



## Evaluation of carbohydrates occurring in food industry waste as potential green inhibitors of calcium carbonate scale in oil and gas production

Ronald Wbeimar Pacheco Ortiz<sup>1</sup>, Jessica Oliveira<sup>1</sup>, Nayanna Souza Passos<sup>1</sup>, Vinicius Ottonio, O. Gonçalves<sup>1</sup>, João Cajaiba<sup>1</sup>, and Vinicius Kartnaller<sup>1\*</sup>

<sup>1</sup>Center of Development of Processes and Chemical Analysis in Real Time, Institute of Chemistry, Federal University of Rio de Janeiro. \*kartnaller@iq.ufrj.br

### Abstract

The development of “green” calcium carbonate scale inhibitors is crucial for reducing the negative environmental impacts of the oil and gas industry. This work evaluates some carbohydrates to inhibit calcium carbonate scale: Glucose, Fructose, Sucrose, Maltose, Maltodextrin, and Soluble Starch, which are biodegradable molecules occurring in carbohydrates-rich food wastes. Calcium carbonate crystallization experiments in the presence of 1000 mg/L of each carbohydrate were carried out in a static system at 30°C and pH 7 by mixing calcium chloride 3963 mg/L and sodium bicarbonate 3000 mg/L. The induction time is longer in the presence of all carbohydrates than in the blank test. Moreover, the drop in pH and the mass of solids recovered are similar for all the carbohydrates, which suggests that the inhibition mechanisms are more related to crystal growth retardation and/or crystal size/shape distortion than to nucleation inhibition. Scanning electron microscopy analysis confirms that the carbohydrates allow the formation of smaller rounded-shaped calcite crystals as well as vaterite crystals for the soluble starch. Soluble starch also is able to delay the calcium carbonate scaling time even at 50 mg/L. Thus, the carbohydrates evaluated show potential to be ingredients in green calcium carbonate scale inhibitors formulations.

### Keywords

Calcium carbonate scale; green scale inhibitor; carbohydrate-rich food waste

### Introduction

The calcium carbonate scale is one of the main flow assurance problems in oil and gas production. This inorganic salt can deposit and accumulate on the surface of pipes, which reduces productivity or even leads to well closure [1]. Moreover, the remediation of this problem involves high costs related to probe rental and acid dissolution treatments, which can lead to additional corrosion and pollution problems. Therefore, nowadays preventive treatments such as the use of scale inhibitors are prioritized [2]. The most commonly used inhibitors are those derived from phosphonic acid. They interact with calcium carbonate preventing the formation of its deposits through various mechanisms: nucleation inhibition, crystal growth retardation, crystal size or shape distortion, and chelating effect. However, depending on their composition and disposal, the scale inhibitors can be also pollutants since they increase the availability of nitrogen and phosphorus in aquatic ecosystems leading to eutrophication [3]. Hence, the development of “green” calcium carbonate inhibitors is essential to decrease the negative environmental impacts of the oil and gas industry. Calcium carbonate can occur in up to five polymorphs (calcite, vaterite, aragonite, ikaite, and

monohydrocalcite) and in the amorphous phase. Composition, temperature, pressure, and ionic strength of the medium influence the stability of each polymorph, which in turn influences properties of calcium carbonate such as solubility, thermal stability, agglomeration capacity, and adhesion [4]. Therefore, controlling the nucleation stage and defining the type of crystalline or amorphous phase is crucial for developing strategies to reduce the accumulation of calcium carbonate oil and gas facilities. Nucleation control is indeed the mechanism used by living organisms in biomineralization processes. They use biomolecules containing specific functional groups such as carboxyl, phosphate, sulfate, hydroxyl, and amino that interact with calcium carbonate to modify its morphology [5]. These biomolecules or molecules with similar structures are therefore potential candidates for the development of green inhibitors. For example, the performance of hydroxylated molecules for inhibiting calcium carbonate scale has already been reported in dynamic studies [6], [7]. The results of these studies show the feasibility of using this type of molecule, emphasizing those that have low toxicity, non-bioaccumulation, and high biodegradability [8]. In this context, food industry wastes and/or by-products rich in carbohydrates constitute a source

of hydroxylated biomolecules that would work as calcium carbonate scale inhibitors [9]. Thus, the purpose of this work is to evaluate the potential of some carbohydrates that can be eventually recovered from carbohydrate-rich food wastes for the development of green inhibitors of the calcium carbonate scale.

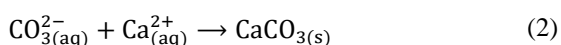
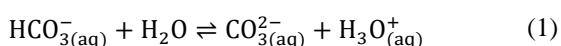
## Methodology

### Materials

The carbohydrates evaluated in this study were: 2 monosaccharides (glucose and fructose), 2 oligosaccharides (sucrose and maltose), and 2 polysaccharides (maltodextrin and soluble starch). All carbohydrates were of analytical grade and purchased from ACS Científica (Sumare, Brazil). Additionally, calcium chloride, sodium bicarbonate, sodium chloride, hydrochloric acid, sodium hydroxide, and ethanol were purchased from Isofar (Rio de Janeiro, Brazil). CO<sub>2</sub> used to adjust the pH of the sodium bicarbonate solution was provided by Eden gases (Rio de Janeiro, Brazil). All the reagents were used with no further purification and Milli-Q® degassed water was used to prepare all the solutions.

### Calcium carbonate crystallization experiments

Calcium carbonate crystallization experiments were carried out at 30 °C, pH 7, and under magnetic stirring of 200 rpm in a static system using an EasyMax® workstation (Mettler Toledo, USA). Here, aqueous solutions of sodium bicarbonate and calcium chloride were mixed in equimolar concentrations, which were 3000 mg/L and 3963 mg/L respectively, according to Eq. (1) and (2)



The pH 7 was previously adjusted by bubbling CO<sub>2</sub> to the sodium bicarbonate solution and by adding HCl 0.1 M or NaOH 0.1 M to the calcium chloride solution. The effect of the presence of each carbohydrate on the calcium carbonate crystallization was evaluated by adding a concentration of 1000 mg/L and monitoring the induction time by RGB (red, green, and blue) image analysis and pH measurement. The induction time was determined at the moment when the RGB color space signal increased due to the production of calcium carbonate solids while the pH decreased due to the production of hydronium ions according to Eq. (1) and Eq. (2). After 1 h from the induction time, the solids formed were vacuum filtered, washed with ethanol, and dried at 50 °C for 1 h. The mass of the recovered calcium carbonate solids was then determined and their morphology was analyzed by Scanning Electron Microscopy (SEM).

## Scale inhibition assessment

The effect of the carbohydrates on the calcium carbonate scale formation was assessed using a dynamic scale loop (DSL) system. This equipment operates by pumping the sodium bicarbonate and calcium chloride solutions into a stainless-steel tube with an inner diameter of 1 mm placed inside a thermostat-regulated oven. Then, the formation of calcium carbonate deposits inside the tube is detected by a differential pressure transmitter. This assessment was carried out under experimental conditions similar to oil and gas production: flow rate of 5 ml/min, 10 bar, 80 °C, pH 7, and 35000 mg/L of sodium chloride. The concentrations of the sodium bicarbonate and calcium chloride solutions were equal to that of the experiments in the static system. Moreover, the carbohydrate was added to the sodium bicarbonate solution in variable concentrations: 1000, 500, 100, and 50 mg/L.

## Results and Discussion

Figure 1 shows the results of the calcium carbonate crystallization experiments in the static system. Both RGB image analysis and pH monitoring were suitable to determine the induction time. Observe that the induction time was longer in the presence of all carbohydrates than in the blank test. Maltodextrin stands out as the molecule that most delayed the formation of calcium carbonate crystals, followed by glucose and soluble starch. Both maltodextrin and soluble starch are polymers of glucose, hence the greater the polymer chain, the greater the number of hydroxyl groups available to interact with the calcium carbonate. However, despite the polymeric chain of maltodextrin being smaller than that of soluble starch, its best performance could be attributed to its greater solubility in aqueous media [10]. Moreover, glucose shows a result similar to fructose, and maltose. Rao et al., [11] reported that fructose and maltose destabilize pre-nucleation clusters of calcium carbonate whereas glucose inhibits its nucleation. Conversely, the shorter induction time in the

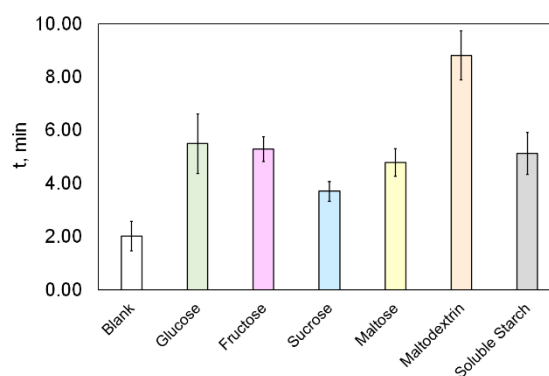


Figure 1. Induction time of calcium carbonate formation in the presence of carbohydrates

However, Figure 2 displays the drop in pH during the crystallization process, which was similar for all the experiments. The drop in pH is due to the hydronium ions produced as the calcium carbonate precipitates according to Eq. (1) and Eq. (2). Therefore, this drop indicates indirectly that the amount of calcium carbonate precipitated is also similar in the presence of all carbohydrates. This can be corroborated by the similar mass of solids recovered in the crystallization experiments, which is shown in Fig. (3). Thus, the inhibition mechanism of the carbohydrates evaluated in this study could be more related to crystal growth retardation and/or crystal size/shape distortion than the nucleation effects described by Rao et al., [11].

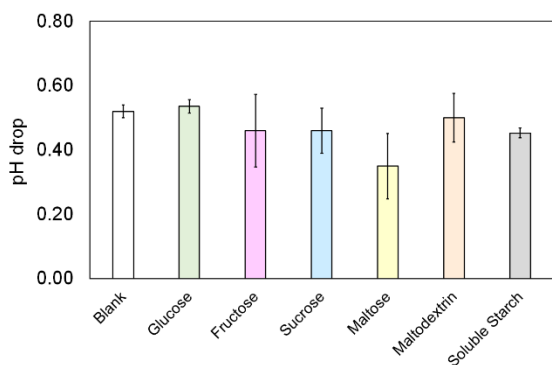


Figure 2. Drop in pH during calcium carbonate crystallization

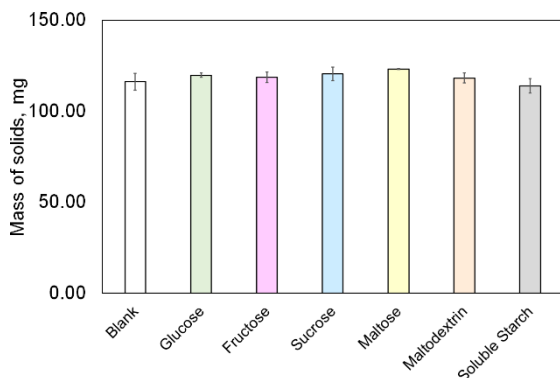


Figure 3. Mass of calcium carbonate solids recovered

The SEM analysis confirms the suggested inhibition mechanisms of the carbohydrates, the images obtained can be observed in Fig. (4). All the carbohydrates change the size and shape of the crystals regarding the blank test. The blank test shows typical calcite crystals, which are the most stable form of calcium carbonate and the main responsible for the formation of scale. The presence of most of the carbohydrates (glucose, fructose, maltose, and maltodextrin) also allows the formation of calcite but with slightly rounded shapes and smaller sizes. Moreover, the presence of soluble starch further decreases the size of the calcite crystals and allows the formation of vaterite, which indicates a greater inhibitory effect [12]. Vaterite is also observed in the presence of

sucrose, although is less perceptible than in the presence of soluble starch. The formation of vaterite in the presence of sucrose by the enhancement of mass transfer of the precipitant ions has been previously reported by Konopacka-Lyskawa et al., [13]. However, sucrose requires more alkaline pHs (close to 9) for this effect to occur.

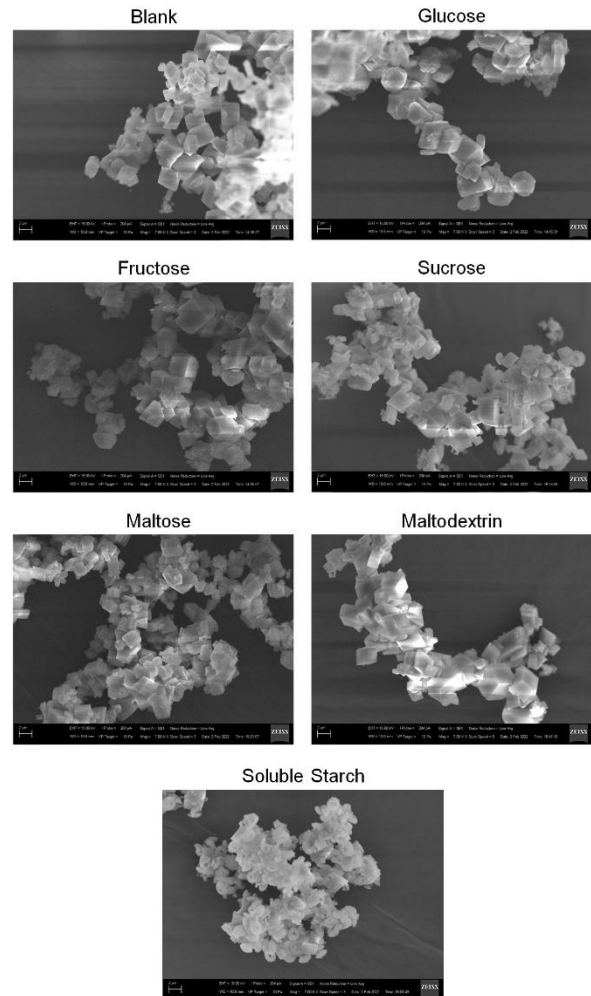


Figure 4. Scanning electron microscopy images of calcium carbonate solids formed in the presence of carbohydrates

Thus, the soluble starch is the carbohydrate that shows the greatest potential to inhibit the formation of calcium carbonate scale, and therefore its performance was assessed in the DSL system. Figure 5 shows that the presence of soluble starch delays the scaling time regarding the blank test even in concentrations of 50 mg/L. Moreover, the scaling time increases with the increasing soluble starch concentration. This indicates that the effect of soluble starch on the size and shape of calcite crystals, in addition to the formation of vaterite crystals, is effective in delaying the calcium carbonate scaling process. The soluble starch is thereby demonstrating its calcium carbonate scale inhibitory potential in the oil and gas industry.

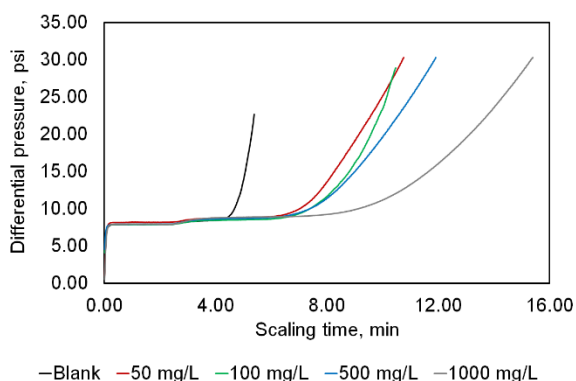


Figure 5. Assessment of calcium carbonate scale formation in the presence of variable concentrations of soluble starch

## Conclusions

As hydroxylated molecules, the carbohydrates evaluated in this work show their effect on the crystallization of calcium carbonate. The presence of the carbohydrates increases the induction time and allows the formation of rounded-shaped calcite crystals smaller than the typical rhombohedron calcite crystals of the blank test. Moreover, the soluble starch allows the formation of even smaller rounded-shaped calcite crystals as well as vaterite crystals. Consequently, the soluble starch is also able to delay the calcium carbonate scaling time. The carbohydrates evaluated in this work are thereby demonstrating their potential as calcium carbonate scale inhibitors. These molecules are biodegradable and can occur in carbohydrates-rich food wastes. Therefore, they would be suitable for the development of green calcium carbonate scale inhibitors. Thus, the use of these carbohydrates would not only reduce the negative environmental impacts of the oil and gas industry but also would be an opportunity for the valorization of carbohydrate-rich food industry wastes.

## Acknowledgments

The authors acknowledge the Human Resources Program of the National Agency of Petroleum, Natural Gas, and Biofuels of Brazil PRH-ANP (in Portuguese) by the financial support of this work with funds from the investment of oil companies qualified in the R&DI Clause of ANP Resolution 50/2015. Additionally, the authors express gratitude to the National Center of Structural Biology and Bioimage of the Federal University of Rio de Janeiro CENABIO/UFRJ (in Portuguese) by providing the infrastructure to perform the scanning electron microscopy analysis.

## Responsibility Notice

The authors are the only responsible for the paper content.

## References

[1] M. Mpelwa and S. F. Tang, "State of the art of synthetic threshold scale inhibitors for mineral

scaling in the petroleum industry: a review," *Pet. Sci.*, 16 (4), 830–849, 2019

- [2] M. S. Kamal, I. Hussein, M. Mahmoud, A. S. Sultan, and M. A. S. Saad, "Oilfield scale formation and chemical removal: A review," *J. Pet. Sci. Eng.*, 171, 127–139, 2018.
- [3] M. Chaussemier *et al.*, "State of art of natural inhibitors of calcium carbonate scaling. A review article," *Desalination*, 356, 47–55, 2015.
- [4] J. Y. Gal, Y. Fovet, and N. Gache, "Mechanisms of scale formation and carbon dioxide partial pressure influence. Part I. Elaboration of an experimental method and a scaling model," *Water Res.*, 36 (3), 755–763, 2002.
- [5] A. Bastrzyk, I. Polowczyk, K. J. Legawiec, J. Chojniak, K. Paraszkiwicz, and G. A. Płaza, "Biomineralization of calcium carbonate controlled by biomolecules produced by *Bacillus sp.*," *IOP Conf. Ser. Mater. Sci. Eng.*, 427 (1), 1–6, 2018.
- [6] V. Kartnaller, F. Venâncio, J. Cajaiba, and F. Do Rosário, "Study of the effect of monoethylene glycol MEG on the precipitation of calcium carbonate in a pressurized dynamic system," *OTC Bras. 2017*, 194–204, 2017.
- [7] V. Kartnaller, F. Venâncio, F. F. do Rosário, and J. Cajaiba, "Application of multiple regression and design of experiments for modelling the effect of monoethylene glycol in the calcium carbonate scaling process," *Molecules*, 23 (4), 1–12, 2018.
- [8] J. Fink, "Scale inhibitors," *Pet. Eng. Guid. to Oil F. Chem. Fluids*, 2nd Edition, 255–278, 2015.
- [9] H. T. N. Hao, O. P. Karthikeyan, and K. Heimann, "Bio-refining of carbohydrate-rich food waste for biofuels," *Energies*, 8 (7), 6350–6364, 2015.
- [10] M. W. Kearsley and S. Z. Dzedzic, "Maltodextrins," in *Handbook of Starch Hydrolysis Products and their Derivatives*, 1st ed., Springer, 1995, 65–81.
- [11] A. Rao, J. K. Berg, M. Kellermeier, and D. Gebauer, "Sweet on biomineralization: effects of carbohydrates on the early stages of calcium carbonate crystallization," *Eur. J. Mineral.*, 26 (4), 537–552, 2014.
- [12] G. Zhang, J. Ge, M. Sun, B. Pan, T. Mao, and Z. Song, "Investigation of scale inhibition mechanisms based on the effect of scale inhibitor on calcium carbonate crystal forms," *Sci. China, Ser. B Chem.*, 50 (1), 114–120, 2007.
- [13] D. Konopacka-Łyskawa, N. Czaplicka, B. Kościelska, M. Łapiński, and J. Gębicki, "Influence of selected saccharides on the precipitation of calcium-vaterite mixtures by the CO<sub>2</sub> bubbling method," *Crystals*, 9 (2), 117, 2019.