

Iron sulfide scale removal: A Environment Friendly Approach.

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Abstract:

Iron sulfide scale is considered a big issue in the oil and gas industry and a very common problem in daily operation bases. Iron sulfide scale forms as a result of the reaction of hydrogen sulfide or mercaptans with carbon steel. The iron scale severely affects the production rates and field operation, as the iron scale precipitation on the well completion tools or the pipelines` inner surfaces will decrease the diameter size and cause flow restriction.

Generally scales can be differed as old age scale and new age scale where new age scale can be removed using mineral acids and to remove old age scale we have to carry out mechanical operation in combination with acid treatment otherwise they can damage our downhole tools and it might require workover operations to cure the problem. Such workover operations add an extra cost for operator. Using HCl as removal can leads to formation H₂S(g) which further can cause corrosion to tubing.

Now a days there are commercial liquids like **THPS ,EDTA,DTPA** delivering good results but our main objective of this study is to find a new environmentally chemical solution to be used for iron sulfide scale removal. Additionally, to study the new fluid performance in terms of solubility for an iron scale (field sample), corrosion effect, and biodegradability for environmentally safe use.

This paper shows a comparison and analysis and study of solubility test and corrosion test done on field scale sample using **NEFAS** and other methods with different concentration and the results from the study showed excellent performance for the scale solubility and for the corrosion rates. The iron scale solubility is 83 g/l after 6 hours at 125°C for the static condition with lower corrosion rates. Thus new **NEFAS** provides very good performance for iron scale removal, with a lower cost than commercial chemicals. Furthermore, the new system is a biodegradable and environmentally safe system.

Area of Interest:

Iron sulfide scale is present in sour oil and gas wells and injectors that are contaminated with sulfate reducing bacteria (SRB). It enhances the corrosion rate of the downhole tubulars, and adversely affects the performance of various wells. It reduces the efficiency of oil-water separation in various GOSPs. Removing iron sulfide scale is a complex process, especially at downhole conditions. Optimizing this process would require full understanding of various chemical interactions.

Introduction:

Iron sulfide species have been known to cause operational problems in the oil and gas industry.

The presence of iron sulfide particles in the injected water can cause loss of injectivity In injectors power water and water disposal wells. Accumulation of iron sulfide and biomass around downhole screens and perforations can cause loss of productivity of water supply wells Build-up of iron sulfide scale in the

tubing can create problems during wireline work and can reduce well deliverability. The presence of fine particles of iron sulfide in the produced crude oil can cause many operational problems in oil-gas separation plants (GOSPs).

Iron sulfide deposits are also present in many types of refining and process equipment. These deposits can significantly reduce the efficiency of heat exchangers, furnaces, and other similar equipment.

Iron sulfide scale forms as a result of the reaction of hydrogen sulfide or mercaptans with carbon steel.¹¹ According to Seto and Beliveau, the known mechanisms of reservoir souring fall under two main categories: biotic and abiotic. An example of the biotic mechanism is the hydrogen sulfide produced in injectors that utilize waters with high sulfate contents, e.g., seawater³ or shallow water aquifers. In these injectors, hydrogen sulfide is produced due to the activities of sulfate reducing bacteria (SRB). For abiotic mechanisms, hydrogen sulfide is produced due to thermochemical sulfur reduction, thermal hydrolysis of organic sulfur compounds, or hydrolysis of metal sulfides.

Unlike common oilfield scales (calcium carbonate, calcium, barium or strontium sulfate), iron sulfide scale has several unique characteristics that should be carefully considered. First, iron sulfide can cause crevice or bimetallic corrosion. According to Smith and Miller,¹⁵ iron sulfide scale can cause bimetallic corrosion of iron in the presence of water. Secondly, Iron sulfide is present in several crystalline forms that have different sulfur to iron ratios. These species have different crystalline forms and, as a result, have different solubilities in mineral acids.^{7,9} Iron sulfide particles are oil-wet and, as a result, they will be coated with oil, condensate, or heavy hydrocarbons. These hydrocarbons will act as a diffusion barrier that will retard acid reaction with the scale.

In addition to the above characteristics, the physical texture and appearance of iron sulfide scale depend on well type. For gas wells, iron sulfide scale is porous, loose, and does not protect the base metal. On the other hand, in water wells, or in the presence of aqueous medium, iron sulfide scale is dense, adherent and protective to the base metal. The objectives of this study are to:

- (1) Identify the nature and composition of iron sulfide scale present in oil, gas and water wells.
- (2) Assess the effectiveness of various methods to remove it.
- (3) Determine an effective method to mitigate this type of scale

Typical Iron Sulfide Scale:

As mentioned earlier, iron sulfide scale has several important characteristics that need to be considered before designing proper treatments to remove the or mitigate scale. To determine these characteristics, various scale samples were collected from oil and gas producers (carbonate and sandstone reservoirs) and water supply wells. The mineralogy, thickness, and acid solubility of the scale were determined. Several interesting findings were noted as follows. Iron sulfide scale was found in sour oil and gas wells and injectors that utilize high-sulfate waters. Iron sulfide scale was detected in several producers in a carbonate reservoir in Saudi Arabia. Reservoir fluids in this field contain 5 mol% CO₂ and 1 to 5 mol% H₂S. The scale was found on the inside wall of the production tubing or as loose particles accumulated in the rat hole.

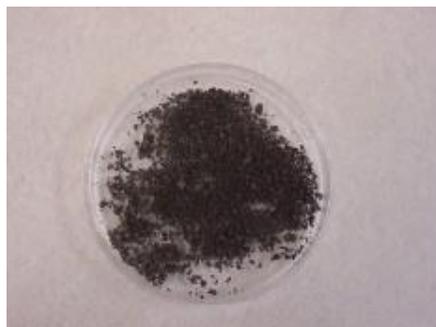


Photo 1. Scale collected from Well -75 at 4055 ft.

Photo 1 shows scale particles collected from Well-75 at a depth of nearly 4,060 ft, an oil well with very low water cut (less than 1 vol%). Iron sulfide scale was also detected in oil producers present in sandstone reservoirs.

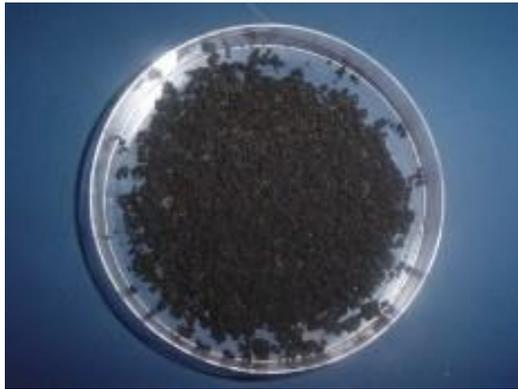


Photo 2. Scale collected from Well-10.

Photo 2 shows the scale sample collected from Well-10, a wet oil producer.

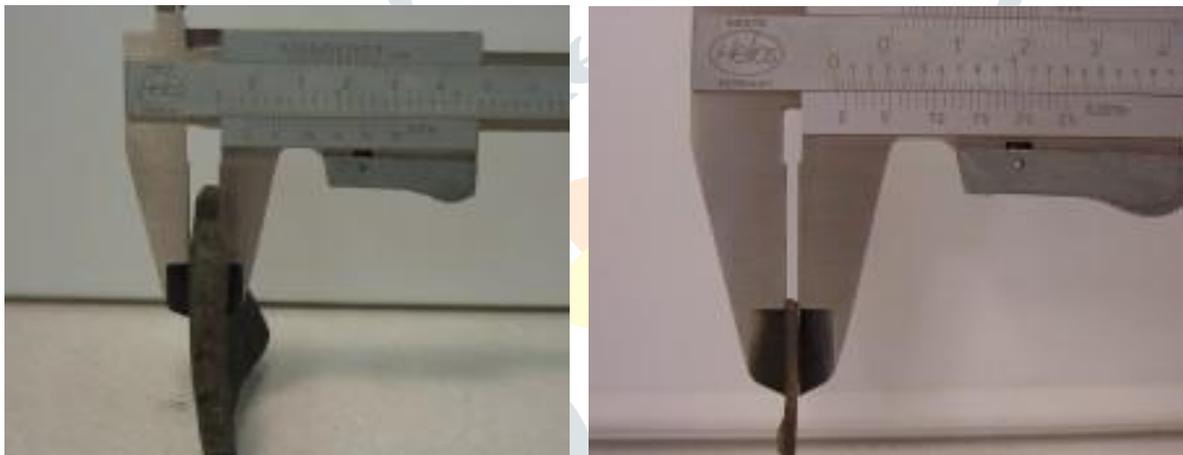


Photo 3. Scale sample collected from Well-895 at 34 ft **Photo 4. Scale sample collected from Well-895 at 680 ft.**

Photos 3 and 4 show scale samples collected from a water supply well with a gas lift. The scale was obtained from 7-inch joints that were retrieved from this well at a depth of 34 and 680 ft, respectively. The scale was consolidated, dense, and adhered to the tubing wall. A hammer was needed to dislodge scale samples from the tubing. Iron sulfide deposits were detected by Kasnick and Engen⁶ in sour gas wells in deep carbonate reservoirs. It is clear from these observations that the texture and composition of the iron sulfide scale depends on well type, which confirm the results obtained by Claassen. Another point regarding iron sulfide scale is the variation in scale thickness along the length of the tubing. Scale thickness was measured in various wells by using gauge cutters or by measuring the thickness of the scale found in the tubing joints retrieved from various wells following workover. The thickness of the scale was found to be a function of depth. For example, in a water supply well with a gas lift (Well-895), the scale thickness was 0.25 inch at 34 ft and nearly 0.05 inch at 680 ft (Photos 3 and 4). In oil wells, the scale thickness varied with depth and several severe constrictions were noted. In deep gas wells, iron sulfide scale was detected in the lower sections of the tubing. Drop out of condensate did help in reducing iron sulfide scale in the upper sections of the tubing.

Source of Iron Sulfide in Sour Wells:

Identifying the source of iron sulfide in sour wells is a difficult task. Iron sulfide present in well tubulars can result from tubing corrosion or simply be deposited on the surface of the tubing. One way to identify the formation mechanism of iron sulfide is to examine the elemental composition of the scale and to compare it with that of the well tubing. For example, J-55 is a low-carbon steel that is used to manufacture most of the tubing strings used downhole. Elemental analysis was conducted on tubing joints that were retrieved from several wells.

The analysis was conducted using an optical emission analyzer (Arc-Met 900). The analysis indicated that the tubing consisted of 98.46 wt% iron, 1.28 wt% manganese, 0.24 wt% carbon and 0.02 wt% silicon. It is important to note that the weight ratio of iron to manganese in this steel was nearly 77:1. It is worth noting that manganese was not detected in any of the scale samples examined in this study. As was mentioned before, J-55 contains 1.28 wt% manganese. Had the scale contained manganese, this would indicate that corrosion of the tubing did contribute to the scale formation in these wells. The scale noted in these wells formed due to the deposition of iron sulfide particles on the wall of the tubing.

Iron Sulfide Removal:

Iron sulfide scale can be removed either by mechanical or chemical means. In general, old iron sulfide scale (mainly FeS₂ species) has low acid solubility. Therefore, this type of scale cannot be effectively removed using mineral acids. On the other hand, new or fresh scale (mainly FeS species) has a high solubility in mineral acids and can be effectively removed by acids. It is very important to note that old scale consists of several iron sulfide species where the location of a given species depends on several operational conditions. For example, several investigators mentioned that iron sulfide deposited close to the tubing wall is FeS, whereas FeS₂ species are concentrated close to the surface of the scale that is exposed to the stream that contains hydrogen sulfide. This radial variation in the scale composition should be considered when designing a treatment to remove it.

Acid Cleaning - Background

Mineral acids can be used to remove fresh scale and can be used in combination with mechanical means to remove old scale. Mineral acids react with iron sulfide (FeS) as follows



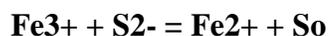
The rate of this reaction was given by Lawson et al

Equation 2:

$$\text{Rate} = k_f[\text{H}^+] - k_r[\text{Fe}^{2+}]^{0.5} (\text{PH}_2\text{S})^{0.5} \quad (2).$$

Where k_f and k_r are the rates of the forward and reverse reactions, respectively. Several important points can be inferred from Equation 2. The rate of dissolution of iron sulfide can be increased by using concentrated acids. This finding was confirmed by Lawson et al.¹⁰ using sulfuric acid and by Nasr-El-Din et al. using hydrochloric acid. Accumulation of hydrogen sulfide will reduce the rate of acid reaction with the scale. Therefore, it is very important to scavenge hydrogen sulfide to be able to dissolve iron sulfide scale. It may be also useful to use an iron chelating agent to maintain the forward reaction. Based on the experimental work performed by Nasr-El-Din et al., 19 HCl at 20 wt% was recommended for field application. Higher acid concentrations are not recommended because the acid becomes very corrosive at high concentrations, especially at high temperatures. High acid concentrations will require large amounts of corrosion inhibitors, which many adversely affect the ability of the acid to dissolve iron sulfide scale. Based on Equation 2, and the nature of iron sulfide scale, the acid should contain the following additives. First, the acid should contain a

corrosion inhibitor to protect the base metal. Secondly, a water-wetting surfactant should be added to the acid to remove condensate and other hydrocarbons from the surface of iron sulfide scale. The surfactant will enhance acid-scale contact. Thirdly, the acid should contain a suitable hydrogen sulfide scavenger. Hydrogen sulfide released during acid reaction with iron sulfide scale is present in a molecular form. It is toxic gas, corrosive and can react with ferrous irons and precipitate elemental sulfur and iron sulfide once the acid is spent and the pH increases above a value of 1.9. Elemental sulfur can precipitate if ferric iron is present



Precipitation of elemental sulfur in the formation can cause formation damage.³² Elemental sulfur is insoluble in hydrochloric acid and can be removed by using expensive organic solvents.³³ Therefore, a suitable hydrogen sulfide scavenger should be added to the acid.³⁴ Hydrogen sulfide scavengers that can be used during acid cleaning include: aldehydes, ketones, and oximes. The performance of various aldehyde-based scavengers was examined by several investigators. Al-Humaidan and Nasr-El- Din, recommended that the scavenger to be added to the acid just before pumping. They should not be used at high concentrations and should be compatible with other acid additives. Another important point is the solubility of the reaction product with reservoir fluids. For example, formaldehyde reacts with hydrogen sulfide and produces trithiane.

By Mechanical means

Removal method	Description	Advantages	Disadvantages
Mechanical mill	Mill Removes deposits by grinding	<ul style="list-style-type: none"> • Can clean hard and thick scale deposition • Positive surface indication by cleaning 	<ul style="list-style-type: none"> • Time consuming • Costly • Can damage tubulars
Jet blaster tools	Fluid Powered by jetting to dissolve scale	<ul style="list-style-type: none"> • cover complete wellbore • Positive surface indication of cleaning 	<ul style="list-style-type: none"> • Costly • Time consuming • Clean scale in tubing only, cannot approach scale deposited in near wellbore

Using chelating agents(EDTA,DTPA)

Using DTPA(20% wt PH11) chelating agent can achieve around 85% dissolution of scale but several catalyst can enhance the rate like potassium carbonate,etc.when solubility test of EDTA conducted with combination of several acids it is shown that at reduced PH solubility rate increases at High concentration and Low PH they are effective, in case DTPA it is also same like at low PH and increased concentration they are effective

By using Biocide

THPS is used in drilling and stimulation fluids to control microbial growth. However, recently THPS is being used as a substitute for hydrochloric acid (HCl) in iron sulfide scale removal from oil and gas wells. THPS showed good dissolution power for iron sulfide scale at pH less than six, however, at this pH the formulation has a high corrosion rate. Ability of THPS decreases as the pH level increases and this occurs at an optimum concentration of 20 wt%.

THPS, being an acidic chelating agent, was combined with EDTA (Ethylenediaminetetraacetic acid) and (DTPA) which are basic chelating agents. The two chelating agents were combined at 20% wt. each to give a basic pH above about 8. This is a suitable environment to prevent corrosion due to acidic medium. The combined chelating agents (THPS and EDTA) yield the maximum solubility in a basic medium of more than 70 % for the field sample

NEFAS

The techniques suggested in previous research proves that using chelating agents like DTPA and EDTA shown good results with around 20% to 25 % wt and PH around 9-11 but it takes around more than 48 hour which is not good, again in case of THPS with different concentrations (from 15 to 75 wt.%) to remove different types of iron sulfide scales. The scale sample was soaked with THPS removal fluid for time periods from 1-24 hours.

Based on the discussed literature, there is a need to develop an environmentally friendly chemical solution for iron sulfide scale removal. The new solution should provide a good removal performance for all types of iron sulfide scales, being non-corrosive and no H₂S gas released after scale reaction

The new environmentally friendly acid system that used in this study is a green acid solution synthesized by a catalytic reagent combination added to HCl creating a biodegradable, non-bio accumulating alternative to HCl. Titration test was conducted to determine the existing HCl percentage in the newly developed system and found that the new system NEFAS 100 wt.% contained 20 wt.% HCl in addition to other additives.

Results and discussion:

According to previous research when solubility and corrosion test were conducted with different concentration of NEFAS (100 wt.% and 75 wt.%) and HCl (15 wt.% and 20 wt.%) it is observed that solubility results for every concentration is same but NEFAS(75% wt) has solubility rate of 83 g/l then the solubility performance for 75% NEFAS was studied with time after completion it is shown that 75 wt.% NEFAS can be used for iron scale removal for only 6 hours with high efficiency and after corrosion test it is shown that NEFAS will not damage the wellbore tubular integrity compared with the HCl that is commonly used in iron scale removal in field applications.

In comparison of other methods like when we use chelating agents at high temperature there is possibility of high corrosion rate so in that situation we have to use corrosion inhibitor therefore using NEFAS will save our money which we spend on corrosion inhibitor

In case of THPS when we use it alone it has poor dissolution rate and high corrosion rate so we have mix with chelating agents and there comes restriction of keeping low PH value. Old techniques of using HCl is not suitable as it leads to higher corrosion rates and production of Hydrogen Sulfide (H₂S) gas and mechanical methods are economically beneficial and again in case of NEFAS (75%wt) the h₂S production is less than the conventional HCl.

Conclusion:

After study of iron sulfide deposition and comparative study on available solution considering there solubility rates and corrosion rates at different concentration, PH and temperature's for various types of iron sulfide scales.

The following conclusions can be obtained from the comparison results of the solubility and corrosion tests:

1. Fresh iron sulfide scale can be effectively removed using mineral acids with suitable additives. On the other hand, old iron sulfide scale can be effectively removed using mechanical means followed by an

acid wash but there is possibility of high corrosion rates of 0.17 lb/ft² and sometimes produce Hydrogen Sulfide (H₂S) gas

2. Chelating agents at high temperature above 100°C has corrosion rates of 0.14 lb/ft²
3. When THPS is mixed with a basic chelating agent such as EDTA and DTPA, This implies that the combined THPS and EDTA or DTPA provide an effective solution for dissolving field iron sulfide scales.
4. NEFAS with a concentration of 75 wt.% presented a high removal performance with a dissolution rate of 83 g/lit for the iron sulfide scale 6 hours.
5. NEFAS evaluation for the corrosion rate found to be 0.04 lb/ft² at 125°C which is lower than the acceptable limit by the field applications in oil and gas industry.

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