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# Performance evaluation of ceiling crystallization for suppressing buoyancy-induced convection in mass transfer applications: An interferometric study

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ABSTRACT

The present study is concerned with the investigation of the phenomena of solute transport in aqueous solution-based crystal growth processes when the growing crystal is fixed in the upside-down (ceiling) configuration. The ceiling crystallization method has been employed for suppressing the adverse effects of buoyancy when the crystal growth experiments are conducted under normal gravity conditions. A Mach–Zehnder interferometer has been employed to record the line-of-sight images of the concentration field. In order to assess the feasibility of the ceiling crystallization approach for creating diffusion-dominated conditions, the results have been compared with that of the conventionally employed approach wherein the growing crystal is platform-supported. Experiments have been carried out for two levels of supersaturation i.e. $\sigma = 2\%$ and 4% and sodium chlorate ($NaClO_3$) has been chosen as the model material. Results have been presented in the form of interferometric images of the concentration field, two-dimensional concentration contours and spatio-temporal variations of supersaturation around the growing crystal in both the configurations considered. Results of the experiments clearly reveal the suppression of buoyancy-induced convection currents and the formation of an extended horizontally stratified depletion zone around the growing crystal in ceiling configuration. The mass transport phenomenon was seen to be diffusion-dominated, thus eliminating the possibilities of sharp variations in the supersaturation levels in the vicinity of the crystal, which otherwise deteriorate the quality of the growing crystal in convection-dominated conditions.

## 1. Introduction

Understanding the phenomena of mass transport is of primary interest in some of the technologically important areas of applications, particularly in chemical industries. Important areas of applications include solidification processes of binary alloys, growth of organic and inorganic crystals from their supersaturated aqueous solutions [1–6]. For instance, large and good quality organic crystals, e.g. protein crystals, are required in biomedical applications for protein structure determination. The quality of structure determinations is often limited by the grown crystal quality. Growth of these crystals involve nucleation, transport of solute particles from the bulk solution to the crystal vicinity and subsequent incorporation of these molecules onto the faces of the growing crystal, a process which is mainly governed by the surface kinetics [7,8]. In order to ensure defect-free and uniform growth, a fine balance needs to be maintained between the rate at which the solute particles are transported from the bulk solution and the rate at which these particles incorporate onto the growing crystal faces. However, under the influence of normal gravity conditions, the buoyancy-driven convection currents act as the main driver of the solute particles from the bulk solution to the crystal vicinity and hence the rate of solute transport increases significantly in comparison with the rate of deposition of these molecules onto the growing crystal, thereby substantially deteriorating the quality of the grown crystal. It has been experimentally established that the three-dimensional and time-dependent nature of these convection currents has an adverse effect on the growth process. In view of this, considerable efforts are currently being made worldwide to suppress the buoyancy-induced convection currents to the maximum extent possible so as to make the growth process diffusion-dominated.

Mass transport by convection and diffusion process is primarily governed by factors like viscosity and density of the solution,

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characteristic dimension, diffusion coefficient of the solute particles and the gravitational force. These two competing modes of solute transport may be conveniently expressed in the form of a non-dimensional number, namely the Rayleigh number given as

$$Ra = \frac{g\beta(\Delta C)L^3}{\nu D} \tag{1}$$

Here, $\Delta C$ is the concentration difference (or the difference in the supersaturation levels), $L$ is the characteristic dimension, $\nu$ is the kinematic viscosity and $D$ is the diffusion coefficient of the solute particles with $g$ being the gravitational acceleration. It is to be seen that for higher values of Rayleigh number, transport of solute particles would be predominantly governed by convection while for values lower than the critical Rayleigh number, the growth process may be considered as diffusion-dominated. Referring to Eq. (1), the plausible ways of suppressing the strength of buoyancy-induced convection currents include:

1. Use of highly viscous growth solutions: For instance, growing crystals in gels as earlier has been demonstrated by Hou et al. [9] wherein the authors made use of the gel as a solvent in order to suppress convection and mimic microgravity environment during the growth process of lysozyme crystals.
2. Decrease the characteristic dimension $L$: Employing very small growth volumes. For instance, Dold et al. [10] studied the effects of mass transport conditions (convection and diffusion-dominated) on the growth process of organic crystals. The authors varied the volume of the growth solution in order to realize the changes in the mass transport conditions.
3. Reduce the gravitational acceleration $g$.

Of the above three plausible approaches, finding ways for reducing the effects of gravitational acceleration has attracted the attention of various researchers in recent times in order to achieve diffusion-dominated growth conditions. Of notable interests are the studies reported by Yin et al. [11] and Ramachandran and Leslie [12] wherein the authors performed crystal growth experiments under the influence of strong magnetic fields for mimicking microgravity environment and to suppress buoyancy-induced convections currents. Similarly, studies concerned with the application of magnetic field for suppressing Rayleigh–Benard convection in a differentially-heated cubic enclosure have also been reported in the literature [13]. A group of researchers have also explored the possibility of conducting these experiments in microgravity conditions created through free fall, parabolic flights and/or space stations and gradient magnetic fields in order to reduce the adverse effects of buoyant convection on the resultant crystal quality [14,15]. However, these approaches for simulating diffusion-dominated growth conditions have inherent disadvantages in terms of the associated cost, inaccessibility of the experiments being carried out at space stations and more importantly the stability problems associated with $g$-jitters.

With this background, the present work employs one of the most simple and innovative ways of creating the diffusion-dominated growth conditions when the crystal growth experiments are performed under normal gravity conditions. The reported experiments make use of ceiling configuration wherein the growing crystal is suspended into its supersaturated solution in an upside-down geometry just below the air-solution interface, as schematically shown in Fig. 1(a). The central idea is to create conditions of stable stratification in the vicinity of the growing crystal with the layer of the lighter solution prevailing over the heavier one, ultimately avoiding the possibility of the occurrence of buoyancy-induced convection currents. The configuration of ceiling crystallization is in contrast to the conventional method of holding the crystal inside the solution in a platform geometry wherein, under the influence of gravitational acceleration, buoyant convection plumes set up due to the presence of concentration gradients in the growth chamber. The inherent drawbacks of the conventional platform technique are associated with the three-dimensionality and time-dependent nature of the convection currents which grow in strength as the crystal size increases with the passage of time.

In the experiments reported in the present work, the process of mass transport has been set up by inserting an earlier grown seed crystal of $NaClO_3$ into its supersaturated solution. Two levels of supersaturation ($\sigma$ = 2% and 4%) have been considered. The growth experiments have been carried out at normal room temperatures. Projection data of the concentration field around the growing crystal has been recorded using a Mach–Zehnder interferometer which is non-intrusive and inertia-free [16]. Experiments have been conducted in wedge-fringe setting mode of the interferometer. The recorded interferograms have been quantitatively analyzed to retrieve the spatio-temporal variation of the two-dimensional concentration field and degree of supersaturation. Based on the distribution of the degree of supersaturation in the growth chamber, it has been demonstrated that the resultant growth conditions in ceiling configuration are predominantly diffusion-dominated in comparison with the convection-dominated mass transport conditions observed with the conventional platform technique.

## 2. Apparatus and instrumentation

The crystal growth experiments reported in the present work have been carried out in a growth chamber cubic in shape (spectrometric cuvette of inner dimensions 30 mm × 30 mm × 30 mm and wall thickness of 2.5 mm), as schematically shown in Fig. 1(a)). The growth chamber is made of quartz material with high optical quality in order to ensure an undisturbed passage of the laser beam for recording the projection data in the form of interferometric images. The temperature of the supersaturated solution was maintained using a water circulation bath (made of copper) placed at the bottom of the growth chamber. Sufficient number of baffles have been fabricated in the copper bath to provide a torturous path to the flowing water. In order to avoid any possibility of the formation of air gaps (pockets) between the base of the growth chamber and the top surface of the water circulation bath, silicone based thermal pad (*thermal conductivity*: 4.1 W/m K) and silver based thermal paste (*thermal conductivity*: 8.7 W/m K) are tightly sandwiched in this space. The inlet and outlet ports of the water circulation bath are connected to a thermostated bath for circulating water at pre-defined temperature levels. A photographic view of the complete experimental set up is shown in Fig. 1(b). Furthermore, the entire crystal growth assembly is covered by a thick layer of asbestos sheet to thermally isolate the experimental apparatus from external fluctuations.

The projection data of the concentration field around the growing crystal has been recorded using a Mach Zehnder interferometer. The optical configuration of the Mach Zehnder interferometry set up is schematically shown in Fig. 2. Experiments have been conducted in wedge fringe setting mode of the interferometer. In this setting, the fringes are representative of concentration profile in the growth chamber. Changes in the refractive index field in the growth chamber result in a difference in path lengths of test and the reference beams. The two beams on superposition at the second beam splitter BS2 produce an interference pattern, which can be observed and recorded. This pattern contains information on the variation of refractive index in the growth chamber. In the present work, the interference patterns are recorded using a monochrome CCD camera (1024 × 768 pixels, *Thorlabs*) coupled with a zoom lens (*Navitar*) at video rates. To compensate the additional path length introduced by the crystal growth chamber in the test