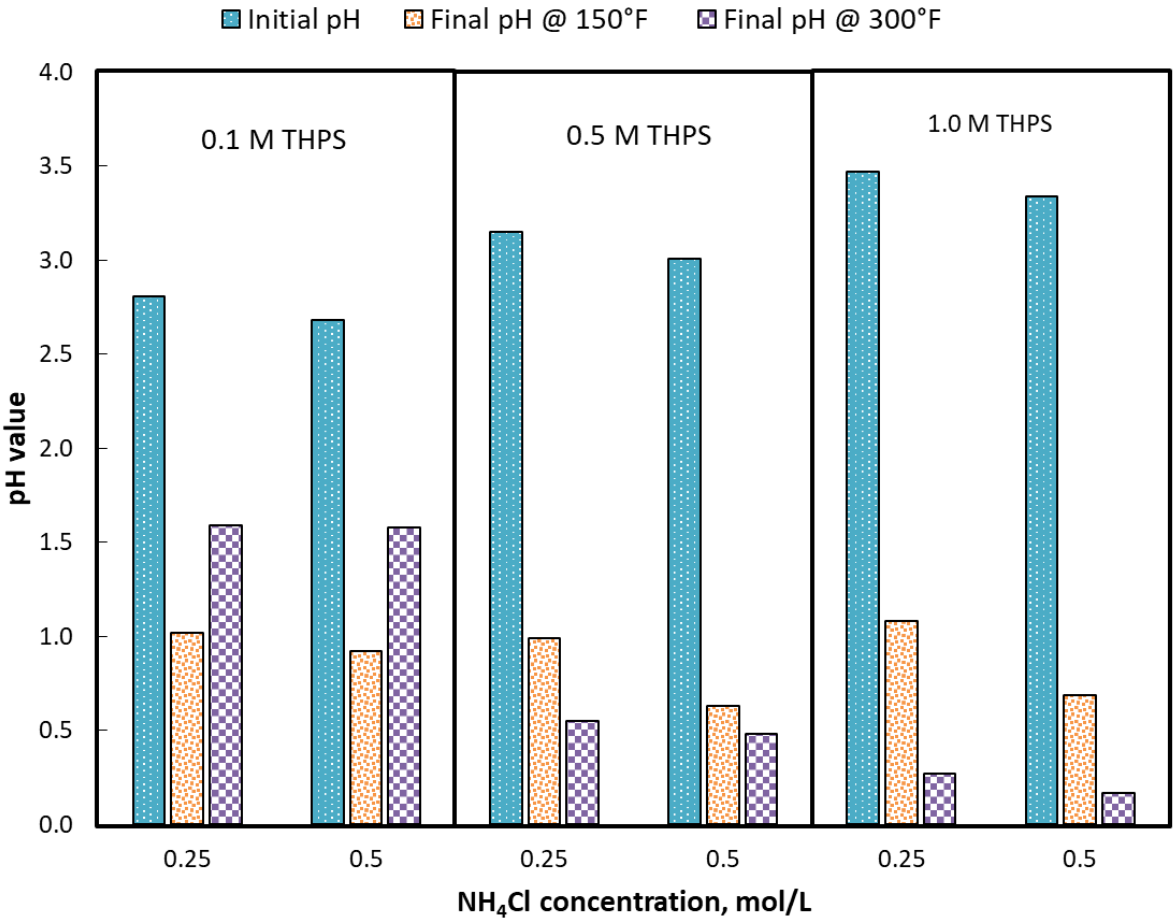


Fig. 17—Effect of temperature on final pH values.

For 0.1 mol/L THPS concentration, final pH values at 150°F were lower than at 300°F. On the other hand, for 0.5 and 1.0 mol/L THPS concentration, final pH values at 150°F were higher than at 300°F. For 0.25 mol/L NH_4Cl concentration, final pH at 150°F was the same (≈ 1.0), but for 300°F, it decreased with increase in THPS concentration. However, for 0.5 mol/L NH_4Cl concentration, final pH decreased with the increase in THPS concentration at both 150 and 300°F. However, the reduction in final pH values was higher in case of 300°F than 150°F temperature.

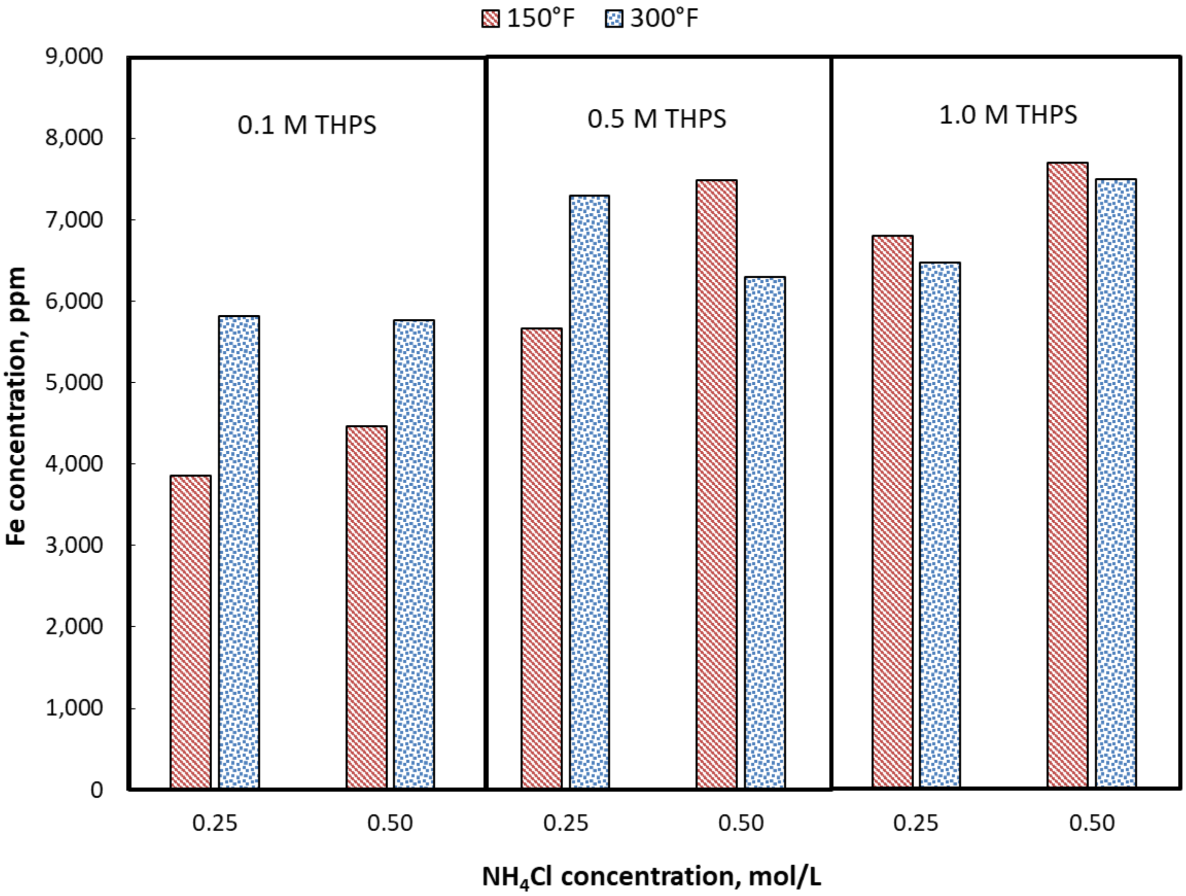


Fig. 18—Maximum dissolution observed at different temperature.

Fig. 18 shows maximum iron ion concentration observed in different dissolvers at 150 and 300°F temperature. According to this chart, at 0.1 mol/L THPS concentration with 0.25 and 0.50 mol/L NH_4Cl, dissolution was higher at 300°F compared to 150°F. Whereas, at 1.0 mol/L THPS concentration with 0.25 and 0.50 mol/L NH_4Cl, dissolution was slightly higher at 150°F compared to 300°F. In the case of 0.5 mol/L THPS concentration, dissolution at 300°F was 7,289 ppm and at 150°F was 5,669 ppm for 0.25 mol/L NH_4Cl concentration, but the opposite trend was observed at 0.5 mol/L NH_4Cl concentration where dissolution at 300°F was 6291 ppm and at 150°F was 7,484 ppm.

This plot provides important information about the temperature effect on the dissolution of iron-sulfide scale using a varying concentration of THPS and ammonium chloride. The same dissolver which can efficiently dissolve iron-sulfide scale at a lower temperature may not be able to dissolve it with the same efficiency at high temperature. At high temperature, the use of high concentrations of THPS and NH_4Cl fails to provide better treatment, but the low concentrations of the dissolver blend can enhance the dissolution.

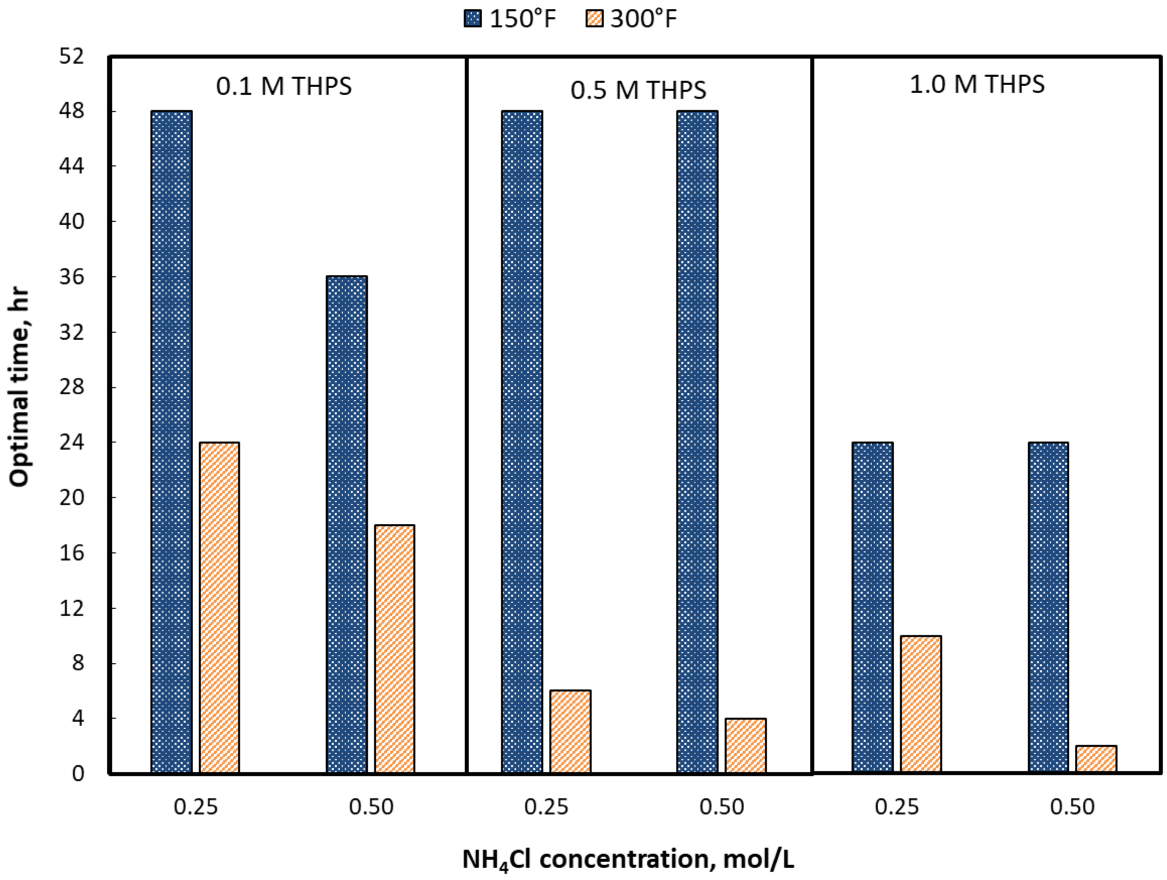


Fig. 19—Effect of temperature on the optimal time for dissolution.

Fig. 19 shows the effect of temperature on the optimal time for dissolution of iron-sulfide scale using different dissolvers of varying THPS and ammonium chloride concentrations. The optimal time for all of the dissolvers decreased with increase in temperature. 0.5 mol/L THPS concentration showed the highest drop in optimal time with an increase in temperature compare to 0.1 and 1.0 mol/L THPS concentrations.

For a constant THPS concentration at 300°F, increasing the concentration of NH_4Cl had a downward trend in optimal time, implying faster reaction for all cases. For a constant NH_4Cl concentration of 0.25 mol/L, optimal time was minimum at six hours when used with 0.5 mol/L THPS concentration and maximum at 24 hours when used with 0.1 mol/L THPS concentrations, but for 0.5 mol/L NH_4Cl concentration, optimal time reduced with an increase in the THPS concentration.

Autoclave Tests

Bottle-test results revealed that low concentrations of THPS have a positive effect on dissolving iron sulfide with an increase in temperature (**Fig. 18**). Gilbert et al. (2002) successfully used standalone THPS to dissolve iron-sulfide scale and found that adding ammonium chloride can strongly improve the performance of THPS. However, these claims have never been discussed in the literature at HP/HT conditions. Therefore, to simulate these observations at HP/HT conditions, autoclave experiments were carried out using 0.1 and 0.2 mol/L concentrations of THPS and 1 wt% ($\approx$ 0.20 mol/L) concentration of ammonium chloride.

These tests were carried out at 150 and 300°F temperature and 1000 psi pressure. Effects of these properties on the dissolution of iron sulfide were observed using these sets of experiments.

Effect of temperature and NH_4Cl concentration on scale dissolution

For this experiments, 40 g of dissolver blend and 2 g of iron sulfide sample were used. Eight different experiments were carried out with 0.1 and 0.2 mol/L THPS concentration, with/without 1 wt% NH_4Cl at 150 and 300°F, to understand the effect of these parameters on the dissolution of iron-sulfide scale.

Fig. 20 shows the effect of ammonium chloride at different THPS concentration at 150°F temperature. Based on this plot, increasing THPS concentration from 0.1 to 0.2 mol/L results in an increase from 3,318 to 4,110 ppm in the dissolution when used standalone without any additive, and an increase from 9,230 to 11,190 ppm when used with 1 wt% NH_4Cl concentration. Adding 1 wt% NH_4Cl resulted in a significant increase in the dissolution for both 0.1 and 0.2 mol/L THPS concentrations.

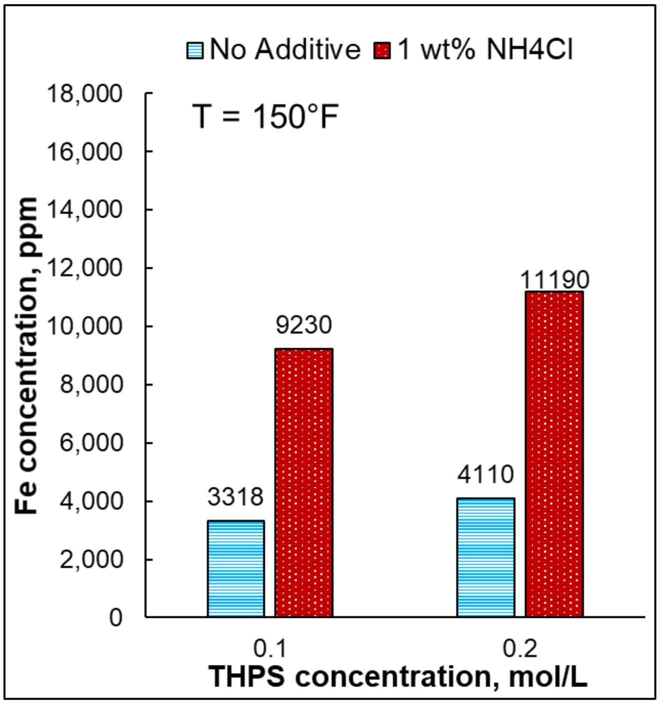


Fig. 20—Effect of ammonium chloride concentration at a temperature of 150°F.

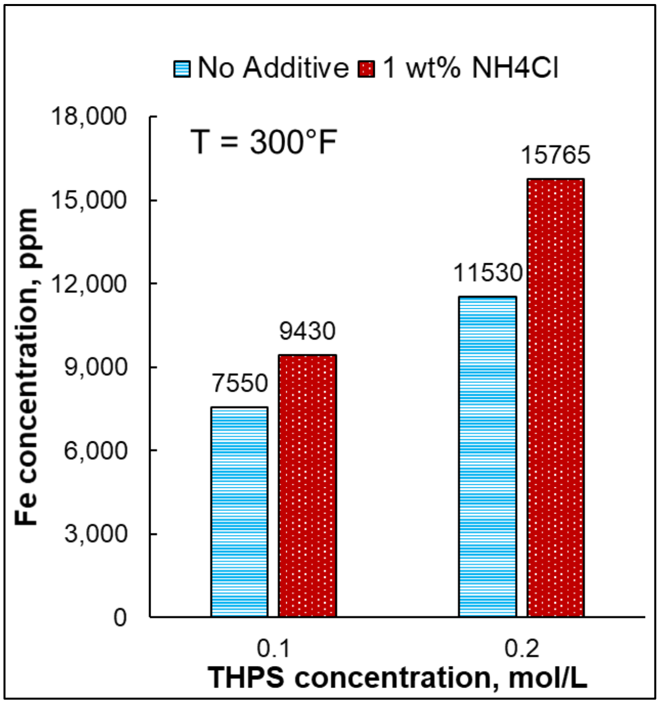


Fig. 21—Effect of ammonium chloride concentration at a temperature of 300°F.

Fig. 21 shows the effect of ammonium chloride at different THPS concentration at 300°F. Based on this plot, increasing THPS concentration from 0.1 mol/L to 0.2 mol/L results in an increase from 7550 to 11530 ppm in scale dissolution when used standalone without any additive and an increase from 9430 to 15765 ppm when used with 1 wt % NH_4Cl concentration. Adding 1 wt % NH_4Cl resulted in an increase in the scale dissolution for both 0.1 and 0.2 mol/L THPS concentration.

Increasing the temperature of the system from 150°F to 300°F increased the dissolution of iron sulfide in all of the dissolvers. 0.1 and 0.2 mol/L THPS standalone can dissolve significantly more iron sulfide at 300°F compared to 150°F. But in cases where 1 wt% NH_4Cl is added into the dissolver, 0.1 and 0.2 mol/L THPS can dissolve iron sulfide slightly better at 300°F than at 150°F.

The increase in temperature appears more effective in iron sulfide dissolution for THPS standalone than in THPS and ammonium chloride blend solutions.

SEM-EDS study

To understand the change in iron-sulfide particles before and after the THPS dissolver treatment, samples of iron sulfide particles before and after the experiment were taken for SEM-EDS study. Scanning electron microscopy (SEM) can provide clear images of solid particle surface topography at micron level, and when combined with energy dispersive x-ray spectroscopy (EDS) can provide elemental analysis of the surface of the sample.

Fig. 22 shows an SEM image of the iron sulfide scale sample before starting the experiment. The image that the surface of the iron-sulfide scale was almost nonporous with some small particles on the surface. It can be proposed based on this image that any dissolver will require better efficiency in creating flow channel in the scale to enhance the surface area and improve dissolution. **Fig. 23** shows an SEM image of the iron-sulfide scale sample after treatment with 0.1 mol/L THPS at 300°F. The scale surface had a different texture than it had before the treatment. Instead of a nonporous flat surface, this image reveals spherical porous balls of iron-sulfide scale with a network of pore spaces, which can help in enhancing the dissolution of iron-sulfide scale. **Fig. 24** shows the SEM image of iron-sulfide scale sample after treatment with 0.1 mol/L THPS and 1 wt% NH_4Cl at 300°F. Based on this image, the change in the scale surface from the initial condition can be easily observed. Porous spherical balls observed in Fig. 23 were also observed in this image, but it also had some flakes, which were more porous compared to spheres and proved the improved dissolution of iron sulfide scale when ammonium chloride additive was added.

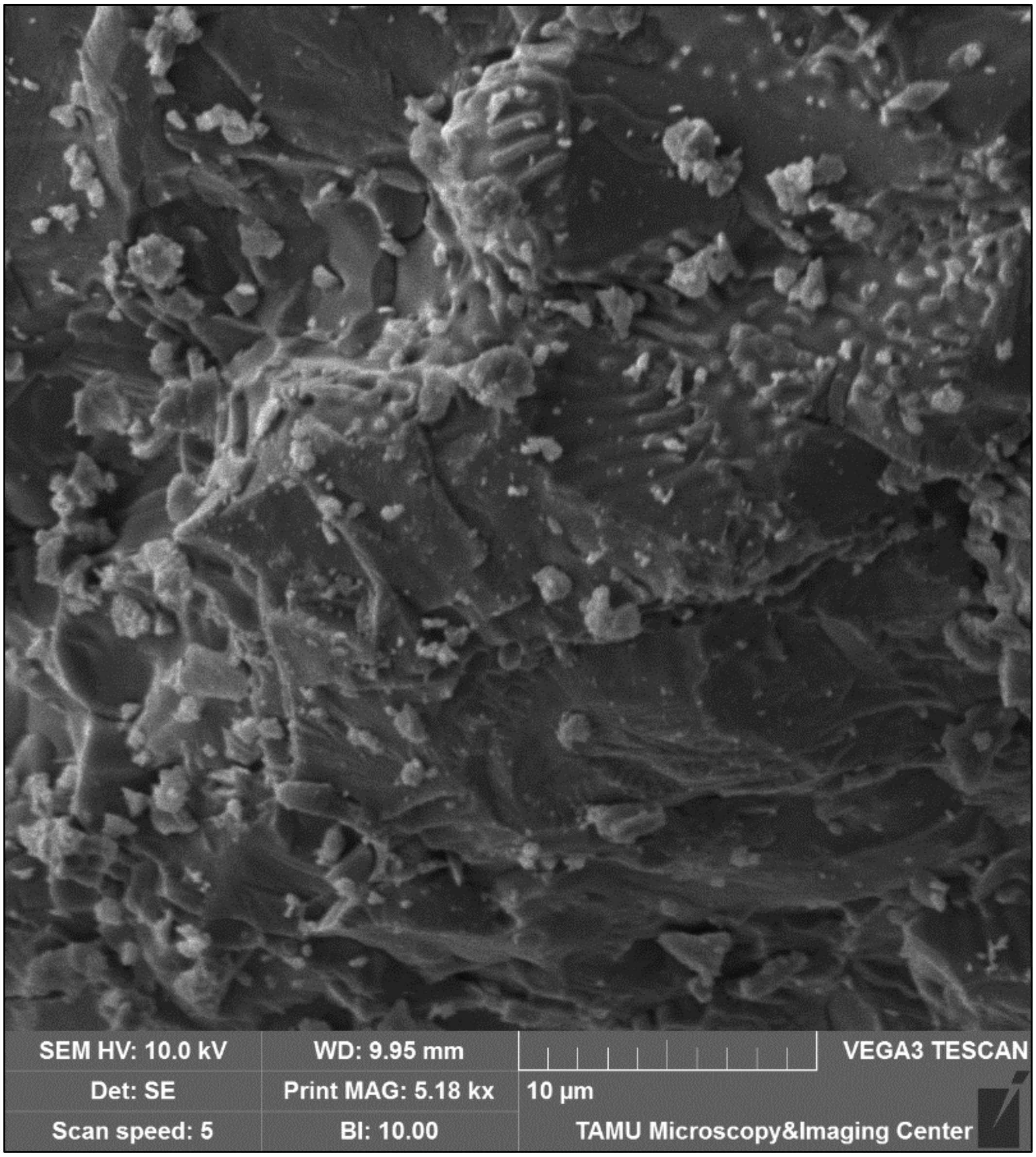


Fig. 22—SEM image of iron sulfide scale sample before the experiment.

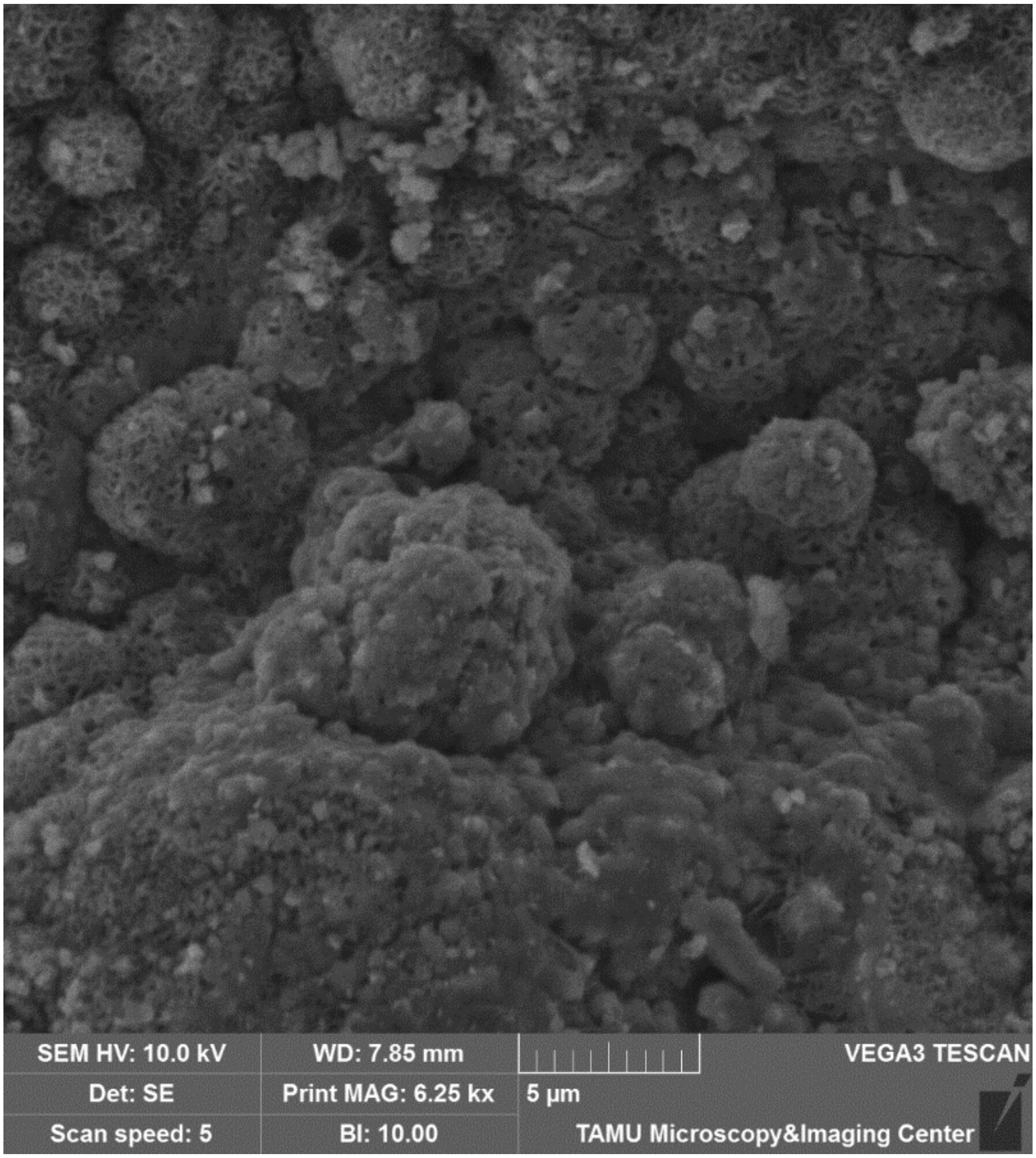


Fig. 23—SEM image of iron sulfide scale sample after treatment with 0.1 mol/L THPS at 300°F.

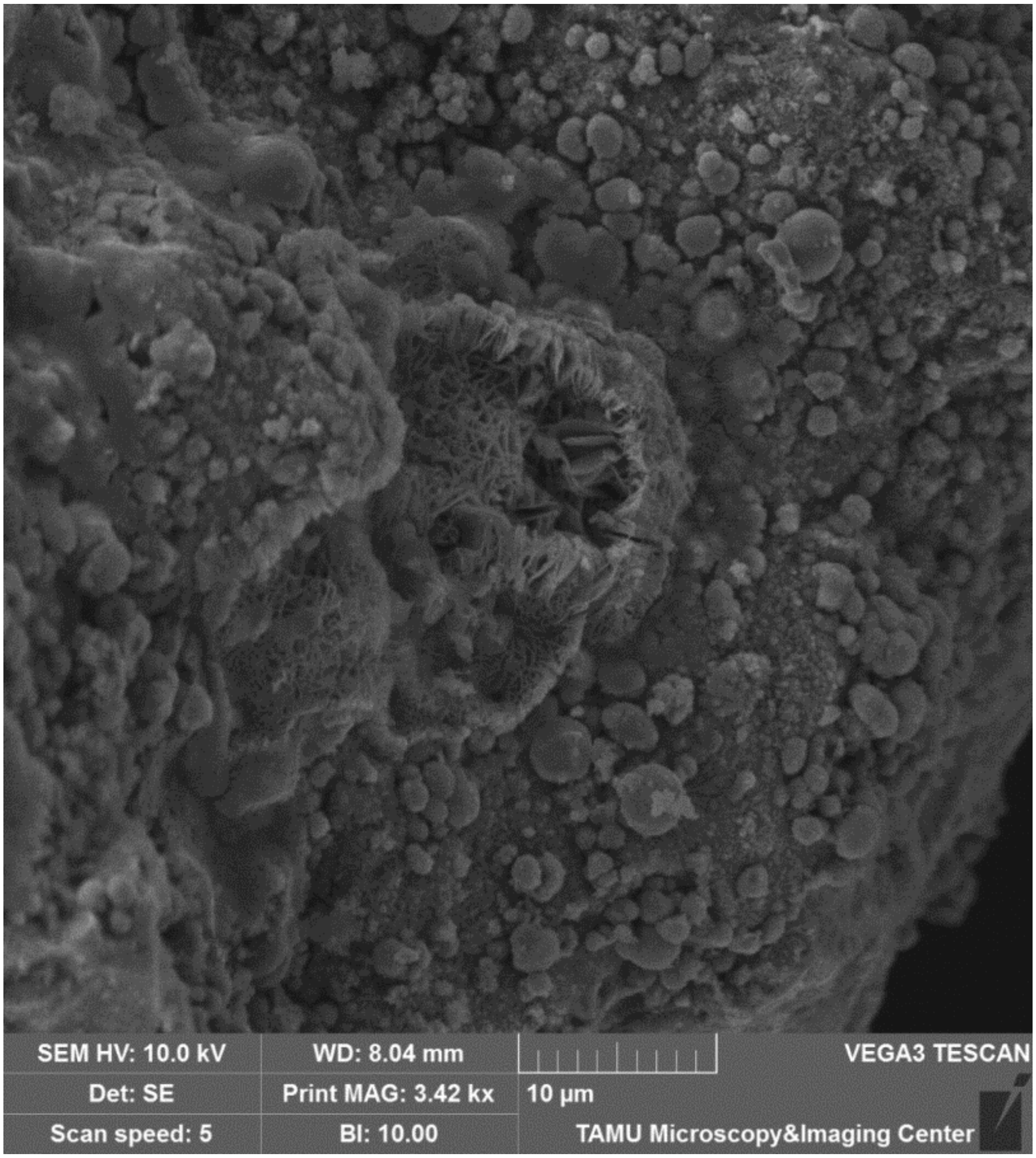


Fig. 24—SEM image of iron sulfide scale sample after treatment with 0.1 mol/L THPS and 1 wt% NH_4Cl at 300°F.

EDS study was carried out on each sample of this scale to measure the elemental composition of its surface (**Table 3)**. After the scale reacted with THPS standalone at 300°F, it showed the presence of new elements phosphorus and carbon, which were building elements of THPS molecule. Hence, it was possible that THPS was sticking to the surface of scale, which can cause a reduction of its dissolution. When the scale reacted with THPS and ammonium chloride it was precipitated chloride ions on the surface of the scale in addition to phosphorus and carbon.

Elements	Before experiment	After treating with 0.1 mol/L at 300°F	After treating with 0.1 mol/L THPS + 0.5 mol/L NH_4Cl
Fe	75.9 %	67 %	47.3 %
S	18.7 %	2.9 %	3.5 %
O	5.6 %	18.7 %	35.2 %
P	-	4.2 %	2.5 %
C	-	7.2 %	10.5 %
Cl	-	-	0.8 %

Table 3—Elemental composition of scale before and after the experiment using EDS.

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One important observation from this study is decreased iron and sulfur concentration but increased oxygen concertation. This behavior can manifest if THPS was only reacting with iron sulfide particles and iron oxide particles were not affected by this process, which can leave oxygen ions as they were before.

Comparison of THPS and NH_4Cl blend with HCl acid to dissolve iron sulfide

Based on previous experiments using bottle tests, one best dissolver (0.5 mol/L THPS + 0.5 mol/L NH_4Cl) was selected for autoclave tests under field conditions. Two different temperature (150 and 300°F) at 1000 psi was used to understand the effect of temperature on dissolution of iron sulfide using THPS and ammonium chloride. For all experiments, 100 cm^3 dissolver was prepared and 1 g of iron-sulfide powder was used. To compare the performance of THPS with hydrochloric acid, one experiment with it was carried out at 150°F temperature.

According to **Fig. 25**, the final pH of the spent dissolver of an experiment carried out at 300°F was slightly lower than that of an experiment carried out at 150°F. In the case of hydrochloric acid, the pH value of the dissolver before and after the experiment was zero.

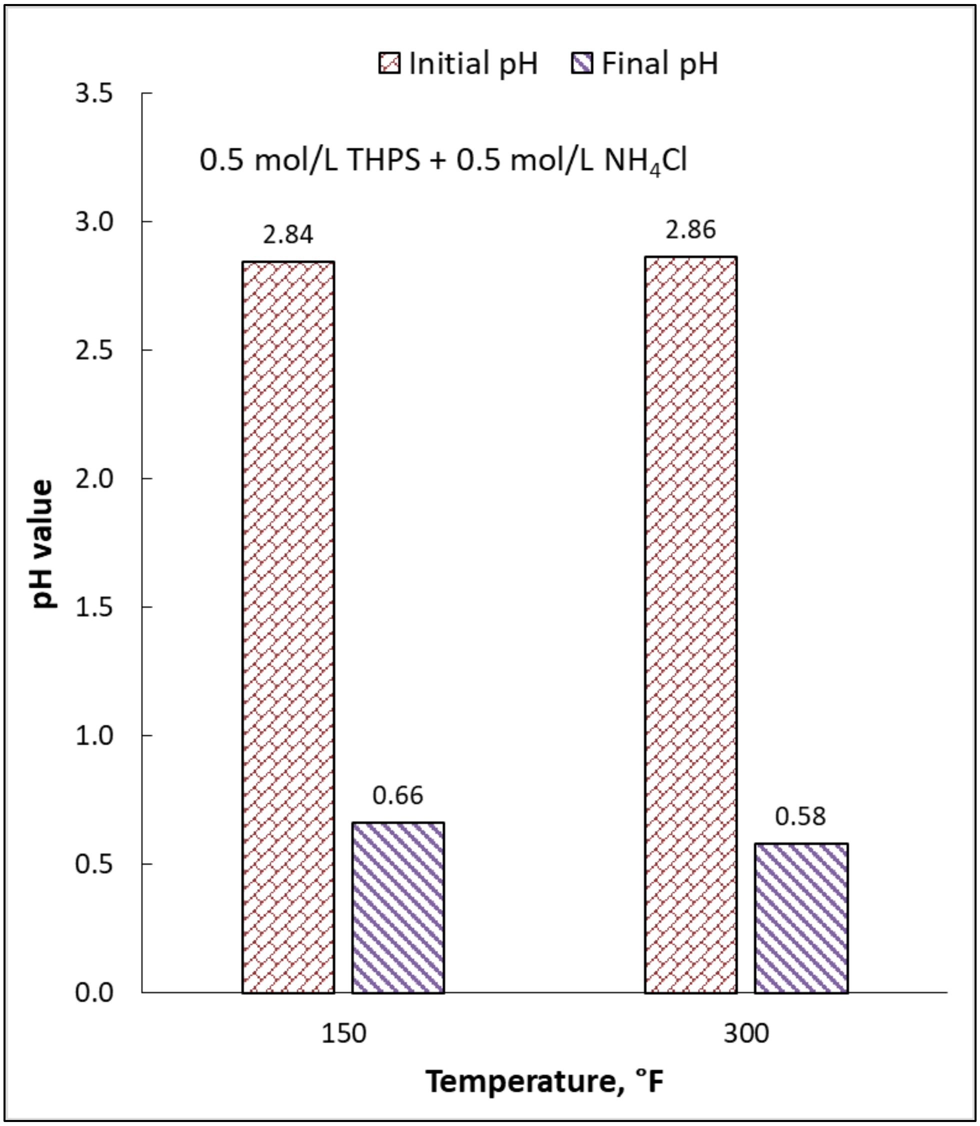

Fig. 25—Effect of temperature on final pH.

Fig. 26 shows the maximum iron ion concentration observed in the different dissolvers. According to this plot, dissolver blend 0.5 mol/L THPS and 0.5 mol/L NH_4Cl could dissolve slightly better than 15 wt % HCl. According to the literature, hydrochloric acid is very effective in dissolving iron sulfide (FeS) scale. Based on this results THPS and ammonium chloride blend was performing as well as HCl. The THPS and ammonium chloride blend showed much better performance in dissolving scale at 300°F compared to 150°F. Unfortunately, the HCl test could not be carried out at 300°F for comparison with THPS blend because HCl is very active and corrosive at high temperatures, which can damage the autoclave reactor.

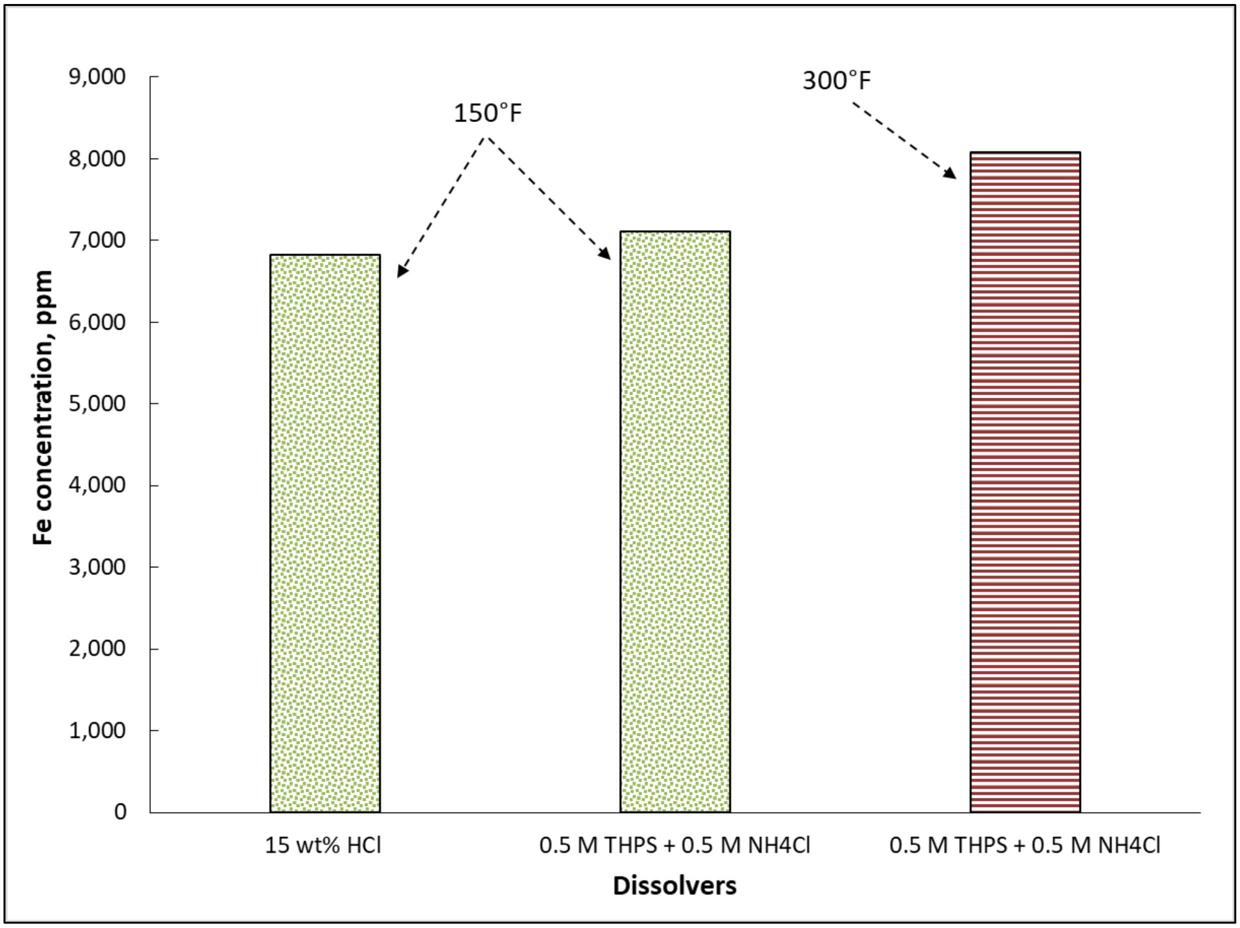

Fig. 26—Maximum dissolution observed for different dissolver at different temperature.

Fig. 27 shows the optimal time for dissolution of iron-sulfide scale using different dissolver blends. 15 wt % HCl took four hours, whereas 0.5 mol/L THPS and 0.5 mol/L NH_4Cl took eight hours for effective dissolution at 150°F. The same THPS and ammonium chloride blend took only one hour to effectively dissolve iron sulfide at 300°F.

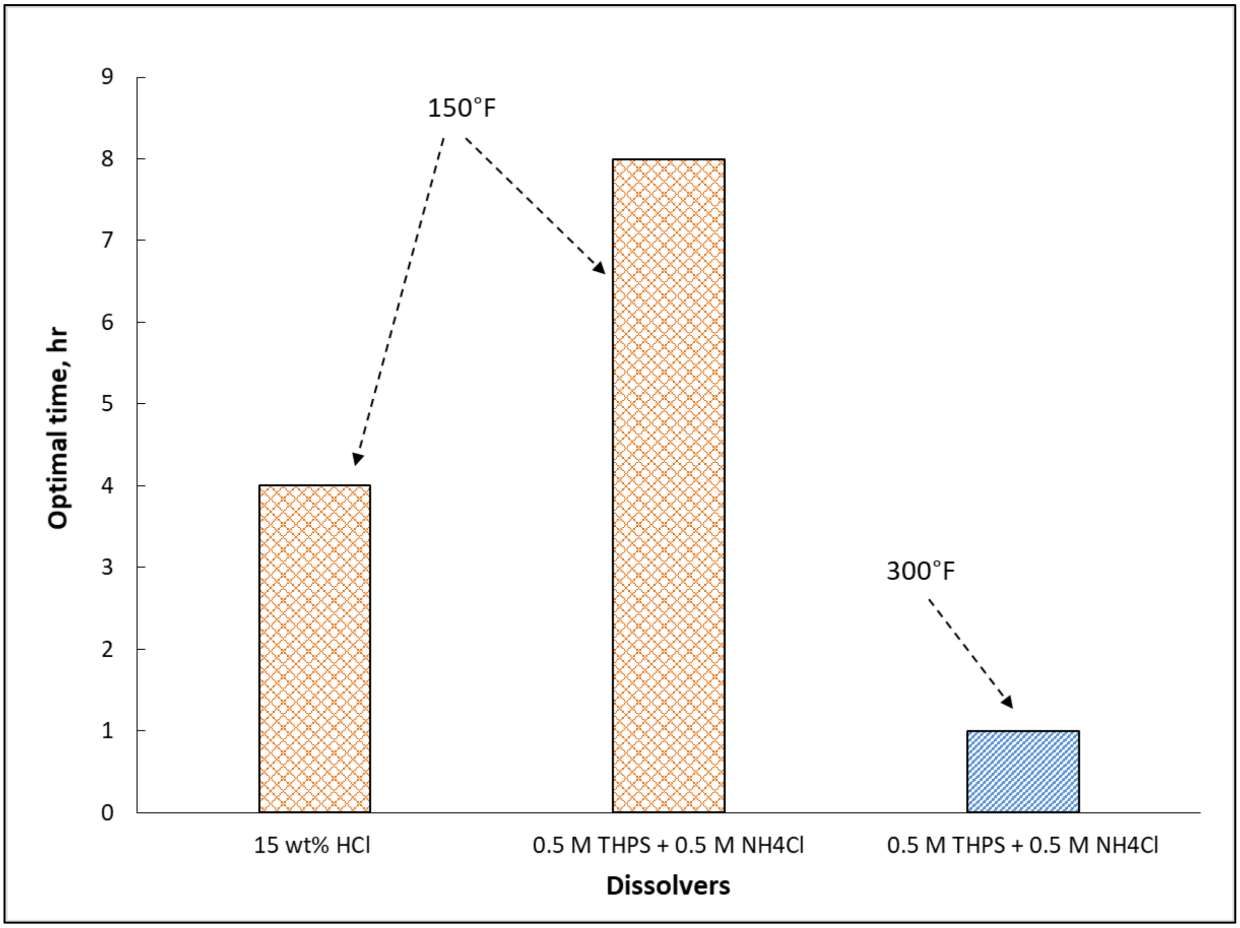

Fig. 27—Optimal time for treatment using different dissolvers at different temperature.

For a better understanding of the dissolution process, H_2S concentration was measured using Dräger tubes after each experiment. There was no H_2S trace when THPS and ammonium chloride blend was used at 150°F, but 70 ppm H_2S concentration was observed when the same dissolver blend was used at 300°F. For an experiment with HCl, 1000 ppm of H_2S was evolved during the reaction process.

Thermal Degradation Tests

To understand the thermal stability of THPS and ammonium chloride blend at high temperature, a thermal degradation study was carried out in an OFITE aging cell. For this study, 1.0 mol/L THPS and 0.5 mol/L NH_4Cl blend were selected and 250 ml of this dissolver was prepared. These tests were carried out at 350 and 400°F for 24 hours. The samples were collected at the end of the experiment for the FTIR study to observe the change in functional groups.

Fig. 28 shows IR patterns of the 1.0 mol/L THPS and 0.5 mol/L NH_4Cl blend before and after thermal degradation test in the OFITE aging cell at 350 and 400°F. This dissolver blend was prepared using water as a solvent, so the peak at 3250 cm^{-1} can be assigned to O-H stretching from water. The peaks at 2920 and 1615 cm^{-1} can be attributed to the N-H stretching and bending, respectively. The source of N-H peaks is the ammonium chloride additive used in dissolver. The blend was prepared using water that has peaks that may overlap with N-H bonds. The peak at 1415 cm^{-1} can be attributed to $R\text{-}CH_2\text{-}OH$, which is a part of THPS molecule. The peaks between 1150 to 920 cm^{-1} occurred because of phosphine oxide, sulfates, and sulfur oxides present in the dissolver.

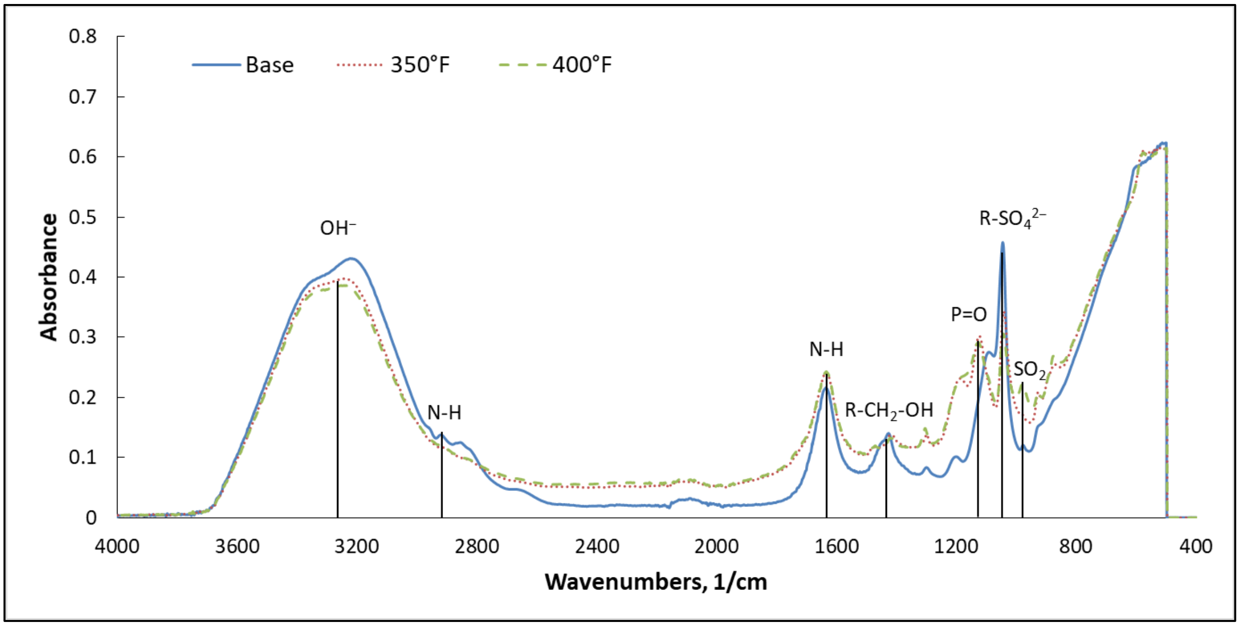

Fig. 28—IR spectrum of 1.0 mol/L THPS and 0.5 mol/L NH_4Cl before and after thermal degradation at 350 and 400°F.

Based on Fig. 2, phosphorus from THPS molecule combines with oxygen when THPS degrades into THPO and BMPA. Because functional groups containing phosphorus and sulfur in THPS molecules changes into different functional groups when degraded in THPO and BMPA. There were no peaks observed for P=O and SO_2 in the dissolver sample before the thermal degradation treatment. Although, alteration of IR spectra in the region of 1150 to 920 cm^{-1} can be observed after the dissolver was degraded. The peak of sulfate was more prominent in the base dissolver compared to degraded dissolvers. The base dissolver did not have peaks for P=O and SO_2, which were part of THPO and BMPA's molecular structure. Hence, THPS degraded into THPO and BMPA.

The difference between IR spectra of degraded dissolver at 350 and 400°F was very minor. The position and intensity of the peaks of all of the functional groups were the same in both IR patterns. These results confirm that the THPS was completely degraded at any temperature greater than or equal to 350°F.

pH values before and after the tests were measured for a better understanding of the thermal degradation reaction. Initial pH of the blend was 3.30, whereas the final pH of the degraded blend was zero at both 350 and 400°F. According to Wang et al. (2015), ammonium chloride degraded and created ammonia and hydrochloric acid. Based on these results, ammonium chloride was also not stable at high temperature. The degradation product of ammonium chloride is hydrochloric acid, which is very corrosive at temperatures greater than 350°F.

CHAPTER V

CONCLUSIONS

Results of this research lead to the following conclusions:

1. For constant THPS concentration, increasing NH_4Cl concentration will decrease the initial and final pH of the dissolver solution.
2. For constant ammonium chloride concentration, increasing THPS concentration will increase initial pH. However, increasing THPS concentration will decrease final pH at NH_4Cl concentration greater than 0.5 mol/L.
3. At 0.25 mol/L NH_4Cl concentration, higher THPS concentration will provide maximum dissolution but at NH_4Cl concentration greater than 0.5 mol/L, using higher THPS concentration will not increase dissolution in a beneficial way.
4. Except for the case of 0.25 mol/L NH_4Cl concentration, all other dissolver achieved a maximum limit of iron sulfide dissolution at around 7700 ppm at THPS concentration of greater than 0.5 mol/L.
5. All of the dissolvers showed flattening of the curve of iron sulfide dissolved as a function of time.
6. Optimal time of treatment decreased with increase in THPS and ammonium chloride concentration.
7. 0.1 mol/L THPS concentration showed high final pH values at 300°F than 150°F but THPS concentration greater than 0.5 mol/L showed the opposite trend.

8. THPS and ammonium chloride blend dissolve more iron sulfide scale at high temperature when used in a concentration lower than 0.5 mol/L. However, a slight reduction in dissolution was observed when used at higher concentration.
9. The optimal treatment time of THPS and ammonium chloride blend with iron sulfide scale reduces drastically when used at high temperature.
10. SEM-EDS study provides evidence of an increase in dissolution, and the surface of an area of scale when treated with THPS standalone or THPS and ammonium chloride blend. Treatment of iron sulfide scale with THPS can result in sticking of THPS and ammonium chloride on the surface of the scale.
11. 0.5 mol/L THPS and 0.5 mol/L NH_4Cl blend showed marginally better performance than 15 wt % HCl when used in field conditions.
12. 0.5 mol/L THPS and 0.5 mol/L NH_4Cl gave better performance at 300°F than 150°F under the pressurized system.
13. The optimal treatment time of 0.5 mol/L THPS and 0.5 mol/L NH_4Cl is higher than HCl at 150°F however reaction process of 0.5 mol/L THPS and 0.5 mol/L NH_4Cl is very fast at 300°F.
14. THPS and ammonium chloride blend degrades at a temperature greater than 350°F within 24 hours.

This work contributes to understanding the effect of tetrakis (hydroxymethyl) phosphonium sulfate and ammonium chloride concentration on the dissolution of iron sulfide scale. Results demonstrate the effect of reaction time for maximum dissolution of iron sulfide. This work also provides thermal degradation data of THPS and NH_4Cl blend that is not available in the literature. This project could lead to optimizing the process for better scale removal and improving project economics.

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