METHODS OF CONTROLLING FERRIC HYDROXIDE PRECIPITATION RESULTS FROM CORROSION IN ACIDIZING TREATMENTS

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ABSTRACT

In acidizing treatment, acid readily dissolves iron scale in surface equipment, casing and tubing, and also attacks iron containing minerals in the formation. This dissolved iron remain in solution until the acid is spent. As the pH of spent acid rises above 2, iron losses its solubility and precipitates. Precipitation of iron compounds from spent acid causes formation damage and reduces the effectiveness of acidizing operation. Thus it is very important that iron control agent be used to avoid this problem.

Cleaning the tubular goods by the acid prior the acidizing treatment can remove rust and scale from equipments, pipes, casing and tubing, and reduce these iron compounds. For cleaning, acid should be displaced to the bottom of tubing and then removed from the well by reverse circulation, swab or gas lift.

INTRODUCTION

Acidizing is one of the oldest technique in well stimulation that is still being used today. The first practical use of acid in an oil well came as a direct result of the development of a corrosion inhibitor to protect the casing from excessive acid corrosion. When appreciable quantities of iron are dissolved by the acid during acidizing treatment, iron precipitation and therefore formation damage may result. Thus it is very important that effective iron control methods be used to avoid this problem.

CORROSION INHIBITORS:

A corrosion inhibitor is a chemical that slows down acid corrosion by the formation of an absorbed barrier layer on the metal surfaces. Inhibitors are used in all acid treatments to protect the surface equipments and downhole casing and tubing. The unit of measurement used to determine the amount of corrosion is lb/ft²: 
Corrosion (lb/ft\(^2\)) = \frac{\text{weight loss in lb}}{\text{Area in ft}^2} - \frac{\text{weight loss in gram \times 2.048}}{\text{Area in cm}^2}

Where 2.048 is conversion factor.

Also acceptable metal loss in acidizing treatment that are recommended by API are as follows:

<table>
<thead>
<tr>
<th>Temperature(°F)</th>
<th>Maximum acceptable weight loss ( lb/ft(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Up to 200</td>
<td>0.02</td>
</tr>
<tr>
<td>210 – 250</td>
<td>0.05</td>
</tr>
<tr>
<td>250 – 275</td>
<td>0.075</td>
</tr>
<tr>
<td>Above 275</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Therefore for a deep well (10,000 to 14,000 ft) with high bottom hole temperature (above 200 °F) in spite of the using corrosion inhibitors, corrosion occurs while acis is in contact with the tubings and this results in formation of Fe\(^{+2}\) and Fe\(^{+3}\) ions.

Precipitation of iron compound from spent acid causes formation damage and reduces the effectiveness of acidizing operation. Therefore it is very important to use an effective chemical for preventing precipitation of Iron compounds.

**SOURCES OF IRON**

There are three source of iron in acidizing operation:

1) Iron from the rust of storage tanks and treating pipes. (These iron compound may include FeO, Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), FeCo\(_3\) and FeS)

2) Iron from the corrosion of casing and tubing.

3) Iron from Iron-Containing minerals such as siderite (FeCo\(_3\)), chlorite [(AlSi\(_3\)O\(_{10}\))Mg\(_5\)(Al,Fe)\(_3\)(OH)\(_3\)], pyrite (FeS\(_2\)) and Ankerite [Ca(Mg,Fe)(Co\(_3\))\(_2\)].
When acid is pumped in the well, it flows for a relatively long time through tubings of the well and then reaches the formation. Mostly, the tubing contains rust which will be dissolved by the acid. Newly manufactured tubings have a layer of the mill scale (magnetite) which is a form of ferric/ferrous oxides. When mill scale is contacted with injected acid, it will be dissolved and forms ferric chloride which enters the formation. The concentration of iron ions due to dissolution of mill scale could be up to 70,000 ppm.

**PRECIPITATION OF IRON COMPOUND**

Iron dissolved during acidizing treatment can exist in oxidation state of either ferric or ferrous iron. The charge on the dissolved iron is a function of the oxidation state of the iron source (well type and history, and formation mineralogy).

Dissolution of red iron rust (hematite) will produce ferric iron and dissolution of mill scale (magnetite) will produce both ferric and ferrous iron. Acid attack will produce only ferrous iron and iron dissolved in acid from the formation can be in either ferric or ferrous oxidation state.

Analysis of returned spent acid sample has shown that most iron dissolved by treating acid is ferrous iron.

It has been estimated that average ratio of ferrous to ferric iron in spent acid is about 5:1. The dissolved ferrous and ferric iron remain in solution until the acid is spent. When the pH increases to about 2.2, the Fe present in the ferric form begins to precipitate and when the pH increases to 3.2 all of the dissolved ferric iron will precipitate as gelatinous ferric hydroxide [Fe(OH)₃]. Ferrous hydroxide will precipitate in the 7-9 pH range[1]. These insoluble precipitations are as follows.

\[
\text{Fe}^{\text{\textsuperscript{2+}}} + 2\text{OH}^- \leftrightarrow \text{Fe(OH)}_2 \quad \text{ferrous hydroxide (PH 7 to 9)}
\]

\[
\text{Fe}^{\text{\textsuperscript{3+}}} + 3\text{OH}^- \leftrightarrow \text{Fe(OH)}_3 \quad \text{ferric hydroxide (PH 2 to 4)}
\]

Solubilities of ferrous and ferric hydroxide is show in Table -1. Since maximum pH of the spent acid is about 5.3, therefore the precipitation of ferrous hydroxide is not a problem.
FACTOR AFFECTING IRON PRECIPITATION

1) Acid dissolution of the rust scale will produce ferric iron. As the acid flows for a relatively long time through tubing in the well, a certain amount of ferric iron is subjected to conversion to ferrous iron by its reaction with the iron pipe by means of the following reaction [2]:

\[ 2\text{Fe}^{3+} + \text{Fe}^0 \rightarrow 3\text{Fe}^{2+} \]

Due to increase in acid injection rate and therefore contact time between acid and tubing, and downhole pressure and temperature the ratio of ferric to ferrous hydroxide will reduce.

2) The presence of H₂S in sour well, changes the nature of the iron precipitation problem. Hydrogen sulfide, a strong reducing agent, will reduce any dissolved ferric iron to ferrous iron as a result of the following reaction. [3],[4]

\[ 2\text{Fe}^{3+} + \text{H}_2\text{S} \rightarrow 2\text{Fe}^{2+} + 2\text{H}^+ + \text{S}^0 \]

This reaction prevents the precipitation of ferric hydroxide but causes sulfur precipitation in both live and spent acids. In addition to the precipitation of sulfur, the reaction between hydrogen sulfide and ferrous iron will produce insoluble ferrous sulfide by means of the following reaction:

\[ \text{Fe}^{2+} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}^+ \]

This reaction will occur in spent acid when pH increases to 1.9 or above. The precipitated FeS in spent acid changes the colour of acid to black[3].

3) Before acidizing operations, acid is in contact with air, and therefore some oxygen will dissolve in acid. This oxygen can oxidize ferrous iron to ferric iron. Investigation shows that maximum dissolved oxygen is 8 mg/litre, and this amount of oxygen can oxidize about 55 ppm of ferrous iron that is insignificant.

( ) mill scale is a surface layer of ferric/ferrous oxide (Fe₃O₄) that forms on steel or iron during hot rolling.
4) Some crude oils tend to precipitate asphaltic sludges in contact with acid. For preventing this problem antisludge additives are usually added to acid. [5]

It has been shown that the presence of dissolved ferric iron in the treating acid aggravates acid sludging. The ferric iron alters the surface charge of asphaltic components and causes these asphaltic materials to precipitate. The iron that has charge of +2 is not a problem.

**METHOD OF CONTROLLING IRON PRECIPITATION**

Ferric hydroxide will not precipitate at spent acid that has a pH below 2. But this is not a reliable method for controlling precipitation because hydrochloric acid spends rapidly and pH of the spent acid will quickly rise above 2.

In sandstone acidizing, if mud acid returns immediately will generally have a pH below 2. But as seen in Fig – 1 a zone of totally spent acid will be formed at the leading edge of reaction front. In addition the acid in the leading edge usually contains more dissolved iron, since it is the first injected acid and contain most of the iron resulting from dissolution of scale in the equipments, pipes and tubing in the well. Concentrations up to 100,000 ppm have been measured. For this reason tubular goods can be treated prior to acidizing operations. It is recommended to use a treating volume of at least 0.1 gal of 15% HCl per Ft² of tubing surfaces. The acid should be displaced to the bottom of tubing, and then removed from the well by reverse circulation, swab, gas lift or using coiled tubing and nitrogen. The required additive for this acid is shown in Table-2.

**Fe STABILIZING AGENTS**

Fe stabilizing agents can be used to prevent the precipitation of ferric hydroxide from spent acid. The most commonly used stabilizing agents are sequestering agent including citric acid, Acetic acid, mixture of acetic and citric acids, EDTA and NTA.

Reducing agents also can be used to prevent precipitation of ferric hydroxide. These agents converts ferric ions to ferrous ions. This eliminates the chance of ferric hydroxide precipitation. Erythorbic acid is the most efficient iron reducing agent. Each of these iron stabilizing agents can be added to the hydrochloric acid in either their acid or as their respective chemical salts. The salts are sometimes used because they dissolved more readily.
in acid and facilitate mixing. In either case, the resulting products are the same. When added to HCL, the chemical salts instantly convert to the acid of the complexing Agents.

Specification of the most commonly used iron stabilizing agents and summary of their respective properties are shown in Table-3. Considerable care should be taken for the type and amount of iron sequestring agents. Since the average ratio of ferrous to ferric hydroxide in spent acid is about 5:1, this ratio must be used for recommending the amount of stabilizing agent to use when only the total iron content of the spent acid from the previous treatment is known. If the treatment is designed for the total iron content, there is a possibility of using more agent than is necessary. This could cause problems because the unused portion of some agents forms insoluble precipitates. For example citric acid in excess of 10 lb per 1000 gal that is not complexed with ferric iron may precipitate as insoluble calcium citrate as the pH rises. Calcium salts of EDTA are much more soluble in spent acid.

ACETIC ACID

A common misunderstanding is that the addition of acetic acid to hydrochloric acid will maintain the pH of the spent acid at a low level, thus preventing precipitation of ferric hydroxide. Fig-2 shows the pH of spent acetic acid. It is seen that the pH of acetic acid even when 50% spent is 4.73. The pH value of spent 15% hydrochloric acid is 5.3 and ferric hydroxide will precipitates at a pH of 2.2, and in the presence of H2S, ferrous sulfide (FeS) will have precipitated when the pH reaches 1.9, therefore acetic acid cannot be used as iron controlling agent.

EFFECT OF TEMPERATURE

Effect of temperature on the performance of iron stabilizing agents are shown in Fig-3& 4. As seen in this figures, citric acid, Nitrilotriacetic acid (NTA), and Tetrasodium Ethylenediamine tetraacetic (Na4EDTA) are effective up to 400 °F [204°C], but acetic acid is ineffective above 150 °F (66 °C). Surprisingly above 200 °F (93 °C) the effectiveness of citric acid, NTA and Na4EDTA seems to increase.
CONCLUSIONS

1) Citric acid and erythorbic acid as reducing agents and EDTA and NTA as chelating agents are very effective Iron stabilizers and can be used at temperatures up to 400 °F (204 °C) in well stimulations. But acetic acid is relatively ineffective above 125 °F (52 °C).

2) In the present of H₂S, ferric iron does not precipitate as Fe(OH)₃ but is converted to Fe(OH)₂, releasing element sulfur and insoluble iron sulfide( FeS) upon spending of the acid. To avoid this problem erythorbic acid in combination with EDTA should be used.

3) The first few barrels of acid pumped down the tubing and into the formation contain high concentration(up to 100,000 ppm) of dissolved iron. To clean the tubing ar, acid must be circulated down the tubing and up the annulus prior to the acid treatment. In low pressure wells, acid must be nitrified or must be removed from the wells by swabbing or gas lift.

4) In water injection well, oxygen dissolved in the water creates corrosion that is ferric type, and when dissolved by the acid will prescavseent more serious precipitation problems. Therefore additional iron stabilizing agent is required in water injection wells.

REFERENCES


3. Hall, B.E. and Dill, W.R. :”Iron control Additives for limestone and sandstone acidizing of sweet and sour wells” paper SPE 1757


Fig-1: Precipitation of ferric hydroxide during sandstone acidizing
Fig. 3 — Effect of temperature on the performance of Fe stabilizers.

Fig. 4 — Performance comparison of erythorobic acid, citric acid, and $\text{Na}_4\text{EDTA}$. 
### Table-1
Solubilities of ferrous and ferric hydroxide in spent acid

<table>
<thead>
<tr>
<th>PH</th>
<th>Maximum Concentration of ferric iron(Fe⁺³) (ppm)</th>
<th>PH</th>
<th>Maximum Concentration of ferric iron(Fe⁺³) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>60,000 below 6 very high</td>
<td>7</td>
<td>90,000</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>8</td>
<td>900</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>9</td>
<td>9</td>
</tr>
</tbody>
</table>

| above 5 | 0 |

### Table-2
TubeClean Composition

<table>
<thead>
<tr>
<th>material</th>
<th>purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>15% HCl</td>
<td>To dissolve iron rust and scale</td>
</tr>
<tr>
<td>Corrosion Inhibitor</td>
<td>To protect exposed metal surface from acid corrosion</td>
</tr>
<tr>
<td>Silt suspending or Foaming agent</td>
<td>To suspend silt or other particulate</td>
</tr>
<tr>
<td>Erythorbic acid</td>
<td>Reduces ferric iron to ferrous form</td>
</tr>
</tbody>
</table>

### Table-3
Specification of Iron Stabilizing Agents

<table>
<thead>
<tr>
<th>stabilizing Agents</th>
<th>form</th>
<th>specific gravity</th>
<th>Amount (lb)</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>citric Acid</td>
<td>powder</td>
<td>1.54</td>
<td>175</td>
<td>Effective at temperature up 400°F (204°C) and above 200°F (93°C) effectiveness increases</td>
<td>will precipitate as calcium citrate when excess quantities are used (above 10 lb/1000 gal of Acid)</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>liquid</td>
<td>1.05</td>
<td>43.5</td>
<td>no problem from possible precipitation as calcium acetate</td>
<td>relatively ineffective above 125°F</td>
</tr>
<tr>
<td>Tetrasodium salt of EDTA</td>
<td>powder</td>
<td>0.72</td>
<td>300</td>
<td>possible precipitation of calcium salt . effective at temp . up to 400°F (204°C)</td>
<td>more expensive than other agents</td>
</tr>
<tr>
<td>Sodium erythorbate</td>
<td>powder</td>
<td>25</td>
<td>25</td>
<td>effective at temperature up to 400°F (204°C) . small quantity required</td>
<td>Decrease effectiveness of corrosion inhibitor</td>
</tr>
<tr>
<td>NTA</td>
<td>powder</td>
<td>175</td>
<td>175</td>
<td>effective at temperature up to 400°F (204°C) . small quantity required</td>
<td>excessive amount will precipitate as calcium salt .</td>
</tr>
</tbody>
</table>