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Mitigation of Barium Sulphate Scale using Red Onion Skin Extract Derivatives

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Abstract

Some oilfield brines contain enough sulphate ion in the presence of barium ions to form barium sulphate ($BaSO_4$) scale. Due to its physical hardness, chemical stability, and thermal stability, barium sulphate scale has been proven to be one of the most difficult scales to remove in oil and gas production systems. As a result, oil and gas producers frequently employ treatment chemicals to inhibit the formation of these scales and reduce their proclivity to adhere to surfaces. However, increasing concern about the environmental friendliness of some of these chemicals necessitates the investigation of green scale inhibitors. In this study, we modified and tested derivatives of Red Onion Skin Extract (ROSE) for their ability to inhibit the formation of Barium Sulphate scales. At the optimum dosage, the unmodified red onion skin extract inhibited 83 percent of the evaluated scale. One of the three modified product blends achieved the highest efficiency of 88 percent, while the other two products achieved efficiency above 50 percent, which can be improved by increasing the scale inhibitor dosage. The results show that ROSE derivatives are effective at inhibiting Barium sulphate scales and are proposed as new green scale inhibitors.

Keywords: *Scale inhibition; Barium sulphate scale; Red onion skin; Green scale inhibitor; Oilfield scale.*

1. Introduction

A common process leading to scale formation is the precipitation of sparingly soluble salts from oilfield brines. The formation of barium sulphate scale ($BaSO_4$) is mostly caused by the mixing of barium-rich formation water and sulphate-rich injection seawater [1-3]. Barium sulphate is difficult to remove once generated and accumulated during oilfield operations, especially in the reservoir, because it is insoluble in most fluids and cannot be easily dissolved by acid [1]. Chemical composition of the brine, temperature, and pressure are the three most obvious physical factors impacting the numerical value of the solubility product of an inorganic salt like $BaSO_4$. When the composition, temperature, or pressure of the brine changes, the $BaSO_4$ solubility product changes as well. The general equilibrium involved in Barium sulphate precipitation [1] is defined as:

$$Ba^{2+}_{(aq)} + SO_{4\,(aq)}^{2-} \leftrightarrow BaSO_{4\,(s)} \quad (1)$$

Barium Scale precipitation could cause various damages in the oilfield and thus should be avoided at all costs. These scales can obstruct fluid flow, promote corrosion, result in production losses, necessitate equipment replacement, cause equipment damage, which may generally influence the economic benefit of a well [1,4-5]. The use of scale inhibitor is a simple, effective, and most economical route for the prevention of barium sulphate buildup [4]. It works by altering the thermodynamic stability of developing nuclei and/or blocking the active sites of crystals, to diminish the driving force for crystallization and subsequent growth [6-10]. The effectiveness of scale inhibitors in preventing scale formation has been extensively studied in the literature using a variety of inhibitors. However, like with other industries, the oil industry suffers from the environmental effects of using harmful chemicals to prevent scale formation. It is obvious that more research on green scale inhibitors will aid in keeping the environment safe while also reducing the scaling phenomenon in porous media. Environmentally friendly inhibitors that are non-toxic, biodegradable, and do not accumulate in the body therefore becomes very important. As a result, this study assesses the inhibitive performance of four new green scale inhibitors derived from onion skin extract on Barium sulphate scale. These new inhibitor blends are designated as ROS, ROG, RUF, and ROF. ROS is the pure red onion skin extract, ROG is glutaraldehyde-modified red onion skin extract, RUF is furfuraldehyde and urea-modified red onion skin extract, and ROF is furfuraldehyde-modified red onion skin extract.

2. Preferred location for barium scale formation

Barium Scale precipitation does not appear to prefer specific locations for deposition. Under field conditions, however, basic thermodynamic laws are employed to forecast the locations and rate of $BaSO_4$ scale formation. During production, barium sulphate scales could form all along the water's flow path where incompatible water mixes at the surface facility as following [1,3]:

- In the reservoir where the mixed injection water and formation water are about to reach the producing well.
- The connection of branched zones where each branch generates different water or the manifold of producing zones where water is produced from different blocks within the same producing zone.
- Topside of side facilities where produced fluids are mixed from multiple production zones to separate oil and gas from water.
- Pipelines that transfer produced fluids to onshore processing facilities, as well as discharge well, where produced water is injected for eventual disposal.

2.1. Key properties of scale inhibitors

Scale inhibitors can work in one or more of three ways as a result of the scaling formation process. Some scale inhibitors can disrupt the nucleation process by diffusing in the bulk liquid and reaching the ion clusters in the liquid or on a solid substrate [2,11]. These inhibitor ions should be large enough to disrupt scaling ion clustering and prevent existing clusters from growing to the critical size where crystallites would form. A good nucleation inhibitor ion must be critical in size while still being able to diffuse in water at an acceptable rate [2].

Some inhibitors do not prevent clustering but rather slow crystal growth by diffusing over the crystal surface and active sites with a high affinity [3,8]. This type of inhibitor must be small enough to diffuse but large enough not to be absorbed by the growing crystals. In contrast to the first type of inhibitor, this type of inhibitor promotes the formation of small crystals in order to reduce supersaturation of the solution and the risk of scaling in subsequent parts of the flow conduit. If the inhibitor is absorbed into the crystal, the resulting scale may be soft, friable, and easily removed.

Some inhibitors have the ability to alter the crystal surface. The transport theory and scale inhibitor models can be found in the literature [2, 3,7-8]. Molecules that are neither nucleation nor crystal growth modifiers can strongly bind to crystal surfaces and prevent crystal attachment.

Field operators are primarily concerned about the performance of scale inhibitors in oilfield operations. Information is required to make effective decisions that ensure scale control and prevention. These decisions are based on a review of scale inhibitor performance under a variety of environmental circumstances. For a chemical substance to be suitable as a scale inhibitor in the industry, many criteria must be addressed. The following are the five most important features for a chemical to be effective as a scale inhibitor [12-14].

1. Scales inhibitors should be compatible with field brines and other chemical additives.
2. The chemical should be able to prevent scale formation even at very low doses, such as 1–50 ppm.
3. Scale inhibitors should be thermally stable.

4. Scaling is uncommon in areas where corrosion is not present in the oilfield. As a result, the scale inhibitor should not cause corrosion or be harmed by corrosion agents. It must be compatible with corrosion inhibitors.

The skin of red onions has been examined and discovered to contain quercetin, a conjugated and electron-rich substance that inhibits corrosion and mineral scale growth (15-17).

2.2 Barium scale inhibitor evaluation methods

2.2.1. Bulk characterization

Conventionally, the bulk precipitation of barium scale has been investigated using a static bulk jar test. Test methods are designed to evaluate the ability of scale inhibitors to inhibit oilfield scale precipitation in a laboratory condition [2, 11, 18].

2.2.2. Turbidity Measurement

Turbidity is a measurement of a solution's degree of "cloudiness" caused by the presence of suspended particles. The solution grows cloudier when the barium sulphate precipitates. The turbidity meter detects how much light is dispersed in a solution by suspended particles [18].

2.2.3. Measurement of conductivity

The ability of a solution to carry electrical current is known as conductivity. It is proportional to the number of ionic species and their concentration in solution. As a result, a conductivity meter can be used to determine the concentration of barium ions. The conductivity of the solution decreases as the scaling process in the bulk solution occurs [18].

3. Materials and methods

3.1.ROSE extraction and synthesis

Soxhlet extractor apparatus was used in this study for extraction, which comprises of a condenser, a reservoir, and an extraction compartment with a siphon tube and a solvent permeable thimble. Acetone and all other chemical reagents/catalysts for synthesis were of analytical grade.

For each extraction cycle, 500g of pulverized red onion skin was placed inside the thimble, and 250ml of acetone was poured into the reservoir. The acetone vaporizes when heated by a heating mantle, then condenses in the condenser and drops into the thimble to extract the red onion skin. This cycle is repeated until all the extract has been removed and the solvent has become colorless. Following the extraction, the solvent was evaporated in a water bath, leaving the ROSE extract behind for further air drying [15,19].

The ROSE structure was then modified with other reagents to produce different products. A total of four (4) products were synthesized in this study by chemically modifying ROSE with furfuraldehyde, glutaraldehyde, and urea in the presence of an appropriate catalyst to produce a compound with a higher molecular weight and that is water soluble. ROS (pure red onion skin extract), ROF (red onion skin extract modified with furfuraldehyde), RUF (red onion skin extract modified with furfuraldehyde and urea), and ROG (red onion skin extract modified with glutaraldehyde) were the Scale inhibitors developed for this study.

3.2. Characterization

The presence of various functional groups was assessed by FTIR (Fourier transform infrared spectroscopy, Agilent Cary 630, US) in transmission mode from 4000 to 650 cm^{-1} at 8cm^{-1} resolutions with 32 scans [17]. Pure ROS extracts and all modified products were all assessed.

3.3. Synthetic water preparation

Synthetic brines were made by dissolving the appropriate inorganic salts in distilled water according to the National Association of Corrosion Engineers (NACE) standard, TM0197-2010, Item No. 21228 [18]. Brine was separated into two solutions: barium brine and sulphate brine as shown in Table 1. These solutions were made separately by weighing the appropriate amount of salts and mixing them with distilled water, then mixing them at a 1:1 ratio during experiment runs. To remove undissolved salts, the two brines were filtered through 0.45m membrane filter paper.

Table 1. Composition of synthetic water

Scale type	Brine concentration, g/L (ACS reagent grade)
$BaSO_4$	A. Barium containing Brine: NaCl = 7.50, $BaCl_2.2H_2O$ = 0.66 B. Sulphate containing Brine: NaCl = 7.50, Na_2SO_4 = 0.80

3.4. Bulk jar test

The bulk jar test was used to assess the ability of developed scale inhibitors (SI) to prevent the precipitation of Barium sulphate from solution under static conditions as described in the NACE standard method for laboratory screening tests [18]. The experiment consists of scaling brines mixed in 100 ml bottles under the test conditions described in Table 2. Following the BaSO4 precipitation, the concentration of barium was measured as a function of time (t), as described in American Society for Testing and Materials (ASTM) D3651 [19]. The test results were calculated as percentage inhibition of BaSO4 for each scale inhibitor concentration, as shown in Equation (2).

$$\text{Percentage inhibition} = \frac{m_2 - m_0}{m_1 - m_0} X\,100 \qquad (2)$$

where m_2 is the mass concentration of Ba^{2+} ions after inhibitor functions (sample); m_1 is the mass concentration of Ba^{2+} ions in the control solution; m_0 is the mass concentration of Ba^{2+} ions of the blank.

The test of the mass concentration of Ba^{2+} ions also followed the method specified by the standard NACE Standard TM0197-2010, Item No. 21228 [18]. Analysis of the blanks establishes the "zero inhibition" concentration of the Ba^{2+} ions for the test. Analysis of the controls establishes the maximum possible (100% inhibition) Ba^{2+} values. The concentration values obtained are required for the calculation of test results in Section 3.

Table 2: Static jar test condition

Scenario	Temperature (°C)	Time (Hrs)	Scenario	Temperature (°C)	Time (Hrs)
Test 1	71	4	Test 3	90	4
Test 2	71	22	Test 4	90	22

4. Results and discussion

4.1. Characterization of ROS

The FTIR spectra shown in Figure 1 were used to confirm the presence of the required functional groups in red onion skin extract. Scale inhibitors typically consist of many active functional groups of similar or different types that have the capability to bind strongly or weakly with the cations of scales or with the forming nuclei or with the growing crystal, thereby holding them in aqueous solution [14].

Figure 1 shows that the peak value around 821.130cm^{-1} was assigned to C-CI stretching vibration of chloro compound. The peaks around 963.027cm^{-1}, 1089.659cm^{-1}, 1130.799cm^{-1}, 1164.260cm^{-1}, 1197.375cm^{-1} and 1272.913cm^{-1} were assigned to C-O stretching vibration of ether compound respectively. The peak values around 1320.930cm^{-1} and 1376.278cm^{-1} were assigned to C=C anti-symmetric vibration of ethene compound respectively. The medium band around 1506.949cm^{-1}, 1599.425cm^{-1} and 1640.911cm^{-1} were assigned to N-H stretching vibration of 1° amine compound respectively. The peak around 1707.152cm^{-1} was assigned to C-O stretching vibration of cyclic ester compound. The absorbance around 2102.246cm^{-1} was assigned to COO stretching vibration of carboxylic acid. The peak around 2344.563cm^{-1} corresponds to C-N stretching vibration of nitrile compound. The weak band around 2851.19cm^{-1} was assigned to C-H stretching of methylene compound. The peak values around 2918.225cm^{-1} were due to SCN stretching vibration of thiocyanate compound. The strong band around 3257.310cm^{-1} was assigned to OH stretching vibration of 1^0 alcohol compound**.** The expected functional groups responsible for the scale inhibition properties have been revealed.

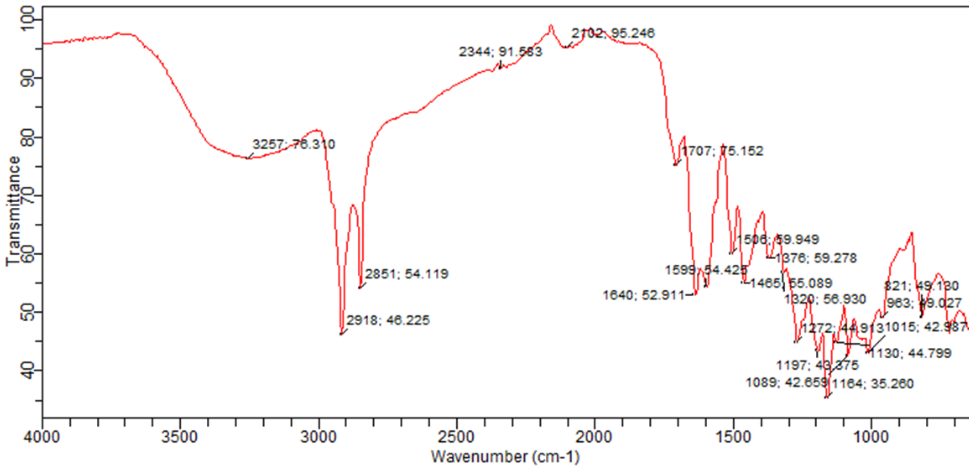

Figure 1. FTIR spectrum of ROS

4.2. Scanning electron microscope (SEM) analysis

Figure 2 shows SEM images of barium sulphate obtained in the absence of an inhibitor and at a low dosage.

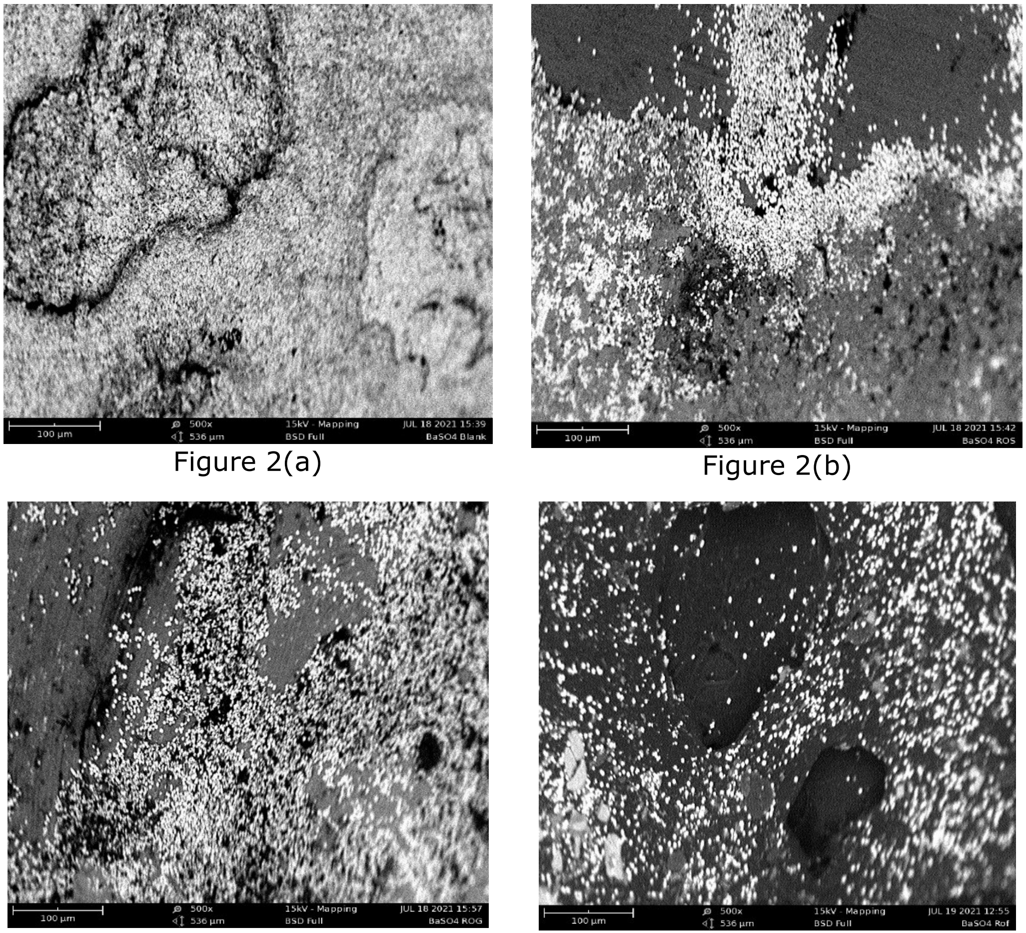

Figure 2(a)

Figure 2(b)

Figure 2(c)

Figure 2(d)

Figure 2. SEM images of $BaSO_4$ without 2(a) and with inhibitor 2(b, c, d)

Figure 2a depicts the structure of barium sulphate scale in the absence of any inhibitor; Figure 2b depicts the structure of barium sulphate scale in the presence of ROS; Figure 2c depicts the structure of barium sulphate scale in the presence of ROG; and Figure 2d depicts the structure of barium sulphate scale in the presence of a low dosage of ROF. When small doses of inhibitors were added to the rule dense-flake crystals, they became loose, indicating that the crystals were suppressed. Furthermore, the diameter of the crystals increases with inhibitor, which could be attributed to the fact that the SI influences the surface phase of the barium sulphate crystal [20].

4.3. Scale inhibition performance

The experiment revealed that increasing the inhibitor dosage increases the inhibition for all tested blends. In addition, once the minimum inhibition efficiency was reached, there was a slight decrease. Figure 3(a,b,c,d) depicts a plot of inhibition versus dosage for all scale inhibitor blends tested. Figure 3(a) depicts the obtained inhibition efficiency for ROG, which has the highest inhibition performance of 88 percent at an 80ppm dosage. Figure 3(b) depicts the calculated ROS efficiency, which has the second-highest inhibition efficiency observed from ROS performance, with 83 percent efficiency at 80ppm. When RUF was used, it inhibited at a rate of 70 % at 100 ppm, while ROF inhibited at a rate of 66 %. These new inhibitor blends have a relatively good inhibition efficiency.

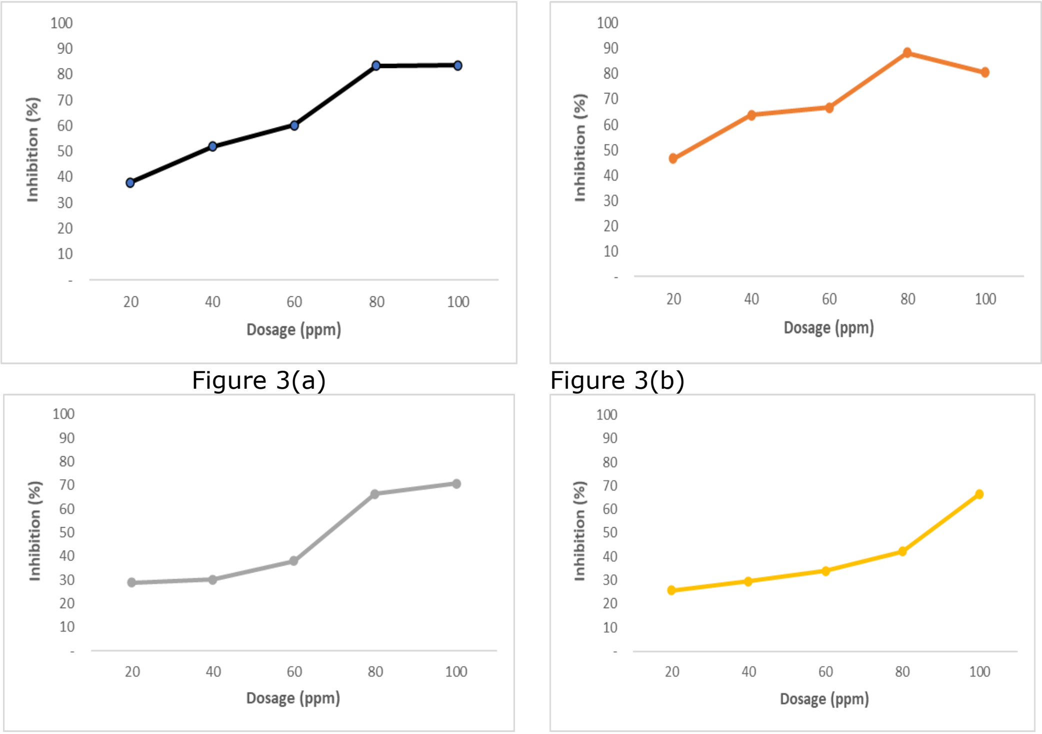

Figure 3(a)

Figure 3(b)

Figure 3(c)

Figure 3(d)

Figure 3(a): Relationship between dosage of ROS and inhibition efficiency; Figure 3(b): Relationship between dosage of ROG and inhibition efficiency; Figure 3(c): Relationship between dosage of RUF and inhibition efficiency; Figure 3(d): Relationship between dosage of ROF and inhibition efficiency (71 °C_22 hrs)

4.4. Effect of temperature on scale inhibitor performance

Figure 4a shows an inhibition rate of 88 percent for ROS at both 71°C and 90°C. Similarly, the graphs of ROG (Fig. 4b), RUF (Fig. 4c), and ROF (Fig. 4d) show no significant increase as temperature rises. As a result, no additional dosage is required for barium sulphate scale inhibition at higher temperatures in the scope of this work.

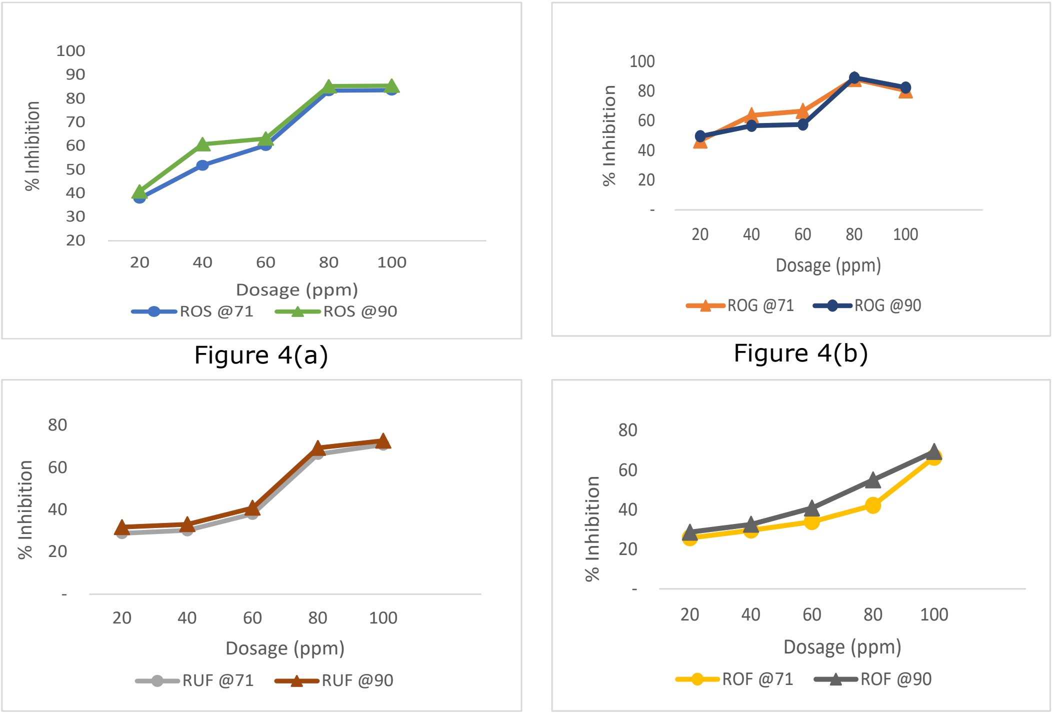

Figure 4(a) Figure 4(b)

Figure 4(c) Figure 4(d)

Figure 4(a), Effect of temperature on the inhibition efficiency of ROS; Figure 4(b), Effect of temperature on the inhibition efficiency of ROG; Figure 4(c), Effect of temperature on the inhibition efficiency of RUF; Figure 4(d), Effect of temperature on the inhibition efficiency of ROF

4.5. Effect of evaluation time on scale inhibition rate

Figure 5a, 5b, 5c, 5d depicts the effect of evaluation time on the performance of scale inhibitors. It demonstrates that for all scale inhibitor blends, the inhibition efficiency at a 22-hour evaluation time is greater than that at a 4-hour evaluation time, indicating that the inhibitors play a continuous inhibition performance.

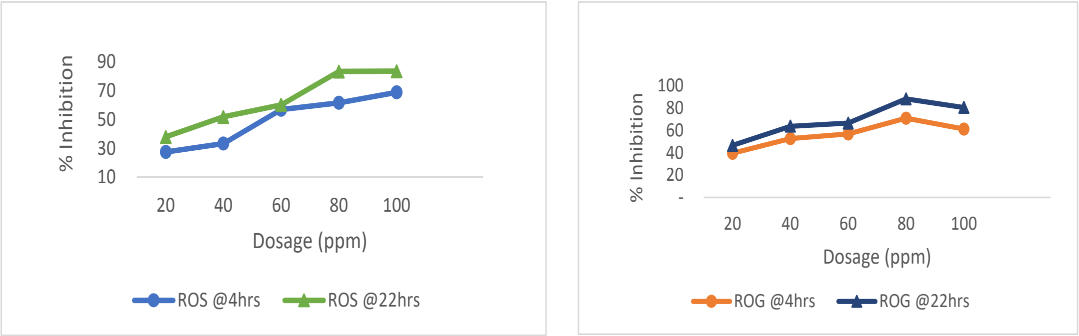

Figure 5(a) Figure 5(b)

Figure 5(a). Effect of evaluation time on the inhibition rate of ROS; Figure 5(b): Effect of evaluation time on the inhibition rate of ROG

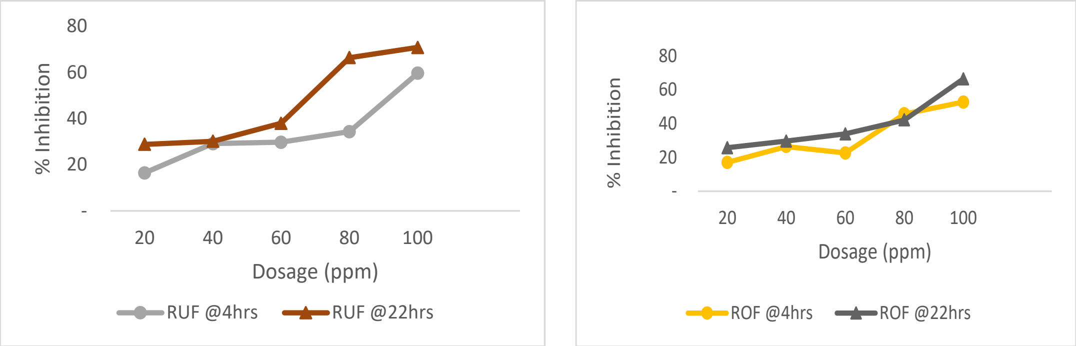

Figure 5(c)

Figure 5(d)

Figure 5(c). Effect of evaluation time on the inhibition rate of RUF; Figure 5(d): Effect of evaluation time on the inhibition rate of ROF

4.6. Comparison of formulated blends with existing scale inhibitor

Figure 6 depicts a comparison of the newly formulated inhibitor blends with an existing conventional inhibitor (CSI) for barium sulphate scale. CSI demonstrated the high inhibition efficiency of 99.83 percent at 80ppm, followed by ROG with 88.23 percent efficiency at 80 ppm. Other inhibitor blends exhibited good efficiency as well. Therefore, this shows that red onion skin exhibits a relatively good inhibition efficiency when compared to an already existing scale inhibitor for barium sulphate scale.

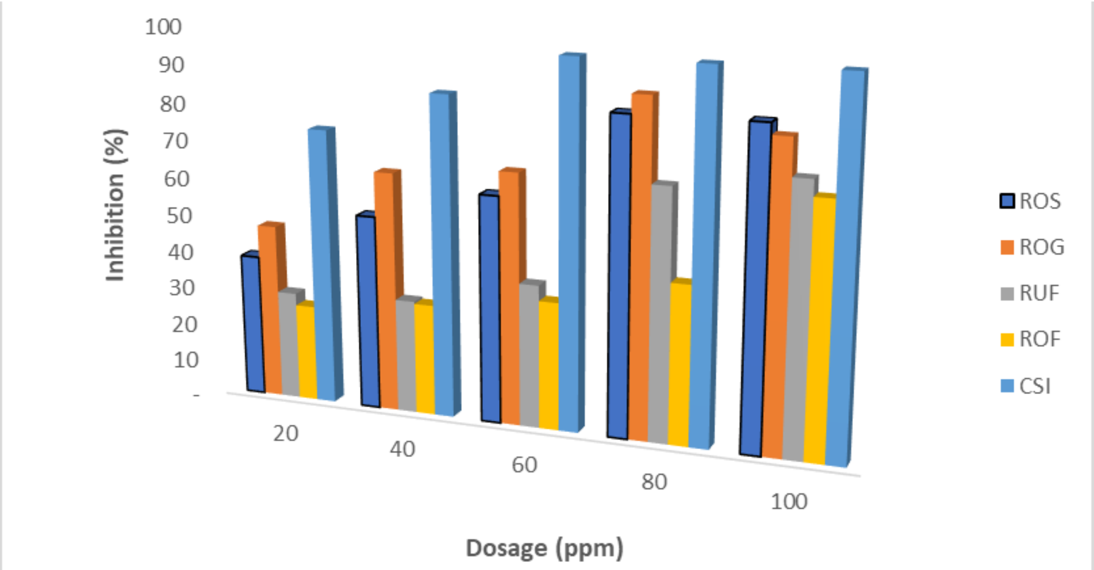

Figure 6. Comparison between CSI and newly formulated scale inhibitor blends

4.7. Modeling of the treatment fluid

To establish optimum treatment concentration of the inhibitor blends, the dosage of each inhibitor was plotted against various concentration. A logarithmic graph with the best regression value and hence most suitable treatment fluid dissolution pattern was established with equation of type:

$$y_{pc_i} = \sum_{k=0}^{n=4} a_k x_i^k \quad ; \quad x_i = {}^{c_i}/_{20}\ , 1 \le i \le 5, n, k \ge 0 \qquad (3)$$

The Model equation therefore becomes:

For ROS $y = -2.4101x^4 + 27.477x^3 - 107.39x^2 + 179.9x - 59.646$ (3a)
For ROG $y = -3.3811x^4 + 39.317x^3 - 158.51x^2 + 268.15x - 98.896$ (3b)
For RUF $y = -2.452x^4 + 26.884x^3 - 96.778x^2 + 140.24x - 39.036$ (3c)
For ROF $y = 0.3592x^4 - 2.9986x^3 + 9.1993x^2 - 8.0881x + 27.269$ (3d)

where y is the inhibition efficiency at various concentrations and x is the concentration of SI; Equation 3a, 3b, 3c, 3d, are the model equations that can be used to obtain the required inhibition of barium scale at different concentration within these experimental conditions.

5. Conclusions

A potential green scale inhibitor for oilfield was developed and tested on barium sulphate. ROG had an inhibition efficiency of up to 88 percent, followed by ROS, which had an efficiency of 83 percent. ROF and RUF, the other inhibitor blends, also achieved a moderate inhibition efficiency of 66 and 70 percent, respectively. To achieve a higher inhibition efficiency, further attempts at increasing the dosage of these two inhibitor blends are required.

No additional antiscalant is required to achieve well-inhibition performance at higher temperatures. At higher temperatures, inhibitor blends remain stable. Because the diameter of barium sulphate formed at low inhibitor dosage is larger than that formed under blank conditions, adequate dosage for barium sulphate prevention is critical. Scale inhibitor blends are non-hazardous to human health, environmentally friendly, and inexpensive.

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Conflict of interest

The authors declare that there is no conflict of interest.

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