



Transmission Electron Microscope as a tool to study the growth and agglomeration processes of calcium carbonate nanoparticles

Vanessa P. Lages^{1*}, Amaro G. Barreto Jr.¹, André Rossi²

¹School of Chemistry, Federal University of Rio de Janeiro, Brazil

²Brazilian Center for Physics Research, Rio de Janeiro, Brazil, *vanessalages@eq.ufrj.br

Abstract

Calcium carbonate scale formation commonly occurs in hard water pipelines and it may result in severe flow assurance problems in the oil industry. Among the inorganic substances, the calcium carbonate scale is one of the most common and your precipitation proceeds via a complex multistage scenario. Understanding the steps that occur until the crystal formation and its adhesion is important to know how to avoid scaling. Transmission electron microscope (TEM) is a powerful tool to investigate the structural characteristics of calcium carbonate nanoparticles during the different stages of synthesis. This work is part of an in-depth research that aims to investigate the intermediate steps of the nanoparticle construction and improve the understanding of the calcium carbonate crystal formation process. Here, the morphological characterization of calcium carbonate nanoparticles in brines with different concentrations of calcium ions is done using TEM in combination with energy dispersive spectroscopy (EDS). The results suggest that part of the free calcium present in the solution can be adsorbed on the surface of the particles.

Keywords

Calcium carbonate; transmission electron microscopy; nanoparticles.

Introduction

Scale formation is characterized by the adhesion of inorganic compounds to walls and often results in severe flow assurance problems in the oil industry. Among the inorganic substances, the calcium carbonate scale is one of the most common, due to the formation of ionic species from dissolved CO₂, which react with the Ca⁺² present in the formation water.

Calcium carbonate precipitation proceeds via a complex multistage scenario involving neutral ion clusters as precursors and amorphous phases as intermediates, which finally transform to crystals. Although the existence of stable clusters in solution prior to nucleation has been demonstrated, the molecular mechanisms by which they precipitate are still obscure [1].

Since understanding the mechanism of a phase transformation requires local, even atomistic information, transmission electron microscopy has proved invaluable in identifying key features of transformations on the nanoscale [2].

Although several excellent reviews of the TEM technique and their various applications already exist [3–6] as well as many important research findings, few works have used this technique to investigate the structural characteristics of calcium carbonate nanoparticles during the different stages of synthesis.

Therefore, the aim of this work is analyze the morphology and structural characteristics of calcium carbonate nanoparticles in brines with

different concentrations of calcium ions using TEM in combination with EDS.

From these preliminary results, we intend to investigate the intermediate steps of the nanoparticle construction and improve the understanding of the calcium carbonate crystal formation process.

Methodology

For morphological evaluation of CaCO₃ nanoparticles in solution, three brines were prepared using deionized water with different concentrations of CaCl₂/NaCl, but with the same ionic strength (0.1M). Ca⁺² ions concentration ranged from 0 ~ 33 mM in the brine, as shown in Tab. 1.

Table 1. Salt concentration used in brines preparation

CaCl ₂ (M)	CaCl ₂ (g/L)	NaCl (M)	NaCl (g/L)
0.033	3.699	0.000	0.000
0.015	1.665	0.055	3.214
0.000	0.000	0.100	5.844

0.6 g of commercial calcium carbonate and 75 ml of each brine was mixed to yield samples at 0.8% by weight. Then, the calcium carbonate suspension was allowed to stand and the supernatant was collected for analysis. The sample was pipetted, and a drop was placed onto a TEM grid covered with a lacey carbon film in an atmosphere of 95% humidity at 25°C.

A JEOL 2100F transmission electron microscope operated at 200 kV and equipped with an energy-dispersive X-ray spectrometer (EDS) (Bruker X-Max 65T) was used, mainly in scanning mode (STEM) using a spot size of 0.7 nm. An 11 megapixel CCD camera (GATAN Orius) was used to acquire TEM images and selected area electron diffraction (SAED) patterns. STEM images were obtained using an annular dark field (ADF) detector. SAED patterns were also obtained from samples at room temperature. EDS spectra were obtained in STEM mode to evaluate the relative Ca/C atomic composition at the nanoscale.

Results and Discussion

Samples with CaCO₃ particles in saline solution with 0; 0.015 and 0.033 M of CaCl₂ were analyzed in TEM.

Morphological analysis shows that calcium carbonate appears as needlelike crystals with a diameter of ~500 nm, which are further composed of well-aligned nanocrystals with a diameter of ~200 nm.

Figures 1, 2 and 3 show TEM images of CaCO₃ particles in brine with CaCl₂ concentration equals to 0.0, 0.015 and 0.033 M, respectively.

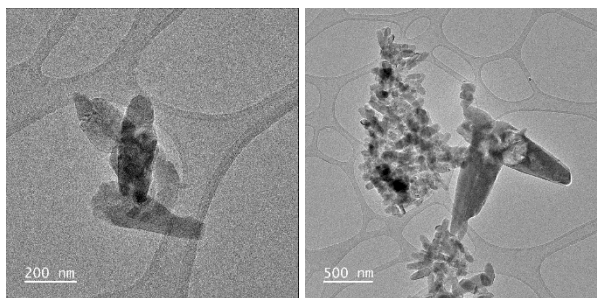


Figure 1. TEM images of CaCO₃ particles in brine with NaCl (Concentration = 0.0M CaCl₂)

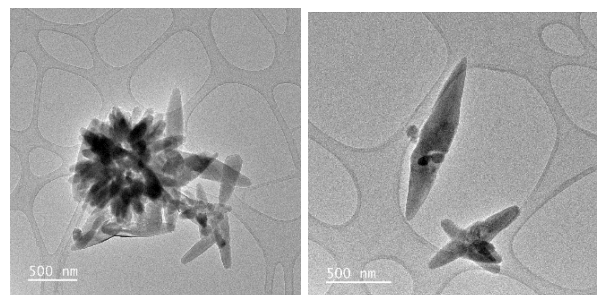


Figure 2. TEM images of CaCO₃ particles in brine with NaCl and CaCl₂ (Concentration = 0.015 M)

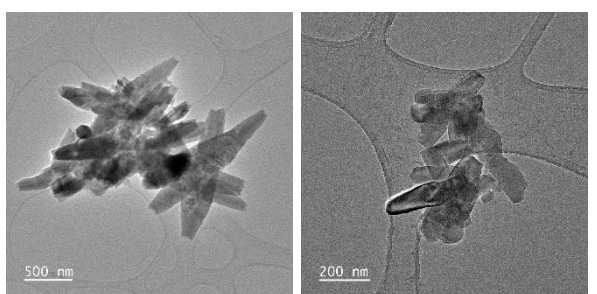


Figure 3. TEM images of CaCO₃ particles in brine with NaCl and CaCl₂ (Concentration = 0.033 M)

In all samples, it was possible to observe isolated particles and agglomerates of CaCO₃ particles with sizes ranging from 200 to 1000 nm.

It was not possible to notice through the images obtained a difference in the morphology of the calcium carbonate agglomerates with the increase of the concentration of calcium ions in the sample. Spectroscopy (EDS) confirmed that the samples are mostly composed of Ca, C and O, with small amounts of Na and Cl. The calcium percentage present in the nanoparticles increased with the increase in the calcium ions concentration in the brine, indicating that part of the free calcium present in the solution can be adsorbed on the surface of the particles.

Figures 4, 5 and 6 show the spectrum obtained from the analyses. The sample with CaCO₃ particles in the brine containing only NaCl (0.0 M of CaCl₂) presented 43.0% of Ca in its composition, while the samples of CaCO₃ in the brine with 0.015 and 0.033 M of CaCl₂ presented 50.1 and 58.4% Ca respectively.

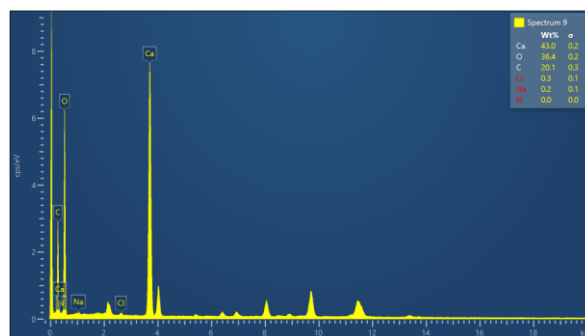


Figure 4. EDS spectra of CaCO₃ particles in brine with NaCl (concentration = 0.0 M CaCl₂).

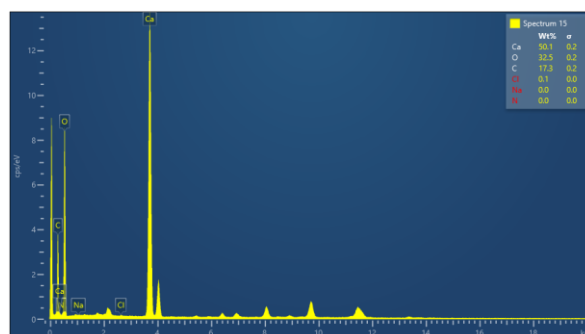


Figure 5. EDS spectra of CaCO₃ particles in brine with NaCl/CaCl₂ (concentration = 0.015 M CaCl₂).

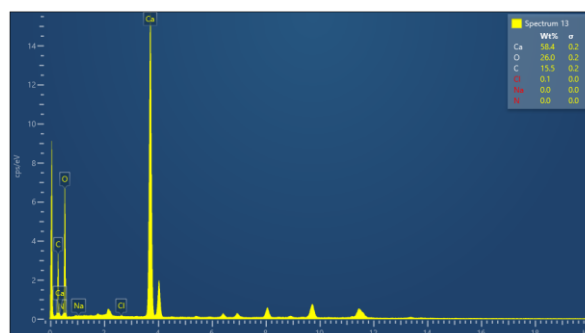


Figure 6. EDS spectra of CaCO₃ particles in brine with NaCl/CaCl₂ (concentration = 0.033M CaCl₂).

Conclusions

Spectroscopy results indicated that the percentage of calcium present in the nanoparticles increased proportionally to the concentration of calcium ions in the brine. It suggests that part of the free calcium present in the solution can be adsorbed on the surface of the particles.

From the images obtained in the TEM, it was possible to observe CaCO₃ particles in the nanoscale order, which proves that this is an important technique that can be used in situ to observe the mechanism of particle formation.

Thus, it is intended to carry out experiments of mixing a supersaturated solution of bicarbonate in a solution of calcium chloride to induce the synthesis of calcium carbonate particles and to be able to analyze how the phase transformations that lead to the formation of crystals in solution.

Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES).

Responsibility Notice

The authors are the only responsible for the paper content.

References

- [1] Kellermeier, M.; Gebauer, D.; Melero-Garcia, E.; Dreschsler, M.; Talmon, Y.; Kienle, L.; Cölfen, H.; García-Ruiz, J.M.; Kunz, W. *Adv. Funct. Mater.* 1-11, 2012.
- [2] Dalmonico, G.M.L.; Lopez, E.O.; Longuinho, M.M.; Checca, N.R.; Farina, M.; Ersen, O.; Rossi, A.M.; Rossi, A.L. *Materials Chemistry and Physics*, 237, 121862, 2019.
- [3] Lee, W.C.; Kim, B.H.; Choi, S.; Takeuchi, S.; Park, J. *J. Phys. Chem. Lett.* 1-25, 2017.
- [4] Tan, S.F.; Chee, S.W.; Lin, G.; Mirsaidov, U. *Acc. Chem. Res.* 50, 1303–1312, 2017.
- [5] Zou, Z.; Xie, J.; Macías-Sánchez, E.; Fu, Z. *Cryst. Growth Des.* 21, 414–423, 2021.
- [6] Yu, L.; Hudak, B.M.; Ullah, A.; Thomas, M.P.; Porter, C.C.; Thisera, A.; Pham, R.H.; Goonatileke, M.A.; Guiton, B.S. *Chem. Mater.* 32, 2, 639–650, 2020.