



Application of Plant Extract as Barite Scale Inhibitor in Water Injection Operation

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ABSTRACT

Water injection into oil reservoirs is a common method to compensate for the pressure drop due to oil production. Injection water is mainly seawater, which contains ions such as sulfate and carbonate. Formation water generally contains cations such as calcium, barium, strontium, etc. Therefore, mineral scales are formed as a result of mixing injection water with formation brine. One of the most important problems in water injection operation is the formation of mineral scales, which causes reservoir damage, loss of production, pressure reduction, depreciation of the wellhead equipment, and in more severe cases, well closure. Using scale inhibitors is an effective method to prevent scale formation. In this study, olive leaf extract was used as a green inhibitor to prevent and reduce barite scale formation. For this purpose, water samples were synthesized according to real ionic composition of formation brine and sea water, and mixed at different mixing ratios. The inhibition performance of olive leaf extract was explored at different concentrations. Characterization of the used extract was carried out using FTIR analysis. The highest amount of barium sulfate precipitation was observed 0.37 gr/l in the mixture containing 90% formation brine. Experimental results indicated that the most effective concentration of the inhibitor for reduction of scale formation is 20 ml/l. Moreover, the effect of pH value and salinity of injection water was investigated and the best performance of inhibitor was observed at 4100 ppm salinity and pH 7.7.

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1. Introduction

Formation damage is one of the most important reasons for declining well injectivity as well as productivity in oil and gas reservoirs. Several mechanisms responsible for formation damage are reported in the literature including fines migration, clay swelling, fluid-fluid incompatibility, phase blocking, scale formation, dissolution and precipitation reactions, and wettability alteration. The formation of mineral scales in hydrocarbon reservoirs and oil field facilities is the main challenge in water injection operations (Asadollahi et al., 2021). Scale formation and deposition can occur during certain operations such as stimulation, production and transportation in petroleum industry. Carbonates, sulfates and sulfides are common scales in oil fields. Usually, these scales are caused by changes in temperature, pressure and mixing of incompatible waters in the reservoir (Merdhah and Yassin, 2007). Controlling and preventing the formation of scales as one of the most effective solutions has been the concern of both research and industry for many years. The most effective method to reduce mineral scales in water injection operations is the use of scale inhibitors, which requires a comprehensive study under different conditions. To select the best type and concentration of scale inhibitor, laboratory tests should be performed on formation brine and injection water. Scale inhibitors have different mechanisms of inhibition. A group of inhibitors can reduce the activities of the ions in the solution and consequently reduce the scale formation. Some types of inhibitors affect the scale after the formation of the solid crystal core and prevent the crystal growth through adsorption to the active sites on the crystal surface. Another inhibition mechanism is the modification of the crystal structure, which often reduces the adhesion of scales on the solid surface. Another category of inhibitors reduces the deposition of scales by increasing the dispersion of solid crystals and reduces the

accumulation and settling of suspended solid particles (Valadbeigian et al., 2023).

For the best inhibitor performance, some factors should be investigated. The scale inhibitor (SI) must be stable against high temperature and salinity. In addition, since the chemistry and ionic composition of sea water and formation water vary at different regions, an effective SI should be compatible with these waters. Hence, a SI that performs well in a given oil field may not do so in another (Tantayakom et al., 2005; Vilorio et al., 2010). Changes in environmental conditions such as pH value, temperature, fluid hydrodynamics, and presence of other chemicals can also influence the performance of a scale inhibitor. Factors such as brine supersaturation and the presence of divalent cations, such as Ca^{2+} and Mg^{2+} ions or even Zn^{2+} can lead to incompatibility between the brine system with the chemical, hence reducing its concentration in solution and its scale inhibition performance (Kan and Tomson, 2012).

Most commercial inhibitors used in oil fields are based on phosphonate and polyacrylate. Phosphonates are phosphorus-containing organic compounds that are not easily hydrolyzed due to the strong bond between phosphorus and carbon in their structure. Phosphorus and nitrogen compounds have been used effectively to prevent inorganic scale formation. Today, chemicals which are toxic and harmful to the environment are severely restricted. Therefore, it is important for the industry to develop alternative solutions, i.e., the use of green and environmentally friendly inhibitors to control the formation of mineral scales. Green chemicals are defined according to three criteria of non-toxicity, non-biological accumulation and possibility of biological degradation (Zojaji, 2020). Various natural products, especially from plants, contain generous amounts of polyphosphates, carboxylic acid groups, alcohol and aromatic amines, which are potential functionalities for adsorption or antiscalming effect of the chemical SIs. Research on

the use of plant materials as oilfield chemicals like drilling mud (Ghazali et al., 2015), biosurfactants (Silva et al., 2014) and corrosion inhibitors (Ituen et al., 2016; Ituen et al., 2017) is very active, but very little has been done to explore some plant materials as SIs. Extracts of natural plants are environmentally friendly, non-toxic, relatively less expensive, readily and sustainably available and also biodegradable. Nevertheless, this biodegradability limits the storage and long-term usage of plant extracts. Leaf extracts of Fig (*Ficus carica* L.) contains β -amyryne, umbelliferone, bergabten, psoralene, β -sitosterol, p-coumaric acid, lupeol and other organic compounds and have been used to inhibit calcium carbonate scales (Abdel-Gaber et al., 2008). Other plants materials reported as efficient scale inhibitors include sea weeds polysaccharides and soybean oil methyl ester (Miksic et al., 2005; Abdel-Gaber et al., 2011), and leaf extracts of *Punicagranutum* (Abdel-Gaber et al., 2017). There are also reports on products or compounds from plants and natural products such as humic acid, leucine, citric acid and xanthan used as scale inhibitors (Chaussemier et al., 2015). Recently, due to the limitations of the world community to protect the environment and also considering the fact that before using any scale inhibitor, laboratory studies of the inhibitor's performance under field conditions are required, environmentally friendly green inhibitors have received much attention by researchers (Zojaji, 2020).

In this research, an attempt was made to investigate the efficiency of olive leaf extract as a green inhibitor to control the formation of barite scales. To ensure the presence of functional groups such as hydroxyl and carboxyl in the olive leaf extract, a fourier transform infrared (FTIR) spectrometer was used for characterizing the extract. Brines compatibility experiments were conducted via standard jar test at reservoir temperature of 90 °C to explore the optimum inhibitor concentration. Furthermore, the effect of salinity and pH value of injected water on inhibition efficiency was also investigated.

2. Experimental Procedure

2.1. Brines Preparation

The formation brine and injection water samples were synthesized by dissolving a certain amount of high purity salts in distilled water. To prepare the injection water sample, 0.47 g sodium sulfate salt and 3.63 g sodium chloride salt were dissolved in 100 cc distilled water. The formation water sample was made by dissolving 0.26 g barium chloride and 14.98 g sodium chloride in 100 cc distilled water. All samples were passed through filter paper in order to remove any solid particles from the prepared solutions.

Olive leaf extract was prepared by two extraction methods using a Soxhlet apparatus and by boiling the powdered leaves in distilled water. In the first method, 100 g of dried olive leaves were ground into powder by grinding in a mortar. Then, 5 g of the powder was mixed with 100 cc distilled water and the extraction process was performed for 6 hours using a Soxhlet apparatus. Finally, the refluxed solution was filtered to remove any contamination and solid particles.

In the second method, 5 g of dried olive leaves that were ground into powder were mixed with 100 cc distilled water and placed on a heater stirrer. After boiling the mixture for 30 minutes, the mixture was filtered using a 0.45 μ m cellulose acetate filter paper and stored in a closed bottle at ambient temperature. A fourier transform infrared (FTIR) spectrometer was used for characterizing the olive leaves extract.

2.2. Brines Compatibility Test

Static jar tests were performed to determine the amount of scale and the performance of olive leaf extract as scale inhibitor. To this end, formation and injection water samples were mixed in different volume ratios in different glass tubes. The glass tubes were kept at constant temperature and pressure

and their content was stirred every 15 minutes to complete the precipitation reaction. After complete mixing of brines, the electrical conductivity and turbidity of the solutions were measured. Finally, by passing each solution through 0.45 μm filter paper, the solid scale was separated, dried, and weighed using a digital balance.

The same procedure was repeated by adding the olive leaf extract at various concentrations (i.e., 20, 40, 50 and 100 ml/l) to the injection water and the amount of the formed scale was measured accurately. Using the experimental data, the percentage of scale inhibition was calculated.

The salinity of injection water is a key factor in designing low salinity water injection operations. In order to observe the effect of the salinity of injected water on the green inhibitor efficiency, 2, 5 and 10 times diluted seawater samples were prepared as shown in (Table 1) and compatibility tests were conducted at different salinities. In (Table 1), SW denotes seawater and SWX indicated X times diluted seawater.

Table 1: Diluted Injection Water Composition

Concentration (ppm)	SW	SW2D	SW5D	SW10D
Na ⁺	13100	6550	2620	1310
Cl ⁻	23800	11900	4760	2380
SO ₄ ²⁻	3200	1600	640	320
TDS	40100	20050	8020	4010

One of the main parameters affecting the solubility of mineral scales is pH value. Therefore, the impact of injection water pH value on the amount of scale and inhibitor efficiency were explored in this study. To this end, the injection water samples were prepared at different pH values by adding a specified amount of Sodium Hydroxide. At each pH value, jar tests were performed at different inhibitor concentrations, and variations in the amount of scale was measured. (Figure 1) demonstrates the procedure of the experiments.

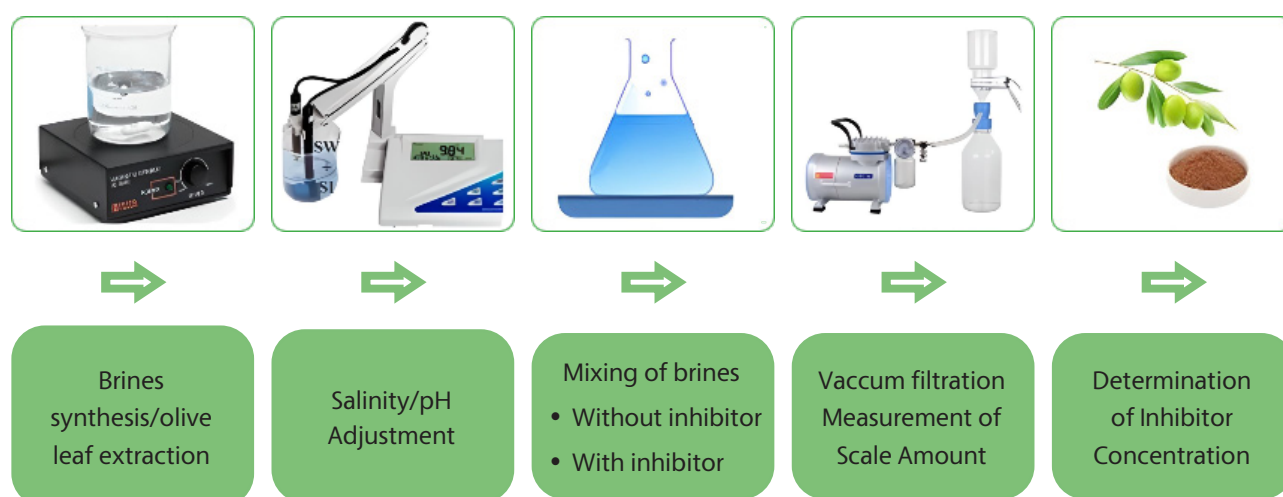


Figure 1. Schematic of the Experimental Procedure

3. Result and Discussion

(Figure 2) illustrates the FTIR spectrum of the olive leaf extract. The observed peak at wavenumber 3428.22 cm^{-1} can be attributed

to the hydroxyl functional group, and the two peaks at 1730.98 and 1631.77 cm^{-1} are related to the C = O bond of the carboxylic group.

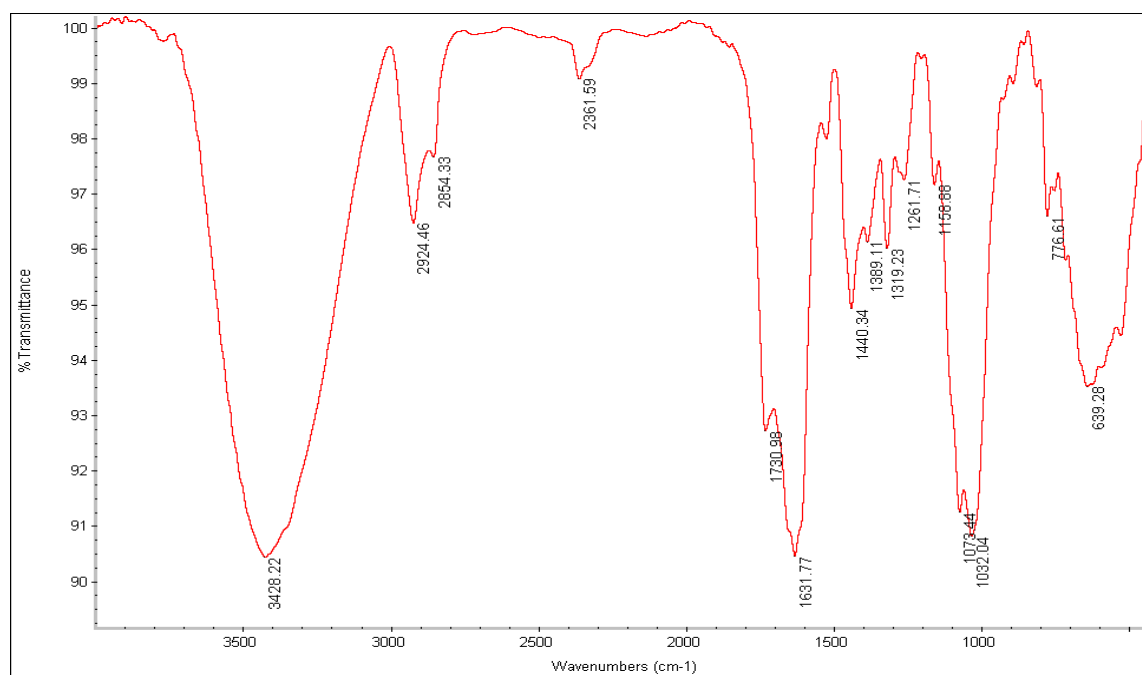


Figure 2. FTIR Spectrum of Olive Leaf Extract

3.1. Effect of Mixing Ratio

In the first set of static tests, the effect of the mixing ratio of formation brine to injection water was investigated. It was observed that with the increase in the volume of formation water more scale is formed due to the increase of barium ions concentration and more reaction with sulfate anions. As shown in (Figure 3), in the mixture containing 50% formation brine and 50% injection water, the amount of scale was measured 0.033 g, and in the solution including 90% formation brine, the amount of scale was

detected 0.074 g. The highest amount of scale was observed in the mixture containing 90% formation water. In fact, with increasing the volume fraction of formation brine, the amount of barium ions in the solution increases, and therefore the chemical reaction of barium sulfate formation (i.e., Eq. 1) proceeds toward the formation of solid phase and the formation of solid crystals of scale.

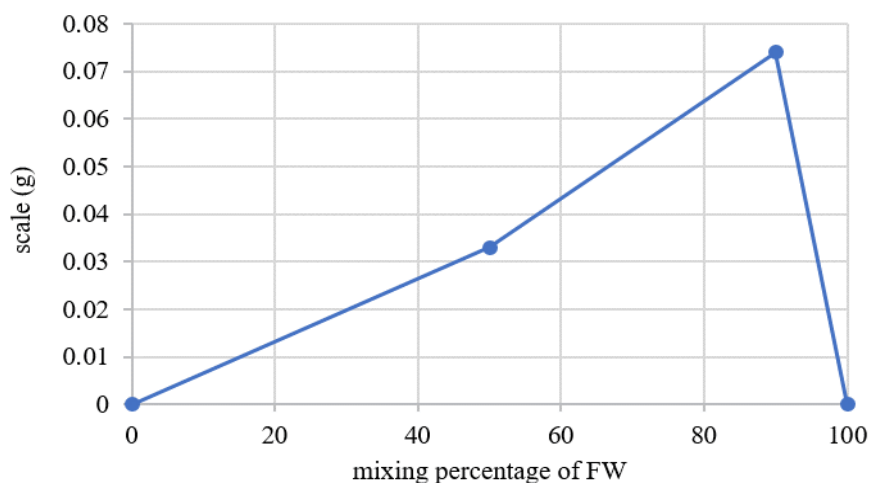
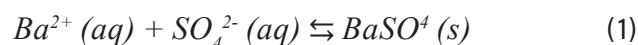


Figure 3. The Amount of Scale at Different Percentage of Formation Water

3.2. Inhibitor Performance Analysis

Static jar tests were performed at different inhibitor concentrations of 20, 40, 50 and 100 ml/liter of injected water. As can be seen in (Figure 4), the lowest amount of scale was formed at inhibitor concentration of 20 (ml/l). Increasing the concentration of inhibitor more than 20 (ml/l) leads to increase the scale amount. In fact, similar to chemical inhibitors, an optimum value for the concentration of green inhibitors should be determined to reach the highest inhibition

efficiency. For olive leaf extraction using a Soxhlet apparatus, the best efficiency was observed at the concentration of 20 ml/l, and the amount of barite scale was decreased to 0.068 g.

For the second method of extraction in which the olive leaf extract was obtained by boiling the powdered leaves in distilled water, static jar tests were repeated. As shown in (Figure 5), the best inhibition efficiency was again detected when the inhibitor concentration was 20 (ml/l).

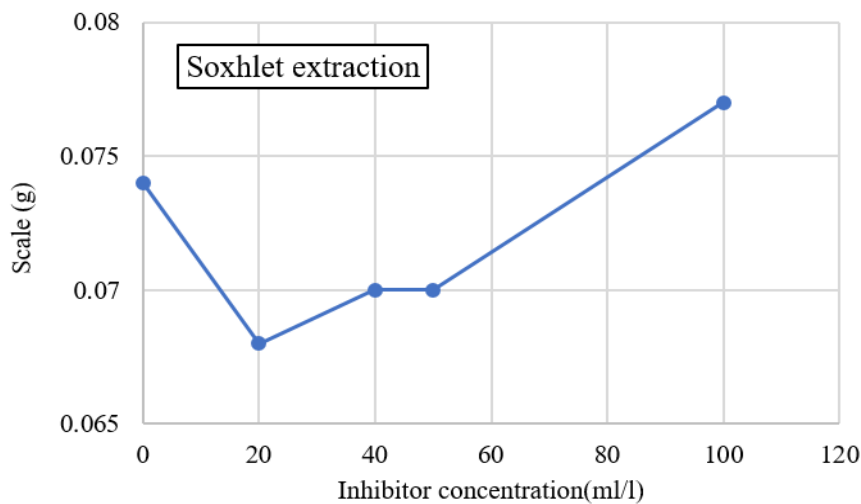


Figure 4. The Amount of Scale at Different Inhibitor Concentrations from Soxhlet Extraction

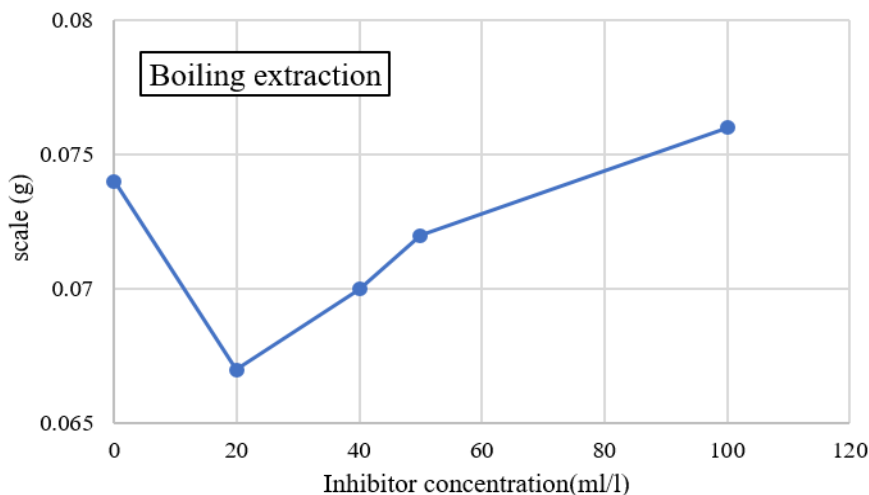


Figure 5. The Amount of Scale at Different Inhibitor Concentrations from Boiling Extraction

By comparing the obtained results of two different extraction methods, it can be concluded that the extracts obtained from both methods were equally effective in reducing

the barite scale. Therefore, the boiling method which is simpler and done in less time can be used as an effective extraction method.

3.3. Effect of Salinity

The effect of injection water salinity on inhibitor performance was explored by diluting the injection water. The measurement of the electrical conductivity of brines mixture containing inhibitor at different salinities showed that the decrease in injection water salinity, decreases

the electrical conductivity, which means that the dissolved ions in the solution are decreased. As can be seen in (Figure 6), with the decrease of injection water salinity and consequently the decrease of electrical conductivity, the amount of barite scale decreases.

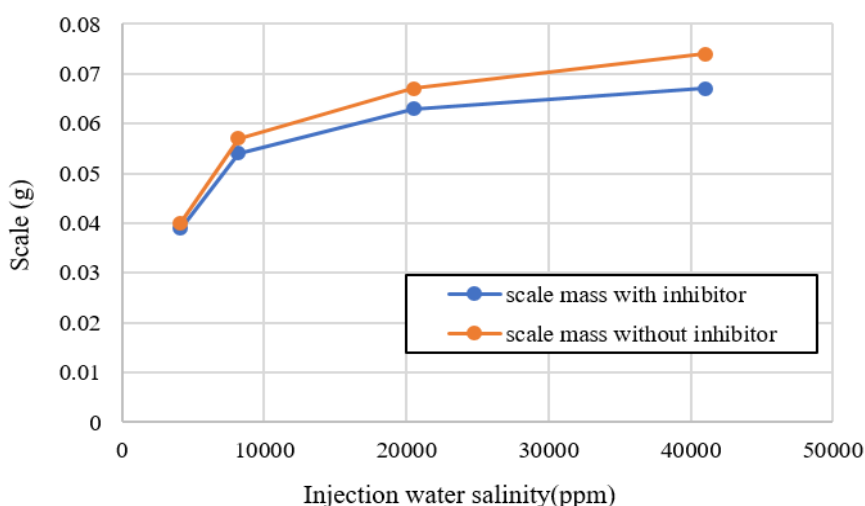


Figure 6. The Effect of Salinity on the Scale Amount

3.4. Effect of pH Value

As most mineral scales are soluble in acidic solvents, the pH value of injection water is an effective factor on inorganic scales. As shown in (Figure 7), pH value has no effect on barium sulfate precipitation in the absence of inhibitor and it can be stated that barium sulfate scale formation is independent of pH value. Similar results have been reported in the experiments of Tantayakom et al. (2005).

The effect of pH value on barite scale is different in the presence of inhibitor. It was found that with increasing the injection water pH value, the amount of scale increases slightly which is in accordance with the results of previous studies (Asadollahi et al., 2021; Merdhaq and Yassin, 2007). The amount of scale formed at pH 8.7, 9.7, and 10.7 was measured 0.070, 0.074, and 0.080 g, respectively.

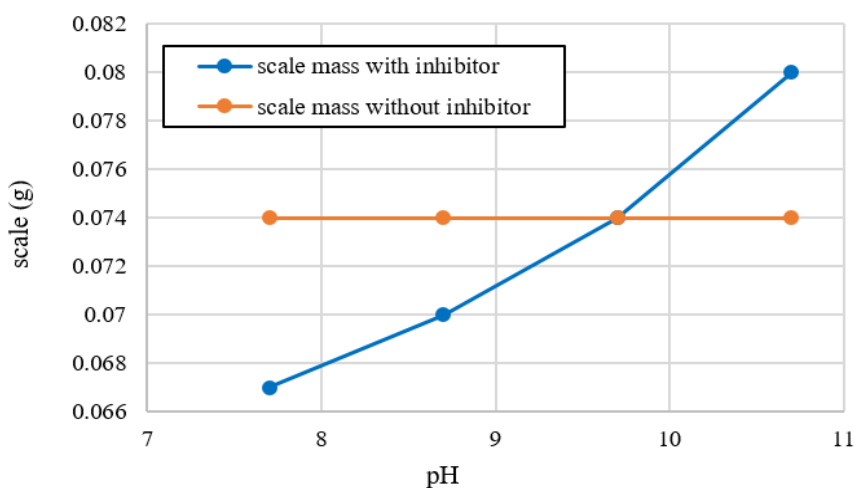


Figure 7. The Effect of pH Value on the Scale Amount

3. Conclusions

In this study, olive leaf extract was used as a novel green inhibitor to prevent and reduce barite scale formation. For this purpose, the brine samples were synthesized according to the ionic composition of formation brine and sea water, and static jar tests were conducted to investigate the efficiency of the proposed inhibitor. The effect of the volume ratio of formation brine to injection water, salinity and pH value of injection water was explored at different concentrations of inhibitor. FTIR analysis of olive leaf extract confirmed the presence of hydroxyl and carboxyl functional groups which are effective chelating agents.

Static compatibility tests showed that the highest amount of barium sulfate scale i.e., 0.37 (g/l) is formed in the mixture containing 90% formation water. By adding olive leaf extract to the brines mixture, first the amount of scale reduces and then increases. The minimum amount of scale was detected when the concentration of green inhibitor was 20 ml/liter. Although in the absence of inhibitor no change in the amount of barium sulfate scale was observed by changing pH value, but the performance of green inhibitor was decreased at higher pH values. The results of experiments at different salinities of injection water indicated that the green inhibitor has a good performance at high salinities. The findings of this study confirm that olive leaf extract can be considered as an alternative to chemical and toxic inhibitors of barite scale.

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کاربرد عصاره‌های گیاهی به‌عنوان بازدارنده رسوب باریت در عملیات تزریق آب

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چکیده

تزریق آب به مخازن نفتی یکی از روش‌های متداول جهت جبران افت فشار ناشی از تولید نفت می‌باشد. آب تزریقی معمولاً آب دریاست که حاوی یون‌هایی نظیر سولفات و کربنات است. آب سازندی اغلب دارای کاتیون‌هایی مانند کلسیم، باریم، استرانسیم و غیره می‌باشد؛ بنابراین در اثر اختلاط آب تزریقی با آب سازندی، رسوبات معدنی تشکیل می‌شوند. یکی از مهم‌ترین مشکلات در عملیات تزریق آب، تشکیل رسوبات معدنی است که موجب آسیب به مخزن، کاهش تولید، افت فشار، استهلاک تجهیزات سرچاهی و در شرایط حاد بسته شدن چاه می‌گردد. استفاده از بازدارنده‌های رسوب روش مؤثری برای پیشگیری از تشکیل رسوبات است. در این مطالعه، عصاره برگ درخت زیتون به‌عنوان بازدارنده سبز جهت کاهش تشکیل رسوب باریت استفاده شد. برای این امر، نمونه آب‌ها بر اساس ترکیب یونی واقعی آب سازندی و آب تزریقی ساخته شدند و سپس در نسبت‌های مختلف حجمی با هم مخلوط شدند. عملکرد بازدارندگی عصاره برگ درخت زیتون در غلظت‌های مختلف ارزیابی شد. مشخصه یابی ترکیبات موجود در عصاره گیاهی مورد استفاده با آنالیز FTIR انجام شد. بیشترین مقدار رسوب سولفات باریم برابر با ۰/۳۷ gr/l در مخلوط حاوی ۹۰ درصد آب سازندی مشاهده شد. نتایج آزمایشگاهی نشان داد که مؤثرترین غلظت بازدارنده برای کاهش تشکیل رسوب، ۲۰ ml/l است. علاوه بر آن، تأثیر pH و شوری آب تزریقی نیز مورد بررسی قرار گرفت و بهترین عملکرد بازدارنده در شوری ۴۱۰۰ ppm و pH برابر با ۷/۷ مشاهده شد.

واژگان کلیدی: آسیب سازند، رسوبات معدنی، بازدارنده سبز، عصاره گیاهی