Effect of the temperature and the CO\textsubscript{2} concentration on the behaviour of the citric acid as a scale inhibitor of CaCO\textsubscript{3}

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Abstract. For all Industrial sector is important to extend the useful life of the materials that they use in their process, the scales of CaCO\textsubscript{3} are common in situation where fluids are handled with high concentration of ions and besides this temperatures and CO\textsubscript{2} concentration dissolved, that scale generates large annual losses because there is a reduction in the process efficiency or corrosion damage under deposit, among other. In order to find new alternatives to this problem, the citric acid was evaluated as scale of calcium carbonate inhibition in critical condition of temperature and concentration of CO\textsubscript{2} dissolved. Once the results are obtained it was carried out the statistical evaluation in order to generate an equation that allow to see that behaviour, giving as result, a good efficiency of inhibition to the conditions evaluated the scales of products obtained were characterized through scanning electron microscopy.

1. Introduction

The scales generation associated with the production of formation and injection water, can lead to oilfield production problems which are often costly to remedy. The calcium carbonate (CaCO\textsubscript{3}) is one of the most common scale that is present in production wells and surface installations. The formation of carbonate scale can affect the production because the pipe and the flow lines lock, equipment fouling and corrosion under deposit [1].

Scale formation from calcium carbonate deposition is a major drawback in many industrial facilities, including oil and gas industry, leading to obstruction problems then causing productivity reduction and economic loss [2]. To solve this phenomenon different alternatives have been proposed, among the scales inhibitor. [3] One of the methods of control of scales more used in refineries and chemical plants is the use of chemicals called incrustation inhibitors [3-7].

Carboxylic Acids have been used as a chemical specie to formulate different scale inhibitors as Polyphosphino carboxylic Acid, carboxymethyl inulin [8]. In the present work, the results of evaluation of citric acid as a scale inhibitor, dosed at different concentrations (15, 25 and 40ppm), are presented under the influence of the critical variables for the formation of CaCO\textsubscript{3} crystals. In order to determine their effectiveness to specific conditions of temperature, flow rate and CO\textsubscript{2} concentration.

2. Experimental procedure

2.1. System used for the tests performed

The experiments carried out for the evaluation of the inhibitor of incrustation composed by acid. Were carried out in the laboratory by means of a closed circuit assembly. The designed system consists of a saturated solution of calcium carbonate that lies in a glass vessel and has agitation as well as constant...
CO₂ flow is driven by means of hoses through a pump at a constant speed towards the test capillary found in a heating bath by means of which the desired temperature is achieved, the solution passes through the Capillary and is redirected to the container containing the solution. For the development of the system used, it was taken as reference the one found in the research. The kinetics of carbonate scaling-application for the prediction of downhole carbonate scaling (See Figure 1) [3].

![Figure 1. System used for the tests performed.](image)

2.2. Material
The material used for the development of the tests corresponds to an AISI 316L stainless steel capillary (AISI 316L stainless steel), with an external diameter of 6.36mm and a wall thickness of 0.89mm and 150mm in length.

2.3. Conditions
The tests performed lasted 36 hours, at temperatures of 70°C and 80°C, CO₂ dosages of 1py3/h and 3py3/hr handling a flow rate in a laminar flow regime (Re=127.46). Once the solution is saturated by the gas it is determined that the pH is 6.80 this is obtained with a pH meter HANNA.

2.4. Brine
A supersaturated solution of calcium carbonate, prepared by weighing 10g of calcium carbonate and 33g of sodium chloride, was used, which were taken to a Beaker and dissolved in water. Then this solution is taken to a 1L balloon to be titrated. This solution is prepared for each test performed [9].

2.5. Calculation of inhibition efficiency
To determine the efficiency of citric acid as a calcium carbonate scale inhibitor, the weight in grams of the crystal layer deposited in the test capillary was taken into account. The calculation of the inhibition efficiency was carried out by the following equation:

\[
Efficiency = \frac{W_{\text{white}} - W_{\text{inhibitor}}}{W_{\text{white}}}
\]

Where, \(W_{\text{white}}\)=scale gained without inhibitor dosage in grams. \(W_{\text{inhibitor}}\)=scale gained with inhibitor dosage in grams.

3. Results and discussion
3.1. Efficiencies obtained and effect of variables
Citric acid very well counteracts the formation of calcium carbonate scale, since it is an organic tricarboxylic acid, these carboxyl groups can lose a proton when they are in solution, producing the citrate ion, said citrate ion, forms salts with metal ions within which calcium is found. For the case under study, calcium carbonate reacts with citric acid to form calcium citrate, CO₂ and water as follows in the Figure 2.
According to the study, citric acid shows good behaviour as a calcium carbonate scale inhibitor, in Table 1, the results obtained are presented, it can be observed that the efficiencies obtained for most cases are found on 98% efficiency.

Table 1. Results of incrustation efficiencies obtained.

| Evaluation Conditions | Dosing of inhibitor (ppm) | Efficiency (%) |
|-----------------------|---------------------------|----------------|
|                       | 15                        | 99.56          |
| 70°C-1ft³/CO₂         | 25                        | 99.34          |
|                       | 40                        | 99.34          |
|                       | 15                        | 99.36          |
| 70°C-5ft³/CO₂         | 25                        | 99.08          |
|                       | 40                        | 99.15          |
|                       | 15                        | 98.08          |
| 80°C-1ft³/CO₂         | 25                        | 94.40          |
|                       | 40                        | 98.73          |
|                       | 15                        | 63.73          |
| 80°C-5ft³/CO₂         | 25                        | 76.21          |
|                       | 40                        | 98.63          |

From the analysis performed, it is determined that as the temperature and the CO₂ concentration in the system increases, the efficiency of the inhibitor is affected, presenting a decrease in the same, thus having a greater influence on the CO₂ dosage, since the stability of the complex that form the chemical species chelating with the metal ion, in this case Ca²⁺, are affected by the changes of pH, which in this case are generated with the addition of CO₂, affecting the way in which the complexes can react. A statistical analysis was performed, which correlates all the studied variables, thus obtaining a mathematical equation that allows predicting the inhibition behaviour of the acid, with which the behaviour previously analysed is corroborated.

\[
%\text{Eficiencia} = 18,07405 + 1,1936T + 96,9002C + 2,0037D + 0,002901D^2 - 1,3850TC - 0,03105TD - 2,4106CD + 0,03443TCD
\]  

(2)

Where T=Temperature, C=Addition of CO₂ and D=inhibitor dosage.

3.2. Morphology and characterization of crystals obtained

Figure 3 and 4, the crystals formed using citric acid inhibitor are shown, they are significantly smaller than those found in tests carried out without the use of inhibitor, in addition there are holes in the embedded material and the Grains formed have a geometry different from that of white tests, which in this case, corresponds to conic forms mostly hollow, all this, is due to the action generated by the
inhibitor in the formation of the incrustation. Calcium carbonate is polymorphic, i.e. it may be formed or existing in more than one crystalline structure. The polymorphs of calcium carbonate are three; Aragonite, vaterite (unstable phases), and calcite (more stable phase). [10-14]. Based on the shape of the crystals obtained, it is determined that the phase that is formed conforms to one of the unstable phases of the calcium carbonate, possibly aragonite. [12]. The morphology shows that, with this inhibitor, the formation of the most stable phase of calcium carbonate is not achieved, as well, it is observed that the formed crystals are significantly smaller than those obtained with the tests without inhibitor use, presenting sizes of 899.9nm and 978.3nm.

3.3. Characterization realized by XRD

The XRD analysis was carried out in order to obtain more information about the chemical composition of the formed incrustations and to identify the present classes. Figure 5 shows the results obtained from XRD analysis on the scale obtained with the use of citric acid inhibitor. In the spectrum, the presence of calcium carbonate, which in this case is presented as aragonite, is present. This result confirms the evidence obtained by scanning electron microscopy, where an elongated and weak crystal morphology is observed, with very thin layers and very small crystals.
4. Conclusions
Evaluation efficiencies using citric acid as a CaCO$_3$ scale inhibitor are found to be above 98% in most cases, this means that the inhibitor exhibits good behaviour against scale. It was found that with this inhibitor, the efficiencies are excellent even when dosed at 15ppm which is the lowest amount used, so in this case this would be the optimal dosage of inhibitor to use.

It was determined that the increase of CO$_2$ to the system decreases the efficiency of inhibition, this is possibly because the behaviour of the molecules as inhibitors depends on the changes pH; The CO$_2$, causes pH in the system to change, thus generating instability in the mechanism of inhibition.

With the use of inhibitor, a remarkable change in the morphology of the crystals is observed, as well as the decrease in the size of the crystals, indicating the positive effect of the inhibitor against the decrease of CaCO$_3$ salt formation.

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