Inhibition of $BaSO_4$ Scale Formation in Oilfield Equipment Using Rutin from Sweet Orange (*Citrus Sinensis L*) Mesocarp Extract (SOMEX)

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***Abstract-** The majority of commercial scale inhibitors used in the oilfield are synthetic, expensive, poisonous, non-biodegradable, ecologically harmful, and non-renewable. The search for a better, and more eco-friendly scale inhibitor alternative to the available ones has remain ongoing. Rutin obtained from sweet orange mesocarp extract (SOMEX) was modified using furfuraldehyde, and urea at varying molar ratios to form a novel green scale inhibitor, namely, Rutin (RU), Rutin-Furfural-modified polyphenolic resin (RFP) and Rutin-Furfuraldehyde-Urea- modified polyphenolic resin (RFUP). In order to create the scale inhibitors RFP and RFUP, the rutin extract, RU was first mixed with Furfuraldehyde in a 2:1 molar ratio and heated to 130ºC with 2 ml of 1% w/v NaOH for 60 minutes to obtain RFP; then mixed with Furfuraldehyde and Urea in a 2:2:1 molar ratio, heated at 70ºC with 2 ml of 1% w/v NaOH for 30 minutes to obtain RFUP. FTIR was used to characterise the inhibitors. Results of analyses show that RU, RFP and RFUP inhibitors are alkaline, thermally stable at a temperature of 130ºC after 24 hours and compatible with the formation brine at a temperature of 25ºC. The inhibitors' efficacy were assessed using* $BaSO_4$ *brine and synthetic formation water that was generated according to the National Association of Corrosion Engineers (NACE) standard. From the results of the inhibitor dosage evaluation test, the lowest effective RU dose of 20 mg/L resulted in an inhibition rate of 70.40% on* $BaSO_4$ *scales formation. As the inhibitor dose was raised above 20 mg/L, the rate of inhibition decreased. Longer contact times result in better inhibitor activity on the formation of* $BaSO_4$ *scales at 71ºC and 78ºC respectively. Additionally, it was noted that the inhibition of RU, RFP, and RFUP on the formation of* $BaSO_4$ *scale rose when the temperature was raised from 71ºC to 90ºC at a process time of 4 hrs. But when the process time was extended to 24 hrs the inhibition efficiency of the inhibitors initially increased with temperature increase up to a pick temperature of 78ºC, after which the inhibition efficiency starts to decrease slowly till it gets to the minimum. The findings of this study demonstrate that rutin derived from SOMEX and its derivatives has a good potential as green scale inhibitor for oilfield operations.**

***Keywords:** Sweet orange mesocarp extract (SOMEX), rutin (RU), RFP, RFUP, Barium sulphate scale* ($BaSO_4$)*, commercial inhibitor (CSI).**

I. INTRODUCTION

Scale formation in oil wells is one of the most common problems confronting oil and gas industries around the world. Scaling presents dual risks to both environmental integrity and economic efficiency in oilfields, not only increasing the costs related to equipment maintenance and replacement but also disrupting production, thereby diminishing overall profitability [1], [2].

Worldwide, scale consequences cost more than $1.4 billion each year, and in Africa almost $160 million yearly [3]. Scaling can be caused by many issues in the oil and gas sector but in simple terms it occurs when dissolved salt ions found in produced water are exposed to a change such as pressure or temperature and during mixing with other produced stream/seawater which contain other dissolved salt ions that are incompatible with them which, once mixed, create a new insoluble salt which then drops out as scale. Drilling wells disturbs the formation's long-term temperature, pressure and chemical stability [4]. Scales are precipitated as the system adjust to achieve a new stability. Potential issues may arise in the event of sudden changes in temperature or pressure, the mixing of various liquids, or the introduction of inappropriate chemicals with undesirable effects [5].

During oilfield exploitation, continuous fluctuations in system pressure, temperature, and pH considerably alter the solubility of ions, including Ba^{2+}, SO_4^{2-}, Mg^{2+}, Ca^{2+}, and CO_3^{2-}, thereby promoting their crystallization and subsequent precipitation as mineral scale [6], [7], [8], [9]. Scale may form in several areas of the petroleum production process, including formation, transfer lines, storage tanks, treatment equipment, tubing, and more. After a coating has been formed, it will only thicken more if without treatment. Depending on the amounts of scale formed this can lead to a restriction in flow or even a blockage.

Most commonly formed scales in the oilfield and gas industry includes – calcium sulphate, calcium carbonate, barium sulphate, strontium sulphate, ferrous carbonate, ferrous sulphide and pyrite [10], [11]. Of all the scales in the oil industry, barium sulfate scales are the most easily precipitated due to the very low solubility (2.3 mg/L at STP) of barite in water [12]. Precipitation of barium sulphate occur when the solution concentration has exceeded its solubility, and attained supersaturation. Barium sulfate scales are precipitated due to the mixing of incompatible waters during waterflooding. Formation water that is highly rich in barium cations when mixed with injection seawater that is enriched with sulphate anions leads to formation of barium sulfate (Equation 1) [13].

Depending on the pH, temperature and pressure, the salts tend to reach a point of super saturation leading to a metastable condition which leads to phase separation (ionic salts convert from dispersed phase to crystals). The salts precipitate by nucleation and crystal growth [14]. Once these crystals are formed, they tend to adhere to form layers or blocks which causes major interference with fluid flow. Besides this process, barium sulfate can also be precipitated due to change in thermodynamic, hydrodynamic and kinetic parameters including sudden change in pressure and temperature in the reservoir or during the processing of the brine on the surface [15], [16], [17], [18].

$$Ba^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \leftrightarrow BaSO_4{}_{(s)} \qquad 1$$

Barium sulphate scales possess capacity to alter the permeability and porosity of oil reservoir as well as triggering considerable alterations in injector and producing reservoirs [19], [20]. It forms a hard, crystalline scale that reduces pipe diameter, damages permeability in formations, and promotes under-deposit corrosion. Barium sulphate scale could be formed at any point in the production system depending on where the formation and seawater mix.

The removal of $BaSO_4$ scale is particularly difficult as it is insoluble in most fluids and cannot be dissolved by acid. Where and when it is possible mechanical methods (e.g., milling, drilling) are required for removal. $BaSO_4$ scale treatment has largely focused mainly on its prevention through the use of scale-control chemicals. The severity of the scaling problem is determined both by the scaling rate and the efficiency of the chemical inhibitors [21].

Scale deposition problems have been managed by injecting scale inhibiting chemicals into the area of interest to inhibit the formation of scale. The use of inhibitors have proved a more efficient way of managing oilfield scales. Scale inhibitors are water-soluble chemicals that are designed to prevent or retard the nucleation and the crystal growth of inorganic scales which can reduce the rate of scale formation to almost zero. Inhibitors are typically used before scaling to prevent scale deposition or after remediation to prevent further scaling. Inhibitors can be used at producing fluids through gas lift, topside injection system, or can be squeezed downhole as cost-effective threshold scale inhibitors. Squeeze treatments is achieved by injecting chemical scale inhibitors in the producers near wellbore [22].

Scale inhibitors have been the preferred downhole treatment for the prevention or control of scale formation and its subsequent deposition, by application in a 'squeeze' treatment [23], [24].

Addition of chemical inhibiting agents, are economical and simple effective means of preventing of scaling [25]. Scale inhibitors have advantage in sustaining formation integrity and improving enhanced oil recovery (EOR). Natural chelating chemicals, as scale inhibitors, are a great alternative to more conventional methods of scale management.

Scale precipitation can be avoided by chelating the scaling cation. The petroleum industry has a long history of using chelating agents namely ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), or diethylenetriaminepentaacetic acid (DTPA) to reduce scale [26]. Chelating agents are capable of dissolving barium sulphate without a separate conversion step. A jar test to evaluate the effectiveness of three different scale inhibitors - Methylene Phosphonic Acid (DETPMP), Poly- Phosphino Carboxylic Acid (PPCA), and Phosphonate-based scale inhibitor (PBSI) on the inhibition of barium sulphate scale formation using a synthetic brine was conducted [27].

The test was carried out at the atmospheric pressure and at different temperatures ranging from 50ºC, 70ºC to 90ºC and a time period of 4h. Inhibitor concentrations of 10 ppm and 30 ppm made up with synthetic seawater were tested.

Their report shows that at higher temperatures the rate of $BaSO_4$ precipitation decreases since the solubility of $BaSO_4$ increases with increasing temperature. At 60ºC temperature, PPCA showed very efficient $BaSO_4$ inhibition effect where it reduced most amount of $BaSO_4$ compared to the DETPMP and PBSI inhibitors. In respect to inhibitor performance at different concentration, the three inhibitors performed better at 30 ppm than 10 ppm. However, the order of performance according to [27] is PPCA >>> DETPMP >>PBSI. [28] synthesized a scale inhibitor by radical polymerization of three monomers – maleic anhydride (MA), maleic acid (MAA), and styrene-butadiene-styrene (SBS) in the ratio 6:1:1 respectively. The inhibition performance of the scale inhibitor was investigated on barium sulphate scale. They reported optimum efficiency of 89.1% at inhibitor concentration of 160 mg/L under the conditions of pH = 7 and 70ºC. A scale dissolver for barium sulphate scale was developed [29]. The composition of the developed dissolver has diethylenetriamine pentaacetic acid (DTPA) as a chelating agent, oxalic acid, and tannic acids as an activator, nonionic surfactant, and water as the base fluid. Two barium sulphate scale samples were used to evaluate the efficiency of the developed dissolver:

sample 1 is 100% barium sulfate and sample 2 has 97.75% barium sulfate and 2.25% of quartz. They reported a dissolution efficiency of 76.9 and 71.2% at 35°C and 91.3 and 78.4% at 90°C for samples 1 and 2, respectively. They also reported that the developed dissolver showed a very low precipitation tendency for the scale dissolved solids (1.9 and 3.2% for samples 1 and 2, respectively) under 35°C for 24 hours. Nevertheless, regardless of their efficacy, the majority of commercial scale inhibitors and chelating agents used in the oilfield are synthetic, expensive, poisonous, non-biodegradable, ecologically harmful, and non-renewable [30]. For the best inhibitory effect, it is essential to choose non-toxic, effective, biodegradable, renewable, and non-absorbed inhibitors [31]. Green antiscalants are renewable, biodegradable, and good for the environment [32]. Additionally, they deal with a growing variety of environmental issues.

The cost and environmental concerns of available scale inhibitors continue to increase the interest of researchers to develop better and cheaper alternative to the available ones. This informed the interest in sweet orange mesocarp extract (SOMEX), a locally abundant renewable source as possible raw material for oilfield scale inhibitors. Sweet orange mesocarp (SOM) is a by-product of sweet orange rinds. Rutin, is a key component of specifics, [33], [34], [35], [36].

It has been extracted from sweet orange mesocarp [37]. Rutin obtained from orange mesocarp has been used to remove some metal ions. Unmodified orange mesocarp residue after extraction of rutin was used to bind 56% of Mg, 81% of Zn, 71% of Cu, 73% of Pb and 85.05% of Cd, while the modified residue using 2,4-Dichloro-6-(Phenoxy-4′-sulphonic acid)-1,3,5-triazine bound 63.05% of Mg, 37% of Zn, 43.25% of Cu, 33.05% of Pb and 86.45% of Cd [38]. Also, rutin extracted from orange mesocarp was modified to obtain Carboxylated-Toluene Di-isocyanate Orange Mesocarp Extract Resin (CTOMER) and Sulphonated-Toluene Di-isocyanate Orange Mesocarp Extract Resin (STOMER). These modified orange mesocarp extract were used to remove zinc, copper, nickel and cobalt ions from aqueous solution [39].

It has been shown that the naturally occurring flavonoid rutin has remarkable metal chelating properties [40], [41]. Multiple studies have shown its complex-forming capabilities with ions of main group and transition metals as well as those from the lanthanide family of metals. Among these ions are

Ca^{2+}, Mg^{2+} Ba^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} [38], [42], [43], [44], [45]. The potential health benefits arising from the antioxidant activities of rutin and its use in binding and removing of metal ions from aqueous solution [38], [39], [46]; stimulated our interest in the study of rutin as scale inhibitor. Rutin is non-toxic, biodegradable and has shown no bioaccumulation [47].

Rutin like other flavonoids, contain functional hydroxyl groups. These functional hydroxyl groups mediate their antioxidant effects by scavenging free radicals and/or by chelating metal ions [48], [49].

The chelation of metals is crucial in the prevention of radical generation which precipitate and deposit as scales [50], [49]. Sweet orange is one of the important fruits in Nigeria, because it is a source of vitamin C. It produces large volumes of wastes, which has caused environmental nuisance in the region. The objective of this study is, therefore, to develop inexpensive, effective, environmentally friendly and renewable inhibitor or chelating agent from sweet orange mesocarp, an agricultural waste which is available in Nigeria.

If such an antiscalant is developed, it may replace the existing commercial scale inhibitors and chelating agents used in the oilfield which are expensive, non-biodegradable, ecologically harmful, and non-renewable. And also assist in combating the menace of barium sulphate scale in oil and gas industries.

II. MATERIALS AND METHODS

Sample collection and Processing

Fresh sweet Orange (Citrus sinensis) fruits were bought from mile 1 market in Port Harcourt, Rivers State, Nigeria. They were washed with deionized water and peeled with kitchen knife to obtain the mesocarp. The mesocarp was air dried, crushed into a fine powder with a commercial grinding machine, sieved to 150µm particles sized and stored in an airtight bottle at room temperature for extraction [37]. The crushing was done to increase the surface area of the sample in order to achieve proper interaction and penetration between the extracting solvent and shell materials during the extraction.

Extraction and purification of rutin from sweet orange mesocarp

The bioflavonoid rutin in the sweet orange mesocarp (SOM) was extracted with ethanol. The study adopted a solvent extraction mechanism [51], [52], and was performed according to [37].

The crude extract was filtered and ethanol was evaporated on vacuum rotary evaporator to obtain a concentrated crude extract. The concentrated extract was further air/sun dried for 24 hours to ensure solvent has completely evaporated and the product is in powder form before storage in an air tight bottle.

Crude extract obtained after the extraction was purified employing two different methods: solvent-solvent extraction using Hexane as solvent and was performed according to [52]. Extraction was done in separating funnel for 1hr to 2hrs and then the two phases: raffinate and extract phases were separated. The sample was collected from both the phases for the estimation of rutin concentration. The raffinate was later filtered and the filtrate discarded to remove fats, waxes and pigments.

Column chromatography using 200-micron particle size silica gel as stationary phase and ethanol as solvent in the column was performed. Rutin content was quantitatively determined by using spectrophotometer according to [53]. The rutin obtained was concentrated again using a rotary evaporator and recrystallized from ethanol to obtain pure rutin. The pure rutin obtained was characterized and verified using infrared spectroscopy and yield and purity of the isolated rutin were determined using GCMS.

Further purification of the sweet orange mesocarp extract was carried out by crystallization according to [37]. A saturated solution of rutin was created by dissolving the concentrated rutin extract in ethanol (solvent). The saturated solution was cooled slowly to a temperature of 4°C. A small amount of pure rutin crystals (seed crystals) were added to the solution to initiate crystallization. The solution was allowed to stand for 24 hrs. At end of 24 hrs, the solution was filtered and crystals of rutin formed were collected. The crystals were washed with a small amount of cold ethanol to remove impurities.

The pure crystals of rutin were dried in a desiccator to remove any remaining solvent. During the process of crystallization, the pH of solution was maintained at pH of 5 to ensure rutin solubility for effective crystallization. Also cooling rate was controlled to prevent rapid crystallization, which can lead to impure crystals.

Modification of rutin with furfuraldehyde

The Rutin extract (10 g, 2 mol) and furfuraldehyde (0.79 g, 1 mol) was charged into a pre-weighed 250 ml round bottom flask (the reactor vessel) and connected to a Dean-Stark trap fitted to a condenser on a retort stand and placed on a hotplate equipped with a mechanical stirrer. The solution mixture was heated to a temperature of 130℃ and the catalyst; 2 ml of 1% w/v NaOH was added followed by refluxing for 1 h under magnetic stirring respectively.

At the end of the reaction (when the volume of water condensed in the dean and stark trap is constant), the flask was allowed to cool, the product weighed using an analytical weighing balance. A portion of this product was dissolved in 10% w/v NaOH and concentrated with a rotary evaporator. The products obtained were both placed in a desiccator to dry and stored in airtight containers for further use. The prepared Rutin-furfuraldehyde resins (RFP) were milky white in color and were characterized using its FTIR spectra.

Modification of rutin with furfuraldehyde and urea

Furfuraldehyde (1.59 g, 2 mol) and Urea (0.50 g, 1 mol) were charged into a pre-weighed 250 ml round bottom flask (the reactor vessel) and connected to a Dean-Stark trap fitted to a condenser on a retort stand and placed on a hotplate equipped with a mechanical stirrer. The solution mixture was refluxed for 30 minutes at a temperature of 70°C. The rutin extract (10 g, 2 mol) and the catalyst; 2 ml of 1% w/v NaOH based on rutin, was added and the mixture refluxed for 60 minutes under magnetic stirring. At the end of the reaction (when the volume of water condensed in the dean and stark trap is constant), the flask was allowed to cool, the product weighed using an analytical weighing balance, placed in a desiccator to dry and stored in an airtight container for further use. The prepared Rutin-furfuraldehyde-urea resin (RFUP) was milky yellow in color and was characterized using its FTIR spectra.

Preparation of synthetic formation water (Brine)

In the laboratory, the protective performance of scale inhibitors was evaluated in synthetic formation water because using synthetic formation water, instead of actual formation water, can improve the reproducibility of test results. The synthetic formation water was prepared based on NACE Standard TM0197-2010 [54], for barium sulphate composition in a produced water.

Two component brines A and B were defined such that when mixed in equal volumes, result in a composite brine with concentrations equivalent to the scaling brine expected to occur in the field. Brine A, contained all Ba^{2+}, and brine B, contained SO_4^{2-}. The remaining ions, such as Na^+ and Cl^-, were allotted such that the ionic concentrations in the two component brines are comparable if not equal. Brines A, and B were prepared according to [54], with the following composition: 7.50 g/L NaCl (ACS reagent grade); 0.66 g/L $BaCl_2.2H_2O$ (ACS reagent grade) for barium containing brine (A), and 7.50 g/L NaCl (ACS reagent grade); 0.80 g/L Na_2SO_4 (ACS reagent grade) for sulphate containing brine (B).

For consistency, very small quantities of insoluble materials remaining after the specified reagents have completely dissolved in solutions were filtered through a 0.45-μm filter. Distilled water was used to prepare chemical solutions of formation water in laboratory experiments. This was done to eliminate the influence on properties of the composition and the results of experiments of ion determination.

Medical syringes and high precision laboratory balances were used for the exact values of the reagent’s masses. This ensures the precision of the required volume of the composition, as well as the precision of concentrations of components, in the preparation of the aqueous formation brine solution.

Evaluation of inhibition efficiency of developed scale inhibitors

The effectiveness of the inhibitor can be evaluated by its effect on real formation water or synthetic formation water. However, the use of synthetic formation water provides a more comprehensive assessment for a specific type of salt [55], [56]. The effectiveness of an inhibitor was evaluated by the mass change of precipitates, which were formed in mineralized water in the presence of inhibitor with respect to water with no inhibitor [57]. The protective effect of an inhibitor was calculated by the following Equation 2:

$$E = \frac{Mo - M}{Mo}\ x\ 100\% \qquad 2$$

where E is the scale inhibitor efficiency; M and Mo are the mass of salt precipitates in water with and without inhibitor, respectively, (mg). Working solutions were prepared for studying the spontaneous process of $BaSO_4$ precipitation in the aqueous solutions in accordance with NACE standard methods. Static Jar test was used to give a measure of the ability of scale inhibitors to prevent the precipitation of barium sulphate from solution at 71°C. The static bottle test gives information about inhibitor's effectiveness and thermal stability in preventing scale formation in the bulk phase and/or bottle surfaces. Tests were conducted at various scale inhibitor concentrations (dosages) to obtain a better understanding of performance under laboratory conditions as set by NACE standard methods. The scale inhibitor concentration required for a field application is likely to be different from that determined under these laboratory conditions

Barium sulphate precipitation test

Barium sulphate ($BaSO_4$) precipitation test was carried out according to [54] procedures. Sufficient quantities of Brine A, and Brine B prepared by weighing out the salts described above and dissolving them in deionized/distilled water to provide the required ionic concentrations. Sufficient buffer was mixed into Brine A so that the composite brine mixtures (A+B) have the required pH at the test temperatures. The required quantity of buffer was determined in advance by mixing, at test temperature, appropriate aliquots of Brine A and Brine B quickly but carefully adding buffer. Each component brine was through a 0.45 µm cellulose acetate membrane filter. The component brines were transferred to labelled flasks fitted with dispensers capable of reproducibly delivering 50.0mL to the test bottles. Flasks were placed into a constant-temperature bath set at 71^{o}C. A stock solution of each scale inhibitor to be evaluated was prepared and measured gravimetrically.

50 mL of component brines were delivered into labelled test bottles. All tests were performed at least in duplicate. Some test bottles containing Brine B were labelled with the designation "Control" while some bottles with no inhibitor doze were given the designation "Blank." A range of aliquots of each scale inhibitor to be evaluated were measured into test bottles containing Brine B. Test bottles were placed into a constant-temperature bath set at the test temperature of 71^{o}C.

At the test temperature, Brine A was mixed with Brine B. Cap was tightly secured and agitated in 10 up-and-down cycles for proper mixing. Immediately, the test bottles were placed back into the constant-temperature bath stabilized at the test temperature and monitored for the test duration which reflects the likely residence time of the scale inhibitor in the field application being modelled.

At the end of the specified test duration, each test bottle was removed, in turn, from the water bath and samples of the brine were immediately taken for analysis. Each analytical sample was filtered without delay through a 0.2 µm syringe filter into a clean glass container for cation analysis. For each scale inhibitor concentration, the test results were calculated and reported as percentage inhibition of $BaSO_4$ using equation 2 or equation 3.

$$\%\ \text{Inhibition} = \frac{Ca - C_b}{C_c - C_b}\ X\ 100 \qquad 3$$

Where: C_a = concentration in the treated sample after precipitation, C_b = concentration in the blank after precipitation and C_c = concentration in the blank before precipitation

The standard deviation was also calculated using equation 4.

$$\%\ \text{Inhibition of } BaSO_4 = \frac{(M^{2+})sample - (M^{2+})blank}{(M^{2+})control - (M^{2+})blank}\ X\ 100 \qquad 4$$

Also, an inhibitor-brine incompatibility investigation was done by treating the theoretically non-scalnhnding mixtures of Brine A and Brine B with the highest concentration of the inhibitor(s) being evaluated, as some inhibitors may be incompatible with highly saline brines or with high concentrations of specific cations resulting in a deposit which may be mistaken for $BaSO_4$ and may remove the inhibitor from the solution

Performance Evaluation of Developed Inhibitors under Operational Variables

Effect of dosage on $BaSO_4$ scale inhibition

A stock solution of each scale inhibitor to be evaluated was prepared and measured gravimetrically. Five different concentrations of a given inhibitor, 20, 60, 100, 200 and 400 mg/L were pipetted into six different test cells. 50 mL of sulfate-containing brine was added to each of the test cell and mixed thoroughly. 50 mL of calcium-containing brine was also added to each of the test cells. Test cells were immediately capped and agitated to mix the brines and the scale inhibitor thoroughly.

Duplicate blanks were prepared by setting aside two samples of the barium containing brine (50 mL each). Barium ion concentration of the blanks were determined before precipitation. Test cells and blanks were immersed to 75% of their lengths in a water bath at 78±1°C for 24 hrs. The test cells were removed after the required time exposure avoiding agitation. Test cells were allowed to cool to 25 ±5°C for a time not to exceed two hours. At the end of the specified test duration, each test bottle was removed, in turn, from the water bath and samples of the brine were immediately taken for analysis. Each analytical sample was filtered without delay through a 0.2 μm syringe filter into a clean glass container for cation analysis. Barium ion concentration was determined by procedures given in ASTM D3651-11 [58], and ASTM D3986 [59]. All tests were performed at least in duplicate. The average of the duplicate barium ion concentration values as mg/L barium sulphate retained in solution for each inhibitor test concentration and the blank was reported. For each scale inhibitor concentration (dosage), the test results were calculated using Equation 2 or 3 and reported as percentage inhibition of $BaSO_4$.

Effect of temperature on $BaSO_4$ scale inhibition

20 mg/L of each scale inhibitor to be evaluated was pipetted into three different test cells. 50 mL of sulfate-containing brine was added to each of the test cell and mixed thoroughly. 50 mL of calcium-containing brine was also added to each of the test cells. Test cells were immediately capped and agitated to mix the brines and the scale inhibitor thoroughly. Duplicate blanks were prepared by setting aside three samples of the barium containing brine (50 mL each). Barium ion concentration of the blanks was determined before precipitation. Test cells and blanks were immersed to 75% of their lengths in three different water baths of different temperatures- 71ºC, 78ºC and 90ºC respectively for 4 hrs and 24 hrs. The test cells were removed after the required time exposure avoiding agitation. Test cells were allowed to cool to 25 ±5°C for a time not to exceed two hours. At the end of the specified test duration, each test bottle was removed, in turn, from the water bath and samples of the brine were immediately taken for analysis. Each analytical sample was filtered without delay through a 0.2 μm syringe filter into a clean glass container for cation analysis.

Barium ion concentration was determined by procedures given in [58], [59]. All tests were performed at least in duplicate. The average of the duplicate barium ion concentration values as mg/L barium sulphate retained in solution for each inhibitor test concentration and the blank was reported. For each scale inhibitor evaluated, the test results were calculated and reported as percentage inhibition of BaSO4 using Equations 2 or 3.

Effect of contact time on $BaSO_4$ scale inhibition

20 mg/L of each scale inhibitor to be evaluated was pipetted into four different test cells. 50 mL of sulfate-containing brine was added to each of the test cell and mixed thoroughly. 50 mL of barium-containing brine was also added to each of the test cells. Test cells were immediately capped and agitated to mix the brines and the scale inhibitor thoroughly. Duplicate blanks were prepared by setting aside four samples of the barium containing brine (50 mL each). Barium ion concentration of the blanks were determined before precipitation. Test cells and blanks were immersed to 75% of their lengths in four different water baths of the same

constant temperature of 71ºC ± 1°C and heated for a period of 4 hrs, 8 hrs, 12 hrs, and 24 hrs respectively.

At the end of the specified test duration, each test bottle was removed, in turn, from the water bath and were allowed to cool to 25 ± 5°C for a time not exceeding two hours. Samples of the brine were immediately taken for analysis. Each analytical sample was filtered without delay through a 0.2 µm syringe filter into a clean glass container for cation analysis. Barium ion concentration was determined by procedures given in [58], [59]. All tests were performed at least in duplicate. The average of the duplicate barium ion concentration values as mg/L barium sulphate retained in solution for each inhibitor test concentration and the blank was reported. For each scale inhibitor evaluated, the test results were calculated and reported as percentage inhibition of BaSO4 using Equation 2 or 3.

The above procedure was repeated by immersing the Test cells and blanks in water baths of constant temperature of 78ºC ± 1°C and heating for a period of 4 hrs, 8 hrs, 12 hrs and 24 hrs respectively.

III. RESULTS AND DISCUSSION

Effect of dosage on $BaSO_4$ scale inhibition

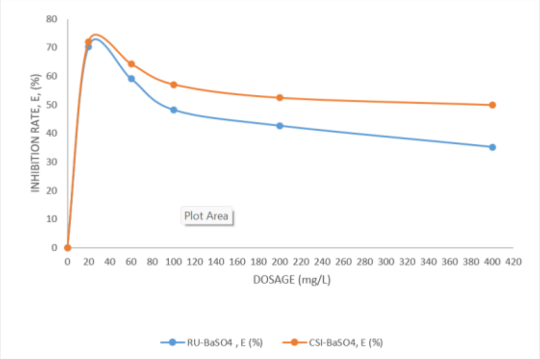

Figure 1: Effect of dosage on the performance of rutin and CSI on $BaSO_4$ scale formation

Figures 1 shows the inhibitor's inhibition performance on the formation of barium sulphate scale at different inhibitor dosages. It was generally observed that increasing the inhibitor dosage increases the inhibition efficiency. When the dosage reaches a critical level, the inhibition rate remains constant or slowly decreases. The rate of inhibition decreased as inhibitor dosage increase from 60 mg/L to 400 mg/L. Figure 1 also shows a comparative inhibitor performance on evaluated scales within the operating condition of 78ºC and 24hrs. From the Figures the optimum inhibition rate of rutin for $BaSO_4$ scales formation was obtained at a low rutin dosage of 20 mg/l as 70.40% while the CSI gave 72.11% optimum inhibition performance for the formation of $BaSO_4$ scales at the same low dosage of 20 mg/L. Comparing CSI to rutin inhibitor shows that rutin has significant potential as green scale inhibitor in the oilfield. Therefore, it can be inferred that rutin has a relatively good inhibition performance on barium sulphate scale formation. The result shows that fewer amounts of the scale inhibitors (20 mg/L) are consumed for reasonable inhibition efficiency.

Optimum inhibition performance at a low scale inhibitor (SI) dosage has been reported as one of the requirements for a high-quality oilfield scale inhibitor. Inhibition efficiency of two green SIs (A) and (B) against gypsum for a specific amount of every SI (300 mg/L) as 60.81% and 10.77% respectively (Leila et al., 2021). They also reported inhibition efficiency of a phosphonate-based commercial scale inhibitor (C) of 99.54% for a 75 mg/L inhibitor dosage.

Performance Evaluation of Effect of Contact Time on inhibitor performance

Effects of contact time on the inhibition performance of rutin

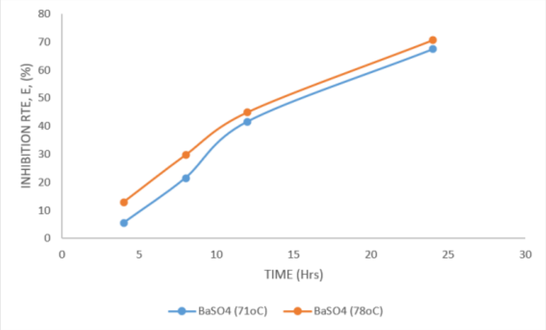

Figure 2: Performance of rutin (RU) on formation of $BaSO_4$ scale at different contact time and different temperature.

Effect of inhibition time on the performance of rutin inhibitor is shown in Figure 2. For barium sulphate deposition inhibition experiments, the scale inhibition rate is increasing as the contact time increases. Also, the inhibition efficiency on barium sulphate scale formation was also increasing at a higher time duration both at 71ºC and 78ºC (Figure 2). At 71ºC obtained inhibition efficiency are 5.56%, 21.54%, 41.62% and 67.45% at time duration of 4hrs, 8hrs, 12hrs and 24hrs respectively. For a temperature of 78ºC inhibition performance are 12.91%, 26.65%, 44.88% and 70.60% at time duration of 4hrs, 8hrs, 12hrs and 24hrs respectively. At an evaluation time of 24 hrs, and at 71ºC $BaSO_4$ scale formation has an inhibition rate of 67.45 % which is higher when compared to 5.56 % obtained for 4hrs inhibition time.

And at 24 hrs and 78ºC, it has 70.60 % when compared to 12.91 % obtained for 4hrs inhibition time. This indicates that the inhibitor plays a continuous $BaSO_4$ scale formation inhibition performance.

Effects of Contact Time on the inhibition performance of RFP

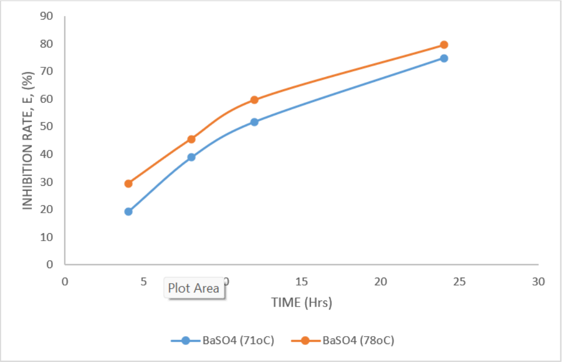

Figure 3: Performance of RFP on formation of $BaSO_4$ scale at different contact time and different temperature.

Figure 3 presents the results of RFP obtained at 4 hrs, 8 hrs, 12 hrs and at 24 hrs for $BaSO_4$ at 71ºC and 78ºC. RFP inhibition performance on $BaSO_4$ scale formation at 71ºC and at 4 hrs, 8 hrs, 12 hrs and at 24 hrs were obtained as 19.24%, 38.86%, 51.74% and 74.82% at 71ºC respectively while at 78ºC and at 4 hrs, 8 hrs, 12 hrs and at 24 hrs inhibition efficiency obtained are 29.39%, 45.54%, 59.60% and 79.52% 12.91% to 70.60% at 78ºC, respectively. For barium sulphate scale formation inhibition evaluation (Figure 3), the inhibition efficiency increased from 19.24% to 74.82% at 71ºC and from 29.39% to 79.52% at 78ºC, when the time of evaluation was increased from 4hrs to 24hrs respectively. It shows that RFP exhibits a continuous scale inhibition effect on $BaSO_4$ scales.

Effects of Contact Time on the inhibition performance of RFUP

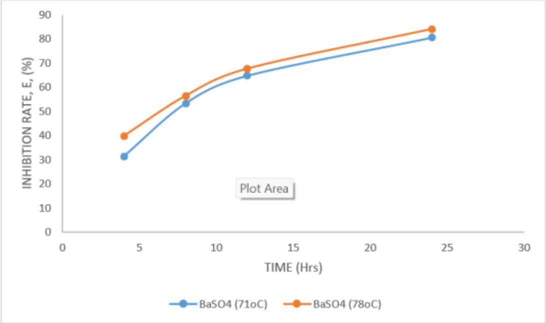

Figure 4: Performance of RFUP on formation of $BaSO_4$ scale at different contact time and different temperature.

Figure 4 shows the effect of evaluation time on the performance of RFUP inhibitor on barium sulphate scales formation. It can be inferred from the figures that increasing the time of contact of scale with the inhibitor improves its performance. The highest inhibition efficiency for barium sulphate scale formation at 4 hrs, 8 hrs, 12 hrs and at 24 hrs at 71ºC were 31.44%, 53.37%, 64.82% and 80.68% while at 78ºC are 39.79%, 56.41%, 67.66% and 84.12% respectively.

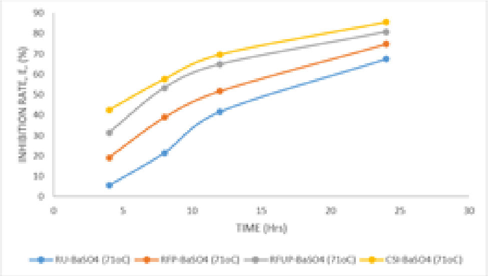

Figure 5: Comparison of the effect of contact time on the performance of inhibitors on formation of $BaSO_4$ scale at 71ºC

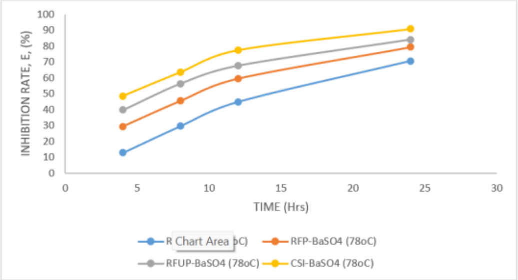

Figure 6: Comparison of the effect of contact time on the performance of inhibitors on formation of $BaSO_4$ scale at 78^{o}C

Effect of Temperature on performance of RU, RFP and RFUP on $BaSO_4$ scale inhibition

Figure 7 and 8 shows the results obtained from the effect of temperature variation on the performance of the inhibitors.

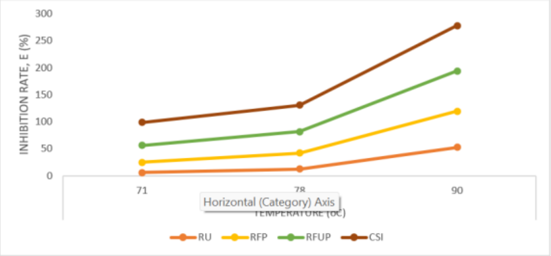

Figure 7: Effect of temperature on performance of inhibitors on formation of $BaSO_4$ scale at 4 hrs

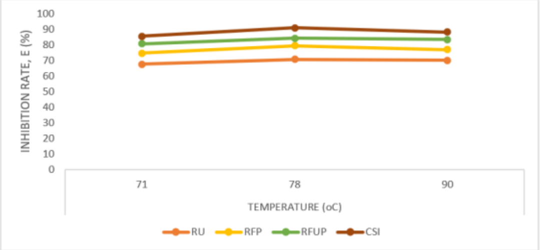

Figure 8: Figure. 4.16d. Effect of temperature on performance of inhibitors on formation of $BaSO_4$ scale at 24 hrs

The effect of temperature on the scale inhibition rate of the three inhibitors (RU, RFP, and RFUP) was evaluated for $BaSO_4$ scale formation using optimum inhibitor dosage of 20 mg/L and heating period of 4 hours (Figure 7) and 24 hours (Figure 8). Temperature was increased from 71^{o}C to 90^{o}C to observe the effect of increased temperature on the performance of scale inhibitors on the formation of barium sulphate scale. The inhibition efficiency of rutin (RU), within 4 hours process time, increases as temperature increases. 5.56%, 12.54% and 52.25% were obtained at 71^{o}C, 78^{o}C and 90^{o}C respectively (Figure 7), and 67.53%, 70.69% and 64.69% inhibition were obtained at 71^{o}C, 78^{o}C and 90^{o}C respectively after 24 hrs process time, (Figure 8). RFP inhibition efficiency obtained at 4 hrs process time are 19.24%, 29.39% and 66.96% at 71^{o}C, 78^{o}C and 90^{o}C respectively (Figure 7); and for 24 hrs process time 74.7%, 79.51% and 77.05% at 71^{o}C, 78^{o}C and 90^{o}C were obtained respectively (Figure 8). For RFUP inhibition performance at 4 hrs process time, we obtained 31.44%, 39.79% and 74.68% at 71^{o}C, 78^{o}C and 90^{o}C respectively (Figure 7), and 80.66%, 84.22% and 83.47% at 71^{o}C, 78^{o}C and 90^{o}C respectively for a 24 hrs process time (Figure 8).

Comparing Figure 7 and 8, for RU, RFP and RFUP inhibition efficiency on barium sulphate scale it was observed that inhibition performance of the three inhibitors at 24 hrs process time were better than for 4 hrs process time. Also, it was observed that, for 4 hrs process time, the inhibition efficiency of RU, RFP, and RFUP increases with increase in temperature respectively (Figure 7). However, a different phenomenon was observed in the three inhibitors (RU, RFP, and RFUP) behaviour when the process time was extended to 24 hrs (Figure 8).

The inhibition efficiency of the inhibitors initially increased as temperature increased reaching to a peak at 78^{o}C and after which inhibition efficiency starts to decrease slowly and steadily till it gets to the minimum. This demonstrates that at a process time of 24 hrs, increasing the temperature beyond 78^{o}C has no significant effect on the performance of RU, FRU, and URU inhibitors on $BaSO_4$ scale formation. The overall effective inhibition performance of three inhibitors is RFUP >> RFP >> RU.

IV. CONCLUSION

The inhibitors' efficacy was assessed using barium sulphate ($BaSO_4$) brines and synthetic formation water that was generated according to the NACE standard. Result of the inhibitor dosage evaluation test, shows the lowest effective RU dose of 20 mg/L resulted in an inhibition rate of 70.40% on the $BaSO_4$ scale formation. As the inhibitor dose was raised above 20 mg/L, the rate of inhibition decreased. This shows that the optimum inhibition rate of rutin for $BaSO_4$ scale formation was obtained at a low rutin dosage. Low inhibitor dosage is one of the satisfactory requirements for a good quality scale inhibitor in oilfield operation.

Figure 7 elucidates the effect of temperature on the inhibition performance of RU, RFP and RFUP on barium sulphate scale formation when the process time is 4 hrs. The Figure shows that inhibition rate increased with increased temperature from 71ºC to 90ºC. When the temperature increased, the barium ions were retarded to be precipitated with sulphate ions. These results on temperature effect are consistent with the previously published data [27], [60], [61], [62].

But when the process time was extended to 24 hrs (Figure 8) the inhibition efficiency of the inhibitors initially increased as temperature increased up to a pick temperature of 78ºC and after which inhibition efficiency starts to decrease slowly till it gets to the minimum. This demonstrates that increasing the temperature beyond 78ºC and at too long process time have no significant effect on the performance of the inhibitors on $BaSO_4$ scale formation. Temperature significantly impacts scale inhibitor performance. Higher temperatures can accelerate the kinetics of scale formation, potentially overwhelming the ability of some inhibitors to prevent or delay scale deposition. As temperature increases, the solubility of certain salts such as barium sulphate decreases [63], leading to increased scaling tendencies, promoting precipitation.

Additionally, results on the effect of contact time shows that longer contact times result in better inhibitor activity for all the three inhibitors on the formation of $BaSO_4$ at 71ºC and 78ºC, respectively. Generally, increasing the contact time between a scale inhibitor and the solution it is treating enhances the inhibitor's performance. This is because longer contact time allows the inhibitor more opportunity to interact with the scaling components and interfere with their ability to form crystals. However, the relationship is not always linear, and there can be diminishing returns or even a decline in effectiveness at extremely long contact times. This study has shown that increasing the contact time of RU, RFP, and RFUP can lead to higher inhibition efficiencies, particularly when dealing with barium sulfate scales.

Therefore, RU, RFP and RFUP function well as scale inhibitors for $BaSO_4$ scale formation although RFUP had a better inhibition efficiency than RU and RFP. The findings of this study demonstrate that rutin derived from SOMEX has potential as a scale inhibitor for oilfield operations. Comparison with an existing commercial inhibitor (CSI) indicate that rutin and its derivatives has a good potential as green scale inhibitor in the oil industry.

REFERENCES

[1] Jing, G.; Tang, S.; Li, X. Analysis and Inhibition of Scale Accumulation for a Producing Well in the Daqing Oilfield. Pet. Sci. Technol. 2013, 31, 1772–1777.

[2] Yi, T.; Jin, Z.; Chuan-Li, X.; Wei-Ying, W. A Bohai Sea SZ36-1 Oil Field Formation Scaling Experimental Study and Scale Inhibitor Optimization. Pet. Sci. Technol. 2014, 32, 2512–2519.

[3] W. Wayne, and M. Frenier, “Formation, removal, and inhibition of inorganic scale in the oilfield environment”. Society of Petroleum Engineers, 2009.

[4] W.W. Frenier, “Novel scale removers are developed for dissolving alkaline earth deposits”. Paper SPE 65027 MS presented at the SPE International Symposium on Oilfield Chemistry, Houston, Texas. 13-16, February 2001, doi: 10.2118/65027-MS.

[5] G.V. Chilingar, R. Mourhatch and G. D. Al-Qahtani, “The fundamentals of corrosion and scaling for petroleum and environmental engineers”, Elsevier Science: Houston, TX, USA, ISBN 780127999913, 2013.

[6] Jing, G.; Tang, S.; Li, X.; Wang, H. The analysis of scaling mechanism for water-injection pipe columns in the Daqing Oilfield. Arab. J. Chem. 2017, 10, S1235–S1239.

[7] Sun, H.; Liu, Y.; Liu, D.; Li, S.; Chen, H.; Han, Z.; Li, L.; Li, X. Enhanced removal of scaling

cations from oilfield produced water by carrier mineral floatation. Water Sci. Technol. 2021, 84, 3629–3640.

[8] M. Chen, Shafer-Peltier, K.; Veisi, M.; Randtke, S.; Peltier, E. Complexation and precipitation of scale-forming cations in oilfield produced water with polyelectrolytes. Sep. Purif. Technol. 2019, 222, 1–10.

[9] L. Mahmoodi, Malayeri, M.R.; Tabrizi, F.F. Abatement of scale precipitation in oilfields using green scale inhibitors. J. Pet. Sci. Eng. 2022, 208, 109237.

[10] T.A. Hoang, H.M. Ang, and A.L. Rohl, "Effects of temperature on the scaling of calcium sulphate in pipes. Powder Technol., 179, 31–37, 2007.

[11] O. Bukuaghangin, S. Olujide, K. Niraj, M. Huggan, A. Neville, and T. Charpentier, "Kinetics study of barium sulphate surface scaling and inhibition with a once-through flow system, Journal of Petroleum Science and Engineering, 2016.

[12] G. V. Chilingar, Mourhatch, R., and Al-Qahtani, G.D. Fundamentals of Corrosion and Scaling - for Petroleum and Environmental Engineers. Book by Gulf Publishing Company, Houston, Texas. ISBN-13: 978-1933762302, 2008.

[13] G. L. Gates, and Caraway, W.H. Oil Well Scale Formation in Waterflood Operations Using Ocean Brines. Book by U.S. Dept. of the Interior, Bureau of Mines, Wilmington, California, 1964.

[14] A. F. Clemmit, Ballance, D.C., and Hunton, A.G. The Dissolution of Scales in Oilfield Systems. Paper SPE 14010 presented at the Offshore Europe, Aberdeen, United Kingdom, 10-13 September 1985, doi: 10.2118/14010-MS

[15] O. J. Vetter, How Barium Sulfate Is Formed: An Interpretation. SPE Journal of Petroleum Technology, 27 (12) :1515-1524.SPE 4217-PA. doi:10.2118/4217-PA, 1975.

[16] A.T. Kan, G. Fu, and M. B. Tomson, "Effect of methanol on carbonate equilibrium and calcite solubility in a gas/methanol/water/ salt mixed system". Langmuir 18 (25): 9713–9725, 2002.

[17] A.T. Kan, G. Fu, and M. B. Tomson, "Effect of methanol and ethylene glycol on sulfates and halite scale formation". Ind. Eng. Chem. Res. 42 (11): 2399–2408, 2003.

[18] H. Lu, A.T. Kan, P. Zhang, J. Yu, C. Fan, and M.B. Tomson, 'Phase stability and solubility of calcium sulfate in the system NaCl/monoethylene glycol/water". In Proceedings of the SPE International Conference on Oilfield Scale (SPE-130697-MS), Aberdeen, UK; pp. 1–26, 2010.

[19] M. H, Al-Khaldi., A. Aljuhani., S. H. Al-Mutairi, and M. N. Gurmen, "New insights into the removal of calcium sulphate scale". In Proceedings of the SPE European Formation Damage Conference (SPE-144158-MS), Noordwijk, Netherlands, 7–10, 2011.

[20] M. Mahmoud, "Effect of elemental-sulphur deposition on the rock petro-physical properties in sour-gas reservoirs". SPE Journal.19, 703–715, 2014.

[21] I. E. Mazzollnl, Betero, L., Truefltt, S.C. Scale prediction and laboratory evaluation of BaSO4 scale inhibitors for seawater flood in a high-barium environment. SPE Prod. Eng. SPE 20894, 186 – 192, 1992.

[22] C. Romero, B. Bazin, A. Zaitoun, and F. Leal-Calderon, "Behavior of a scale inhibitor water-in-oil emulsion in porous media". SPE- 98275-PA, 22 (02), 191−201, 2007.

[23] O.J. Vetter, "Oilfield scale-can we handle It?" SPE Journal of Petroleum Technology, 28 (12), 1402-1408. SPE 5879-PA. doi: 10.2118/5879-PA, 1976

[24] K. Sorbie, M. Yuan, G. Graham, and A. Todd, "Appropriate laboratory evaluation of oilfield scale inhibitors". Advances in Solving Oilfield Scaling Problems, Aberdeen, UK., 1992

[25] W. Dickson, R. Griffin, L. Sanders, C. Lowen, and Kemira, "Development and performance of biodegradable antiscalants for oilfield applications". In: Offshore Technology Conference, Houston, USA, 2–5, 2011.

[26] M.S. Kamal, I. Hussein, M. Mahmoud, A. S. Sultan, and M.A.S. Saad, "Oilfield scale formation and chemical removal": A Review. Journal of Petroleum Science and Engineering 171: 127-139, 2018.

[27] Amer Badr BinMerdhah. Inhibition of barium sulfate scale at high-barium formation water. Journal of Petroleum Science and Engineering 90–91 (2012), 124–130.

[28] Wu, D.; Liu, D.;Wang, J.; Zhao, H.; Dong, Y.;Wang, X. High-Performance Barium Sulfate Scale Inhibitors: Monomer Design and Molecular Dynamics Studies. Processes 2025, 13, 660. https://doi.org/ 10.3390/pr13030660

[29] H. Gamal, Saad Al-Afnan, Salaheldin Elkatatny , and Mohamed Bahgat. Barium Sulfate Scale Removal at Low-Temperature. Dhahran 31261, Saudi Arabia, 2021.

[30] O. Claudia, and R. Jaime, "EDTA: The chelating agent under environmental Scrutiny". Quim. Nova, Vol. 26, No. 6, 901-905, 2003.

[31] A. A. Olajire, "A review of oilfield mineral scale deposits management technology for oil and gas production", Journal of Petroleum Science and Engineering, 135: 723-737, 2015.

[32] G. Jing, and S. Tang, "The summary of the scale and the methods to inhibit and remove scale formation in the oil well and the gathering line". Recent Patents Chem. Eng., 4, 291–296, 2011.

[33] A. A. Akaho, U. J. Chukwu, and O. Akaranta, "Synthesis and evaluation of iron (iii)-red onion skin extract azo complexes as pigments for surface coatings in oilfield environment". Chemical Sciences International Journal, 25(3): 1-9, 2018.

[34] H. S. Sayed, H. N. M. Hassan, and M. H. A. El, "The effect of using onion skin powder as a source of dietary fiber and antioxidants on properties of dried and fried noodles". Current science Journal, 3(4): 468-475, 2014.

[35] O. Benavente-Garcıa, J. Castillo, FR. Marin, A. Ortuno, JA. Del Rıo, "Uses and properties of citrus flavonoids". Journal of Agricultural and Food Chemistry 45:4505-4515, 1997.

[36] D. E. Okwu, "Citrus fruits a rich source of phytochemicals and their roles in human health": A Review. Int. J. Chem. Sci: 6(2), p. 451 – 471, 2008.

[37] G. A. O. Ajoku and I. J Otaraku, "Extraction of rutin from sweet orange (Citrus sinensis L) mesocarp using soxhlet extractor", American Journal of Sciences and Engineering Research E-ISSN– 2348–703X, Vol. 9, Issue 1, pp. 50 – 60. January 2026.

[38] RE. Ogali, O. Akaranta, and VO. Aririguzo, "Removal of some metal ions from aqueous solution using orange mesocarp". Afr. J. Biotechnol., 7(17): 3073-3076, 2008.

[39] M. U. Ibezim-Ezeani, F. A. Okoye, and O. Akaranta, "Kinetic studies on the removal of some metal ions from aqueous solution using modified orange mesocarp extract". International Journal of Water Resources and Environmental Engineering Vol. 4(6), pp. 192-200. DOI: 10.5897/IJWREE11.088; ISSN 1991-637X ©2012 Academic Journals, 2012.

[40] S. H. Hassanpour, and A. Doroudi, "Review of the antioxidant potential of flavonoids as a subgroup of polyphenols and partial substitute for synthetic antioxidants". Avicenna J Phytomed; 13(4): 354-376, 2023.

[41] S. S. Liew, W. Y. Ho, S. K. Yeap, and S. A. B. Sharifudin, "Phytochemical composition and in vitro antioxidant activities of Citrus sinensis peel extracts", Peer J. 6: doi: 10.7717/peerj.5331, PMC6078072 PMID: 30083463, 2018.

[42] VA. Kostyuk, AI. Potapovich, EN. Vladykovskaya, LG. Korkina, and IB. Afanas'ev, "Influence of metal ions on flavonoid protection against asbestos-induced cell injury". Arch Biochem Biophy, 385, 129-137, 2001.

[43] Z. Radovi, and D. Malešev, Pharmazie 39, 870, 1984.

[44] Z. Radovi, and D. Malešev, Arch. Pharm. 320, 188, 1987.

[45] J. M. D. Markovic, Z. S. Markovic, T. P. Brdaric, and N. D. Filipovi, "Comparative spectroscopic and mechanistic study of chelation properties of fisetin with iron in aqueous buffered solutions: Implications on in vitro antioxidant activity". Dalton Transactions, 40: 4560-4571, 2011.

[46] A. Filipiak-Szok, M. Kurzawa, and E. Sz_lyk, "Determination of anti-oxidant capacity and content of phenols, phenolic acids, and flavonols in Indian and European gooseberry", 2012.

[47] J. Gupta, and A. Gupta, "Isolation and identification of flavonoid rutin from rauwolfia serpentine". International Journal of Chemical Studies, 3(2): 113 – 115, 2015.

[48] S. Kumar, T. K. Naiya, and T. Kumar, "Developments in oilfield scale handling towards green technology-A review". Journal of

Petroleum Science and Engineering. 169, 428–444, 2018.

[49] S. Kumar, A. Mishra, and A. K. Pandey,"Antioxidant mediated protective effect of Parthenium hysterophorus against oxidative damage using in vitro models," BMC Complementary and Alternative Medicine, vol. 13, article 120, 2013.

[50] M. Leopoldini, N. Russo, S. Chiodo, and M. Toscano, "Iron chelation by the powerful antioxidant flavonoid quercetin," Journal of Agricultural and Food Chemistry, vol. 54, no. 17, pp. 6343–6351, 2006.

[51] A. A. Akaho, U. J. Chukwu, and O. Akaranta, "Cu (II)-red onion skin extract-azo metal complex - a potential for oilfield", Article in Chemical Science International Journal, Article No. CSIJ.47803, ISSN: 2456-706X, 2019,

[52] N. M. Parvathi, and M. Vangalapati, "Extraction, modelling and purification of flavonoids from Citrus medica peel". Int. J. Appl. Sci. Biotechnol, Vol. 3(4): p. 588 – 591. DO1: 10.3126/ijasbt. v3i4.13360, 2015.

[53] N. P. Pawar, and V. R. Salunkhe, "Development and validation of UV Spectrophotometric method for simultaneous estimation of rutin and gallic acid in hydroalcoholic extract of Triphala churna. International Journal of Pharm Tech Research. 5(2): 724-729, 2013.

[54] NACE Standard TM0197-2010 Standard Test Method: Laboratory Screening Test to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Barium Sulfate or Strontium Sulfate, or Both, from Solution (for Oil and Gas Production Systems). NACE International.

[55] JM. Matty, and MB. Tomson, "Effect of multiple precipitation inhibitors on calcium carbonate nucleation". Appl Geochem.; 3(5): 549–56. doi:10.1016/0883-2927(88)90026-1, 1988.

[56] C. Tortolano, T. Chen, and P. Chen, "Mechanisms, new test methodology and environmentally acceptable inhibitors for codeposition of zinc sulfide and calcium carbonate scales for high temperature application". In: SPE international oilfield scale conference and exhibition, 14–15 May, Aberdeen, Scotland; doi: 10.2118/169810-MS, 2014.

[57] I. Drela, P. Falewicz, and S. Kuczkowska, "New rapid test for evaluation of scale inhibitors". Water Res.; 32(10):3188–91.doi:10.1016/S0043-1354(98)00066-9, 1998.

[58] ASTM (5) D3651 (latest revision), "Standard Test Method for Barium in Brackish Water, Seawater, and Brines" (West Conshohocken, PA: ASTM).

[59] ASTM D3986 (latest revision) "Standard Test Method for Barium in Brines, Seawater, and Brackish Water by Direct-Current Argon Plasma Atomic Emission Spectroscopy" (West Conshohocken, PA: ASTM).

[60] A. A. Rocha, Frydman, M., Fontoura, B.A.S., Rosario, F.F., Bezerra, M.C.M. Numerical Modeling of Salt Precipitation During Produced Water Reinjection. The 2001 SPE Third International Symposium on Oilfield Scale. January 30–31 2001, Aberdeen, UK, vol. SPE 68336, 1–8 pp.

[61] F. F. Rosario, Bezerra, M.C.M. Scale Potential of a Deep-Water Field-Water Characterization and Scaling Assessment. The 2001 SPE Third International Symposium on Oilfield Scale. January 30–31 2001, Aberdeen, UK, vol. SPE 68332, 1–5 pp.

[62] L. Ying-Hsiao, Crane, S. D., Coleman, J.R. A Novel Approach to Predict the Co- Precipitation of BaSO4 and SrSO4. The SPE Production Operation Symposium. April 2– 4 1995, Oklahoma City, Oklahoma, vol. SPE 29489, 447–461pp.

[63] M. Merdhah, & A. Badr, The study of scale formation in oil reservoir during water injection at high-barium and high-salinity formation water. Universiti Teknologi Malaysia, Faculty of Chemical and Natural Resources Engineering, 2008.