Lab Investigation of Inorganic Scale Removal Using Chelating Agents and Hydrochloric Acid Solutions

Abstract

One of the most important damages to the oil and gas reservoirs, are inorganic scales resulted from precipitation of different inorganic solids with low solubility in near wellbore area. Remedial actions to remove inorganic scales depend on characteristics of these scales. Various solutions can be applied to remove scales that include injection of HCl acid and chelating-based solutions. Chelating agents have the ability to chelate and sequester many metal ions in water–based fluids. As a result, they can remove inorganic scales from wellbore and near wellbore area. Ethylenediaminetetraacetic acid (EDTA) and related salts are chelating agents that can remove inorganic scales. In this study, experimental investigations are conducted to measure the solubility of different scales in chelating agents (Na_4EDTA and iron chelating agents) and HCl acid solutions. In addition, optimum EDTA concentration is obtained. Results of this study show that sulfate scales demonstrate good solubility in Na_4EDTA, and other scales (iron scales) have good solubility in HCl solutions. Furthermore, Iron chelating-based solutions can completely dissolve iron (II) sulfate. However, calcium sulfate solubility in these solutions is very low.

Keywords: Inorganic Scales, Scale removal, Chelating agents, EDTA, Stimulation, Hydrochloric acid.

Introduction

Scale formation is associated with water production or injection. Inorganic scales can precipitate in tubing, in perforations, and back in formation. Water is a good solvent and can carry large quantities of scaling minerals. Scales form under conditions of lowered pressure and/or reduced temperature, allowing scale to crystallize or solidify out of solution. In addition, scales can be formed when incompatible waters are mixed. Calcium carbonate ($CaCO_3$), Calcium sulfate ($CaSO_4$), Barium sulfate ($BaSO_4$), Iron sulfate ($FeSO_4$), Iron sulfide (FeS), and Iron oxides (Fe_2O_3) are the main inorganic scales that can precipitate and decrease well productivity.

Hydrochloric acid can easily react with carbonate scales and remove them. In addition, most iron scales can be treated with this acid. Proper iron control agent should be used to maintain soluble material in solution. Other scales are only slightly soluble in acid, and are partially soluble in chelating agent-based fluids such as EDTA.

Chelating agents are materials used to control undesirable reactions of metal ions. In field treatments, chelating agents are frequently added to stimulation fluids to prevent precipitation of solids (mainly iron hydroxides and iron (II) sulfide) as acid spends on the treated formation. In addition, chelating agents are used in scale removal applications. EDTA has been used extensively for iron control and scale removal. As an example, Figure 1 shows the chelating process of $BaSO_4$ in EDTA solution. An EDTA molecule shares electrons from nitrogen and oxygen with barium ions, forming a barium-EDTA complex compound (top picture). The chelating process can help to chelate barium sulfate scale (bottom picture).

EDTA type chelating agents have been proposed as main fluid for matrix acidizing of carbonates by Fredd and Fogler [1]. Two types of EDTA salts, disodium EDTA (Na_2H_2EDTA) and tetrasodium EDTA (Na_4EDTA), are the most effective ones for scale removal purposes. [2] Tetrasodium EDTA solution is preferable to other alternatives for removing scales because of its higher pH (about 10.6). The dissolution process is increased at higher pH. Additionally, tetrasodium EDTA has mush higher solubility limit than the more acidic EDTA salts.

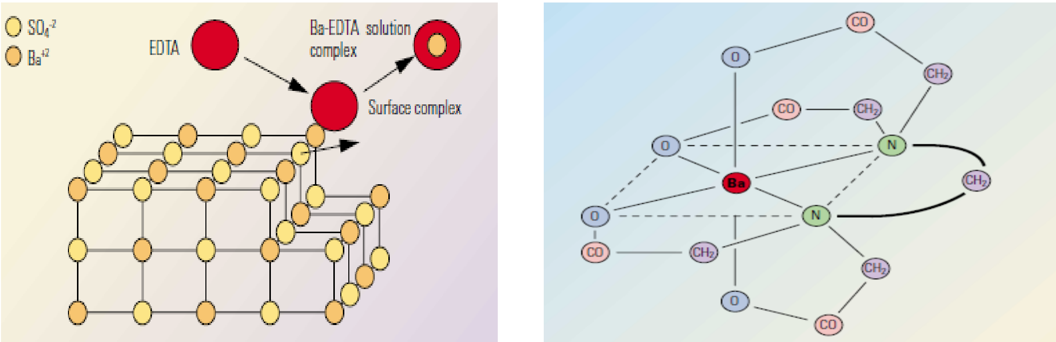

Figure 1: The chelating process of Ba^{2+} ion in EDTA. [3]

In this study, HCl (10% and 15% HCl), Na_4EDTA (4%, 12%, 16%, and 20% Na_4EDTA), and iron chelating-based solutions are used to test the solubility of different scales. All the experiments are conducted at high temperature conditions (about 95 ˚C). In addition, compatibility tests were performed on all solutions to investigate the possible incompatibilities. Results of this study show that 12 wt% Na_4EDTA has the optimum concentration to dissolve scales. Sulfate scales are highly soluble in EDTA, however, FeS and $BaSO_4$ are not soluble in it. In addition, HCl acid can dissolve iron scales. It should be noted that, dissolved scales in EDTA are only stable at alkaline conditions and will precipitate if pH of solution decreases to acidic values. Furthermore, Iron chelating-based solutions can completely dissolve iron (II) sulfate. However, calcium sulfate solubility in these solutions is very low.

Experimental studies

Scale solubility experiments with HCl acid, EDTA solutions are conducted in Mehran Acid Lab. Below sections present materials used in experiments and conducted test procedures.

Materials

Hydrochloric acid is titrated with 1 N sodium hydroxide solution to obtain its concentration which is 30 wt.%. All solutions are prepared using fresh water

(FW) at room temperature. In addition, commercial stimulation additives (acid corrosion inhibitor, non-emulsifier, iron control agent, H_2S scavenger, and Surfactant) and tetrasodium EDTA salt are used in experiments.

Tests procedures

The procedure of solubility test of scale samples in acidic, EDTA, and iron control solutions are as follows:

1- Put the scale sample in oven (95°C) for 1 hr.
2- Weight 5g of scale sample.
3- Prepare the 100 cc planned fluid solutions (HCl, Na4EDTA, and iron chelating agents) in 250 cc beakers.
4- Put the scale sample in the prepared fluid at desired temperature (95°C)
5- After designed soaking time (6 hours) filter the remained residue, dry it and weight.
6- Add HCl acid to EDTA filtered solutions and investigate any precipitation.

Below tables show recipe of 10% HCl, 12% Na4EDTA, and iron chelating-based solutions:

Table 1: Recipe of 10% HCl solution

Name	Per 1000 cc	unit	Lab Quantity/ 100 cc	Lab Unit
Fresh water	651	cc	65.1	cc
Cor-inhibitor	6	cc	0.6	cc
Non Emulsifier	5	cc	0.5	cc
Iron Control	10	cc	1	cc
H_2S Scavenger	20	cc	2	cc
Surfactant	4	cc	0.4	cc
HCl 30%	304	cc	30.4	cc

Table 2: Recipe of 12% Na4EDTA solution

Name	Per 1000 cc	unit	Lab Quantity/ 100 cc	Lab Unit
Fresh water	876	cc	87.6	cc
Surfactant	4	cc	0.4	cc
Na_4EDTA	120	gr	12	gr

Table 3: Recipe of iron chelating-based solution

Name	Per 1000 cc	unit	Lab Quantity/ 100 cc	Lab Unit
Fresh water	986	cc	98.6	cc
Surfactant	4	cc	0.4	cc
Iron chelating agent A or B	10	cc	1	cc

Results and discussions

Experimental studies are conducted according to previously mentioned test procedures. Results of these tests are observed and solubility of each scale is measured. This section presents the results obtained from this experimental study.

Compatibility test of HCl and EDTA solutions

Compatibility tests of all designed/ fluids are checked in bottom-hole temperature (95˚C) for 6 hours. The solutions are filtered, and possible solids/emulsions are weighted and investigated. As an example, figure 2 shows the compatibility of 12% Na_4EDTA and 10% HCl solutions. Table 4 shows results of compatibility tests of all prepared fluids. It should be noted that no precipitation is observed on the filter paper for 4%, 12%, 16%, and 20% Na_4EDTA compatibility tests. According to table 4, prepared fluids are compatible with each other and results are acceptable. In addition, no dispersed particles or emulsions are observed in solutions.

Figure 2: compatibility test of 12% Na_4EDTA and 10% HCl solutions

Table 4: Results of compatibility test of Na_4EDTA and HCl solutions

Fluid Type	Fluid volume (cc)	time (hr)	T (°C)	Residue (gr)
10% HCl	100	6	95	0
15% HCl	100	6	95	0.011
4% Na_4EDTA	100	6	95	0.006
12% Na_4EDTA	100	6	95	0.202
16% Na_4EDTA	100	6	95	0.233
20% Na_4EDTA	100	6	95	0.348

Scale solubility in HCl solutions

HCl solutions were prepared based on 10 and 15 wt% recipes. Solubility of different scales is investigated in hydrochloric acid. Table 5 shows the solubility of each scale in HCl. In addition, figure 3 shows the results schematically. As per table 5, $FeSO_4$ and $CaCO_3$ have the highest solubility in HCl acid, and barite ($BaSO_4$) is partially soluble in HCl acid. Iron scales show good solubility in hydrochloric acid and effect of acid concentration on solubility is small.

Table 5: Scale solubility in HCl solutions

Scale Type	Fluid Type	Fluid Volume (cc)	Soaking time (hr)	T (°C)	Initial Weight (gr)	Final Weight (gr)	Solubility (%)
FeS	10% HCl	100	0.5	95	5	2.465	50.7
$FeSO_4$	10% HCl	100	0.5	95	5	0.088	98.2
CaSO4	10% HCl	100	0.5	95	5	1.929	61.4
$CaCO_3$	15% HCl	100	6	95	5	0.171	96.6
FeS	10% HCl	100	6	95	5	1.035	79.0
FeS	15% HCl	100	6	95	5	0.97	80.6
$FeSO_4$	10% HCl	100	6	95	5	0.100	98.0
$FeSO_4$	15% HCl	100	6	95	5	0.327	93.5
Fe_2O_3	15% HCl	100	6	95	5	2.152	56.9
CaSO4	10% HCl	100	6	95	5	1.806	64.0
BaSO4	10% HCl	100	6	95	5	3.518	30.0

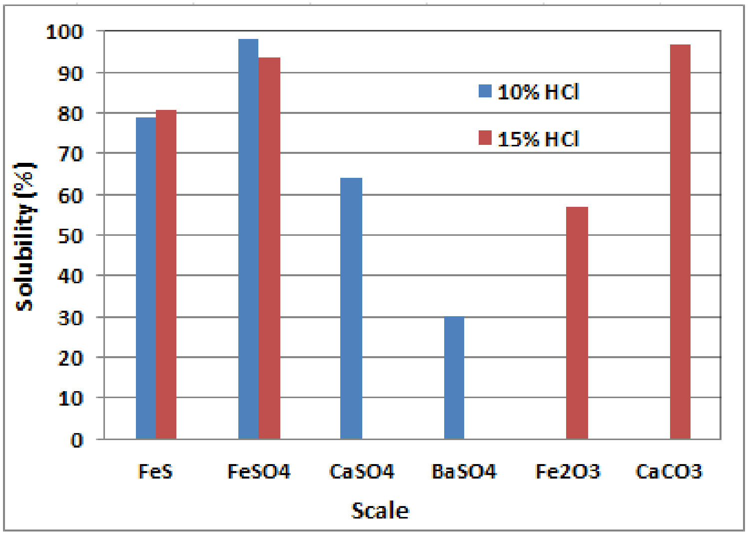

Figure 3: Solubility of various Scales in HCl solution after 6 hours

Scale solubility in Na_4EDTA solutions

Tetrasodium EDTA solutions are prepared based on 4 to 20 wt%. Solubility experiments are conducted for various scales. The solubility of scales and optimum Na_4EDTA concentration are investigated. Table 6 shows the results of solubility experiments in Na_4EDTA and figure 4 shows the variation of solubility with concentration of this solution.

Table 6: Solubility of Various scales in Na_4EDTA

Scale Type	Fluid Type	Fluid Volume(cc)	Soaking time (hr)	T (°C)	Initial Weight (gr)	Final Weight (gr)	Solubility (%)
$CaSO_4$	4% EDTA	100	6	95	5	3.327	33.5
$CaSO_4$	12% EDTA	100	6	95	5	0.314	93.7
$CaSO_4$	16% EDTA	100	6	95	5	0.356	92.9
$CaSO_4$	20% EDTA	100	6	95	5	0.409	91.8
BaSO4	4% EDTA	100	6	95	5	4.393	12.1
BaSO4	12% EDTA	100	6	95	5	4.411	11.8
BaSO4	20% EDTA	100	6	95	5	4.845	3.1
FeSO4	4% EDTA	100	6	95	5	0.289	94.2
FeSO4	12% EDTA	100	6	95	5	0.277	94.4
FeSO4	20% EDTA	100	6	95	5	0.391	92.2
FeS	4% EDTA	100	6	95	5	4.915	1.7
FeS	12% EDTA	100	6	95	5	4.784	4.3
FeS	20% EDTA	100	6	95	5	4.95	1
50% CaSO4 + 50% FeSO4	4% EDTA	100	6	95	5	2.409	51.8
50% CaSO4 + 50% FeSO4	12% EDTA	100	6	95	5	0.293	94.1
50% CaSO4 + 50% FeSO4	20% EDTA	100	6	95	5	0.348	93.0

As per figure 4 and table 6, $CaSO_4$, $FeSO_4$ and the mixture of these scales are highly soluble in Na_4EDTA solutions. Solubility of calcium sulfate and its mixture with iron (II) sulfate increases with increasing EDTA concentration from 4% to 12%, and after that, it does not change significantly. In addition, FeS and $BaSO_4$ are not soluble in Na_4EDTA. According to figure 4, optimum Na_4EDTA concentration is 12 wt%, and solubility remains approximately constant at higher concentrations.

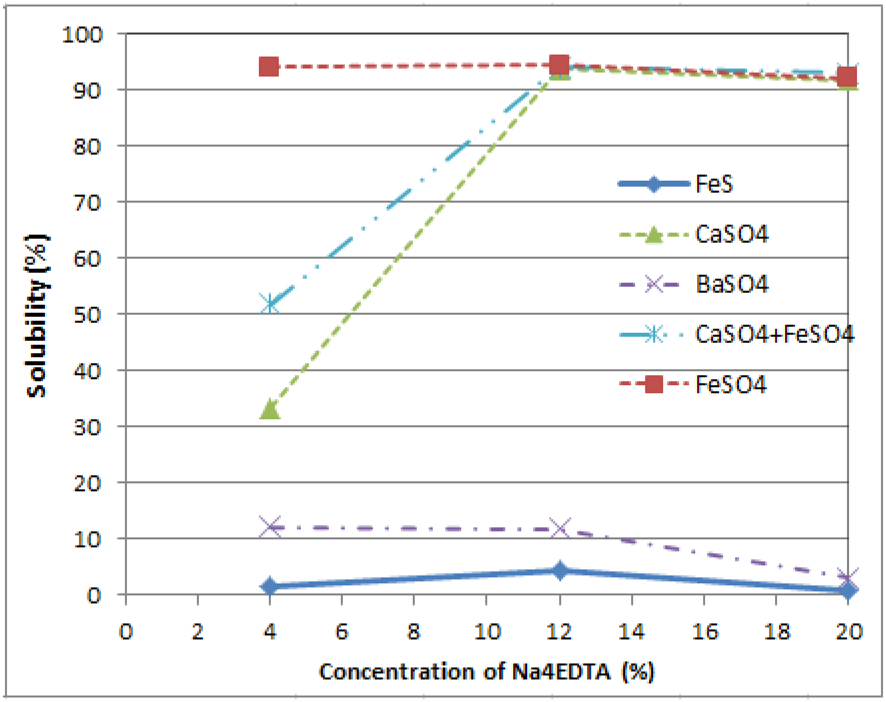

Figure 4: Scale solubility versus Na_4EDTA concentration

Corrosion test of EDTA solutions

An advantage of treatment with EDTA is that EDTA solution does not need corrosion inhibitors. The corrosion tests of 12% Na_4EDTA were conducted in HT condition on both CRA and CT coupons. The aforementioned corrosion test results are listed below:

- 6 hours corrosion test of 12% Na_4EDTA with CRA sample: Corrosion rate is obtained 0.00073 lb/ft^2.
- 6 hours corrosion test of 12% Na_4EDTA with CT sample: Corrosion rate is obtained 0.014 lb/ft^2.

According to obtained results, the corrosion rate of EDTA solution is in acceptable range (below 0.05 lb/ft^2). As a result, EDTA solution can be used without any corrosion inhibitor and there will be no concern of corrosion problems.

Stability of soluble complexes in acidic condition

Most of the EDTA solutions have alkaline pH after chelating scales. Possibility of re-precipitation of complexes (such as $CaNa_2EDTA$) resulted from solution of scales in Na_4EDTA are investigated by adding HCl acid (to create acidic conditions, pH=0) to filtered solutions. Table 7 shows the results of stability test for 20% Na_4EDTA. The resulted solution with possible precipitations is filtered after 12 hours. The amount of residue on filter paper is reported in table 7.

Table 7: Stability test of 20% Na_4EDTA solutions at acidic condition

Scale Type	Initial pH	Residue (gr) at pH=0	Status after adding HCl acid (pH=0)
$BaSO_4$	11	5.945	Changed color immediately, after 15 minutes, dispersed particles are observed at solution and precipitated. White powdered residue is observed on the paper
$FeSO_4$	11	NA	No precipitation or dispersed particles was observed immediately.
$CaSO_4$	11	30.186	No dispersed particles are observed immediately, but after 15 minutes, many white colored crystal particles precipitated. White powdered residue is observed on the paper
FeS	11	12.638	No dispersed particles are observed immediately, but after 15 minutes, some crystal particles precipitated. Greenish crystalline residue is observed on the paper.
$CaSO_4$+ $FeSO_4$	11	8.500	Initially, changed color to yellow from reddish with no precipitation (clear solution). After 15 minutes, many particles precipitated. Solution segregated to solid and liquid phases. Slightly yellow to white powdered residue is observed on the paper
Comp. 20% EDTA	11	4.208	No dispersed particles are observed immediately, but after 15 minutes, some precipitation occurred. White powdered residue is observed on the paper

According to Table 7, EDTA solutions with dissolved scales are stable at alkaline condition (high pH values). Adding HCl acid to solutions decreased the pH to zero and resulted in huge precipitation of different EDTA compounds. One of these compounds can be $CaNa_2EDTA$. As a result, EDTA treatments have not to be followed by HCl injection, because of severely damaging the near wellbore area. Most of EDTA compounds will precipitate at low pH values.

Solubility test of scales in iron control chelating agents

Solubility test of scales in iron control chelating agents are designed to study the solubility of scales ($CaSO_4$ and $FeSO_4$) in iron chelating-based solutions. Two commercial iron chelating agents, A and B, are used in this study. Table 8 shows the results of these tests. As per table 8, Iron chelating agents A and B, completely dissolved $FeSO_4$. However, $CaSO_4$ solubility is very low.

Table 8: Solubility of $CaSO_4$ and $FeSO_4$ in iron chelating-based solutions

Scale Type	Iron control	Fluid Volume (cc)	Soaking time (hr)	T (°C)	Initial Weight (gr)	Final Weight (gr)	Solubility (%)
$CaSO_4$	A	100	6	95	5	4.548	9.0
$CaSO_4$	B	100 cc	6	95	5	4.538	9.2
$FeSO_4$	A	100 cc	6	95	5	0.025	99.5
$FeSO_4$	B	100 cc	6	95	5	0.018	99.6

Conclusions

Following conclusions can be drawn from the results of performed experiments:

- Iron scales are soluble in HCl acid. $FeSO_4$ is dissolved in Na_4EDTA, too. However, FeS is only soluble in HCl acid.
- $BaSO_4$ is partially soluble in HCl, and its solubility in Na_4EDTA is very low.
- $CaSO_4$ is highly soluble in Na_4EDTA , and partially soluble in HCl acid.
- Optimum concentration of Na_4EDTA to dissolve scale is 12 wt.%, and higher concentrations are not economical.
- Corrosion rate of Na_4EDTA solutions without corrosion inhibitor on both CRA and CT samples are very low. As a result, Na_4EDTA can be applied without any corrosion inhibitor.

- Although, dissolved scales in Na_4EDTA solution are stable at alkaline conditions (high pH values), they will precipitate at acidic conditions (low pH values).
- $FeSO_4$ completely dissolved in both iron chelating-based solutions. However, $CaSO_4$ solubility is very low in prepared solutions.

Acknowledgements:

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