



## Aspects of calcium carbonate formation in the presence of hydrate inhibitors

Elvio B. M. Filho<sup>1,2\*</sup>, Jonathan S. Lobo<sup>1,2</sup>, Hosana O. A. Neta<sup>1,2</sup>, Fabiane S. Serpa<sup>1</sup>, Fábio C. Dossi<sup>1</sup>, Gustavo R. Borges<sup>1,2</sup>, Cláudio Dariva<sup>1,2</sup>, Elton Franceschi<sup>1,2</sup>

<sup>1</sup>Center for Studies on Colloidal Systems (NUESC)/Institute of Technology and Research (ITP), Brazil

<sup>2</sup>Postgraduate Program in Process Engineering (PEP), Tiradentes University (UNIT), Brazil, \*ebmf12@hotmail.com

### Abstract

The formation of organic and inorganic scales during the production and transport operations of multiphase fluids represents a challenge for the oil industry. Thermodynamic inhibitors are commonly employed to avoid the formation of hydrates, favoring the precipitation of salts present in the produced water. In particular, scales formed by calcium carbonate are common and its polymorphic phases present different levels of solubility in the liquid mixture, which influence the nucleation kinetics, growth, and crystal deposition. Within this context, the proposed work seeks to evaluate the influence that the addition of hydrate inhibitors (ethanol, monoethylene glycol, and glycerol) in different concentrations (0–30 wt.%) may have on the polymorphic and morphologic characteristics of calcium carbonate in brine solutions at 70 °C and batch condition of precipitation with time. Scanning electronic microscopy and Fourier transform infrared spectroscopy techniques were applied to characterize solids. The results showed that the additives interacted to favor the transformation of polymorphic phases - thus changing morphology as well as the size of formed solids. The effects associated with the addition of glycerol were more pronounced. The existing differences amongst the chemical structures and the viscosity of the hydrate inhibitors within investigated conditions influenced the process.

### Keywords

Morphology; polymorphism; calcium carbonate

### Introduction

High demand for natural gas production causes operational problems related to flow assurance, such as scale formation. Problems such as these must be solved and/or minimized so the exploration of this resource may be deemed economically viable. Hydrates represent a serious issue for the oil industry. To guarantee favorable conditions for the process, the injection of hydrate-formation inhibitors is performed within the well. Nowadays, thermodynamic inhibitors such as methanol, ethanol, and glycols are the most used since they can inhibit the nucleation of the hydrate thus modifying the balance of conditions towards the formation of crystals [1].

However, the use of these inhibitors induces the supersaturation of the system and favors the precipitation and deposition of inorganic salts. The inorganic scales decrease the rate of well production, and that of the rock permeability found near the production well [2]. Particularly, scales formed by calcium carbonate (CaCO<sub>3</sub>) are often found in the oil industry.

Various factors affect the polymorphism of calcium carbonate (anhydrous and metastable) including pH values, ionic concentrations, temperature, and chemical additives [3-5]. These phases show

different levels of solubility in the liquid mixture, which influence the nucleation kinetics and the growth of carbonate crystals [3]. It is necessary to investigate the phenomena associated with the formation of inorganic salts to assist with the development of techniques and strategies to control scales and improve production efficiency. Hence, this work aims to perform an experimental study of the kinetic behavior of CaCO<sub>3</sub> in aqueous solutions in the presence of hydrate formation inhibitors.

### Methodology

Precipitation analyses in the batch condition consisted in the preparation, initially, of synthetic saline water (similar that of industry). This composition was based in the work by Rosa et al. (2016) [6], as shown in Tab. 1. Besides the materials shown in Tab. 1, the following compounds were employed as hydrate inhibitors: absolute ethyl alcohol (99.5%, Synth), glycerol (99.5%, Synth) and monoethylene glycol (99.5%, Synth).

Table 1. Composition of the synthetic brine used to obtain CaCO<sub>3</sub> scale experimental data.

Ion	Concentration (ppm)
Na <sup>+</sup>	39020
Sr <sup>2+</sup>	290
Ba <sup>2+</sup>	570
Ca <sup>2+</sup>	2040
Mg <sup>2+</sup>	530
K <sup>+</sup>	1090
HCO <sub>3</sub> <sup>-</sup>	1000

All samples were prepared gravimetrically. The solutions were purified using a filtration system using a 0.45 μm nylon filter. To allow for the agitation of solutions, a magnetic stirring was utilized.

Anion and cation solutions (~50 mL each) were placed separately into glass jars (100 mL) having been sealed and heated in an oven for 2 h at temperature of 70 °C. Afterwards, the solutions were mixed in equal amounts and kept under heat for 24 h. The analyses were performed both with and without hydrate inhibitors. In the absence of the inhibitor, the solutions of cations and anions were mixed. In the case of the experiments carried out with scale inhibitor, different concentrations of the inhibitor's ethanol, monoethylene glycol and glycerol (10-30 wt.%) were added to both ionic solutions. All experiments were performed twice. Samples were collected after 2 h and 24 h after the mixing of the saline waters. Then, the samples were filtered and dried under 70 °C for 24 h.

The morphologic identification in nanoscale, elementary chemical composition, and the polymorphic phase of the salt crystals obtained from the static precipitation tests were acquired by scanning electronic microscopy SEM (JEOL JSM, model IT200LA) and Fourier transform infrared spectroscopy – FTIR (Bruker, model Invenio R).

## Results and Discussion

The evaluation on the addition of hydrate inhibitors ethanol, monoethylene glycol and glycerol (0-30 wt.%) upon the transformation of the solid phases precipitated in batch condition were performed as a function of time (2 h and 24 h) at 70 °C.

Fundamental vibrations of the carbonate ion were observed through FTIR spectra for the different crystal structures of CaCO<sub>3</sub>. Figure 1 shows infrared spectra obtained after 24 h of precipitation in aqueous systems in the absence and presence of scale inhibitors. Wavelengths referring to the crystalline phases calcite (713, 871, 874, 1396 cm<sup>-1</sup>), aragonite (700, 712, 713, 844, 854, 1083 cm<sup>-1</sup>) and vaterite (744, 876, 1087 cm<sup>-1</sup>) were considered [7,8,9].

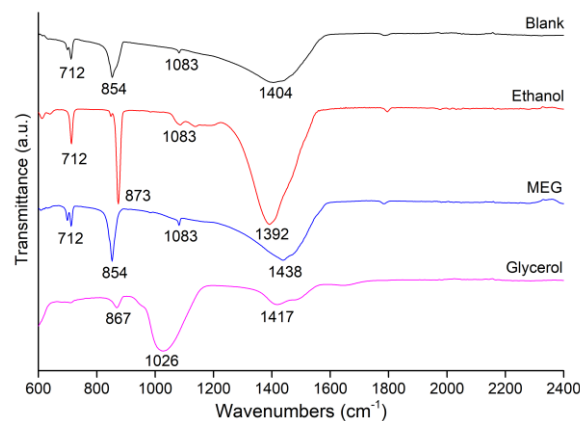


Figure 1. FTIR spectra of anhydrous crystalline phases of CaCO<sub>3</sub> obtained in absence and presence of hydrate inhibitors (30 wt.%).

In relation to polymorphism, it is possible to note a tendency in the formation of more intense peaks at the positions corresponding to the aragonite and calcite. The literature reports that the formation of polymorphs is governed by kinetic and thermodynamic phenomena. Calcite is thermodynamically stable and least soluble form while vaterite has higher solubility and lower thermodynamic stability [10, 11]. However, the aragonite is favored in higher temperatures [12-14]. Crystal stability can also be controlled by mechanisms associated with the presence of other ions, ionic concentration, additives [11,15-18]. The addition of inhibitors promoted an increase in the viscosity of the solution which hindered the adhesion of the formed crystalline nuclei and the development of the crystals as compared with pure water thereby encumbering the mobility of the formed particles and reducing the kinetics of growth and the development of clusters [5,19,20]. Hydrate inhibitors form hydrogen bonds with the water molecules present in the solution. The ethanol, monoethylene glycol and glycerol inhibitors presents one, two, and three functional hydroxyl groups in its structure, respectively. Thereby, the molecular structure tends to have an influence in the process of precipitate development, which then promotes changes in the morphology and in the polymorphism of the formed solids.

Figure 2 shows the variation of the FTIR spectra obtained during the precipitation of CaCO<sub>3</sub> in aqueous solution at different times. It is possible to notice typical peaks of calcite and aragonite, in the absence of inhibitor. The presence of glycerol induced the formation of peaks in other vibrational bands, in the initial hours of the experiment.

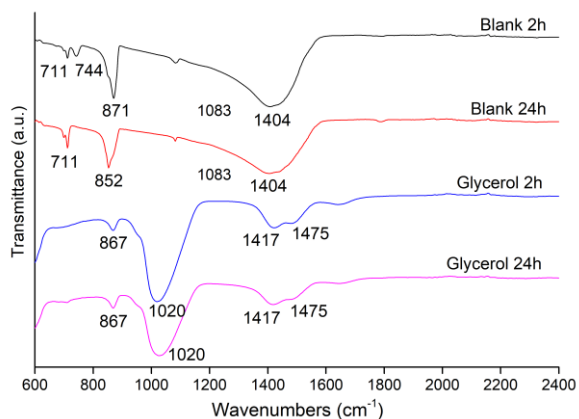


Figure 2. FTIR spectra of  $\text{CaCO}_3$  at different reaction time (2 h and 24 h) in absence and presence of glycerol (10 wt.%).

Figure 3(A - D) shows the experimental results related to the precipitation of  $\text{CaCO}_3$  in systems containing ethanol, monoethylene glycol or glycerol (20 wt.%), at 70 °C using the SEM technique. The micrographs corroborate the data obtained by spectroscopy.

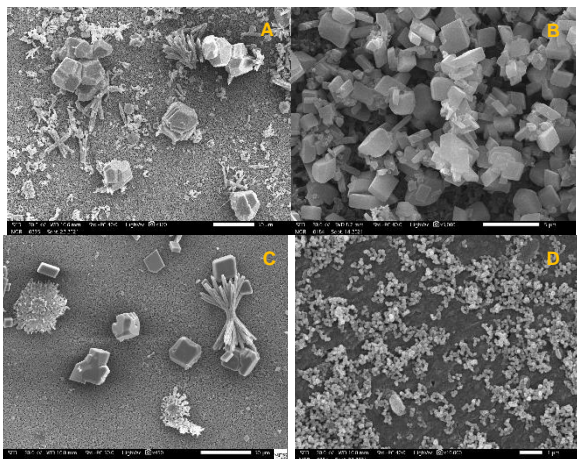


Figure 3. Scanning electron micrographs of  $\text{CaCO}_3$  obtained in the presence of hydrate inhibitors (20 wt.%): (A) without inhibitor (x370); (B) ethanol (x5000); (C) monoethylene glycol (x450); (D) glycerol (x10000).

In the absence of inhibitor, the predominance of particles with morphology similar to calcite and aragonite was observed. However other morphologies can also be observed, such as vaterite. Throughout the growth of the crystals, the inhibitors are absorbed in different concentrations and in different facets of the crystal - therefore hampering the transformation of the calcium carbonate to its most stable form, calcite. The inhibitor promoted changes in morphology and reduced the size of  $\text{CaCO}_3$  crystals. The effects associated with the addition of glycerol were more pronounced when compared to the monoethylene glycol and less so by the ethanol.

## Conclusions

In lower alcohol concentrations, the supersaturation controls the process. However,

there is an inhibitory effect in high concentrations that is greater than that of the supersaturation effect, which fosters the formation of  $\text{CaCO}_3$  particles in reduced sizes. Throughout the growth of the crystals, the inhibitors are absorbed in different concentrations and in different facets of the crystal - therefore hampering the transformation of the calcium carbonate to its most stable form, calcite. Furthermore, the addition of these compounds promoted an increase in the viscosity of the solution, hindering the adhesion of the formed crystalline nuclei and the development of the crystals, reducing the growth kinetics and the formation of agglomerates. Crystal stability can also be controlled by mechanisms associated with the presence of other ions, ionic concentration, additives.

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## Responsibility Notice

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