

Scale Formation and Wetting of Surfaces: A Microfluidics Investigation

A. Tzachristas^{1,2}, R.E. Malamoudis¹, D.G. Kanellopoulou^{1,2}, J. Parthenios²,
P.G. Koutsoukos^{1,2}, C.A. Paraskeva^{1,2}, V. Sygouni^{1,2}

¹Department of Chemical Engineering, University of Patras

²Institute of Chemical Engineering Sciences, Foundation for Research and
Technology, GR26504 Patras, Greece

ABSTRACT

Multiphase flow processes taking place in oil production operations, CO₂ and/or natural gas storage in underground reservoirs, in geothermal energy production, membrane operations etc., are accompanied with undesirable scale deposits formation either on rocks or on the walls of pores or metallic equipment, rendering the corresponding operations significantly less efficient. Scale formation depends not only on the morphology and structure but also on the wetting properties of the substrates on which scale is deposited or formed through nucleation and crystal growth. In the present work, in situ nucleation and growth of calcium carbonate is investigated in a microfluidics cell both in the absence of organic phase. Nucleation and crystal growth were directly observed in both hydrophobic and hydrophilic microchannels. Results are compared with work done in batch reactors, which showed that the presence of organic, water immiscible phase accelerated the formation of calcium carbonate, while depending on the solution supersaturation different metastable calcium carbonate phases were stabilized. The confinement of the supersaturated solutions in the microchannels revealed that the mechanisms changed from bulk to surface diffusion, depending on the flow rates of the supersaturated solutions in the microchannels.

Keywords: microfluidics, calcium carbonate, scale, mixed solvents

INTRODUCTION

Sparingly soluble salt deposits are often encountered in industrial applications, in the aquatic environment and in various biological processes. Oil and gas production industry is faced with the efficient confrontation of scale deposits tenaciously adhering on process equipment parts resulting to serious operational problems.^{1,2,3} Similar problems due to the formation of various insoluble salts on membranes are encountered in water desalination,^{4,5} in heat exchangers in geothermal energy production plants and in CO₂ storage operations.^{6,7} In oil and gas industry calcium carbonate and calcium sulfate deposits are commonly encountered,⁸ while other salts form to a much lower extent. The cause of the formation of the salt deposits, as a rule is due to increase of the respective supersaturations because of temperature and pressure changes, which in turn affect the solubility of the respective salts. Among others, wettability and surface structure have been reported to affect the propensity of surfaces to form calcium carbonate scale deposits. Wettability of materials by fluids, is a property strongly dependent on the physicochemical affinity of the respective

material with a fluid or with a system of fluids. A drop of a liquid may either spread freely or shrink on a solid surface. In the former case the solid is termed as liquid-wet while in the latter as non-wetting. In oil and gas production industry, the respective reservoirs consist of heterogeneous formations of minerals with different extent of wetting from water. The presence of oil inside their pores affects fluids flow and may change pore surface wettability to more oil-wet.¹⁰ According to recently published work involving mineralization of calcium carbonate in two phase systems consisting of water supersaturated with respect to calcium carbonate and an immiscible with water organic phase, showed that the precipitated calcium carbonate includes all calcium carbonate polymorphs: vaterite, aragonite and the thermodynamically most stable calcite.^[11] In the present work, we have investigated the precipitation of calcium carbonate from supersaturated solutions using a microfluidic approach aiming at further understanding the formation of this salt in the pore's environment. The microfluidics approach offers a unique opportunity to monitor the process at different solution conditions, as it offers the possibility to visualize the nucleation and growth of solids and to vary the wettability of the substrates on which the formation of sparingly soluble salts takes place.¹² More specifically, the precipitation of calcium carbonate in supersaturated solutions (saturation ratio values, SR, 40.5 and 61.7) was investigated in a microfluidic reactor system with the possibility of using either hydrophobic or hydrophilic micro-channel. The formation of the mineral phase was monitored with a video-camera. The time of the observation of the first crystal past mixing (and therefore of the establishment of supersaturation) and the crystal growth were recorded. Raman spectroscopy analysis was used for the mineralogical characterization of the crystals. To our knowledge, it is the first time that the effect of wettability is investigated in microchips.

EXPERIMENTAL PROCEDURE

The precipitation of calcium from supersaturated solutions was done directly inside the microchip shown in Figure 1. The channel used for this study, was the Y-shaped channel with two inlets and two outlets. This geometry allowed the mixing of the solutions of calcium chloride and sodium bicarbonate which were prepared from the respective crystalline solids and standardized by atomic absorption spectrometry. Two types of channels were used: one hydrophilic and one hydrophobic and the solutions mixing was done using a Y junction microchip. The dimensions of the cell were 22.5 mm x 15.0 mm x 4 mm (length x width x height).

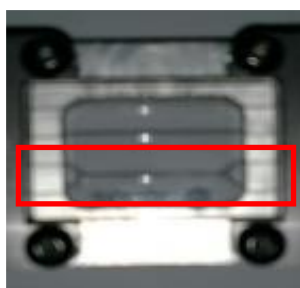


Figure 1: Picture of the microchip. Encircled is the Y-shaped microchannel reactor used in this study.

The Y-junction microchannel (Dolomite) is of 100 μ m depth and 205 μ m width. Two different microchips were used; the hydrophilic which is made of glass and the hydrophobic which is of the same geometry and topology but with silane coated surface. The hydrophilic microchip is compatible with most of the organic and inorganic compounds, including hydrochloric acid and sodium hydroxide, methanol and acetone while the hydrophobic microchannel is not compatible with dense hydrochloric acid and sodium hydroxide solutions. The reactant solutions were pumped with microfluidic

pumps (P) (Figure 2) connected with air pump (AP) to ensure constant flux at the inlets of the micro-channel (C) in which, the reactant solutions mixing was done. The total flux of the fluids in all experiments was equal to $0.5\mu\text{L}/\text{min}$ and the value of Reynolds number was equal to 5.7×10^3 . A microscope and a video-camera (MVC) were used to monitor the precipitation inside the microchannel and a computer (C) was used for pictures recording (Figure 2).

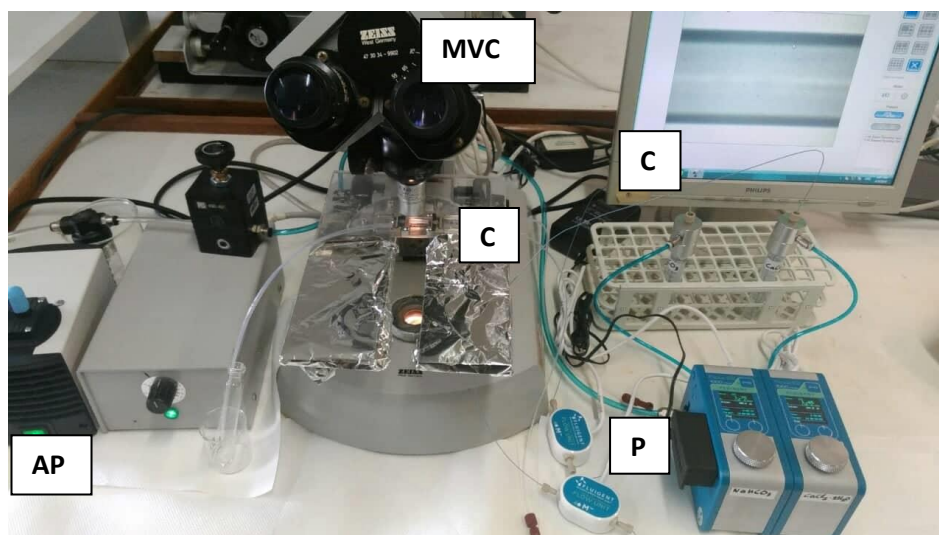


Figure 2: Microfluidic experimental setup for the investigation of the precipitation of calcium carbonate inside the microchannel cell.

In all cases, the calculations of the saturation ratio of calcite in the supersaturated solutions were performed using the equilibrium software Multiscale 6.1®.^[13] All experiments were done at constant temperature 25°C . The ionic strength of the solutions was adjusted to 0.15M , with the addition of the appropriate amount of sodium chloride stock solution. At the micro-channel outlet, samples were collected at least daily, filtered and the filtrates were analyzed for calcium content by atomic absorption spectrometry. The formation of the deposit crystals was monitored directly using a camera adapted to an optical microscope (Figure 2). Using image analysis of many pictures, particle size distribution estimates were obtained as a function of time.

RESULTS AND DISCUSSION

Typical results of precipitation of calcium carbonate inside the micro-channel for solutions for which past their mixing are shown in the graph of figure 3a. A sequence of snapshots of calcium carbonate crystals formed at SR 61.7 at different times (at 8, 12 and 24hrs) are shown in Figure 3b. It should be noted that at the SR conditions of the experiment, the formation of the first crystal inside the microchannel was recorded past 4h from the mixing of the two solutions in the microchannel reactor. All crystals increased in size forming the nucleus of a larger aggregate of crystals the size of which increased with time, and with respect to the number of crystals of the cluster. As may be seen in Figure 3(a) the encircled crystal (Figure 4(b)) was progressively associated with additional crystallites forming a cluster.

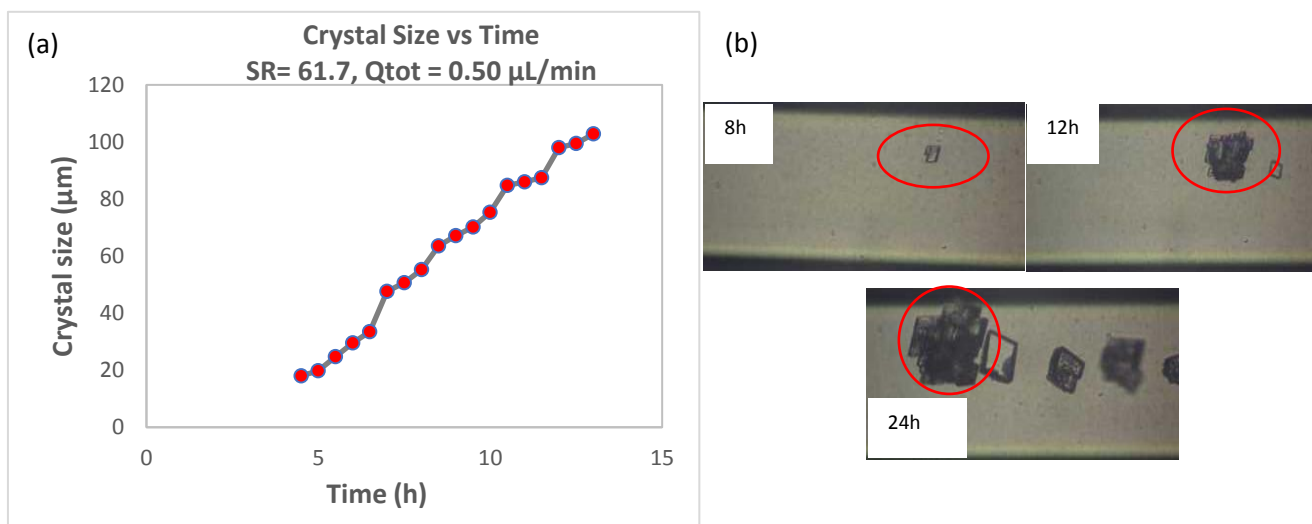


Figure 3: Calcium carbonate precipitation from supersaturated solutions inside the microchannel; SR = 61.7, Ionic strength 0.15 M NaCl, pH~7, 25°C: (a) Variation of crystal size as a function of time; (b) Snapshots of the crystals formed inside the micro- channel at 8,12, 24hrs past mixing of the CaCl_2 .

From Figure 3a, a linear rate of growth of $5.5 \times 10^{-10} \text{ m} \cdot \text{s}^{-1}$ was calculated. Linear rates of this order of magnitude have been reported for the crystal growth of calcium carbonate at ambient conditions ¹⁴. In Figure 4, the sequence of pictures during the precipitation inside the microchannel is presented. As may be seen, the growth of crystals takes place in the center of the channel.

It is interesting to note that despite that the supersaturation ratio with respect to calcium carbonate was very high, nucleation was observed past the lapse of induction time which was 4hrs. This fact suggested that nucleation in the confined space of the micro-channel is mainly homogeneous. The formation of calcium carbonate in the hydrophilic microchip was moreover investigated at a lower supersaturation value, SR=40.1 (Figures 5 and 6). The formation of the first crystal was recorded past 8hrs from the reagents mixing. This induction time was clearly significantly longer in comparison with the case of supersaturated solutions at SR=61.7. In Figure 6(a) the crystals formed along the microchip over a time period of 24hrs and at the end of the experiment (48hrs) may be seen. It should be noted, that past 48hrs, the solutions inlet was almost completely clogged by crystal agglomerates. Along the microchip, the morphology of the crystals formed varied (Figures 5 (b) and 6). As a rule, the three different calcium carbonate polymorphs have distinctly different morphologies. To investigate whether changes in morphology were due to the formation of different calcium carbonate polymorphs or to differences of the kinetics of formation of crystal faces of one polymorph, the mineral deposits were characterized by *in situ* Raman spectroscopy. The analysis of the space resolved spectra, confirmed the presence of metastable