

Pore wall deformation due to sodium chloride crystallization in a microfluidic device

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1 Introduction

During the drying of porous media, dissolved salts can reach a very high concentration that they crystallize. Crystals can partially or totally clog pores, modifying the porous medium transport properties, or causing damages in the porous material [1]–[3]. Understanding the crystallization process is therefore important for many fields; mostly in the field of civil engineering, to prevent the destruction of building materials or cultural heritage, in the field of CO₂ sequestration [4] in order to avoid the well bore clogging during the gas injection, or in the field of the erosion of natural rocks.

In this context, a key parameter is the local supersaturation, i.e. the amount of ions in excess at the liquid crystal interface in comparison with a solution at equilibrium with salt crystals. It affects the kinetics of growth as well as the level of the crystallization pressure [5]; which is the pressure that a crystal can exert on a wall. Thus, in order to predict the crystallization pressure, it is important to well describe all the coupled phenomena which control the crystal growth at the scale of a single crystal [6]: nucleation, crystal growth kinetics, and ions transport through the solution.

In spite of the numerous studies performed on crystal nucleation and growth in solutions (e.g [7] and references therein) these phenomena are still not perfectly described.

In recent years, microfluidics has been used as a valuable tool to characterize and control the crystallization process [8]. In particular, it provides well-controlled experimental conditions and enables to isolate small volumes in which only one nucleation event can occur [9]. The deformability and photoelasticity properties of PDMS were used in [10] to observe the crystallization pressure induced by halite crystal growth. In that paper, crystallization was induced in a large microchannel by cooling and controlled by diffusion.

In our study, we develop a quite simple microfluidic device to perform a local study of crystallization in a single straight channel. It can be seen as a model system for the study of porous media [11]. This device allows us to trigger the crystallization by evaporation of a sodium chloride solution in a trapped volume as small as picoliters (10^{-12} L). Thus, we can precisely observe the onset of crystal nucleation and growth. Moreover, numerical simulations are performed to analyse the experimental results.

2 Materials and methods

Experiments are performed on a microfluidic chip as represented in Figure 1a. It is composed of a large channel which is used to supply the fluids. Experimental observations are done in dead-end pores which are perpendicular to the large channel. Two cross sections are used: $5 \times 5 \mu\text{m}^2$ and $20 \times 20 \mu\text{m}^2$ in order to see the crystallization dependence on pore size. The chips are made of PDMS and glass. Pore channels are initially saturated by a salt solution which evaporates by diffusion. A flow of nitrogen is maintained in the large channel during the whole experiment. Crystallization is recorded at 1000 frames per second on an inverted microscope. In order to analyse the experimental results, a numerical model is developed with Comsol multiphysics 5.2© to simulate the crystal growth of an initial nucleus in a solution. The transport of dissolved salt by diffusion and convection is taken into account as well as the crystal growth by reaction. The problem is considered axisymmetric and the crystal is at the middle of the pore. Because of symmetry, only a quarter of the problem is modelled to speed up the computation (Figure 1c).

3 Results

Unlike [10], our experimental setup allows us to record all the crystallization process from the nucleation (Figure 1b). The kinetics of crystal growth extracted during the first 10ms show that it is at least 2 orders of magnitude faster than those reported in literature [6], [12]–[14]. Thanks to a theoretical model and numerical computation (Figure 1c), this discrepancy is explained by the fact that the measurements in literature are done after a longer time; when the growth is limited by diffusion and not by the reaction process. Thanks to our high frame acquisition rate, we are able to propose a new value for the kinetics parameter of crystal growth rate by reaction $k_r \sim 10^{-2}$ m/s for sodium chloride.

Besides, different crystal shapes are observed depending on the pore channel cross section; “compact” crystal in case of higher geometrical confinement and “star” crystal in lower confinement (Figure 1b).

The deformation of pore walls because of crystallization pressure can also be observed (Figure 1b, left). This deformation corresponds to a maximum applied pressure around 0.5MPa when the crystal touches the pore. The pressure is evaluated from elastic deformation computations with a finite volume method. To generate such a pressure, the supersaturation has to be equal to 1.005. This is in good agreement with our computation of the dissolved salt concentration field at the crystal surface performed with our value of k_r .

In summary, this work sheds light on the mechanism of stress generation on pore walls due to sodium chloride crystallization. The key new feature is that the stress generation is a highly transient process directly related to the supersaturation level in the vicinity of the crystal when it is about to touch the walls during its growth. This opens up the route to understand this transient process within a porous medium.

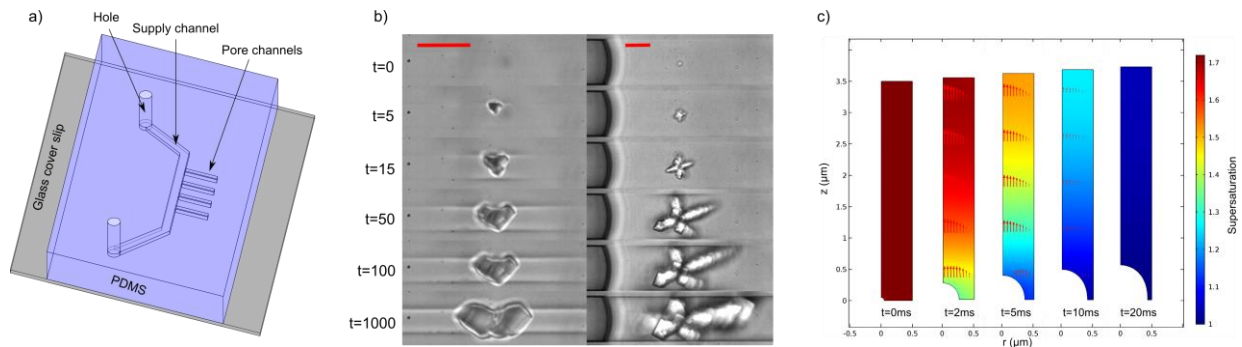


Figure 1: a) Scheme of the microfluidic chip. b) Crystal growth recorded at 1000 frames per second (red scale bar represents 10 μm). c) Computation of the supersaturation during the crystal growth.

References

- [1] G. W. Scherer, Stress from crystallization of salt, *Cem. Concr. Res.*, 34, 1613 (2004).
- [2] R. M. Espinosa-Marzal et al., Advances in understanding damage by salt crystallization., *Acc. Chem. Res.*, 43, 897, (2010).
- [3] H. Derluyn et al., Deformation and damage due to drying-induced salt crystallization in porous limestone, *J. Mech. Phys. Solids*, 63, 242 (2014).
- [4] M. Kim, et al., Aquifer-on-a-Chip: understanding pore-scale salt precipitation dynamics during CO₂ sequestration., *Lab Chip*, 13, 2421(2013).
- [5] M. Steiger, Crystal growth in porous materials- I: The crystallization pressure of large crystals, *J. Cryst. Growth*, 282, 455 (2005).
- [6] A. Naillon et al., Evaporation with sodium chloride crystallization in a capillary tube, *J. Cryst. Growth*, 422, 52, (2015).
- [7] J. W. Mullin, *Crystallization*, 4th editio. Elsevier, 2001.
- [8] J. Leng et al., Microfluidic crystallization., *Lab Chip*, 9, 24-34 (2009).
- [9] R. Grossier, et al., Predictive Nucleation of Crystals in Small Volumes and Its Consequences, *Phys. Rev. Lett.*, 107, 25504 (2011).
- [10] K. Sekine et al., In situ observation of the crystallization pressure induced by halite crystal growth in a microfluidic channel, *Am. Mineral.*, 96, 1012–1019, (2011).
- [11] W. L. Olbricht, Pore-scale prototypes of multiphase flow in porous media, *Annu. Rev. Fluid Mech.*, 28, 187-213 (1996).
- [12] R. Grossier et al., “Ultra-fast crystallization due to confinement,” *J. Cryst. Growth*, 312, 487-489 (2010).
- [13] S. Al-Jibbouri et al, “The growth and dissolution of sodium chloride in a fluidized bed crystallizer,” *J. Cryst. Growth*, 234, 237 (2002).
- [14] N. Shahidzadeh et al., “Damage in porous media: role of the kinetics of salt (re)crystallization,” *Eur. Phys. J. Appl. Phys.*, 60, 24205 (2012).