



## The combined effect of hydrates and scale formation inhibitors on the formation of scale

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### Abstract

During the production and transport of multiphase fluids, the formation of hydrates and scales is common due to the contact of water, gas, and light hydrocarbons under severe conditions of temperature and pressure. In order to minimize this problem and ensure the flow of production, the oil industry uses chemical additives that inhibit the formation of hydrates, such as monoethylene glycol (MEG), and scale inhibitors such as [((2-Hydroxyethyl)imino)bismethylene] bisphosphonic acid] (briquest 22150A). Understanding how the combination of these inhibitors impacts on salt precipitation is fundamental to flow assurance in the oil industry. In this context, the proposed work aims to evaluate the influence of the MEG inhibitor at different concentrations (20-60 wt.%) on the formation of calcium carbonate in aqueous solutions, at a temperature of 120 °C and pressure of 132 psi under dynamic precipitation conditions using the Dynamic Scale Loop (DSL) technique; and the combination of hydrate inhibitors and scale inhibitors at fixed concentration of 10 ppm. Based on the results obtained from the use of scale and hydrate inhibitors in a combined way, it appears that scaling time increases due to an increase in viscosity as well as an alteration in the morphology and size of crystals formed.

### Keywords

Scale inhibitor; hydrate inhibitor; calcium carbonate

### Introduction

Operations of oil exploration and production represent challenges due to the production and transport of oil and natural gas in locations with severe temperature and pressure conditions and high levels of dissolved carbon dioxide and salinity, which are typical of deepwater reservoirs. The presence of water produced during oil extraction, along with other factors, conveys a variety of problems. Among them, the development of inorganic scaling and the formation of hydrates stand out, which may interrupt well productivity, cause output loss and higher costs [1-3].

A common technique to avoid the formation of hydrates is the injection of inhibitors, such as the monoethylene glycol [4,5]. However, it has been noted that the presence of these hydrate formation inhibitors has a direct effect upon the thermodynamic balance of saline solutions, thus favoring the precipitation of salts present in the water of formation [6,7].

As for the saline scales, the main salts which may precipitate during the oil and natural gas production process are as follows: barium sulfate, strontium sulfate, and calcium carbonate - being calcium carbonate the most common. Several methods to inhibit or minimize the development of scale within streaming systems are employed as well, given

that the use of inhibitors is the most common one towards preventing scale - aside from being the most economical and cost-effective [8-10].

A widely used inhibitor type is that of organophosphates. They are indeed advantageous, given they do not hydrolyze easily and can support large temperature ranges. They are used in low concentrations (between 1 and 5 mg L<sup>-1</sup>) and also work as corrosion inhibitors. However, their use is considerably limited due to their environmental implications and high cost [8,11].

This scenario allows for an investigation about the mechanisms associated with formation of precipitate and scale of inorganic salts during oil production and transport, natural gas and water produced in reservoirs, producing wells and surface equipment. Hence, there is a need to evaluate the behavior of scale inhibitors and those of hydrates along with the behavior of salts in pressurized conditions.

Amongst the methodologies aimed at to study the effect of inhibitors upon the process of salt scale, a technique called Dynamic Scale Loop has shown itself as one of the most relevant ones, since it is capable to simulate the conditions of both temperature and pressure of the real process -

aside from being a swift, scalable, and accurate method [12].

Thus, this work aims to experimentally study the kinetic behavior of inorganic salts in aqueous solutions with scale and hydrate inhibitors at high temperature and pressure.

## Methodology

This section shows the experimental methodology applied in evaluating the efficiency of scale inhibitors and/or that of hydrates in saline water with the use of the DSL technique.

### Experimental Procedure

The scales tests in the DSL apparatus consisted in preparing, initially, synthetic brines with a saline composition. In these conditions, the precipitated salts of interest were obtained from a mixture of two brine (cation and anion water) of different chemical compositions (Tab. 1). These compositions are typical of produced water derived from pre-salt reservoirs.

Table 1. Composition of the synthetic saline solution used in the dynamic efficiency tests.

Cation solution	
Ion	Concentration (ppm)
Na <sup>+</sup>	50496
Sr <sup>2+</sup>	252
Ba <sup>2+</sup>	284
Ca <sup>2+</sup>	792
Mg <sup>2+</sup>	305
K <sup>+</sup>	391
Cl <sup>-</sup>	79229
Anion solution	
Ion	Concentration (ppm)
HCO <sub>3</sub> <sup>-</sup>	1544
SO <sub>4</sub> <sup>-</sup>	46
C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	138

In addition to the materials shown in Tab. 1, the following additives were used: briquest 22150A (Italmatch Chemicals) and monoethylene glycol (99.5%, Synth).

The main active of briquest 22150A is the [[(2-Hydroxyethyl)imino]bismethylene]bisphosphonic acid] as it is considered to be from the organophosphate class.

All samples were gravimetrically prepared as each salt was weighted separately with the use of an analytical balance with a precision of 10<sup>-4</sup> g. The solutions were filtered (0.45 µm nylon filter) and to promote the agitation of solutions, a magnetic stirrer was used.

### Apparatus and experimental procedure

Dynamic Scale Loop, by Scaleval, manufactured by Vinci Technologies (Fig. 1)

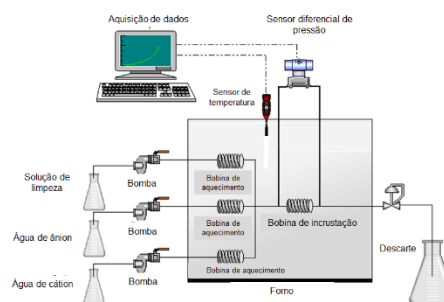


Figure 1. Dynamic Scale Loop unit.

To perform the blank tests (those without an inhibitor), equal volume mixtures of two incompatible saline solutions are injected through distinct pipelines with the help of positive displacement pumps to a total rate of 10 mL min<sup>-1</sup> under the operational pressure of 132 psi. Prior to proceeding with the mixture, the anion and cation solutions, are heated in the oven until the desired temperature. Should conditions be favorable, precipitation and deposition of solid take place somewhere in the capillary tube. As the precipitation of salt ensues, the pressure after the capillary tube increases, meaning that the differential of pressure as a function of time indicates that a salt deposition took place on the internal tube wall.

The tests with inhibitors may be conveyed with the preparation of the solutions with inhibitors of distinct concentrations. These solutions may be injected by a third positive displacement pump or may added to the anion solution. At the end of each test, the solution is discarded and an acid and/or basic solution is pumped alternatively with ultrapure water into the tube for about 30 minutes at the rate of 10 mL min<sup>-1</sup> and at room temperature in order to clean the entire unit to remove any trace of deposited salt that may be present in the capillary.

All investigated experimental results were performed at least twice, of which the standard deviations were calculated. A softening treatment was performed taking into consideration the average of the experimental replicates as well as the moving average of the obtained data.

## Results and Discussion

When utilizing the DSL with the methodology described in the previous topic, it was possible to evaluate the performance of the scale inhibitor (briquest 22150A) in different concentrations, or the effect of the hydrate inhibitor in different concentrations at the scale as well as the combined effect of these two chemical products.

Figure 2 shows the influence of the scale inhibitor on the CaCO<sub>3</sub> precipitation under a pressure of 132 psi and temperature of 120 °C. It is noted that an increase in the scaling time of all concentrations took place as compared to the blank tests. It corresponds to a decrease in the rate of CaCO<sub>3</sub>

crystal deposition and consequentially an adhesion to the capillary surface. The lengthening of the scaling time may be attributed to the preferential adhesion of inhibitors within developing nuclei - thus hindering growth beyond the critical size as necessary for precipitation [12].

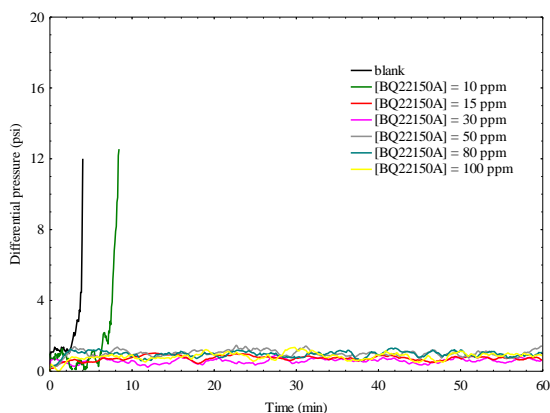


Figure 2. Effect of the addition of the scale inhibitor on the formation of  $\text{CaCO}_3$  when applying the DSL technique at 120 °C and 132 psi.

During crystal growth, scale inhibitors are generally adsorbed in different concentrations and on different types of crystal facets. Due to differing levels of growth retardation towards different facets of the crystal at hand, its shape is changed during growth and one or more crystals may appear or disappear - hence changing its morphology. The literature shows that the scale inhibitor may form complexation links with the cations, which avoids nuclei development, and consequently, incrustation formation [13].

The inhibitor adsorbed into the crystal nuclei blocks the growth area acting as a growth inhibitor of crystals [14]. In other words, the inhibitor may act in both phases: be it inhibiting nucleation or inhibiting crystal growth.

According to Shaw et al. (2012) [15], during the process of inhibition, these compounds tend to form chelated rings with the cations present in the solution. Such rings may have 5-6 or 7-8 components, being that the larger ones show a lesser thermodynamic stability due to being less rigid, rendering a lower entropy within its formation process, and consequently, reducing its inhibitory effect. Therefore, the used scale inhibitor presents itself with 5-component rings, which guarantees greater stability and inhibitory effect.

Figure 3 is the result of the effect of adding the hydrate inhibitor (MEG) into the calcium carbonate scale formation at different concentrations (20- 60 wt.%) under temperatures of 120 °C and pressure of 132 psi when applying the DSL method.

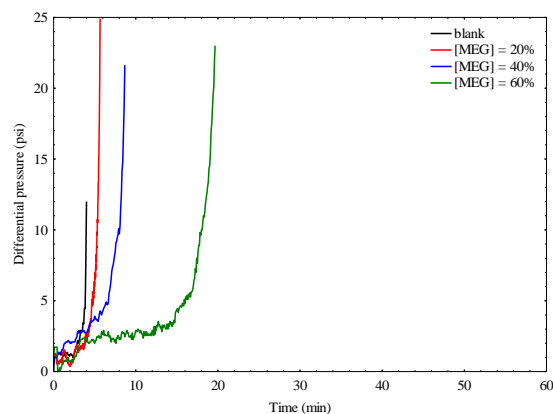


Figure 3. Effect of adding MEG hydrate inhibitors (mass basis) upon the formation of salt scale at 120 °C and 132 psi when employing the DSL method

Data shown in Fig. 3 indicate that the addition of the hydrate inhibitor increased the scaling time as observed at the instant at which the system pressure differential increases. These results are coherent with data available in the literature [6,11,16,17]. The authors observed similar behaviors associated with the induction time to the precipitation (or to that of incrustation) for lower concentrations of alcohols (< 40%).

In lower concentrations of alcohol, the supersaturation controls the process, though under higher concentrations there is an inhibiting effect which is more pronounced than the supersaturation effect itself - which encourages the increase in the timing to induce precipitation. Works in the literature [8,11,17] attributed this inhibiting effect to the increase of the solution viscosity present with these alcohols. Changes in viscosity may affect the ion transport during nucleation and crystal growth. Besides, it is known that alcohols change the interaction between solute-solvent, the dielectric constant of solution, and its viscosity, which consequently influence the formation of precipitate in the line [16,18].

The combined effect between the briquest 22150A (scale inhibitor) and the MEG (hydrate inhibitor) upon salt scale development were evaluated (Fig. 4). A given concentration of scale inhibition (10 ppm) was considered. In this condition, this compound was not effective to inhibit scales as it would be possible to observe how the alcohol would act within the system. Different concentrations of hydrate inhibitors were adopted (20-60 wt.%).

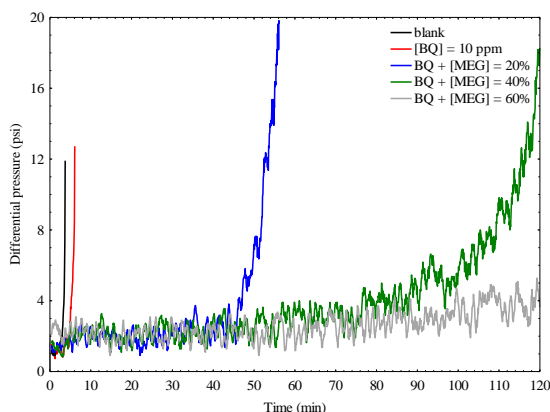


Figure 4. Effect of simultaneous addition of incrustation and hydrate inhibitors in the scale of salts under temperatures of 120 °C and pressure of 132 psi employing the DSL method.

As expected, the simultaneous addition of inhibitors increased the scaling time as compared to the tests performed in the presence of the scale inhibitor alone. It is suggested that this may be attributed to the increase in the solution viscosity and size of the formed crystals, therefore hindering both growth and aggregation of crystalline nuclei. The increase in the alcohol concentration minimized the adhesion of calcium carbonate crystals onto the metal of the pipe surface. The scale inhibitor rendered itself compatible with the hydrate inhibitor thus boosting the inhibition effect for the  $\text{CaCO}_3$  scale.

## Conclusions

The investigated results pointed to the efficiency of the commercial scale inhibitor, and that the minimum concentration required to inhibit  $\text{CaCO}_3$ , under temperature of 120 °C and pressure of 132 psi, is that of 15 ppm.

Tests performed with glycol showed a reduction in the size of the crystals which suggests that the nucleation is affected by the cosolvent. When it comes to greater MEG concentrations, the kinetics of crystal growth is reduced. Effects are associated with solution viscosity as well as the intermolecular interactions between the MEG functional groups and water.

The simultaneous addition of MEG and briquest 221-50A inhibitors demonstrated compatibility, which lengthened the timing of the salt scale inhibition. It can be attributed to the sum of the individual traits of these additives.

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## Responsibility Notice

The authors are the only responsible for the paper content.

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