



Use of Design of Experiments (DoE) on assessment of commercial inhibitors of calcium carbonate scale in O&G production: how good could it be?

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Abstract

Inorganic fouling (scale) is a physicochemical process of precipitation of ions derived from the formation water, which come across different pressure and temperature conditions throughout the production process, affecting the flow assurance management. It is mitigated mostly by using chemical additives (inhibitors). However, the evaluation of a potential compound to become a commercial inhibitor is laborious and demands a great number of experiments. The present study aimed to use a design of experiments (DoE) to evaluate the most impactful parameters on the efficiency and suitability of using a commercial scale inhibitor. The assessed variables were temperature, inhibitor, calcium and bicarbonate concentrations and salinity. The experiments followed a fractional factorial design with center points. The results expressed temperature as the most influential variable, followed by bicarbonate and calcium concentration. Even though the inhibitor studied showed promising efficiency for some scenarios, complete inhibition (> 60 min) was only achieved for a few experiments. Hence, no substantial effect was seen in the factorial design dependent on the inhibitor. Nonetheless, it still showed how the method can be used to assess factors that influence the scaling process and that the design of the experimental variables' range is crucial for a good modeling.

Keywords

scale; design of experiments; calcium carbonate

Introduction

The investigations on Flow Assurance Management have been growing due to the rising complexity of exploratory schemes for petroleum generation. One of its issues is the inorganic scale. Scale is caused by the deposition and adherence of inorganic deposits on pipelines, vessels, and surface facilities, such as heat exchangers [1,3], which can seriously block the flow in valves and pipes, impacting on the well production [4] and demanding process shutdowns. The ions forming those precipitates come from the formation (or injection) water, after changes in conditions such as temperature and pressure leads to its supersaturation [5]. When the precipitates are formed, they may adhere on the surfaces, causing the scale formation process. The predominant precipitates are calcium carbonate [3, 6], calcium/barium/strontium sulfate [7,8] followed by other types of carbonates, halite [9] and to a smaller extension, some oxides, hydroxides and silicates [1]. Among them, calcium carbonate is especially interesting due to carbonate rocks and the pre-salt scenario [10], besides its phenomenal decreasing solubility as the temperature increases [11], unlike most salts.

To mitigate scale, the best cost-efficiency solution is by chemical inhibition. An ideal inhibitor must be soluble in water [12], compatible with sea and formation water [13], thermally stable, effective at large pH ranges, efficient at small inhibitor concentrations to retard and/or prevent the scaling process [14,1], minimally toxic, greatly biodegradable, not expensive and released gradually and continuously on the production water [15]. Undoubtedly, it is difficult to gather all those qualities on a single compound, but the previous laboratory steps are fundamental to reach them as much as possible. Amongst them, the efficiency is one of the main parameters for field application. It can be evaluated by static and dynamic tests, which are complementary to each other. The first gathers information about the mechanisms by which the compound inhibits. The second simulates the dynamic conditions of production by a continuous flow of the ion solutions on a metallic tube, allowing homo- and heterogeneous nucleation to take place, alongside adherence and agglomeration. The output pressure is set and the input changes over the scaling formation process, as the tube is gradually blocked. The differential pressure (dP) *per* time is plotted. This second method is also called Dynamic Tube Blocking Test (TBT) [6,16, 17].

However, the water composition changes from one scenario to another. Therefore, estimating the efficiency of a chemical is dependent on the water composition considered, requiring constant laboratory analyses wherever there is a new formation water composition. There are several variables involved on the scaling process, which can interact with one another. Besides the concentration of the precipitating ions, pressure, salinity, temperature, flow rate, inhibitor concentration, pH and magnesium (II) concentration interfere on calcium carbonate scale formation. Understanding their influence alongside their interactions can be done by a mathematical model, as the one built on the work of Karnaller *et al.* (2018). They have explored the influence of 5 variables: temperature, pressure, calcium and bicarbonate concentrations and their relation to MEG concentration, a hydrate inhibitor, on calcium carbonate scaling formation. They concluded pressure is a statistically insignificant variable, unlike the others assessed.

The present study aims to continue this investigation on the same variables, except the pressure which will be changed by salinity, and their relation on a commercial scale inhibitor efficiency. This method is an initial proposition on a different way to evaluate inhibitors, aiming to propose future application and technologies for mathematical modeling, which would assess product evaluation with less experiments.

Methodology

Variables and range selection

The five variables related to calcium carbonate scale evaluated on this work were: temperature; inhibitor, calcium and bicarbonate concentrations and salinity (determined as sodium chloride concentration). The range of each parameter was chosen based on literature [3,6,16] alongside the expertise of the research group. For defining the inhibitor range, there different inhibitors were tested on the critical condition (100°C, [Ca²⁺] = 7000 ppm, [HCO₃⁻] = 3500 ppm) and, afterwards, on the moderate condition (80°C, [Ca²⁺] = 4000 ppm, [HCO₃⁻] = 2000 ppm). The salinity was kept at the central level (100,000 ppm) for both assays. The pressure was set to 75 bar; the pH, to 7.0; and the flow rate of each pump, to 5 mL min⁻¹.

Design of Experiments (DoE) selection

The fractional factorial design 2⁵⁻¹ alongside 6 replicates of the center point was chosen for screening purposes. The experimental spreadsheet was made manually, under the NIST/SEMATECH Handbook guidelines. For screening purposes, the Pareto diagrams were performed on *Statgraphics 19*©.

Inhibitor selection

The first inhibitor (Inhibitor A) used was tested on the drastic condition, on the concentrations of 0, 10, 50, 100 and 500 ppm. Two other commercial

inhibitors (Inhibitors B and C) were examined on the critical and, later, on moderate conditions, at concentration of 500 ppm. Inhibitor B was chosen for the following steps. The inhibitor center point was set as 750 ppm.

Laboratory analysis

The resulting DoE spreadsheet carried out can be seen on Tab. 1, where X1 = temperature, X2 = [inhibitor], X3 = [Ca²⁺], X4 = [HCO₃⁻], X5 = [NaCl]. The temperature is expressed on degrees Celsius and the concentrations on ppm.

Table 1: Experimental table of the DoE.

EXPERIMENT	X1	X2	X3	X4	X5
1	80	667	4000	2000	116667
2	100	667	4000	2000	83333
3	80	833	4000	2000	83333
4	100	833	4000	2000	116667
5	80	667	7000	2000	83333
6	100	667	7000	2000	116667
7	80	833	7000	2000	116667
8	100	833	7000	2000	83333
9	80	667	4000	3500	83333
10	100	667	4000	3500	116667
11	80	833	4000	3500	116667
12	100	833	4000	3500	83333
13	80	667	7000	3500	116667
14	100	667	7000	3500	83333
15	80	833	7000	3500	83333
16	100	833	7000	3500	116667
17-22	90	750	5500	2750	100000

The experiments were performed randomly on a Dynamic Tube Blocking Test (TBT) equipment, where two solutions were mixed: the cations and the anions. The inhibitor was always added to the anion solutions. The preparation of the cation solution was made from the dilution of a calcium stock solution, prepared by the dissolution of the reagent CaCl₂·2H₂O on type-I water, dissolving the corresponding amount of NaCl. Before performing the analysis, the solution was degassed by using a vacuum system and the pH was adjusted for 7.0±0.1. On the other hand, the anion solution was prepared immediately before the analysis. The corresponding volume of type-I water was degassed by the same vacuum system and afterwards, it solubilized the corresponding NaCl and NaHCO₃ weights until the precise volume. Its pH was also adjusted for 7.0±0.1. Afterwards, the inhibitor was added. The pressure was maintained on 75 bar and the flow rate of each pump was kept 5 mL min⁻¹ for every analysis.

Results and Discussion

A first commercially available inhibitor (Inhibitor A) was chosen and tested in different concentrations. Figure 1 shows the results of its efficiency after the Dynamic Tube Blocking Test. It can be seen that in the critical condition, the inhibitor has proven inefficient, even on the higher (500 ppm)

concentration tested. Greater concentrations were not performed, because the aim of the study focused on industry-applicable inhibitor conditions. Therefore, concentrations greater than 1000 ppm cause logistics concerns, being undesirable.

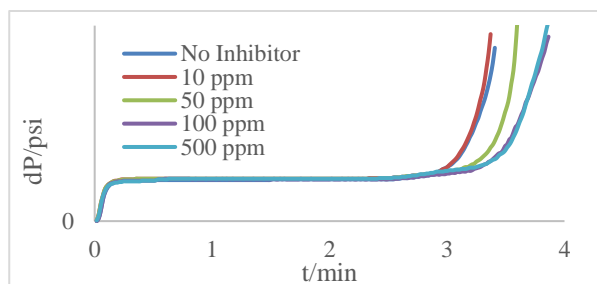


Figure 1: TBT evaluation of inhibitor A at critical conditions.

Other 2 inhibitors were examined on the same condition, as indicated on Fig. 2. Inhibitors B and C showed some inhibition, however for a little period, showing that the chosen condition is indeed critical and exceeds the inhibition capacity of all selected inhibitors.

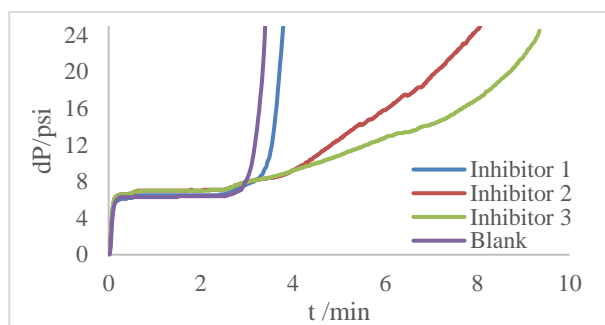


Figure 2: TBT evaluation of inhibitors A, B and D on concentration of 500 ppm at critical conditions.

Inhibitor B was also tested on a moderate condition, where temperature and ion concentrations were lower. In this condition, the inhibitor was able to stop the scale formation for over than 60 min at 500 ppm, as shown on Fig. 3. According to protocols commonly used for evaluating the inhibitors efficiency, this time is enough to approve a product.

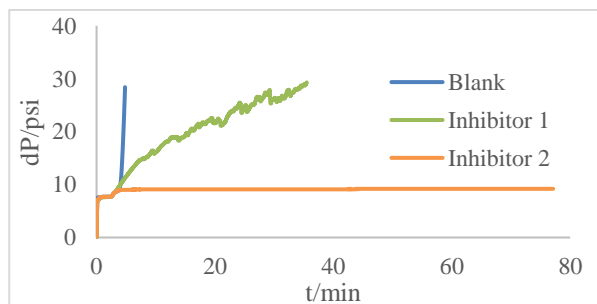


Figure 3: TBT evaluation of inhibitors A and B at moderate conditions.

Based on their performance, Inhibitor B was chosen as a model to test conceptually the DoE

methodology for variable screening. The idea was to assess if a model could be constructed for scenarios ranging from subsea to topside applications, as normally used by the industry. Subsea application tends to happen in lower temperatures and higher pressures, whilst topside application is the opposite. Also, a very large range in calcium and bicarbonate concentrations were used, as to assess for possibly most of the scenarios found in real applications.

However, after performing all experiments, it could be seen that for most experiments, the inhibitor wasn't effective as expected. Only for a few experiments with selected combination of variables, the inhibitor was effective. Nonetheless, the influence of each variable and their interactions were evaluated. The resulting Pareto diagram is indicated on Fig. 5. The response used for the modeling was the scaling time to reach the differential pressure of 0.5 psi.

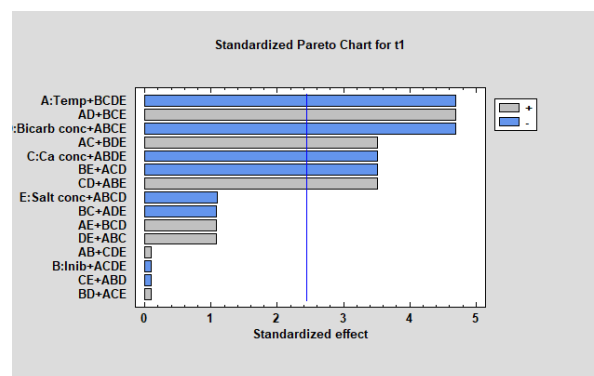


Figure 5: Pareto diagram for the response, showing the influence of each variable and interaction.

It is quite clear that temperature has the greatest effect on the process, which is understandable due to the increasing scaling potential as the temperature increases, caused by the lower solubility of calcium carbonate at high temperatures, in accordance with previous works [11,16]. Bicarbonate concentration was notably important, followed by another variable's interactions and then, calcium concentration. However, salinity has proven to be not statistically significant alongside the chosen inhibitor concentration. This is problematic since the intended purpose of the methodology was to assess the influence of the inhibitor effect over the scaling process. This lack of response is not due to the methodology being wrong, but how the design of experiment was conceived.

The best scenario when trying to model complex processes was that one single model could be able to understand all the natural behavior existing in it. However, trying to get much information leads to the overlooking of crucial aspects of the process. When dealing with scale inhibition, most of the commercial inhibitors will not be suited for all types of applications. Depending on how it will be used, formulations

can be made to best stabilize the product for higher temperatures or higher calcium concentration, etc. When trying to build a model for all scenarios, chances are that the inhibitor will only work for a set of combinations, as was encountered in this design of experiment.

Although the screening was not able to directly assess the inhibitor's effect over the process, results are important for the following works regarding mathematical modelling of the scaling process. In a world where artificial intelligence and computational modeling are gaining power, is important to first understand the chemical stability and application of the inhibitors to decide the set of experiments to perform for data generation.

Conclusions

The variables evaluated for the screening were temperature, inhibitor, calcium and bicarbonate concentrations and salinity. Results showed temperature was the variable of greatest impact on calcium carbonate scaling, followed by bicarbonate and, after, calcium concentrations. Results also led to the conclusion that the inhibitor chosen had little effect to on the scaling process. However, this precedent raises a flag on the importance of understanding the application of the inhibitors and formulations, rather than trying to construct a model with large ranges of temperature and concentrations. Of course, the best scenario would be a unique model that could predict product's behavior for subsea and topside conditions; however, dealing with this type of ranges may not be suited when using the design of experiment approach, as it may lead to combinations where the inhibitor does not work for most of the experiments. This way, this set of combinations are not representative on how the inhibitors work, leading to weak results.

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Responsibility Notice

The authors are the only responsible for the paper content.

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