Effect of Growth Rate History on Current Crystal Growth: A Second Look at Surface Effects on Crystal Growth Rates

Pareena Pantaraks and Adrian E. Flood*

School of Chemical Engineering, Suranaree University of Technology, Nakhon Ratchasima, 30000 Thailand

ABSTRACT: The effect of a crystal's growth rate history on the current growth behavior was investigated as a cause of crystal growth rate dispersion (GRD), which is a significant problem in crystallizer design and modeling. The solute used in the experiments was sucrose, a high production commodity still crystallized mainly in batch crystallizers, where GRD is most significant. The results show that the growth history of a crystal has a significant effect on the crystal growth rate of that crystal. In particular, a history of rapid crystal growth under high supersaturation causes a roughening of the crystal surface, apparently due to poor surface integration, and subsequent growth occurs at lower rates than would be expected without this growth history. The process of crystal surface healing occurs at low levels of supersaturation over periods of several hours of growth and results in the crystals again reaching their normal growth rate levels. The growth layer formed to heal the surface of the crystal is greater than 100 μm thickness, far in excess of the scale of the apparent surface roughness. This study shows that the crystal perfection near the growing surface of the crystal may be a more significant indicator of crystal growth rate than the overall average perfection in the entire crystal.

Introduction

Crystal growth rate dispersion is a phenomena encountered in crystallization that describes how seemingly identical crystals in the same conditions of temperature, pressure, composition, and flow grow at different rates. Since the initial study of White and Wright[1], a large amount of research has been conducted to determine the causes and mechanisms of GRD, but the mechanism responsible for the phenomenon is still little understood. The mechanism initially proposed involved a variable amount of molecular scale surface roughness between different crystals, due to a varying surface concentration of screw dislocations. From modern models of surface integration kinetics, such as BCF theory, it was assumed that the growth rate of an individual crystal was related to the number of screw dislocation sites on its surface. However, the idea that molecular scale surface roughness is relevant to the study of GRD was discounted by Herden and Lacmann[2] in their study of potassium nitrate. The relation between the overall lattice perfection of a crystal and its growth rate was proposed by Ristic et al.[3] and subsequent studies have both agreed (i.e., Mitrovic,[4] Ristic et al.,[5] and Zacher and Mersmann[6]) and disagreed (i.e., Herden and Lacmann[2] and Harding et al.[7]) with their conclusions. Herden and Lacmann[2] suggested that there is no correlation between face-specific growth rates of KNO$_3$ and Laue quality. The difficulty in correlating Laue quality with growth rates may be explained by the fact that the Laue quality is determined for the whole crystal, while the growth rate is face-specific and related to surface features only. A correlation between Laue quality and growth rate is possible, but it is unlikely that it is sufficient to describe the mechanism or cause of GRD.

Tanneberger et al.[8] observed the influence of pulse changes in supersaturation ($\sigma_1:\sigma_2:\sigma_1$ with σ_2 either more than or less than σ_1) on the growth rate of potassium alum (KAl(SO$_4$)$_2$·12H$_2$O). The results showed that the growth rate decreases with decreasing supersaturation σ_2 and increases with increasing supersaturation σ_2, but it does not return to the previous value after the second supersaturation change (returning to σ_1) in a short time period. Herden and Lacmann suggested that the effect might be explained by a change of the surface structure of the crystal, which is then responsible for a change in growth rate.[2] This situation could be quite important during the nucleation period in a batch crystallizer; the initial nuclei form at a higher supersaturation than later nuclei, which may relate to differences in initial growth rates for apparently identical nuclei. If the suspension of a continuous crystallizer was not sufficiently mixed, a similar mechanism could be created by spatial variation in the solute concentration. The current study, therefore, investigates whether the growth rate history of individual crystals is related to crystal growth rate dispersion.

Experimental Procedures

Materials. Solutions were produced from commercial grade white sugar of approximately 99.9% purity (Mitr Phol, Thailand) and water treated by reverse osmosis. Sucrose seed crystals were taken from the same source, with a narrow seed size distribution achieved by selecting crystals of approximately the same size using inspection under a microscope. Seed crystals of unusual shape or containing obvious surface features were excluded. The crystal size distribution of a seed sample used in the batch crystallization study is shown in Figure 1.

Apparatus. Crystallization experiments were performed in both a single-crystal growth cell and a batch crystallizer. The single-crystal growth cell is depicted in Figure 2. A single crystal was mounted between two pins, at the center of the

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* Corresponding author. E-mail: adrianfl@ccs.sut.ac.th.