Experimental Study of Scale Inhibitors for Prevention of Calcium Carbonate Deposition in Synthetic Formation Water

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Abstract

Mixing of incompatible waters during flooding and changes in thermobaric conditions of oil production are the main causes of salt deposition. Forecast of salt formation process during oil production is an essential part of measures to prevent it. In this work, synthetic formation water, which contains ions with different concentrations, is used. Then, the possibility of calcium carbonate precipitation is tested in mixing with the injection water by ion saturation index measurement of carbonate salt at various temperatures and pressures. The effects of temperature and pressure changing on the calcium carbonate scale are considered. To prevent the formation of calcium carbonate, one new composition has been made and two appropriate scale inhibitors (SNPH-5312 and PAF-13A) were selected and their efficiencies were analyzed. The synergistic inhibitory effect has been considered for mixtures of inhibitors. Synergistic effect reached to 1.37 in low dosing rates of scale inhibitor for mixture of made composition with SNPH-5312. The used scale inhibitor is evaluated by influence on the corrosion inhibitor. The used materials were effective for calcium carbonate scale prevention up to 92%.

1. Introduction

The modern methods of oil production are characterized by the need to produce significant amounts of associated water, which is injected back into the oil reservoirs. Inorganic salts deposition occurs during the mixing of different waters which are incompatible with each other in the oil reservoirs, formations, production equipment and electrical submersible pumps [1-3]. These combinations of waters can be done during water flooding into the reservoirs to pressure maintenance. Production rate and equipment life are reduced by the formation of the salts.
Experience in fighting with the deposition of the inorganic salts shows that the most effective methods are based on the prevention of salt deposits [4]. To prevent the scaling, the following methods are used: technological, physical and chemical methods. Inhibitors are used as the chemical reagents for scale prevention. In the first place, scale inhibitors are applied to protect the submersible pumps because the salt deposits in operating parts of this high technology equipment significantly complicate its work. Inhibitors are oil-soluble and water-soluble, single-and multi-component. In practice, water-soluble inhibitors are the most widely used.

Scale inhibitors are not universal; each one prevents only the deposition of a certain group of salts. Suggested effective dosing rate of the scale inhibitors are conducted in the technical conditions for their use [5]. However, practice shows that the efficiency of recommended dosages of scale inhibitors for specific well conditions must be verified by laboratory tests by considering formation water salinity and hydrochemical conditions of formation [6]. In laboratory conditions, it is necessary to determine the compatibility of the scale inhibitor with the water in which the inhibitor solution is planned to prepare for bottom hole treatment [7].

2. Methodology

With proper selection of inhibitor and appropriate technology of its application, the complete prevention of deposition of the inorganic salts can be achieved technologically on the entire flow path of well productions from the bottom of well to the preparation points of oil and water [8].

In describing and predicting the process of formation of calcium carbonate, only chemical (ion concentration and ionic strength of the solution) and thermodynamic characteristics (pressure and temperature) are usually used. According to the equation of prediction of calcium carbonate formation, saturation index (SI) for calcium carbonate by gas phase absent is defined as follows [9]:

$$SI = \log \left[ \frac{[Ca^{2+}][HCO_3^-]}{[Ca^{2+}]_{aq}[HCO_3^-]_{aq}} \right] + 3.63 + 8.68 \times 10^{-3}T + 8.55 \times 10^6T^2 - 6.56 \times 10^7P - 3.42S_i^{0.5} + f S_i^{0.5} T + 1.373S_i$$

Where T is temperature (°F), P is pressure (psi) and S_i is the ionic strength (M).

When SI>0 calcium carbonate falls and the opposite (SI<0) no sediment is formed. Obviously, this prediction equation describes the case of the formation of calcium carbonate for single layer wells with considerable changes of the temperature and pressure conditions [10]. In this work, saturation index for synthetic formation water is considered by mixing the synthetic formation water with injection water (sea water).

Efficiency of scale inhibitors and their compositions determined by equation (2) [11]:

$$E\% = \frac{C_i - C_w}{C_0 - C_w} \times 100$$

(2)
Where $E$ is the efficiency of inhibitor, $c_i$, $c_w$ and $c_0$ are ion concentrations in the solution with inhibitor, without inhibitor and in the source water with initial concentration in milligram per liter, respectively. 

Ion concentration measurement can be measured by the methods of titration or by the apparatus of capillary electrophoresis Kapel-104T.

For quantitative evaluation of the synergistic effect, the ratio of efficiency of mixtures of inhibitors ($E_m$) to the efficiency of inhibitor components, which is calculated by the additivity rule ($E_a$), is applied; i.e. the sum of the efficiencies, which constitute the inhibitor mixtures at respective concentrations [12]. Obviously, if ($E_m/E_a > 1$), the synergistic effect manifests and if ($E_m/E_a < 1$), the antagonistic effect occurs [13].

The additive inhibition efficiency of the mixture is calculated by equations (3, 4):

$$E_a = E_1 n_1 + E_2 n_2 + E_3 n_3 + \ldots + E_p n_p$$

$$n_1 + n_2 + n_3 + \ldots + n_p = 1$$  

Where $E_a$ and $E_p$ are the additive concentrations of the mixture and the $p^{th}$ component of the mixture in milligram per liter, respectively and $n_p$ is the mass fraction of the $p^{th}$ component.

After the scale inhibition experiments, the selected scale inhibitor must be tested for interaction with corrosion inhibitor [14]. Corrosion inhibition efficiency is determined by equation (5) [15, 16]:

$$Z\% = \frac{V_1 - V_2}{V_1} \times 100$$

Where $V_1$ and $V_2$ are the corrosion inhibition rates of the samples in uninhibited and inhibited environments in g.m$^{-2}$.h$^{-1}$, respectively and $Z$ is the corrosion inhibition efficiency.

The corrosion inhibition rate is defined by the equation (6):

$$V = \frac{m_1 - m_2}{s \times t}$$

Where $m_1$ and $m_2$ are the mass of the metal samples before and after the test in gram, respectively, $S$ is the surface area of samples in m$^2$, $t$ is the test time in hour and $V$ is the corrosion rate of the used sample in g.m$^{-2}$.h$^{-1}$.

### 3. Results and discussion

The titration method has been used for the analysis of the synthetic formation water. The ion concentration of water is shown in Table 1. Clearly, that the water composition has a high concentration of calcium, carbonate and bicarbonate ions. pH value of the water is equal to 7.1.
Table 1: Ionic composition of synthetic of formation water

<table>
<thead>
<tr>
<th>pH</th>
<th>Ion contents (mg/l)</th>
<th>Total dissolved salts (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl(^-)</td>
<td>CO(_3^{2-})</td>
</tr>
<tr>
<td>7.1</td>
<td>231</td>
<td>12610</td>
</tr>
</tbody>
</table>

To determine the possibility of deposition of salts, it is necessary to calculate the saturation index by using the equation (1). This equation is based on the concentration of the cation, anion and the solubility product constant. Solubility product constant depends on temperature, pressure, pH, ionic strength and some empirical parameters that have different values for salts. Salt precipitates in the positive values of the saturation index. The saturation index was analyzed for calcium carbonate precipitation. Figure 1 shows the dependence of the saturation index (SI) with respect to the ratio of the injected water to the formation water at different temperatures in the constant pressure (3000 psi) for calcium carbonate. The analysis revealed that the probability of calcium carbonate deposition increases with increasing temperature. As shown in Figure 1, at high temperatures for a low ratio of injected water to the synthetic formation water saturation index rises sharply.

The changes of saturation index are for ratios of injected water to the synthetic formation water in different pressures shown in Figure 2. As shown in Figure 2, saturation index increases with increasing the ratio of injected water to the formation water, also saturation index decreases with increasing the pressure at constant temperature (50 °C). From this figure it is clear that the increase in
the saturation index at low ratio of the two kinds of waters is high. The negative values of saturation index are obtained at low ratios.

![Graph showing saturation index](image)

Fig. 2: Prediction of scale formation in different pressures for synthetic formation water

Scale inhibitors should have the following properties: compatible with the formation water, adsorption-desorption capacity, low corrosivity and be environmentally safe. The composition of scale inhibitors is shown in Table 2. Composition number one is made from the three acids, ammonium chloride and water. They are mixed in mass percentage. The other two inhibitors are selected for comparison and mixing with the composition No. 1. They are applied for the prevention of calcium carbonate formation in the field.

Table 2: Composition of scale inhibitors

<table>
<thead>
<tr>
<th>Scale inhibitor</th>
<th>Scale inhibitor composition</th>
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<tbody>
<tr>
<td>No. 1</td>
<td>Oxiethilendiphosphene acid 5%, ammonium chloride 4%, polyethylene polyamine-N-methylphosphonic acid 4%, hydrochloric acid 6%, water – remainder</td>
</tr>
<tr>
<td>SNPH-5312</td>
<td>Based on the composite reagent of phosphorus</td>
</tr>
<tr>
<td>PAF-13A</td>
<td>Aqueous solution of polyamino methylene phosphonates</td>
</tr>
</tbody>
</table>

Figure 3 shows the dependence of scale inhibition efficiency in the inhibitor dosing rate for three compositions. Dosing rates are from 10 mg/l to 100. The raising of efficiency is high in the low dosing rates, especially in composition No. 1 and SNPH-5312. From the Figure 3, the most effective inhibitor is the composition No. 1. Scale efficiency increases with increasing the dosing rate for all inhibitors. Growth of efficiency of composition No. 1 is insignificant after consumption of 60 mg/l.
Figure 3: The dependence of the efficiency of scale inhibitors on the scale dosing rate of inhibitors

Figure 4 and Figure 5 show the synergistic inhibitory effect of mixtures of inhibitors of calcium carbonate. As shown in the Figure 4, high synergistic effect of the mixtures of No. 1 with SNPH-5312 occurs at a mass ratio of 70:30 in low dosage rates, but in the higher mass ratios antagonistic effect occurs. Figure 4 show that the mixture has a synergistic effect on the rate of 10 mg/l at any ratio of two inhibitors. Also from this figure it is clear that the mixture has an antagonistic effect from rate of 40 mg/l to 100 at any ratio except at ratio 70:30.

Figure 5 illustrates the change of the ratio of $E_m/E_a$ for mixture of composition No. 1 with inhibitor PAF-13A. From this figure, it is clear that the highest synergistic effect is obtained at mass ratio 60:40. In this mixture, the antagonistic effect occurs at high flow dosing rates in any mass fraction.
this case, the antagonistic effect takes place in a ratio range from 0:100 to 50:50 and from 80:20 to 100:0 in low dosing rates (even 10 mg/l).

Figure 6 depicts the dependence of the effectiveness of inhibitors from the dosing flow for different compositions. As shown in this figure, the efficiency of mixture of composition No. 1 with SNPH-5312 is more than the efficiencies of both inhibitors in individual states. It means that this mixture from these two inhibitors gives the highest effectiveness for prevention of the calcium carbonate deposition in the synthetic formation water. For a mixture of composition No. 1 with PAF-13A, the results show that the mixture has good action until the mass ratio of 40:60, after that the effectiveness decrease with increasing the mass ratio of composition No. 1 in the mixture.

Fig. 5: The dependence of ratio $E_m/E_a$ of mixture composition No.1 with PAF-13A on the content of composition No.1

Fig. 6: The dependence of the efficiency of scale inhibitor compositions and mixtures on the dosing rate
Figure 7 and Figure 8 illustrate the polynomial dependence of scale inhibition effectiveness on the mass fraction of the inhibitors in the mixtures at two dosing rates of 20 mg/l and 40. With a sufficiently high coefficient of determination, it was found that efficiency increases with increasing the content of composition No.1 in the mixtures to the point in which the highest synergistic effect occurs. The efficiency of the mixture of composition No.1 with the inhibitor SNPH-5312 is higher than the efficiency of the mixture of composition No.1 with the inhibitor PAF-13A in a mass ratio of 10:90.
The study revealed that the inhibitor in mixture of composition No. 1 with SNPH-5312 has the highest efficiency of prevention of the calcium carbonate formation. Therefore, this mixture has been used for corrosion analysis. Chemical reagent of SNPH-6418 was used as corrosion inhibitor. In Table 3, the results of this study are shown. According to the table, addition of the scale inhibitor into the corrosion inhibitor does not considerably affect. Corrosion protection effectiveness is reduced by increasing the dosing rate of a scale inhibitor.

Table 3: Corrosion inhibition protection

<table>
<thead>
<tr>
<th>Corrosion inhibitor dosing rate (mg/l)</th>
<th>Scale inhibitor dosing rate (mg/l)</th>
<th>Corrosion rate (g.m$^{-2}$.h$^{-1}$)</th>
<th>Corrosion inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-</td>
<td>0.0945</td>
<td>68.3</td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>0.0638</td>
<td>78.6</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>0.0328</td>
<td>89.0</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>0.1001</td>
<td>66.4</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
<td>0.0718</td>
<td>75.9</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
<td>0.0349</td>
<td>88.3</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>0.1058</td>
<td>64.5</td>
</tr>
<tr>
<td>50</td>
<td>40</td>
<td>0.0778</td>
<td>73.9</td>
</tr>
<tr>
<td>100</td>
<td>40</td>
<td>0.0384</td>
<td>87.1</td>
</tr>
</tbody>
</table>

4. Conclusions

The following conclusions can be drawn from this research:

i. Analysis of the deposition of calcium carbonate showed that the precipitation of calcium carbonate crystals occurs in most cases. Saturation index has been increased with increasing the temperature and decreasing pressure.

ii. The high efficiency (up 92%) inhibition of calcium carbonate was obtained by using the composition No. 1 with SNPH-5312 at doses greater than 50 mg/l. The optimal inhibition rate of scale inhibition is in the range of 40-60 mg/l. The mixture of composition No. 1 with SNPH-5312 is recommended in dosing rate of 60 mg/l for the prevention of calcium carbonate formation.

iii. The high synergistic effect is obtained at low rate of scale inhibition. The high synergistic effect of the mixture of composition No. 1 with SNPH-5312 is at a ratio of 70:30 and for the mixture of the No. 1 with PAF-13A at 60:40.

iv. Effectiveness of the protection against corrosion in the presence of scale inhibitor insignificantly decreases while remaining at a high level. In connection with this combined use of scaling inhibitor and corrosion is recommended to prevent deposition of calcium carbonate.
References


