

PREDICTION AND INHIBITION OF INORGANIC SALT FORMATION UNDER STATIC AND DYNAMIC CONDITIONS—EFFECT OF PRESSURE, TEMPERATURE, AND MIXING RATIO

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ABSTRACT

As a result of waterflooding, inorganic salt precipitation occurs in the different parts of an oil production system, thereby leading to damage of production equipment. Different parameters affect the kinetics of salt precipitation. Scale inhibitors are widely used to prevent inorganic salt formation. In this study, the effect of reservoir pressure, temperature, and mixing ratio of injection to formation water on calcium sulfate and barium sulfate precipitation was investigated. For this purpose, two different formation waters and one injection water were used. In addition, the effect of temperature and mixing ratio on inhibition performance was studied. Four different existing industrial scale inhibitors and one new scale inhibitor were used. The performance of the scale inhibitors was determined under static and dynamic conditions. Results of the study showed that calcium sulfate precipitation increased with an increase in temperature and a decrease in pressure. Barium sulfate precipitation was found to increase with a decrease in the temperature. The effect of pressure on barium sulfate formation was negligible. The developed scale inhibitor showed the highest performance for the prevention of calcium sulfate and barium sulfate formation. A change in temperature from 60°C to 120°C reduced the inhibitor performance by 3%. In the cases of calcium sulfate and barium sulfate, the minimum performance of the scale inhibitor was observed when the mixing ratios of injection to formation waters were 60:40 and 50:50, respectively.

Keywords: Formation damage; Formation water; Injection water; Salt precipitation; Scale inhibitor

1. INTRODUCTION

Waterflooding is widely used as a secondary oil recovery method to increase oil production (Haghtalab et al., 2014; Moghadasi et al., 2003). As a result of this operation, inorganic salt precipitation occurs in different parts of the production system. Precipitates accumulate in the pore channels of the reservoir rocks and reduce their permeability (Khormali et al., 2015; Moghadasi et al., 2004). In addition, salt is formed on the surface of production equipment and in pipeline systems (Senthilmurugan et al., 2011b). The salt formation leads to high material costs and significant losses in oil production.

The main source of inorganic salt precipitation is a mixture of two incompatible waters if they have a large amount of dissolved mineral salts (Haghtalab et al., 2014; Khormali et al., 2015; Mollakhorshidi et al., 2012). Moreover, a change in the reservoir pressure and temperature

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provides the conditions for salt precipitation from saturated solutions containing ions (Amiri et al., 2012). The most common types of salts formed during oil production are sulfate (calcium sulfate, barium sulfate, and strontium sulfate) and carbonate (calcium carbonate and magnesium carbonate).

The mechanism of salt formation involves a set of processes that lead to precipitation accumulation (Al-Roomi & Hussain, 2016). The deposition of salts during oil production is due to the crystallization from supersaturated solutions that occurs under complex hydraulic and thermodynamic conditions (Van Berk et al., 2015). Scale formation occurs because of salt nucleation and growth in the solution through homogeneous and heterogeneous mechanisms. In homogeneous nucleation, salt nucleation begins in a saturated solution in the form of unstable clusters of atoms. In heterogeneous nucleation, the salt can precipitate on the surface of existing defects such as the nonuniform surface of a liquid and pipe (Fathi et al., 2006; Melia & Moffitt, 1964).

The prediction of salt formation is significant in its prevention. To determine the possibility of salt formation, the evaluation of water saturation is usually performed. In this method, an analytical prediction of salt formation is used under specific reservoir conditions (Amiri et al., 2012). This is carried out on the basis of the physical and chemical composition of reservoir waters. The method facilitates the prediction of the possibility of salt formation in all parts of oil production systems. However, the assessment of water saturation is an approximate method (Kan & Tomson, 2012; Moghadasi et al., 2003).

Control of salt precipitation during oil production is carried out using its prevention and removal methods. Removal methods are classified into chemical and mechanical methods. The methods for preventing salt formation are divided into reagentless and chemical methods. At present, the most effective method for preventing salt formation is the use of chemical reagents-inhibitors (Gu et al., 2013; Li et al., 2014). In this case, the following factors are taken into account: geological and physical conditions of oil occurrence, ion content analysis of formation and injection waters, simulation and evaluation of the salt formation tendency, injection of selected or developed scale inhibitor, and systematic monitoring of oil well parameters (Senthilmurugan et al., 2011a; Shaw & Sorbie, 2015; Vazquez et al., 2016). All these treatments and activities are designed to ensure the efficient and reliable operation of wells. In addition, they are aimed at improving informed choice about technologically advanced methods for oil production (Guo et al., 2012; Vazquez et al., 2012).

Specific requirements are established for the scale inhibitors used in the oil industry. In particular, the scale inhibitors are regulated using such major indicators: high performance of inhibition process, low corrosion activity, compatibility with formation water, rock and other reagents, and absence of any negative effect on the oil treatment processes (Tantayakom et al., 2005; Wang et al., 2014). The effectiveness of scale inhibitors significantly depends on the properties of reservoir fluids. The type and ion content of formations considerably affect the scale inhibitor performance (Tomson et al., 2003).

The objectives of this research are the investigation of the effect of reservoir pressure, temperature, and mixing ratio of injection to formation waters (thereafter referred to as mixing ratio) on inorganic salt formation (calcium sulfate and barium sulfate). In addition, the performance of five scale inhibitors, including one new scale inhibitor for preventing salt precipitation was examined. Inhibition of inorganic salt was performed under static and dynamic conditions. Core flood experiments were carried out on the carbonate type of core samples.

2. MATERIALS AND METHODS

2.1. Scale Formation and Prediction

To predict the precipitation of inorganic salts, two different synthetic formation waters and one injection water were prepared. The ionic composition of these waters is shown in Table 1. The table shows that formation water No. 1 and injection water contain a high concentration of calcium and sulfate ions, respectively. Therefore, a mixture of formation No. 1 and injection water provides the appropriate conditions for calcium sulfate (CaSO_4) precipitation. As shown in the table, formation water No. 2 contains barium ions that form barium sulfate (BaSO_4) when mixed with the injection water. All waters have high concentrations of total dissolved salts. Therefore, they are prone to form salt under reservoir pressure and temperature.

Table 1 Formation and injection waters

Water	pH	Ion content (mg/L)								Total dissolved salts (g/L)
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Ba^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	
Formation water 1 (for CaSO_4)	6.83	38542	1649	16813	619	0	91990	627	53	150.293
Formation water 2 (for BaSO_4)	7.41	42066	1836	469	703	208	69315	233	62	114.892
Injection water	7.55	11002	348	323	1425	0	20138	2479	74	35.789

The investigation of scale formation and precipitation for CaSO_4 and BaSO_4 was performed using OLI Studio program (OLI Systems, Inc., NJ, USA). The program is one of the industrial programs for designing the water injection operation into reservoirs. This program can determine the possibility of salt formation in a mixture of injection water and formation water under reservoir conditions. In this study, the scaling tendency and amount of salt precipitation were studied on the basis of the reservoir pressure, temperature, and mixing ratio. The saturation index (SI) is used to determine scale formation, and it is defined as the logarithm of scaling tendency that is obtained by the program. Positive values of SI indicate inorganic salt formation (Amiri et al., 2012; Moghadasi et al., 2003).

2.2. Scale Inhibition

To prevent the precipitation of the inorganic salts, different scale inhibitors were used, as listed in Table 2. As shown in the table, DTPMP and ATMP are phosphonate scale inhibitors. PPCA is a polymeric scale inhibitor. PBTC is a liquid inhibitor with a density of about 1300 kg/m^3 . Inhibitor No. 5 is a recently developed scale inhibitor that is composed of two phosphonate scale inhibitors and other additives (Khormali & Petrakov, 2016). The efficiency of the scale inhibitors was evaluated under static and dynamic conditions.

Table 2 Scale inhibitors

Inhibitor number	Abbreviation	Composition
1	DTPMP	Diethylenetriamine penta (methylene phosphonic acid)
2	ATMP	Aminotrimethylenephosphonic acid
3	PPCA	Poly-phosphino carboxylic acid
4	PBTC	2-phosphonobutane-1,2,4-tricarboxylic acid
5	New inhibitor	1-Hydroxyethylidene-1,1-diphosphonic acid, NH_4Cl , polyethylene polyamine-N-methylphosphonic acid, HCl , $\text{C}_3\text{H}_8\text{O}$, water

2.2.1. Inhibition performance under static conditions

The efficiency of the scale inhibitors under static conditions was investigated using a jar test. In

this case, the cation concentration in the solution of formation and injection waters was measured with and without scale inhibitors. In further tests, 30 mg/L of scale inhibitors were used. Therefore, the inhibitor performance is determined as follows (Kumar et al., 2010; Senthilmurugan et al., 2011b):

$$E\% = \frac{C_2 - C_1}{C_0 - C_1} \times 100 \quad (1)$$

where C_0 , C_1 , and C_2 are the cation concentrations in the solution before testing, after testing without the scale inhibitor, and after testing with the scale inhibitor in mg/L, respectively.

2.2.2. Inhibition performance under dynamic conditions

Core flood experiments were performed to measure the effectiveness of scale inhibitors in preventing salt precipitation in core samples. The diagrammatic representation of the experimental apparatus is shown in Figure 1. This apparatus simulates reservoir conditions. Two solution tanks were used to mix formation and injection waters at the required ratio. The scale inhibitor was added to the injection water. Then, an aqueous scale inhibitor solution was prepared and injected into the core samples. The injection rate was 7 mL/min and the core samples were carbonate type. The reduction in the permeability (formation damage) due to salt precipitation in the core samples was determined using Darcy's law. In this study, the ratio of damaged permeability to initial permeability was studied with and without the scale inhibitor.

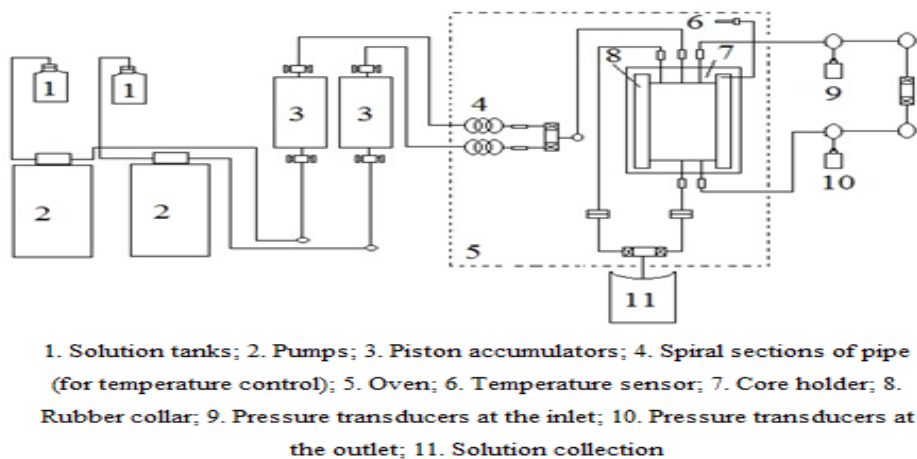


Figure 1 Experimental apparatus for inhibitor injection into core sample

3. RESULTS AND DISCUSSION

3.1. Datasets

The amount of salt precipitation was obtained using OLI Studio program. CaSO_4 precipitation is presented in Figure 2. As shown in Figure 2, CaSO_4 precipitation depends on pressure, temperature, and the mixing ratio of injection water to formation water No. 1. CaSO_4 is formed at temperatures higher than 40°C at a constant pressure of 20 MPa. At the constant pressure, CaSO_4 precipitation was found to increase with temperature. In this case, at temperatures lower than 85°C , the highest salt precipitation occurred when the mixing ratio was 60:40. At temperatures higher than 85°C , the highest salt precipitation occurred at a mixing ratio of 80:20. In addition, the dependence of CaSO_4 precipitation on pressure demonstrates that more salt was formed at lower pressures. The salt precipitation was rapidly reduced with an increase in pressure. At a constant temperature and lower pressure, higher values of CaSO_4 precipitation

were obtained at a mixing ratio of 80:20. However, at a higher pressure (more than 10 MPa), the highest amount of salt precipitation was observed at a mixing ratio of 60:40.

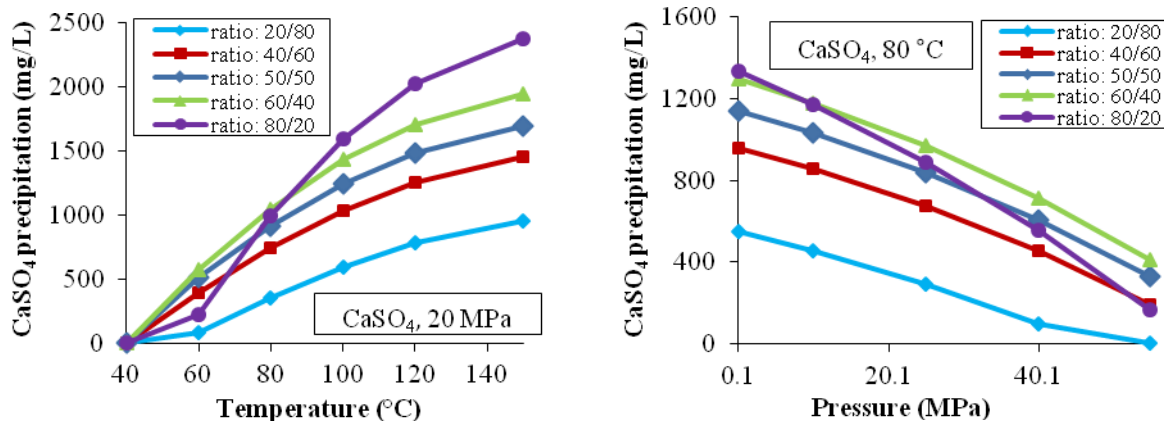


Figure 2 Effect of temperature, pressure, and mixing ratio on CaSO₄ precipitation

Figure 3 shows the SI values of BaSO₄ versus the percentage of injection water in the mixture with formation water No. 2 at different temperatures and pressures. A salt is formed if the SI value is more than zero. As shown in the figure, the SI of BaSO₄ decreases with increasing temperature at a constant pressure. The maximum amount of BaSO₄ was formed when the mixing ratio of injection water to formation water No. 2 was 60:40. In the solution of injection water without formation water, BaSO₄ was not formed because the injection water did not contain any barium ion. As shown in Figure 3, the pressure does not affect the SI of BaSO₄. Formation water No. 2 (a solution without injection water) had a high tendency to precipitate BaSO₄ at any pressure and temperature.

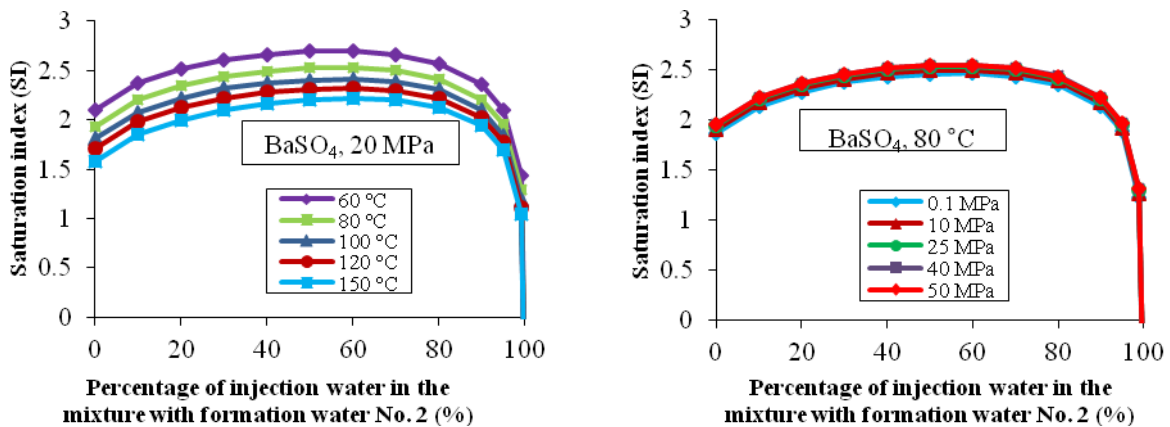


Figure 3 Effect of temperature, pressure, and mixing ratio on BaSO₄ saturation index

3.2. Results of Scale Inhibition

3.2.1. Preventing salt formation under static conditions

The efficiency of preventing inorganic salt formation for all the scale inhibitors was determined under static conditions in a concentration range from 5 mg/L to 50 mg/L. The investigation was performed at a constant temperature of 80°C. All tests were performed at a 50:50 mixing ratio. The efficiency was measured using Equation 1. The results of this investigation are presented in Figure 4. As shown in the figure, the developed scale inhibitor (No. 5) has the highest efficiency for preventing CaSO₄ and BaSO₄ formation. The optimum concentration of this inhibitor was 30 mg/L. At this concentration, the scale inhibitor performance was 90% and

higher. DTPMP and PBTC had a high inhibition efficiency for CaSO₄ scale formation in the mixture of injection water and formation water No. 1. These two inhibitors reached the maximum value of performance at 40 mg/L. For preventing BaSO₄ scale formation, excluding the new inhibitor, the efficiency of PPCA was found to be higher than those of other industrial scale inhibitors. Figure 4 shows that the inhibition performance increases with the inhibitor concentration.

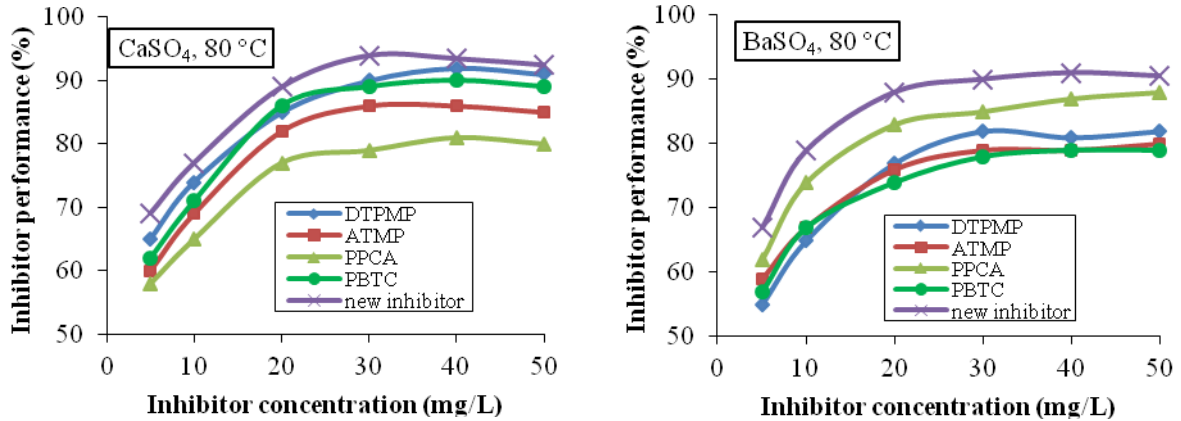


Figure 4 Scale inhibitor performance for CaSO₄ and BaSO₄ prevention versus the inhibitor concentration at a constant temperature

As observed in Figure 4, the new inhibitor has the highest performance for preventing inorganic salt precipitation. Therefore, the effect of temperature and mixing ratio on the performance of the new inhibitor was investigated. The results of the study are presented in Figure 5. In this case, the inhibitor was used at a constant concentration of 30 mg/L under static conditions. The mixing ratio was 50:50 when studying the effect of temperature. Figure 5 shows that the inhibitor performance for preventing CaSO₄ scale formation does not considerably reduce (3%) with an increase in temperature. In addition, in the case of BaSO₄, the performance increased by 3% with an increase in temperature from 60°C to 120°C. As shown in the figure, at a constant temperature, the inhibition performance for CaSO₄ and BaSO₄ scale formation reduces with an increase in the mixing ratio of injection to formation waters until a specific value. Then, the performance increases with the mixing ratio. The minimum performance of the scale inhibitor for preventing CaSO₄ and BaSO₄ formation was observed at 60% and 50% of injection water in the mixture with formation water, respectively.

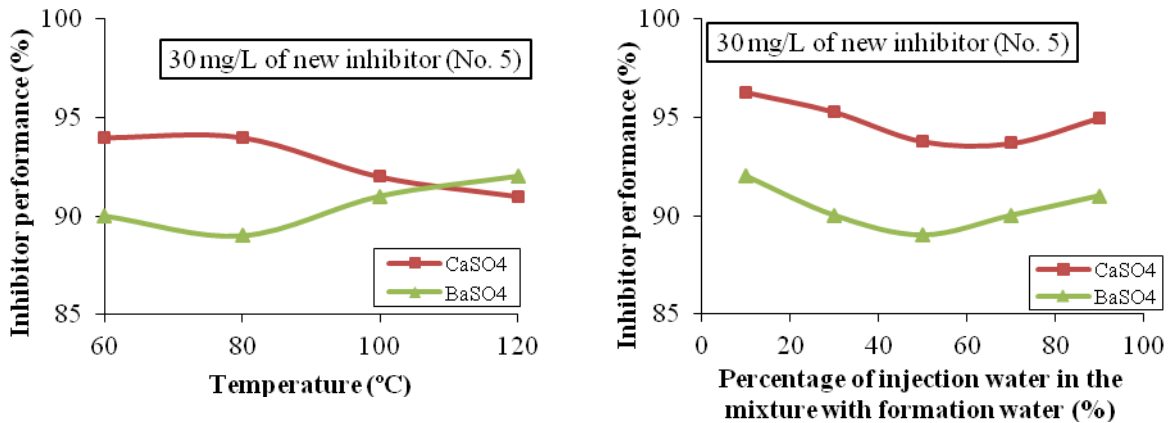


Figure 5 Effect of temperature and mixing ratio on the performance of the new inhibitor (No. 5)

3.2.2. Preventing salt formation under dynamic conditions

The results of CaSO_4 precipitation in the core sample and its inhibition using the new inhibitor (No. 5) are shown in Figure 6. The figure presents the formation damage owing to CaSO_4 precipitation in a carbonate core sample with and without the injection of the inhibitor. Moreover, Figure 6 illustrates the effect of temperature on CaSO_4 precipitation under dynamic conditions. As shown in the figure, the permeability decreases with an increase in temperature. Inhibitor No. 5 effectively prevented CaSO_4 formation at any temperature in the core sample. In the case of inhibitor injection, at first, the permeability ratio was found to decrease with time. However, after a defined period of inhibitor injection into the core samples, the permeability ratio remained constant. For higher temperatures, this constant value was reached earlier.

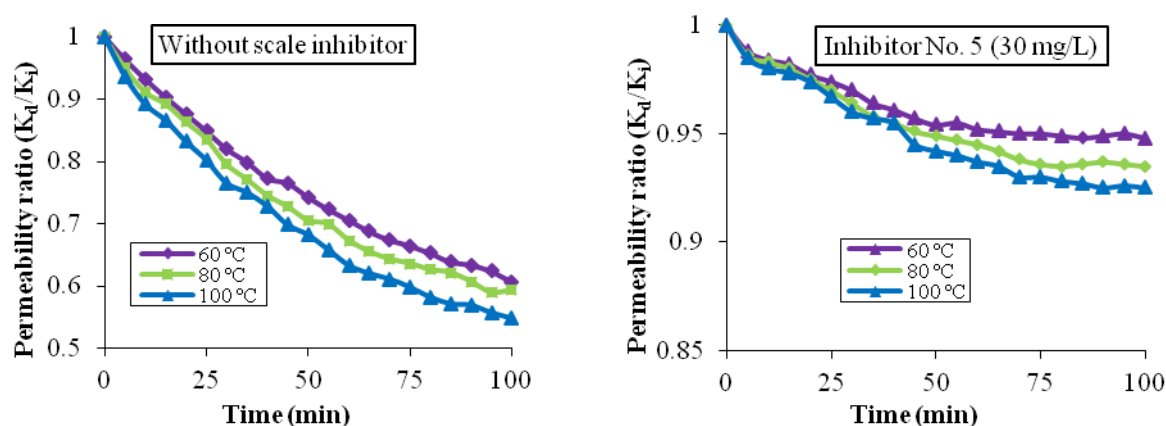


Figure 6 Change in the permeability ratio because of CaSO_4 precipitation at different temperatures

4. CONCLUSION

In this study, the effect of reservoir temperature, pressure, and mixing ratio of injection to formation waters on the precipitation of calcium sulfate and barium sulfate was investigated. The prediction of scale formation and its precipitation was determined using the OLI Studio program. In addition, the inhibition efficiency of different scale inhibitors was measured under static and dynamic conditions. Based on the results obtained in this study, the following conclusions can be drawn:

1. Calcium sulfate precipitation increased with an increase in temperature and a decrease in pressure at different mixing ratios of injection to formation waters. The highest amount of precipitation occurred when the mixing ratio was 80:20 at higher temperatures and lower pressures. Moreover, at lower temperatures and higher pressures, the highest values were observed when the mixing ratio was 60:40. The highest amount of barium sulfate precipitation occurred at a mixing ratio of 60:40. Pressure did not affect barium sulfate formation. The possibility of barium sulfate formation decreased at higher temperatures.
2. Under static conditions, the new scale inhibitor showed the highest level of efficiency for preventing the formation of calcium sulfate and barium sulfate precipitates. The industrial inhibitors DTPMP and PBTC showed sufficient inhibition performance for preventing calcium sulfate formation. The polymeric scale inhibitor PPCA prevented barium sulfate formation better than other industrial inhibitors.
3. The efficiency of the developed scale inhibitor did not significantly change with the temperature and mixing ratio. The inhibitor showed a high efficiency at any temperature (60°C to 120°C) and mixing ratio for preventing calcium sulfate and barium sulfate formation. The injection of the inhibitor into the core samples reduced formation damage,

and permeability ratio value was increased up to 0.95. Temperature did not significantly affect the inhibitor performance under dynamic conditions.

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