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Inhibition of $CaSO_4$ Scale Formation in Oilfield Equipment Using Rutin from Sweet Orange (*Citrus sinensis L*) Mesocarp Extract (SOMEX)

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Abstract: Scale formation in oil wells is one of the most common problems confronting oil and gas industries around the world. Although great technologies have been developed by engineers to combat scale formation, yet the problem remains without an effective solution. Scale deposition problems have been managed by injecting scale inhibiting chemicals into the area of interest to inhibit the formation of scale. However, 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. Rutin obtained from SOMEX was modified using furfuraldehyde, and urea at varying molar ratios to form a novel green scale inhibitors, namely, Rutin (RU), Rutin-Furfural-modified polyphenolic resin (FRU) and Rutin-Furfuraldehyde-Urea- modified polyphenolic resin (URU). In order to create the scale inhibitors FRU and URU, the rutin extract, RU was first mixed with Furfuraldehyde in a 2:1 molar ratio and heated to 130°C with 2 ml of 1% w/v NaOH for 60 minutes to obtain FRU; then mixed with Furfuraldehyde and Urea in a 2:2:1 molar ratio, heated at 70°C with 2 ml of 1% w/v NaOH for 30 minutes to obtain URU. FTIR was used to characterise the inhibitors. Results of analyses show that RU, FRU and URU inhibitors are alkaline, thermally stable at a temperature of 130°C after 24 hours and compatible with the formation brine at a temperature of 25°C. The inhibitors' efficacy were assessed using $CaSO_4$ 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 62.35% on $CaSO_4$ 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 $CaSO_4$ scales at 71°C. Additionally, it was noted that the inhibition of RU, FRU, and URU on the formation of $CaSO_4$ scale rose when the temperature was raised from 71°C to 90°C. 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), FRU, URU, Commercial Inhibitor (CSI), Calcium Sulphate Scale ($CaSO_4$).*

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I. INTRODUCTION

Scaling has remain one of the major challenge confronting the oil and gas industry. Scale consequences cost Africa almost $160 million yearly, which is a huge economic burden and its management is one of the most expensive operational expenses in the oil and gas industry, which represents 28% of crude production loss [1]. 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 [2]. 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 [3]. 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,

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barium sulphate, strontium sulphate, ferrous carbonate, ferrous sulphide and pyrite [4], [5]. The precipitation of calcium sulphate scale phases is often a consequence of mixing of incompatible waters during waterflooding. Also, calcium sulphate precipitation can result from a pressure drop when production is from a reservoir where the brine is saturated with calcium sulphate, or from an increase in temperature during the processing of the brine on the surface (e.g., heater), during membrane filtration, during steam flood, or when large quantities of thermodynamic hydrate inhibitors are used for hydrate control [6], [7], [8]. Three calcium sulphate phases commonly occur as scales, they differ by the number of water molecules in the crystal formula. Gypsum ($CaSO_4 \cdot 2H_2O$) is the stable calcium sulphate phase at low temperatures (from room temperature up to approximately 40 to 90 °C). Above approximately 120 °C, anhydrite ($CaSO_4$) is the commonly reported phase. At intermediate temperatures, hemihydrate ($CaSO_4 \cdot ½H_2O$), also called "plaster of Paris," is often reported in brines with high total dissolved solids (TDS) content [9]. The transition temperatures are strongly dependent on the salt content of the brine and other specific chemical species. At any specific temperature, a higher concentration of salt will tend to favour the formation of a solid calcium sulphate phase with fewer water-of-hydration molecules in the crystal formula. The details of how and which solution conditions affect the phase relationships for the calcium sulphates are not known well enough to be predictive, but it is certainly related to the water activity. In the presence of methanol or monoethylene glycol (MEG), as hydrate inhibitors, anhydrite was observed at much lower temperatures than expected because of the lowering water activity in the presence of methanol or MEG [7], [8]. It has been confirmed that calcium sulphate scale could trigger considerable alterations in injector and producing reservoirs [10]. Calcium sulphate scales in the oil reservoir possess capacity to alter the permeability and porosity of reservoir [11]. The possibility of calcium sulphate scale deposition around electric submersible pump placed in the reservoir was investigated, calcium sulphate crystals were observed in three different forms namely hydrous, hemihydrates, and anhydride with a complicated formation at lower temperature [12]. Similarly, deposition of anhydrate forms of calcium sulphate is possible at higher deposition surface temperatures. As temperature increase, solubility of calcium, sulphate scales increased till 40 ^oC, and at temperatures above 40 ^oC, solubility decreases [9]. Several researchers have reported that the correct prediction for formation and deposition of calcium sulphate is complicated. However, when temperature is above 40 ^oC, solubility of calcium sulphate seems to be high for anhydrite calcium sulphate. Usually, calcium sulphate is less soluble at low pressures, and the solution contains high pH value. Its solubility could also be influenced by ionic capability of the solution, by increasing ionic capacity, the solubility of this scale could be maximized ([13], [14]). Solubility of calcium sulphate decreases with decrease in pressure which trigger scale precipitation in oil well reservoir and oil wells surface thus reducing their performance and productivity with time [15].

Generally, removal of calcium sulphate scale involves a two-step process – conversion and acidification. The insoluble calcium sulphate scale is first converted into a more soluble form (calcium carbonate) by treating it with a solution of ammonium carbonate, sodium hydroxide, or ammonium bicarbonate. The resulting calcium carbonate is then removed by soaking in acids such as 5 – 7% hydrochloric acid (HCl) or acetic acid. Alternatively, a high pH conversion method using potassium carbonate has shown to give a high efficiency removal. By this method up to 100% removal can be achieved using 7wt % HCl or acetic acid on pre-converted 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 [16]. 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 ([17], [18]). Addition of chemical inhibiting agents, are economical and simple effective means of preventing of scaling [19]. 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 [20]. Chelating agents are capable of dissolving calcium sulphate without a separate conversion step. 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 [21]. For the best inhibitory effect, it is essential to choose non-toxic, effective, biodegradable, renewable, and non-absorbed inhibitors [22]. Green antiscalants are renewable, biodegradable, and good for the environment [23]. Additionally, they deal with a growing variety of environmental issues.

Sweet orange mesocarp (SOM) is a by-product of sweet orange rinds. Rutin, is a key component of specifics, [24], [25], [26], [27]. It has been extracted from sweet orange mesocarp [28]. 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

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Cd [29]. 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 [30]. It has been shown that the naturally occurring flavonoid rutin has remarkable metal chelating properties [31], [32]. 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+} [29], [33], [34], 1987 [35], [36]. The potential health benefits arising from the antioxidant activities of rutin and its use in binding and removing of metal ions from aqueous solution [29], [30], [37]; stimulated our interest in the study of rutin as scale inhibitor. Rutin is non-toxic, biodegradable and has shown no bioaccumulation [38]. 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 [39], [40]. The chelation of metals is crucial in the prevention of radical generation which precipitate and deposit as scales [41], [40].

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, environmental 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.

II. MATERIALS AND METHODS

- *Sample Collection and Processing*

Fresh sweet Orange (Citrus sinensis L) 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 [28]. 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 [42], [43], and was performed according to [28]. 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 bottles. Crude extract obtained after the extraction was purified employing two different methods: solvent- solvent extraction using Hexane as solvent and was performed according to [43]. 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 [44]. 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 [28]. 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 ^{o}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°C 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 (FRU) 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

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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 (URU) 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 TM0374-2007 for calcium sulphate composition in a produced water. $CaSO_4$, synthetic brines were prepared with distilled water, with the following composition: **7**.50 g/L NaCl (ACS reagent grade); 11.10 g/L $CaCl_2 \cdot 2H_2O$ (ACS reagent grade) for calcium-containing brine, and 7.50 g/L NaCl (ACS reagent grade); 10.66 g/L Na_2SO_4 (ACS reagent grade) for sulphate-containing brine [45]. The saturation ratio (SR) was calculated using equation 1.

$$SR = \frac{(C_a^{2+})(CO_3^{2-})}{K_{sp CaCO_3}} \quad (1)$$

And scaling tendency was expressed in terms of Saturation Index (SI) as the Logarithm of the Saturation Index:

$$SI = \log_{10} SR \quad (2)$$

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 reagents 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 [46], [47]. 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 [48]. The protective effect of an inhibitor was calculated by the following Equation 3:

$$E = \frac{Mo - M}{Mo} \, x \, 100\% \quad (3)$$

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 $CaSO_4$ 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 calcium 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.

- *Calcium Sulphate Precipitation Test*

$CaSO_4$ scale inhibition test was carried out according to NACE Standard TM0374-2007 procedures. The desired amount of scale inhibitor was pipet into each test cell using the 1 wt% and 0.1 wt% dilutions. The 0.1 wt% dilution was used for tests in which scale inhibitor loadings are less than 10 mg/L. Duplicate blanks were prepared by setting aside two samples of the calcium containing brine (50 mL each). Calcium ion concentration of the blanks were determined before precipitation. 50 mL of sulphate-containing brine was added to the test cell and mixed thoroughly. 50 mL of calcium-containing brine was also added to the test cell. Test cell was immediately capped and agitated to mix the brines and the scale inhibitor thoroughly. Test cells and blanks were immersed to 75% of their lengths in a water bath at 71±1 °C for 4hrs 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. About 1mL of the test brine was pipet into a suitable vessel, avoiding the transfer of calcium sulphate crystals, and diluted with distilled water, deionized water, or as otherwise specified in the calcium determination method to be used [45]. Calcium ion concentration was then determined by procedures given in ASTM D 511, ASTM D 1126, and APHA Standard Methods for the Examination of Water and Wastewater (Part 300) [49], [50]**.** The average of the duplicate calcium ion concentration values as mg/L calcium sulphate retained in solution for each inhibitor test concentration and the blank was reported. Inhibition efficiency was calculated in accordance with Equation 4 below or Equation 3 above.

$$\% \text{ Inhibition} = \frac{Ca - C_b}{C_c - C_b} \, X \, 100 \quad (4)$$

Where: $C_a = C_a^{2+}$ concentration in the treated sample after precipitation, $C_b = C_a^{2+}$ concentration in the blank after

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precipitation, $C_c = C_a^{2+}$ concentration in the blank before precipitation.

➢ *Performance Evaluation of Developed Inhibitors Under Operational Variables*

- *Effect of Dosage on $CaSO_4$ 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 calcium containing brine (50 mL each). Calcium 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. Calcium ion concentration was determined by procedures given in ASTM D 511, ASTM D 1126 and APHA Standard Methods for the Examination of Water and Wastewater (Part 300) [49], [50]. All tests were performed at least in duplicate. The average of the duplicate calcium ion concentration values as mg/L calcium sulphate retained in solution for each inhibitor test concentration and the blank was reported. Inhibition efficiency was calculated in accordance

- *Effect of Temperature on $CaSO_4$ 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 calcium containing brine (50 mL each). Calcium ion concentration of the blanks were 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. Calcium ion concentration was determined by procedures given in ASTM D 511, ASTM D 1126, and APHA Standard Methods for the Examination of Water and Wastewater (Part 300) [49], [50]. All tests were performed at least in duplicate. The average of the duplicate calcium ion concentration values as mg/L calcium sulphate retained in solution for each inhibitor test concentration and the blank was reported. Inhibition efficiency was calculated in accordance with Equation 4 and reported.

- *Effect of Contact Time on $CaSO_4$ 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 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 four samples of the calcium containing brine (50 mL each). Calcium 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. Calcium ion concentration was determined by procedures given in ASTM D 511, ASTM D 1126, and APHA Standard Methods for the Examination of Water and Wastewater (Part 300) [49], [50]. All tests were performed at least in duplicate. The average of the duplicate calcium ion concentration values as mg/L calcium sulphate retained in solution for each inhibitor test concentration and the blank was reported. Inhibition efficiency was calculated in accordance with Equation 3.4 and reported. 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.

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III. RESULTS AND DISCUSSION

➢ *Effect of Dosage on CaSO4 Scale Inhibition*

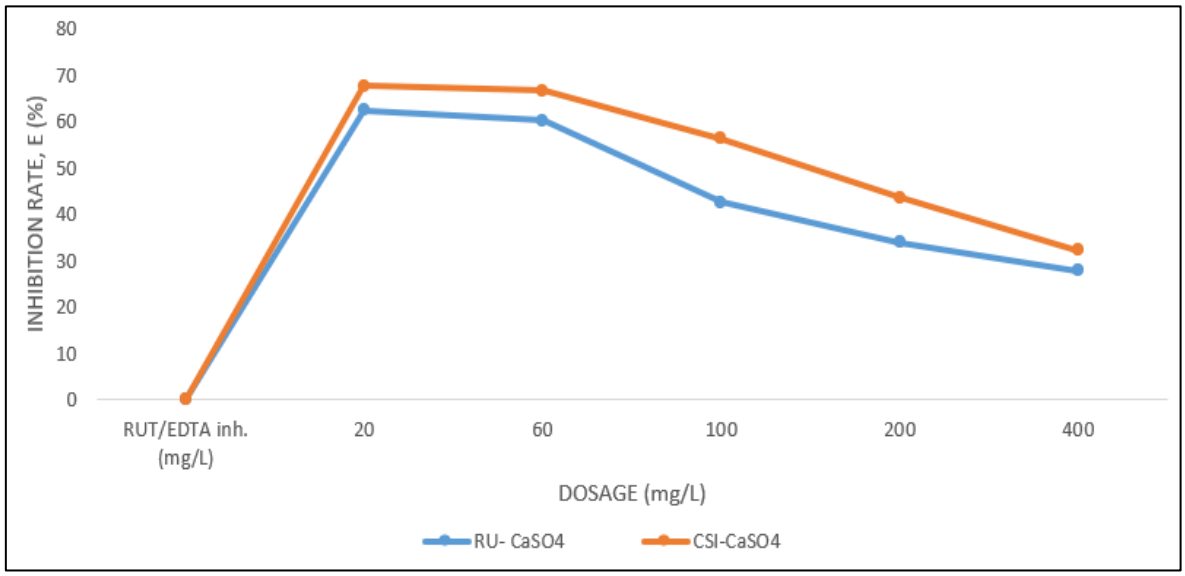

Fig 1 Effect of Dosage on the Performance of Rutin and CSI on $CaSO_4$ Scale Formation

Figures 1 shows the inhibitor's inhibition performance on the formation of calcium 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 78°C and 24hrs. From the Figures the optimum inhibition rate of rutin for $CaSO_4$ scales formation was obtained at a low rutin dosage of 20 mg/l as 62.35% while the CSI gave 67.64% optimum inhibition performance for the formation of $CaSO_4$ 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 calcium 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 requirement 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 [51]**.** They also reported inhibition efficiency of a phosphonate-based commercial scale inhibitor (C) of 99.54% for a 75 mL/L inhibitor dosage.

➢ *Effect of Contact Time on $CaSO_4$ Scale Inhibition*

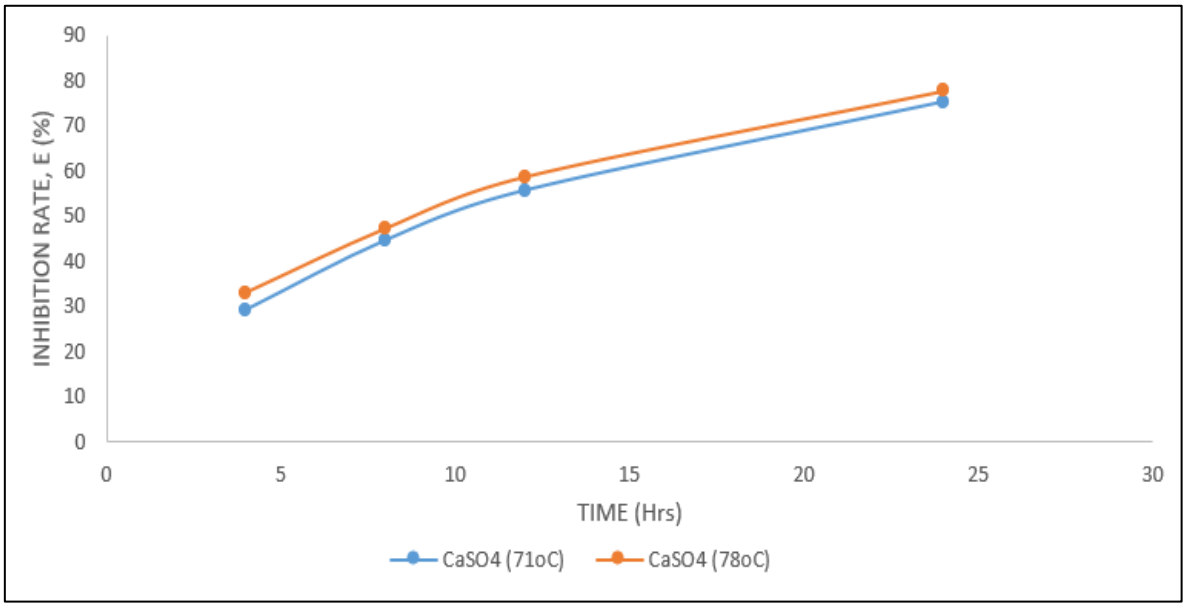

Fig 2 Performance of Rutin (RU) on Formation of $CaSO_4$ Scale at Different Contact Time and Different Temperature.

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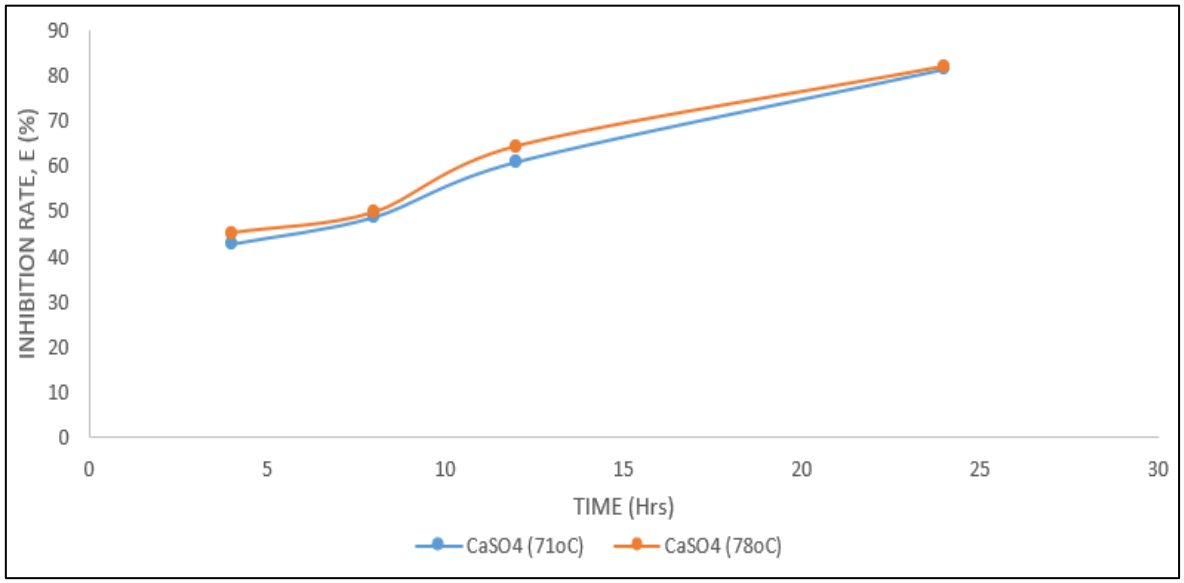

Fig 3 Performance of FRU on Formation of $CaSO_4$ Scale at Different Contact Time and Different Temperature.

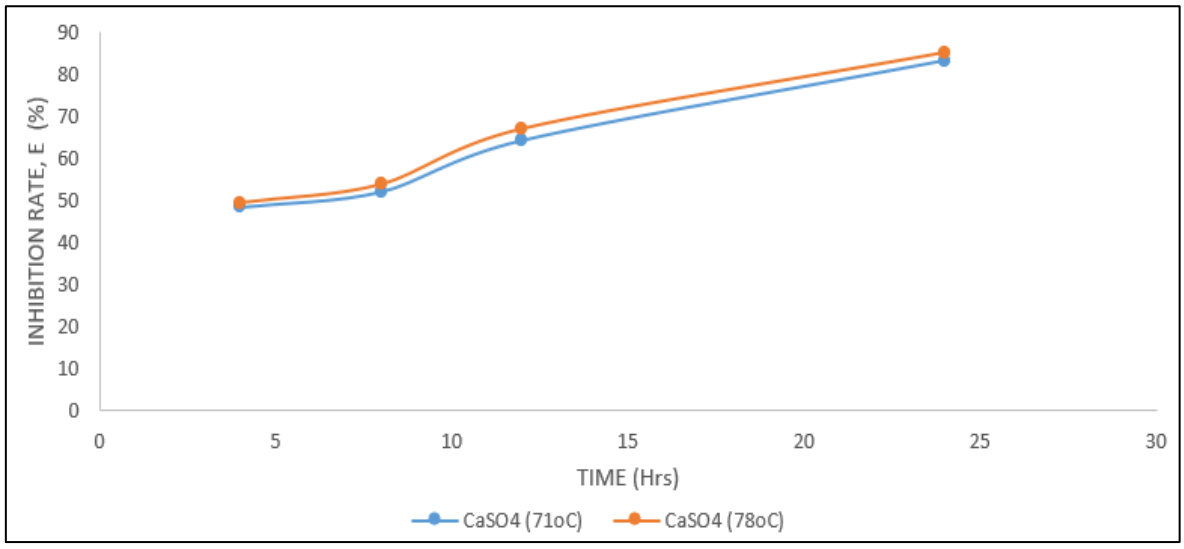

Fig 4 Performance of URU on Formation of $CaSO_4$ Scale at Contact Different Time and Different Temperature.

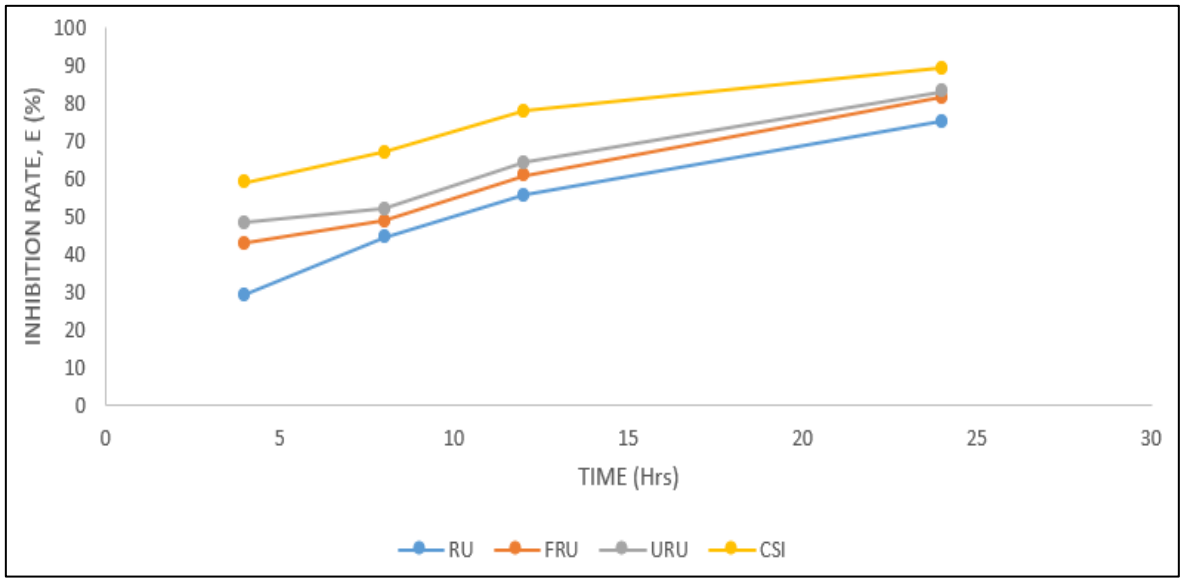

Fig 5 Effect of Contact Time on the Performance of Inhibitors on Formation of $CaSO_4$ Scale at 71 ^{o}C

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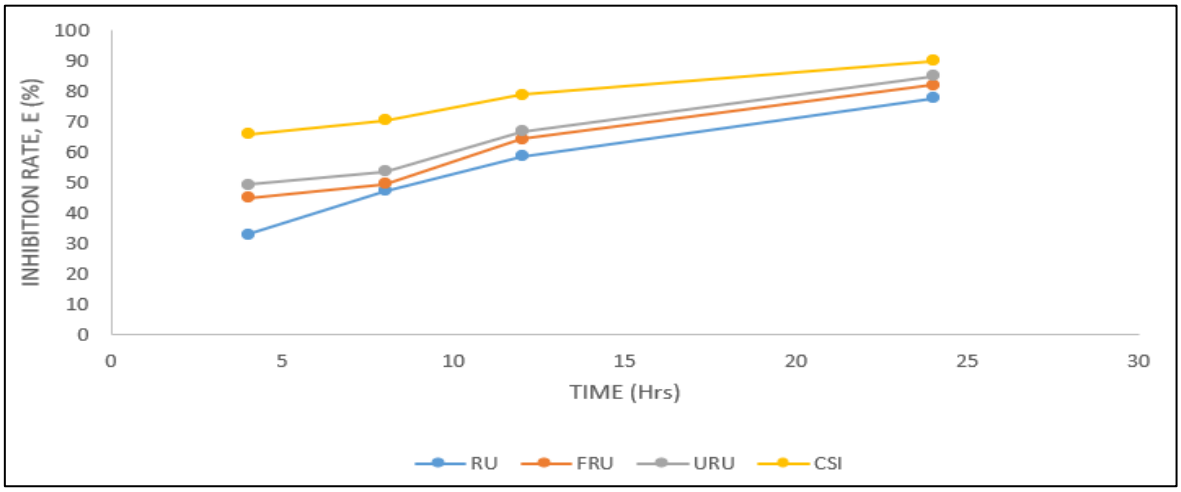

Fig 6 Effect of Contact Time on the Performance of Inhibitors on Formation of $CaSO_4$ Scale at 78 ^{o}C

➢ *Effects of Contact Time on the Inhibition Performance of Rutin*

Effect of inhibition time on the performance of rutin inhibitor is shown in Figure 2. For calcium sulphate deposition inhibition experiments, the scale inhibition rate is increasing as the contact time both at 71 ºC and 78 ºC. At 71ºC obtained inhibition efficiency are 29.18%, 44.58%, 55.69% and 75.25% at contact time duration of 4hrs, 8hrs, 12hrs and 24hrs respectively. For a temperature of 78 ºC inhibition performance are 33.02%, 47.23%, 58.66% and 77.70% at time duration of 4hrs, 8hrs, 12hrs and 24hrs respectively. At an evaluation time of 24 hrs, and at 71ºC $CaSO_4$ scale formation has an inhibition rate of 75.25 % which is higher when compared to 29.18 % obtained for 4hrs inhibition time. And at 24 hrs and 78 ºC, it has 77.70 % when compared to 33.02 % obtained for 4hrs inhibition time. This indicates that the inhibitor plays a continuous $CaSO_4$ scale formation inhibition performance. The rutin inhibitor was observed to have a higher inhibition efficiency on $CaSO_4$ scale formation.

➢ *Effects of Contact Time on the Inhibition Performance of FRU*

Figure 3 presents the results of FRU obtained at 4 hrs, 8 hrs, 12 hrs and 24 hrs for $CaSO_4$ at 71 ºC and 78 ºC. FRU inhibition performance on $CaSO_4$ scale formation at 71 ºC and at 4 hrs, 8 hrs, 12 hrs and at 24 hrs were obtained as 42.78%, 48.72%, 60.53% and 81.41% respectively while at 78 ºC and at 4 hrs, 8 hrs, 12 hrs and at 24 hrs inhibition efficiency obtained are 45.08%, 49.65%, 64.34% and 82.09% respectively. It shows that FRU exhibits a continuous scale inhibition effect on $CaSO_4$ scale.

➢ *Effects of Contact Time on the Inhibition Performance of URU*

Figure 4 shows the effect of evaluation time on the performance of URU inhibitor on calcium 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 calcium sulphate scale formation at 4 hrs, 8 hrs, 12 hrs and at 24 hrs at 71 ºC were 48.35%, 52.01%, 64.21% and 83.16% while at 78 ºC are 49.31%, 53.70 %, 66.92% and 85.06 % respectively.

➢ *Effect of Temperature on Performance of RU, FRU and URU on $CaSO_4$ Scale Inhibition*

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

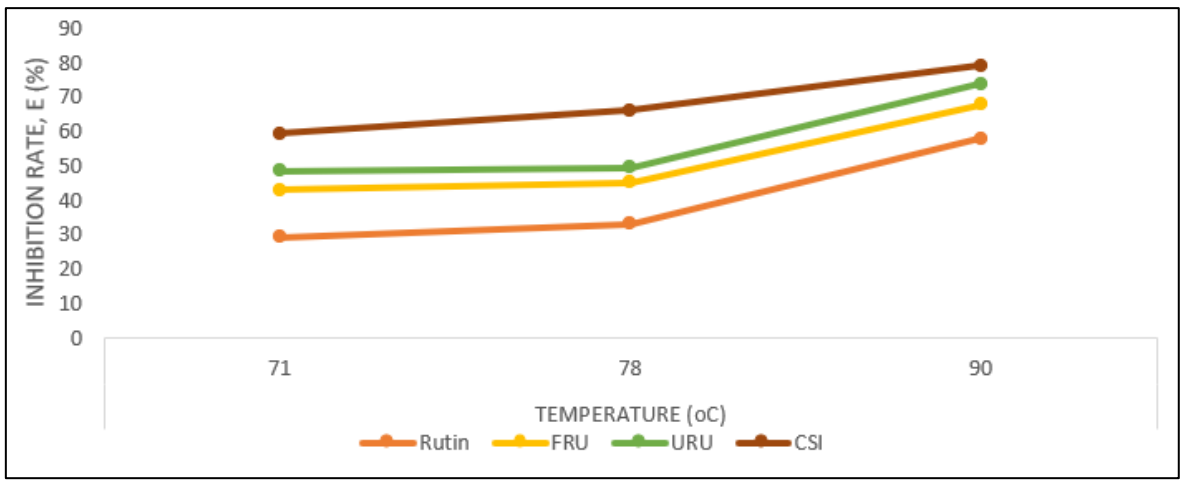

Fig 7 Effect of Temperature on Performance of Inhibitors on Formation of $CaSO_4$ Scale at 4 Hours

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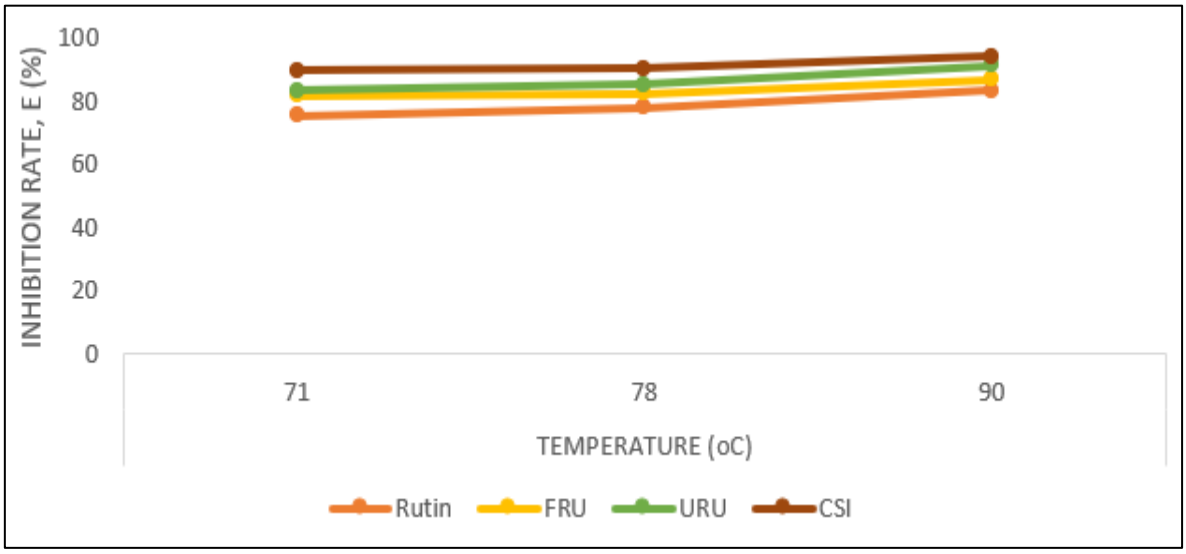

Fig 8 Effect of Temperature on Performance of Inhibitors on Formation of $CaSO_4$ Scale at 24 Hours

The effect of temperature on the scale inhibition rate of the three inhibitors (RU, FRU, and URU) was evaluated for $CaSO_4$ scale formation using optimum inhibitor dosage of 2 mg/L and heating period of 4 hours (Figure 7) and 24 hours (Figure 8). Temperature was increased from 71 ºC to 90 ºC to observe the effect of increased temperature on the performance of scale inhibitors on the formation of calcium sulphate. The inhibition efficiency of rutin (RU), within 4 hours process time increases as temperature increases. 29.18%, 33.02% and 57.73% were obtained at 71 ºC, 78 ºC and 90 ºC respectively (Figure 7). Figure 8 depicts also the performance of rutin as the process time is extended to 24 hrs. It was observed that inhibition efficiency of rutin increases as temperature increases. 72.26%, 77.71% t and 83.20% efficiency were obtained at 71 ºC, 78 ºC and 90 ºC respectively after 24 hours process time.

Comparing Figure 7 and 8, for FRU and URU inhibition efficiency on calcium sulphate scale formation. For calcium sulphate scale formation at a process time of 4 hours, FRU inhibition evaluation, increases as temperature increases. From Figure 7 inhibition efficiency obtained for calcium sulphate scale formation are 42.76%, 45.10% and 67.62% at 71 ºC, 78 ºC and 90 ºC respectively for 4 hours contact time while in Figure 8, FRU inhibition efficiency for calcium sulphate at 24 hours were 81.40%, 82.09% and 86.44% at 71 ºC, 78 ºC and 90 ºC respectively.

URU performance on calcium sulphate scale formation inhibition at 4 hours and 24 hours are shown in Figures 7 and 8 respectively. In both Figures, URU inhibition performance increases at increased temperature. Calcium sulphate scale formation inhibition evaluation, 48.35%, 49.29% and 73.64% were obtained at 71 ºC, 78 ºC and 90 ºC respectively for 4 hours process time (Figure 7). But inhibition evaluation at 24 hours (Figure 8) are 83.14%, 85.08% and 90.96% inhibition efficiency obtained at 71 ºC, 78 ºC and 90 ºC respectively. URU inhibition performance increased as process temperature and as process time increases reaching above 90 percent at 90 ºC. From Figures 7 and 8, it can be observed that the three inhibitors inhibition performances for 24 hours process time were better than for 4 hours. Also the effective inhibition perforce is URU >> FRU >> RU.

IV. CONCLUSION

The inhibitors' efficacy were assessed using calcium sulphate ($CaSO_4$) 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 62.35% on the $CaSO_4$ 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 $CaSO_4$ scale formation was obtained at a low rutin dosage. Low inhibitor dosage is one of the satisfactory requirement for a good quality scale inhibitor in oilfield operation.

The evaluations on the effect of temperature on the inhibition performance of RU, FRU and URU scale inhibitors shows that inhibition rate increased from 71ºC to 90ºC for $CaSO_4$ scale formation. 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 $CaSO_4$ 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 have shown that increasing the contact time of RU, FRU, and URU can lead to higher inhibition efficiencies, particularly when dealing with calcium sulfate scales. Therefore, RU, FRU and URU function well as scale inhibitors for $CaSO_4$ scale formation although URU had a better inhibition efficiency than RU and FRU.

The findings of this study demonstrate that rutin derived from SOMEX has potential as a scale inhibitor for oilfield

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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.

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