Simulations of Crystal Shape Distributions in the Presence of Crystal Growth Modifiers

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1. Motivation

- Crystal shape distribution plays a crucial role in determining product quality and efficiency of down stream processes
- Crystal growth modifiers (CGMs) are often used to obtain desired crystal shape distribution in the industries
- Sometimes CGM in the form of impurities are unavoidable
- A modelling framework and simulation results that can be used to predict crystal shape has been presented

2. How Crystal Growth Modifiers Work

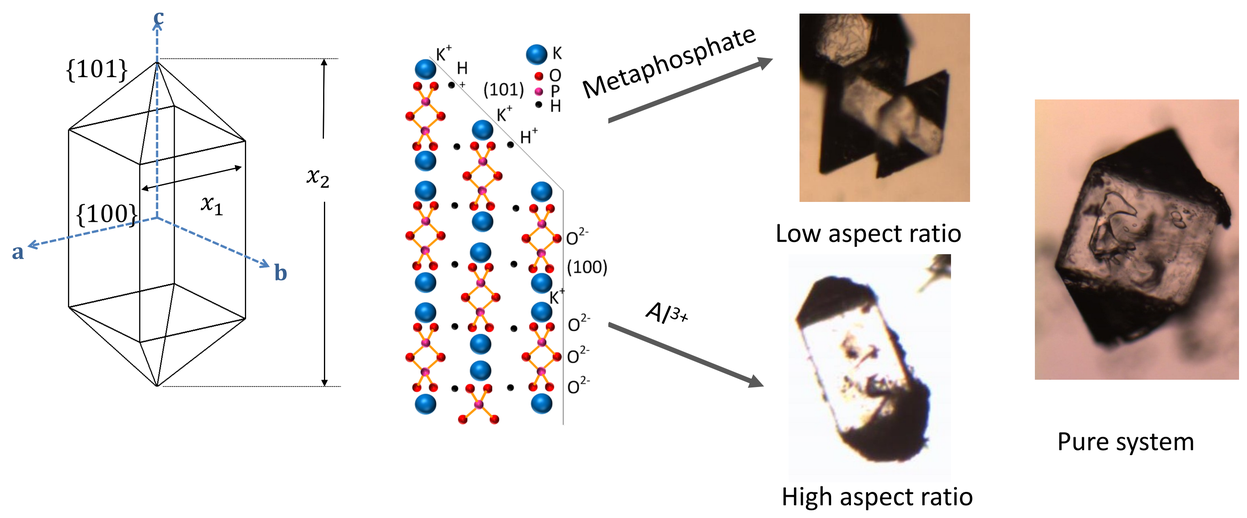

Figure 1: Schematic of potassium dihydrogen phosphate (KDP) crystals. Presence of cations (e.g., Al^{3+}) produce high aspect ratio crystals. On the other hand, in the presence of anions with strong capacity for hydrogen bonding (e.g., metaphosphate) produce crystal with low aspect ratio.

- CGMs with cations get adsorbed on the negatively charged prismatic faces {100}, hinders growth of that face and produces high aspect ratio crystals
- Anions with strong capacity of hydrogen bonding get adsorbed on the pyramidal {101} faces and produce low aspect ratio crystals
- Growth inhibition of a particular crystal face is caused by the pinning of steps by CGM/impurity molecules at the kinks [3]

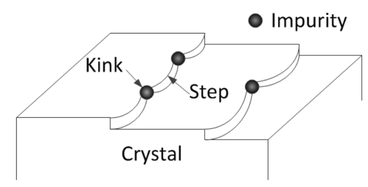

Figure 2: Impurity adsorption at the surface kinks hindering step movement

3. Modeling of Shape Evolution

- Modified growth rate in the presence of CGM [1]

$$G_i = G_{0i}(1 - \alpha\theta)$$

$$\theta = \frac{KC_i}{1 + KC_i}\left[1 - \exp\left(-\frac{\eta}{\tau}\right)\right]$$

G_{0i} is the growth rate in pure system, α is the effectiveness factor for the CGM, θ is the surface coverage, K is the Langmuir constant, C_i is the CGM concentration, η is the contact time, τ is the time constant.

- Population balance model (PBM) for shape evolution [2]

$$\frac{\partial n}{\partial t} + \nabla_{\boldsymbol{x}} \cdot (\boldsymbol{G}n) + \frac{\partial n}{\partial \eta} = B_0 \delta(\boldsymbol{x} - \boldsymbol{x_0})(\eta - 0);\ x = \{x_1, x_2\}$$

n is the distribution function, B_0 is the nucleation rate

- Appropriate mass and energy balance equation also required

4. Simulation Results

Case study 1: Crystallization of a model compound described by 1D PBE

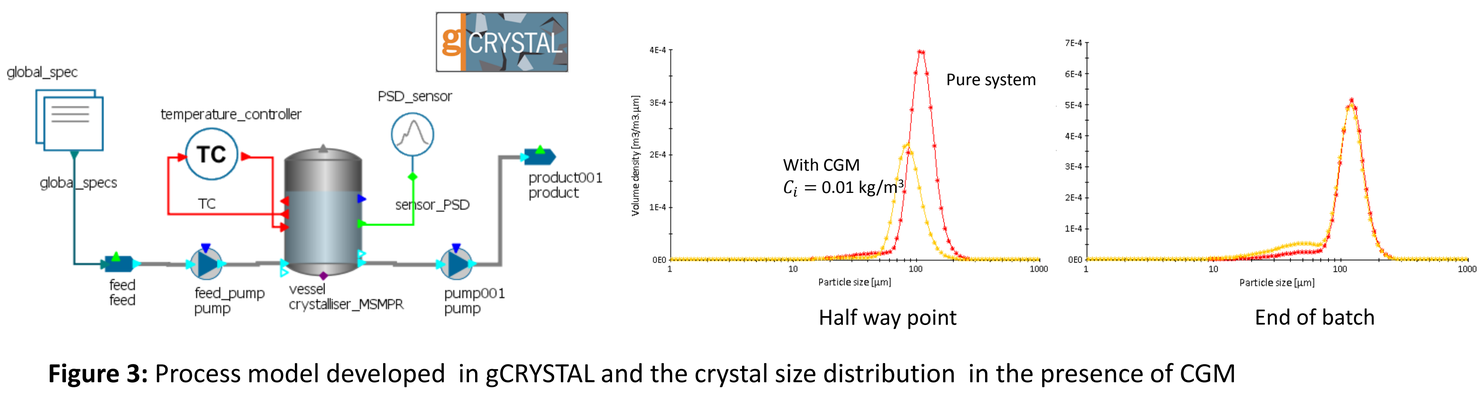

Figure 3: Process model developed in gCRYSTAL and the crystal size distribution in the presence of CGM

Case study 2: Crystallization of potassium dihydrogen phosphate (KDP) in water

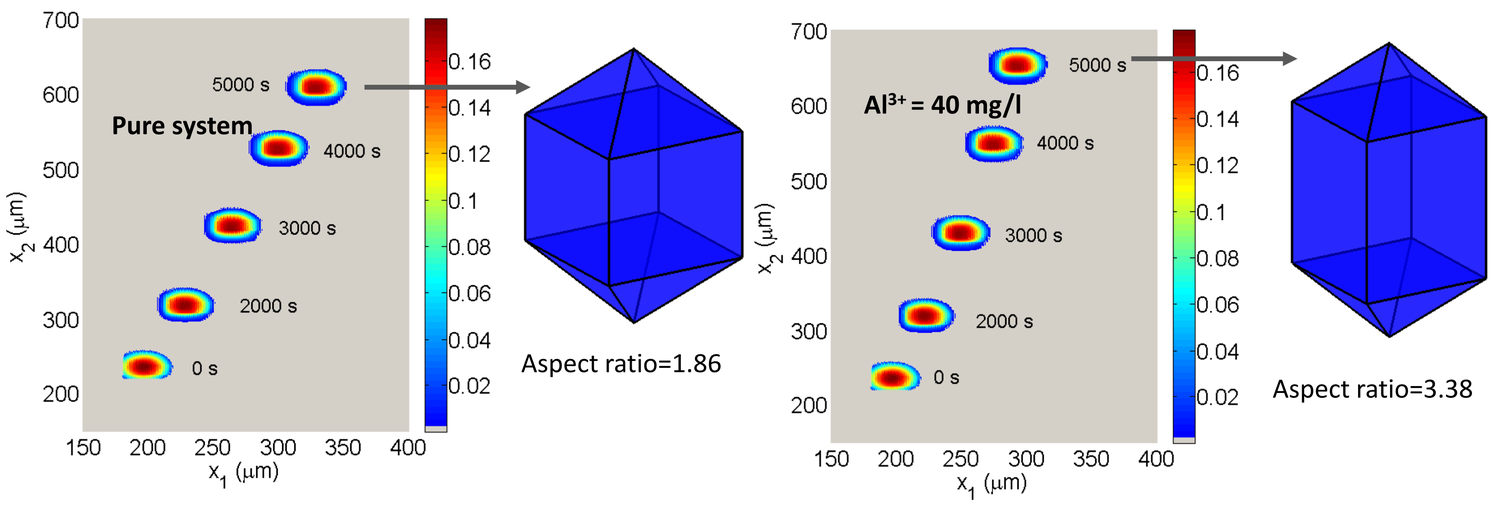

Figure 4: Evolution of the crystal size distribution for KDP-water system. In pure system crystals with low aspect ratio are produced. When Al^{3+} is added as CGM, growth in x_1 direction is hindered and crystals with high aspect ratio are produced.

5. Discussions

- Adsorption model of CGM on crystal surface is combined with the morphological PBEs to describe the evolution of the crystal shape
- The model is implemented in gCRYSTAL for 1D PBEs with modified growth rate
- Cooling crystallization KDP-water system described by 2D PBEs is simulated in Matlab
- Simulation results with experimentally determined parameters show the prediction of the crystal shape distribution
- These results are qualitatively verified by experiments
- In future experiments will be performed to control crystal shape using CGM

References

[1] Kubota et al., *Cryst. Growth Des*. 2004, 4(3), 533-537.
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[3] Kubota, *Cryst. Res. Technol.,* 2001, 36(8-10), 749-769.

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