



Enhancing the Efficiency of Scale Inhibitor Squeeze for Mature Fields of the Campos Basin – RJ Using Ca²⁺ Bridging Ion

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Abstract

The Campos Basin is one of the main sedimentary areas already explored in the Brazilian coast, with mature fields, which are in an advanced stage of production, of which some use seawater injection as recovery method. The seawater injected can be incompatible with the formation water, and with the production, can precipitate insoluble inorganic compounds, in this case barium and strontium sulfates (BaSO₄ and SrSO₄). The main method of preventing scale in the reservoir is periodic scale inhibitor squeeze surrounding the production well. In this work, coreflood laboratory tests were performed using phosphonate inhibitor and Ca²⁺ as an additive. The objective was to access Ca²⁺ as an additive to increase the squeeze lifetime, reducing well interventions for the sandstone reservoirs of the Campos Basin. The results showed that Ca²⁺ as an additive resulted in an increased performance of the scale inhibitor squeeze treatment.

Keywords

flow assurance; scale remediation; scale inhibitor squeeze; inhibitor retention; squeeze life.

Introduction

The Campos Basin is the second most oil and gas producing sedimentary area already explored at the Brazilian coast. It stretches from the southern of Espírito Santo state, to Arraial do Cabo – RJ, with approximately 115,800 km². Its exploration activities began in 1968 and its first discovery of oil was the Garoupa field in 1974⁵.

These fields require recovery methods for supplementing the energy (pressure) of the reservoir for production maintenance¹. Many of these fields are producing large amounts of water associated with oil.

A mature field example of the Campos Basin is the giant Marlim field, discovered in 1985, which is at an advanced stage of production with high water cut. In Marlim field the injection of seawater is used as recovery method (rich in sulfate ions). This injected water is incompatible with the formation water (rich in barium and strontium), precipitating inorganic scale (mainly barium sulfate) in the reservoir, especially in the

surrounding of the producing wells, resulting in production loss due to reduction of permeability^{6,7}.

The main technology used for sulfates scale management in the surroundings of the production wells is called a scale inhibitor squeeze, which consists of the sequential injection of treatment fluids into the reservoir of the producing well^{9,14,15}. The scale inhibitor is retained in the pores of the reservoir rock and then released gradually, when the well returns production, avoiding the formation of scale for a certain period. Currently, we seek to test an additive that can increase the efficiency of treatment and the lifetime thereof^{16,18}.

This study evaluated Ca²⁺ as an additive to a phosphonate scale inhibitor, in laboratory tests using core samples of natural sandstone reservoirs of the Campos Basin. A numerical simulation was also performed, using a commercial simulator, with the data obtained in laboratory, upscaling the results for a real field.

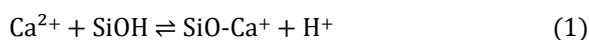
Methodology

The overwhelmingly anionic nature of the inhibitor molecules results in an electrochemical repulsion to the negative charges of the silica surface of the sandstone reservoirs, at high pH values. Increasing inhibitor retention by adsorption, requires the modification of the rock surface, creating a positively charged surface and less repulsive to the negatively charged inhibitor ^{4, 11, 12}.

Additives are evaluated to contain the desired functionality to adsorb the negatively charged surface of the rock, which present more positively charged surface, facilitating the adsorption of the inhibitor at pH values between 2 and 6 ¹¹.

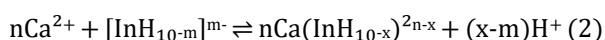
Increased adsorption of the inhibitor can be achieved by the mechanism of connecting bridges electrostatic forces due to the presence of Ca²⁺, which can alter the electrochemical properties of the solid rock surface ^{3, 13}.

It is reported that the addition of a divalent cation (Ca²⁺) to the aqueous phase binds to the solid surface via the oxygen of SiOH group. When the Ca²⁺ is adsorbed to surface SiO₂, each Ca²⁺ is connected to a SiOH group, releasing only one hydrogen given by the reaction in Eq. (1).



This reaction occurs more heavily at high pH (especially above pH 5) and adsorbed amount is proportional to the surface area. Ca²⁺ adsorbed on the rock can act as a bridge between the surface and the anionic molecule inhibitor ^{8, 13}.

Ca²⁺ may also react with the phosphonate inhibitor, according to the reaction in Eq. (2).



This complex can rapidly adsorb to the rock face, whereas high pH and high concentrations favor the interaction of calcium with the phosphonate inhibitor ^{2, 10, 13}.

Experimental Procedure

Several tests were performed to evaluate Ca²⁺ ion as an additive to a phosphonate scale inhibitor solution. The selected scale inhibitor properties are shown in Tab. 2.

Table 2. Properties of the scale inhibitor

Density (g/cm ³)	1.1425
Phosphorus concentration (mg/l)	38,980
Solubility	Water
pH	4.6
μ (cP) @ 4.44°C	14.8

Compatibility test

A 10% v/v inhibitor solution was mixed with the additive at a set of predetermined concentrations. The Tests were carried out at room temperature (21 °C) and 75 °C, where the solutions were heated (in ovens), separately, then mixed and monitored for 24 hours.

Efficiency test

A Dynamic Scale Loop (DSL), with a constant flowrate of 10 ml/min, Fig. (1), was used to evaluate scale inhibitor efficiency in the field scenario: a mixture of 70% seawater and 30% formation water (Tab. 1), 70 °C and 100 psig.

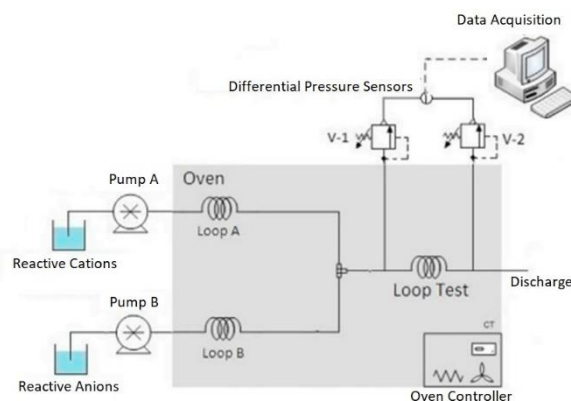


Figure 1. Dynamic Scale Loop (DSL)

Table 1. Chemical composition of the water used in the efficiency test (concentrations in mg/l)

Na ⁺	16,315
K ⁺	164
Mg ²⁺	871
Ca ²⁺	661
Ba ²⁺	23
Sr ²⁺	103
Cl ⁻	28,371
Br ⁻	38
SO ₄ ²⁻	1,454
HCO ₃ ⁻	270
pH @ 25°C	7.3
Total salinity as NaCl	46,768

Coreflood test

This test simulates a scale inhibitor squeeze treatment, evaluating the performance of the inhibitor. Core samples from oil-producing sandstones of the Campos Basin were used. The same water composition of the efficiency test was used, without HCO₃⁻ and SO₄²⁻, and mixture of mineral oils with similar viscosity to the field. The procedure was carried out according to the following steps:

1. The core sample is placed inside the core holder and conditioned to the test conditions (temperature and confining pressure).
2. Measurement of oil permeability at irreducible water saturation, K_{oi} (S_{wi}), using an oil-water separator (OWS) to determine the S_{wi}.

- Measurement of water permeability at residual oil saturation, K_{wi} (S_{or}) using an OWS for determination of S_{or} .
- Main treatment of inhibitor solution (6 Pore Volumes of inhibitor solution) in reverse flow.
- 24 hours shut-in, maintaining a constant temperature and confinement pressure.
- Injection of approximately 800 Pore Volumes (PV) of water, collecting the effluent for further analysis of the released inhibitor.
- Redo steps 2 and 3 to measure K_{wf} (S_{or}) and K_{of} (S_{wi}).
- Calculation of the damage coefficient in the sample due to the scale inhibition treatment performed, Eq. (3).

$$DAMAGE = (1 - K_f/K_i) * (100) \quad (3)$$

Results and Discussion

Compatibility test

The selected scale inhibitor is known for its tolerance to high concentrations of calcium, Ca^{2+} . Therefore, solutions containing 10% v/v of inhibitor and 10,000 to 40,000 mg/l of Ca^{2+} were evaluated. The inhibitor and the additive were fully compatible, as the solutions did not show visual changes such as precipitation and turbidity.

Efficiency test

Fig. (2) shows the scale inhibitor efficiency test results. A Minimum Inhibitory Concentration (MIC) of 70 ppm was considered, as it is the lowest concentration evaluated for which there was no increase in pressure differential due to the occurrence of scaling.

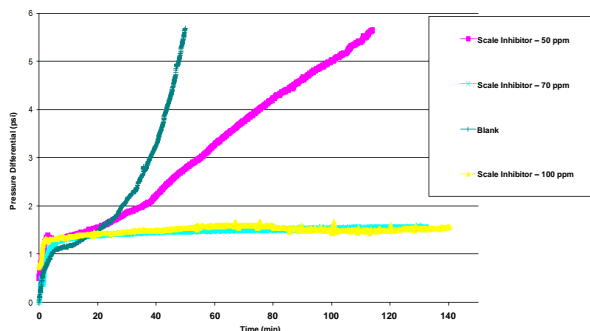


Figure 2. Efficiency test results

Coreflood tests

Three two-phase flow tests in porous media were performed to evaluate the effect of the additive on retention and release of the scale inhibitor.

Coreflood test 1 – Ca^{2+} 10,000 mg/l as an additive: the release curve from test 1 showed better performance compared to the curve for a treatment without additives (reference treatment), reaching the MIC at approximately 130 PV versus 20 PV for the reference treatment, as shown as Fig. (3).

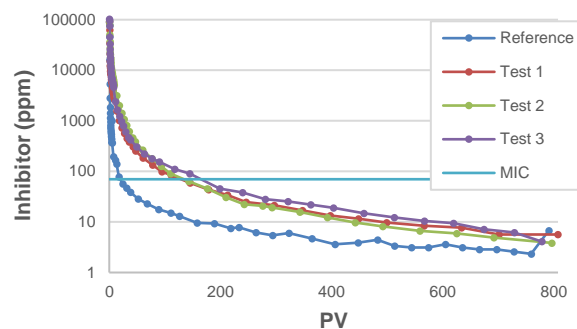


Figure 3. Inhibitor release curves – inhibitor concentration in the effluent versus the pore volume of the effluent sample

The release curve of test 1 also tended to stabilize at a constant concentration above the stabilization of the reference treatment. If the MIC changes to a lower value than the current one in future production scenarios of the studied field, the test 1 formulation can result in even greater gains in squeeze lifetime.

Both test 1 and the reference treatment showed damage to oil permeability lower than 10%.

Coreflood test 2 – Ca^{2+} 20,000 mg/l as an additive: the release curve from test 2 did not perform better compared to the curve from test 1, reaching the MIC at similar PV, as shown as Fig. (3).

For concentrations lower than the MIC, the release curve of test 2 also tended to stabilize at a constant concentration below the stabilization of the test 1. If the MIC changes to a lower value than the current one in future production scenarios of the studied field, the test 2 formulation may result in lower squeeze lifetime gains compared to the test 1 formulation.

Test 2 showed damage to oil permeability lower than 10%.

Coreflood test 3 – Ca^{2+} 10,000 mg/l as an additive and pH adjusted to 6.0: the release curve from test 3 showed better performance compared to the curve from test 1, reaching the MIC at approximately 170 PV versus 130 PV for the test 1, as shown as Fig. (3). When compared with the reference treatment, test 3 reached the MIC approximately 155 PV later (approximately 7.7 times the number of PV), as shown in Fig. (3).

The release curve of test 3 also tended to stabilize at a constant concentration above the stabilization of both the reference treatment and test 1. If the MIC changes to a lower value than the current one in future production scenarios of the studied field, the test 3 formulation can result in even greater gains in squeeze lifetime.

Test 3 showed damage to oil permeability of 22.2%.

Laboratory to field simulation

A numerical simulation was performed to evaluate the behavior of the retention curve and release of scale inhibitor, generated in the laboratory coreflood tests, and to design a squeeze treatment for a real field in the Campos Basin, using SQUEEZE8 software.

All tests' formulations showed positive results in lifetime extension in the simulation of treatment scale inhibitor squeeze in the studied field. The formulation of test 3 presented the longest treatment lifetime in the real field simulation, followed by the formulation of test 1, reaching lifetimes of respectively 207 and 171 days. For comparison, the expected lifetime for the additive-free scale inhibitor solution is of 51 days.

Conclusions

The results confirm the increase in the lifetime of treatments with phosphonate squeeze inhibitor using Ca^{2+} as an additive by increasing the release/retention ratio of the inhibitor.

The test with the use of phosphonate 10% v/v and 10,000 mg/l Ca^{2+} proved to be a better alternative, combining longer lifetime with less damage to effective oil permeability, at irreducible water saturation, caused by the treatment.

The SQUEEZE 8 simulator enabled the squeeze design by calculating the lifetime of an inhibitor squeeze treatment for a real case from laboratory data.

These results contributed to the validation of a technological solution for scale management, delivering a formulation containing a phosphonate inhibitor and Ca^{2+} for use in siliciclastic reservoirs (sandstones). It should be noted extending the lifetime of a squeeze treatment reduces risks and operational costs of contingency in wells, with production stoppages.

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