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Scale Inhibitor Qualification: Evaluation for Treatment in Brazilian Pre-salt fields

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Abstract

Inorganic scale deposition is one of the main challenges related to the flow assurance in the Oil & Gas Industry. The pre-salt oilfields has been becoming very important, especially for the Brazilian market. The operational conditions in these types of scenarios are extremely favorable for precipitation of salts. The main factors for this include high salinity, high temperature and considerable changes on the pH of the produced fluid. For this work, it was possible to predict the scale indexes of some scenarios from Brazilian pre-salt fields throughout software simulations and then, a development of a suitable scale inhibitor. The chemistry showed great performance in avoiding scale precipitation for a long period of test as well as compatibility with high calcium brines. The analyzes carried out included projections on the Scale Soft Pitzer software to evaluate the thermodynamic conditions of the system, compatibility tests with brine, and tests on the DSL ("Dynamic Scale Loop") equipment, in order to verify the performance of inhibitors under dynamic conditions. The MIC, "minimum inhibition concentration", found for the PAPEMP based chemical evaluated, was the lowest one compared to other commercial grades, resulting in a very economical solution for applications in Pre-Salt fields.

Keywords
Scale inhibitor; Pre-salt; High salinity

Introduction

In the South Atlantic area, it is possible to found huge reserves of Pre-Salt fields which are common on the coast of Brazil and West Africa. According to available data, the huge oil and natural gas reserves are located below about 2000 m thick layer of salt which covers the sedimentary basins of Campos, Santos and Espírito Santo. Below it there is a large oil reserve estimated in approximately 150.000 km^2 and 300 km from the coast. This area is known as "pre-salt polygon" (REUTERS, 2020).

The discovery of the pre-salt represented self-sufficiency in Oil for Brazil, since historically the country has always needed to import it. According to the IBP (Brazilian Petroleum Institute), by 2035, Brazil will stop importing and will become an energy exporter

The first Pre-Salt Oilfield was discovered by Petrobras in the Santos Basin in 2006 and, since then, this type of application has grown fast and become very important. This boosted the demand of oilfield production chemicals, such as scale and corrosion inhibitors, emulsion breakers, biocides, among others, in order to ensure the treatment of several operational issues in these types of scenarios (HUSSEINI, 2018). Among the main problems on operations are the appearance of inorganic salts scale, which can be difficult to remove and cause significant production losses.

There are different types of scale deposits in oilfields, the most common being calcium carbonate and sulfate scales (barium, strontium or calcium). Carbonate deposits, for example, are formed mainly due to the decrease in pressure and the increase in temperature. The solubility of $CaCO_3$ decreases with increasing temperature. Through the release of carbon dioxide from oil during its production process, an increase in the pH of the medium is observed, which can promote, for example, the occurrence of carbonate incrustations.

The study of scale inhibitors with strong chelating properties, high thermal stability and huge calcium tolerance had fundamental importance in this work. The development of a high-performance solution was achieved after dynamic performance evaluation, saturation index and mass of precipitate prediction of pre-salt fields conditions, as well as the chemistry type impact on brine compatibility, especially when submitted to high-stress scenarios. A promising PAPEMP based scale inhibitor was developed after achievement of satisfactory test results.

Methodology

The methodology for this work includes initially software simulation to predict the saturation indexes of the brine as well as the theoretical deposition rates based on thermodynamic conditions.
As next steps, it was performed brine compatibility tests and dynamic tests in the DSL in order to evaluate the efficiency of inhibition considering not only thermodynamic conditions of scale precipitation but also the kinetics ones. Two of the most severe scenarios of Pré-salt were selected to evaluate the performance of the scale inhibitor developed, named in this paper as “Scenario A”, Sc. A, and “Scenario B”, Sc. B.

Experimental Procedure

Software Simulations

For all the conditions tested, Saturation Indexes (SI) and mass of precipitate to re-establish the equilibrium (ppt), were calculated by Scale Soft Pitzer software, the software developed by the Brine Chemistry Consortium at the Rice University (M. Thomson’s and A. Khan’s group).

Pre-salt dynamic scale inhibition performance test.

Dynamic scale inhibition tests have been performed by using a Dynamic Scale Rig (Techbox Systems H400) with automatic data recording of differential pressure through a stainless-steel coil. The instrument is equipped with two double pistons pumps (Knauer Azura P4.1S), one used for cationic brine and one for anionic or “inhibited anionic” brine and the cleaning solutions. The oven (Memmert UF55Plus) set is suitable for temperature up to 300°C.
In this test, anionic and cationic brines are pumped separately through two 2-m-long Hastelloy pre-heating coils and then combined by a union tee in a 1-meter stainless-teel coil (ID 1mm or 0.5mm). Differential pressure between the inlet and outlet of the coil is measured by a pressure transducer until it reaches the designed threshold value. Temperature, pressure and flow rate are set up based on field conditions and customer’s requirements. The pH of anionic brine is buffered by bubbling a mixture of CO_2 and N_2 while to buffer the pH of cationic brine HCl and NaOH solutions are used. After each test, 10% acetic acid solution, 5% alkaline EDTA solution and DI water are used to clean and restore the coil. In each experiment, a successful test is when the pressure drop does not achieve the target threshold after a time equal to 60 or 120 minutes. The experiment is designed as a single dosage test, where only cationic and inhibited anionic brine are used. The inhibited anionic brine contains 2x the inhibitor concentration to be tested in the DSL. When a concentration step is not successful – which means that the threshold differential pressure value is achieved – a new inhibited anionic brine with a different dosage has to be prepared.
$BaCl_2$*$2H_2O$), $CaCl_2$*$2H_2O$, NaCl), KCl, $SrCl_2$*$6H_2O$ (ACS Reagent, Sigma Aldrich) and $MgCl_2$*$6H_2O$ (ACS Reagent, Sigma Aldrich) had been used for the preparation of cationic brine.
$NaHCO_3$ (ACS Reagent, Sigma Aldrich), $NaSO_4$ and NaCl (ACS Reagent, Sigma Aldrich) had been used for the anionic brine. All these inorganic salts were ACS reagents of Sigma Aldrich commercial grades. For evaluating the effect of iron, $FeCl_2$*$4H_2O$ (ACS Reagent, Sigma Aldrich) was the source of Fe^{2+}. Both cationic and anionic brines had been prepared by adding all the required number of salts to DI water. Brines were left under stirring overnight, then filtered with a 0,45 µm pore size membrane. $NaHCO_3$ were added prior each test. After the completely dissolution of this salt both brines had their pH adjusted and then the DSL test were started.

Compatibility Tests

Compatibility tests had been performed removing scaling anions (sulfate and bicarbonate) from testing brine. Product was added to the brine in order to have final concentrations up to 5000 or 300000 ppm. After shaking, vials were stored in oven for 24h at testing temperature, and the visual aspect were registered after 1h, 2h and 24h. Scale inhibitor is considered approved in compatibility if in all concentrations up to 300000ppm as product no turbidity and/or precipitation or phase separation is observed after 24h.

Results and Discussion

The simulation data obtained under the conditions of Scenario A are summarized in Tab. 1. Based on this data, very high mixed carbonate and sulfate scales are predicted with high SI and deposit rates.

Table 1. SI and Deposit rate predicted for Sc. A

Scale	SI/Deposit rate
Calcite	2.21 / 718
Celestite	1.40 / 3,039
Barite	1.46 / 26
Anhydrite	0.33 / 1,285
Gypsium	0.17 / 988

DSL result for Scenario A is presented in Fig. (1) as well as the conditions of the test.

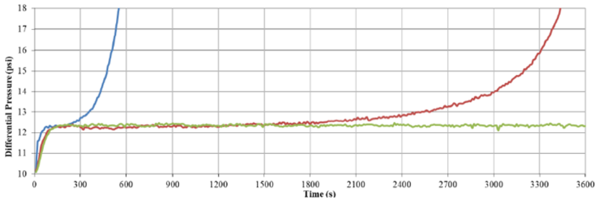

Figure 1: DSL results for Sc. A

Compatibility test for Scenario A is presented in Fig. (2).

	COMPATOBILTY TEST SCENARIO A x DEQUEST 2076A												
	0	100	250	500	1000	2500	5000	10000	20000	50000	100000	200000	300000
t=0													
t=1h													
t=2h													
t=24h													

Clear Cloudy Precipitate

Figure 2: Compatibility test for Sc. A

According to the results obtained, the PAPEMP based scale inhibitor provided excellent performance in DSL tests with only 75 ppm as MIC, showing a very good threshold effect. Furthermore, it is fully compatible with Scenario A brine up to 300000 ppm as product.

Table 2 summarize the simulation data obtained under the conditions of Scenario B. The predictions are positive SI for Calcite, Barite, and strontium sulfate, being calcite the most concerning one. In terms of, deposit rate, Calcite is by far the most critical scale with high amount of strontium sulfate expected as well.

Table 2. SI and Deposit rate predicted for Sc. B

Scale	SI/Deposit rate
Calcite	2.49 / 1,287
Celestite	0.85 / 809
Barite	0.11 / -

Figure (3) shows the DSL result for Scenario B as well as the conditions of the test.

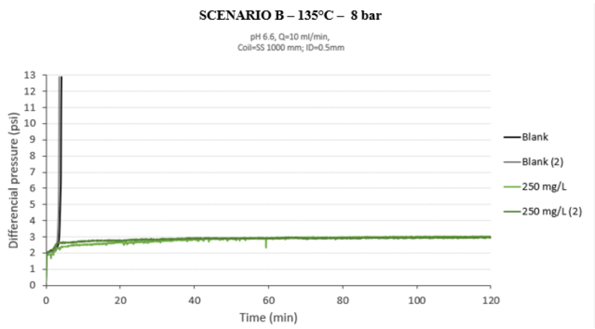

Figure 3: DSL results for Sc. B

Figure (4) shows the Compatibility test for Scenario B.

	COMPATOBILTY TEST SCENARIO B x DEQUEST 2076A									
	0	100	250	500	1000	2500	5000	10000	20000	50000
t=0										
t=1h										
t=2h										
t=24h										

Clear Cloudy Precipitate

Figure 4: Compatibility test for Sc. B

PAPEMP based scale inhibitor provided excellent results at 250 mg/L as product in DSL test performed under conditions of Scenario B, that shows the chelation/threshold effect expected for the product Moreover, is fully compatible with the brine at the concentrations tested up to 5000 ppm.

Conclusions

Pre-Salt applications are growing fast in Brazil making this country one of the most important Oil producers. Therefore, scale inhibitors demand is growing as well.

Typical conditions and brines can vary a lot depending on which field is considered. In most of the cases, Calcite is the typical scale with SI usually high and theoretical deposit rate that can reach very high values, up to 1.512 mg/L or even more.

In order to face this issue, PAPEMP based scale inhibitor was developed. As described in the paper, it overcomes standard chemistries in inhibiting Calcite under these conditions, also inhibiting other scales formations as sulfates, with high efficiency by delivering a great cost-benefit to the treatment. Further advantages are detectability, mild pH (> 4.5) which makes handling safer AND good solvent compatibility are additional benefits.

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Responsibility Notice

The authors are the only responsible for the paper content.

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