

THE INFLUENCE OF pH AND CONCENTRATION OF PHOSPHONATE INHIBITOR - TESTS ON CHANGE OF BARIUM SULFATE SCALE MORPHOLOGY BY USING SCANNING ELECTRON MICROSCOPE

by
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I. INTRODUCTION

Water injection is often used to keep maintaining reservoir pressure. Injected water (high in sulphate) mixes with formation water (high in barium) leading to the deposition of barium sulfate scale in the near wellbore, reservoir, production tubulars and topside equipment. Barium sulfate scale is unique scale deposit and the least soluble of the scales. The deposition of oil field scale is a potentially damaging problem which reduces fluid flow resulting in a decline in oil production.

The best approach to solving the problems of scale formation is to prevent or inhibit deposition and this is more effective than scale removal. The use of scale inhibitor can be effective method for preventing scale although their effectiveness is controlled by experimental conditions. Therefore, it is very important to know factors that influence barium sulfate scale. The main topic of this paper is *“The Influence of pH and Concentration of Inhibitor Solution - Tests on Change of Barium Sulfate Scale Morphology by Using Scanning Electron Microscope”*.

Hopefully, the results of laboratory test presented this paper give useful and valuable information not only for LEMIGAS, but also for oil industry, chemical manufacturers and universities, then other institutions.

II. SCOPE OF LABORATORY TESTS

To see the change of barium sulfate scale morphology caused by pH and concentration of inhibitor, the scope of laboratory tests outlined in Section II can be divided into four main parts:

A. Water analysis

Significant constituents that are in formation water (FW) and injected water (IW), are analyzed to know the chemical compositions in both formation and injected waters to be mixed.

B. Optimum mixing ratio test

This test is carried out to know the condition of mixing ratio between formation water (FW) and injected water (IW) that results in maximum barium sulfate scale deposit.

Experimental condition :

FW : IW = 80 : 20 (sample 1).

FW : IW = 80 : 20 (sample 2).

FW : IW = 80 : 20 (sample 3).

FW : IW = 80 : 20 (sample 4).

at H 6.0 and temperature 30° C.

C. Identification of barium sulfate scale form as standard/comparison

It is necessary to identify barium sulfate scale form at optimum mixing ratio condition by using scanning electron microscope (SEM). This result can be used as standard for comparison with the results of barium sulfate scale identification caused by the influence of pH and inhibitor concentration factors.

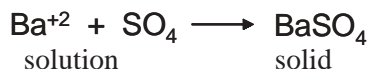
D. The Influence of pH and inhibitor concentration on BaSO₄ morphology

The influence of pH and phosphonate inhibitor concentration on BaSO₄ scale morphology is identified by using SEM at optimum mixing ratio and temperature 30° C for the analyzed samples:

- at pH 3.0, 0 ppm inhibitor, 2000 x magnification.
- at pH 3.0, 0 ppm inhibitor, 10000 x magnification.
- at pH 3.0, 25 ppm inhibitor, 2000 x magnification.
- at pH 3.0, 25 ppm inhibitor, 10000 x magnification.
- at pH 6.0, 0 ppm inhibitor, 2000 x magnification.
- at pH 6.0, 0 ppm inhibitor, 10000 x magnification.
- at pH 6.0, 25 ppm inhibitor, 2000 x magnification.
- at pH 6.0, 25 ppm inhibitor, 10000 x magnification.

III. BARIUM SULFATE SCALE

The extreme insolubility of BaSO₄ makes it very likely that scaling will occur if both Ba⁺² and SO₄⁻² ions are present in a water. Generally, the process of scale deposition occurs when the product solubility of a compound considered is exceeded. The reaction is as follows:



The following table compares the solubility of the three types of scale, such as calcium carbonate, calcium sulfate and barium sulfate in distilled water at 25°C:

Table 3.1.
Comparative solubilities

Scale	Solubility (mg/l)
Gypsum	2080
Calcium carbonate	53
Barium sulfate	2.3

Source: Oilfield Water System by Patton

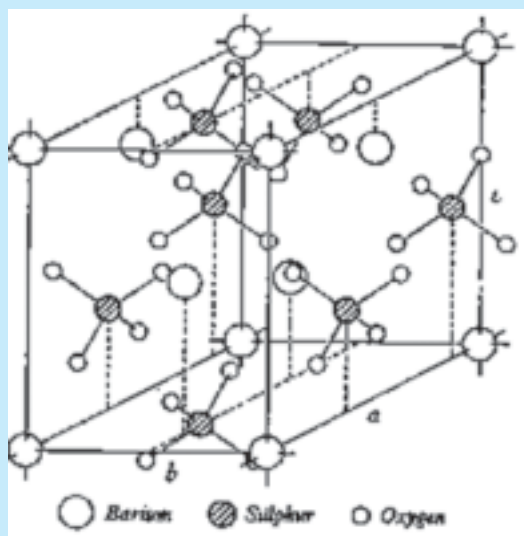


Figure 3.1
Perspective view of the structure of barite

In 1925, James and Wood determined the structure of barite natural barium sulfate.

is called barite or barytes. The orthorhombic unit cell is shown in perspective view in Figure 3.1.

IV. PROCEDURE

A. Water analysis

Chemical compositions and physical properties of formation water and injected water are analyzed based on API – RP45.

B. Optimum mixing ratio

1. Preparation of formation water (FW) and injected water (IW) based on the chemical composition of water analysis.
2. FW and IW are filtered by using 0.45 µm filter paper.
3. FW and IW are mixed in plastic bottles at different mixing ratio (see Section 2.2).
4. Each sample is shaken and barium sulfate scale deposit starts to form and it is left for 24 hours at room temperature in order to get more deposit.
5. Each sample is filtered with 0.45 µm filter and put in the oven at temperature 40° C.
6. The formed deposit for each sample is weighed.
7. The mixing ratio FW : IW in samples no. 1, 2, 3 and 4 that result in maximum barium sulfate scale deposit, is called with optimum mixing ratio.

C. Barium sulfate scale form as standard/ comparison

There are two sources of barium sulfate scale deposit form that is used as standard/comparison

1. Reference from SEM Petroleum Atlas Book, Joann E.Welton, Chevron Oil Field Research Company.
2. LEMIGAS laboratory test result.

Weigh 0.4445 gram of BaCl₂.6H₂O and dissolve in 1 litre aquadest. Weigh 4.3769 gram of Na₂SO₄ and dissolve in 1 litre aquadest. Then, both solutions are mixed, leave it for 20 hours, and it will result in barium sulfate scale deposition. Identification of the formed scale is made by using SEM and the results can be used as comparison.

C. The influence of pH

1. Carry out step no. 1 and 2 Section 4.2.
2. pH of FW and IW are adjusted to pH 6.0 and 3.0 with 10 % HCl solution.

3. FW and IW are mixed into a plastic bottle at experimental conditions (see Section 2.4).
4. Each sample is shaken and barium sulfate scale deposit starts to form and leave it for 24 hours at room temperature.
5. Each sample is filtered by using 0.45 µm filter and put in the oven at temperature 40° C.
6. Identification of the formed scale at experimental conditions by using SEM.
7. Photo of barium sulfate scale identification results caused by the influence of pH are compared to photo of barium sulfate scale formed as standard/comparison from reference/literature and LEMIGAS laboratory result as well.

E. The influence of inhibitor concentration

1. Carry out step no. 1 and 2 Section 4.2.
2. Add Inhibitor of 25 ppm concentration into injected water.
3. FW and IW are mixed into a plastic bottle at experimental conditions (see Section 2.4).
4. Each sample is shaken and barium sulfate scale deposit starts to form and leave it for 24 hours at room temperature.
5. Each sample is filtered by using 0.45 µm filter and put in the oven at temperature 40° C.
6. Carry out identification of the formed scale at experimental conditions with using SEM.
7. Photo of barium sulfate scale identification results caused by the influence of inhibitor concentration are compared to photo of barium sulfate scale form as standard/comparison from reference/ literature and LEMIGAS laboratory results as well.

V. LABORATORY TEST RESULTS

This section shows the laboratory test results that involves water analysis, optimum mixing ratio, photo of barium sulfate scale as standard, the influence of pH and inhibitor concentration on change of barium sulfate scale morphology by using SEM.

A. The results of water analysis

Section 1 has explained that the occurrence of barium sulfate scale caused by incompatible waters, when the injected water (containing sulphate ion) mixes with formation water (containing barium ion) leading to the deposition of barium sulfate scale (BaSO₄).

Chemical compositions in formation water and in-

jected water have been analyzed, and the results are tabulated in Table 5.1. The results of water analysis show that the content of barium ion is 250 ppm in formation water and sulfate ion is 2960 ppm in injected water.

B. The result of optimum mixing ratio test

To know optimum mixing ratio FW : IW condition, mixtures of formation water and injected water are made

Table 5.1
Water analysis results for formation water and injected water

Chemical compositions (ppm)		
Types of cation/ anion	Formation water FW (ppm)	Injekted water IW (ppm)
Na ⁺	29400	10890
Ca ⁺²	2800	428
Mg ⁺²	500	1368
K ⁺	370	460
Sr ⁺²	575	-
Ba ⁺²	250	-
Cl ⁻	52674	19766
SO ₄	-	2960

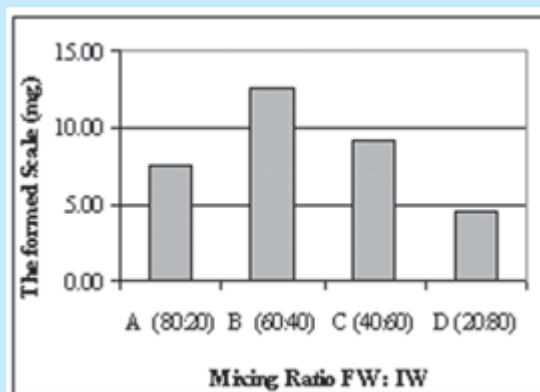


Figure 5.2
Mixing ratio FW : IW vs the formed barium sulfate scale

at different mixing ratio, pH 6.0 and temperature 30°C. The amounts of barium sulfate scale deposit formed are as follows :

- FW : IW = 80 : 20 = 7.40 mg
- FW : IW = 60 : 40 = 12.60 mg
- FW : IW = 40 : 60 = 9.10 mg
- FW : IW = 20 : 80 = 4.59 mg

The data of the formed scale (mg) are plotted against the mixing ratio and are shown in Figure 5.2 The results indicate that mixing ratio of FW : IW = 60 : 40 results in the maximum amount of barium sulfate formed (12.60 mg). This is called with *optimum mixing ratio*.

At *optimum mixing ratio* condition (FW : IW = 60 : 40), where formation water (containing 250 ppm) and injected water (containing 2960 ppm) start mixing (t = 0 second), the obtained concentration of barium is $0.6 \times 250 \text{ ppm} = 150 \text{ ppm}$ and concentration of sulfate in the mixture $0.4 \times 2960 \text{ ppm} = 1184 \text{ ppm}$.

C. Barium sulfate scale form as standard/ comparison

As mentioned in Section 4.2 that there are two sources of barium sulfate scale deposit form as standard/comparison:

- Photo of barium sulfate scale from SEM Petroleum Atlas Book, Chevron Oil Field Research Company (see Figure 5.3.1).
- Photo of barium sulfate scale identification result by using SEM, investigated by LEMIGAS (shown in Figure 5.3.2).

D. The influence of pH and inhibitor concentration on change of barium sulfate scale morphology

The results of barium sulfate scale identification test caused by the influence of pH and inhibitor concentration factors, are as follows:

- For the analyzed sample at pH 3.0, 0 ppm inhibitor, 2000 x magnification (see Figure 5.4.1).
- For the analyzed sample at pH 3.0, 0 ppm inhibitor, 10000 x magnification (see Figure 5.4.2).
- For the analyzed sample at pH 3.0, 25 ppm inhibitor, 2000 x magnification (see Figure 5.4.3).
- For the analyzed sample at pH 3.0, 25 ppm inhibitor, 10000 x magnification (see Figure 5.4.4).
- For the analyzed sample at pH 6.0, 0 ppm inhibitor, 2000 x magnification (see Figure 5.4.5).
- For the analyzed sample at pH 6.0, 0 ppm inhibitor, 10000 x magnification (see Figure 5.4.6).



Source: SEM Petroleum Atlas Book, Joann E.Welton, Chevron Oil Field Research Company

Figure 5.3.1
Photo of barium sulfate scale from Chevron Oil Field Research Company



Figure 5.3.2
Photo of barium sulfate scale, identified by LEMIGAS Laboratory

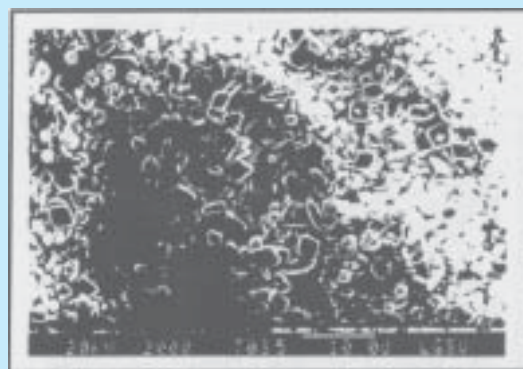


Figure 5.4.1
Photo of barium sulfate scale for pH 3.0, blank, 0 ppm inhibitor, magnification 2000 x



Figure 5.4.2
Photo of barium sulfate scale for pH 3.0, blank,
0 ppm inhibitor, magnification 10000 x

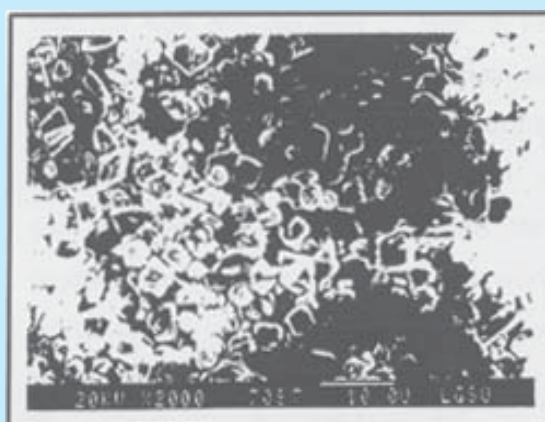


Figure 5.4.5
Photo of barium sulfate scale for pH 6.0, blank,
0 ppm inhibitor, magnification 2000 x

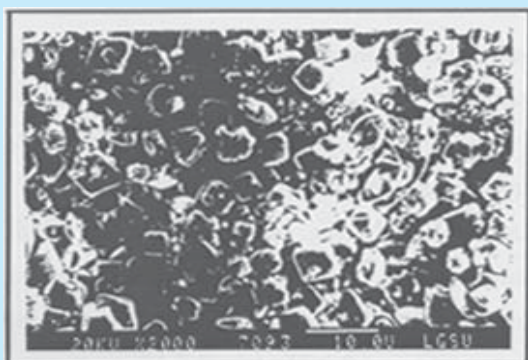


Figure 5.4.3
Photo of barium sulfate scale for pH 3.0,
25 ppm inhibitor, magnification 2000 x



Figure 5.4.6
Photo of barium sulfate scale for pH 6.0, blank, 0
ppm inhibitor, magnification 10000 x



Figure 5.4.4
Photo of barium sulfate scale for pH 3.0,
25 ppm inhibitor, magnification 10000 x

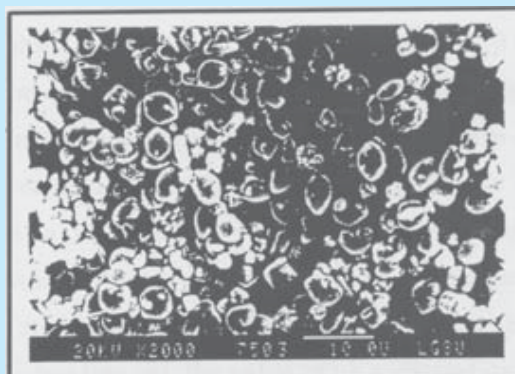


Figure 5.4.7
Photo of barium sulfate scale for pH 6.0, 25 ppm
inhibitor, magnification 2000 x

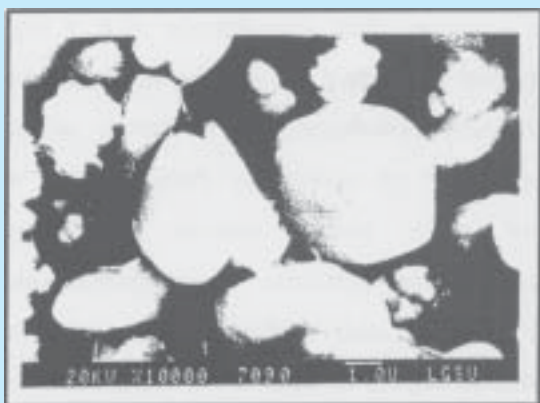


Figure 5.4.8
Photo of barium sulfate scale for pH 6.0, 25 ppm inhibitor, magnification 10000 x

- For the analyzed sample at pH 6.0, 25 ppm inhibitor, 2000 x magnification (see Figure 5.4.7).
- For the analyzed sample at pH 6.0, 25 ppm inhibitor, 10000 x magnification (see Figure 5.4.8).

Section 5.3 and Section 5.4 have shown the results of barium sulfate scale form identification by using scanning electron microscope (SEM).

Identification of barium sulfate scale form for the analyzed samples for blank sample (without inhibitor) and sample (containing 25 ppm phosphonate inhibitor) as well at pH 3.0 and pH 6.0 conditions, are compared to barium sulfate scale form based on reference/literature (see Figure 5.3.1) and LEMIGAS laboratory result (see Figure 5.3.2) as “*comparison*”.

It is very clear, that photo of barium sulfate scale form for blank sample (without inhibitor) at conditions 0 ppm inhibitor concentration, pH 3.0 and 2000 x and 10000 x magnification indicate ortho- rhombic crystal (Figure 5.4.1 and Figure 5.4.2)

On the other hand, Figure 5.4.3 and Figure 5.4.4 show photo of barium sulfate scale form for sample containing inhibitor with concentration 25 ppm, at pH 3.0 and 2000 x and 10000 x magnification. The form of barium sulfate scale obtained at very low pH condition indicates that it is still orthorhombic crystal. It means that phosphonate inhibitor scale does not work effectively to prevent the occurrence of barium sulfate scale at very low pH.

Subsequently, photo of barium sulfate scale for blank sample (without inhibitor) at conditions of 0 ppm inhibi-

tor concentration and pH 6.0 indicates orthorhombic crystal in Figure 5.4.5 for 2000 x magnification and Figure 5.4.6 for 10000 x magnification.

It is very clear that there is a change of barium sulfate scale morphology from orthorhombic to be oval (egg-shaped) form for sample containing inhibitor at pH 6.0, 25 ppm inhibitor concentration and 2000 x and 10000 x magnification (see in Figure 5.4.7 and Figure 5.4.8).

Figure 5.4.3 and Figure 5.4.7 show the influence of pH (3.0 and 6.0) on the change of barium sulfate scale morphology qualitatively, where the form of scale barium sulfate at pH 3.0 (the value of pKa dissociation = 2.8) is orthorhombic, while at pH = 6.0 forms oval (egg-shaped) (the value of pKa dissociation = 6.38). By increasing pH, the value of pKa dissociation will raise, so that the effectiveness of an inhibitor in preventing barium sulfate will also increase. At high pH condition (pH = 6.0), phosphonate scale inhibitor is adsorbed actively on the surface of barium sulfate crystal, so that phosphonate inhibitor is able to work effectively to block the growth of barium sulfate scale. So, phosphonate scale inhibitor work more effectively by at pH 6.0 than pH 3.0 in preventing the occurrence of barium sulfate scale. In qualitative analysis, the effectiveness of a scale inhibitor in preventing barium sulfate scale is indicated by the change of barium sulfate scale morphology.

VI. CONCLUSIONS

Based on the results of barium sulfate scale identification test to see the influence of pH and concentration of inhibitor on the change of barium sulfate scale morphology, it can be concluded as follows :

1. The occurrence of barium sulfate scale is caused by incompatible waters, formation water (containing barium ion) mixes injected water (containing sulfate ion) leading to the deposition of barium sulfate scale (BaSO_4).
2. Based on the results of water analysis, the content of barium ion is 250 ppm in formation water and 2960 ppm sulfate ion in injected water.
3. Mixing ratio between formation water and injected water FW : IW = 60 : 40 results in maximum amount of barium sulfate scale formed maximum (12.60 mg), it is called optimum mixing ratio.
4. The form of barium sulfate scale is identified by using scanning electron microscope (SEM), the results of blank sample (without inhibitor) and sample (containing 25 ppm phosphonate inhibitor) as well at pH 3.0 and pH 6.0 conditions, are compared to the form

- of barium sulfate scale based on reference and LEMIGAS laboratory result as "*comparison*".
5. The form of barium sulfate scale at pH 3.0 shows orthorhombic crystal, while at pH = 6.0, it is oval/egg-shaped.
 6. Phosphonate scale inhibitor work more effectively at pH6.0 than pH 3.0 in preventing the occurrence of barium sulfate scale.
 7. pH and concentration of inhibitor factors play important role to influence the change of barium sulfate scale morphology.

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