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## Dynamic features of the CSD obtained during batch crystallization operations in the presence of impurities.

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The final CSD of particles generated during batch cooling solution crystallization is known to be largely determined by the development of nucleation phenomena and, therefore, of supersaturation. This is why mastering the final quality of crystals is often related to the application of appropriate temperature control policies. Griffiths<sup>1</sup> early suggested that supersaturation "showers" illustrated in Fig.1 should be avoided in view of controlling the product CSD<sup>2</sup>. Later, inappropriate cooling policies, among which the so-called "natural cooling", were also shown to entail detrimental nucleation "showers". More generally, the pattern in Fig.1 indicates that at any one time when supersaturation exceeds the limit of metastable zone an undesirable burst of nuclei should be produced<sup>3</sup>.

The idea of avoiding undesirable nucleation burst is clearly not questionable, but we propose that the way how nucleation showers happen is an important fundamental question that deserves to be thoroughly analyzed. We propose that two distinct ways of generating multiple nucleation showers should actually be differentiated. While papers dealing with temperature control in batch crystallization address the problem of "regulating" nucleation kinetics in pure media, we suggest that in industrial crystallization practice where impurities are almost unavoidable, the mechanisms determining the generation of particles is different. In the absence of inhibition effects, double nucleation peaks are rather frequent, but they do not seem to produce oscillatory supersaturation profiles exemplified in Fig.1a. Such nucleation peaks are referred to as "Simple Nucleation Peaks (SNP)" in the sequel. Multiple nucleation events arising from oscillations of supersaturation might be possible only when inhibition effects are induced by impurities in solution. In this second case, referred below to as Impurity-Induced Supersaturation Peaks (IISP), we show that both the nucleation rate and the supersaturation trajectories can exhibit two or more sustained oscillations.

To investigate the dynamics of batch operations performed in the presence of impurities, the cooling crystallization of ammonium oxalate (AO) was monitored using ATR FTIR spectroscopic measurements of supersaturation. Small amounts of NiSO<sub>4</sub> were dissolved as impurity in the initial solution<sup>4</sup>.

A model of the crystallization was developed, based on Kubota-Mullin's pinning mechanism<sup>5</sup>. The PBEs (Population Balance Equations) were solved and the related kinetic parameters were identified to simulate the experimental behavior of the process.

While SNPs occur in pure crystallization media, IISPs were never experimentally observed before (to the best of our knowledge). ATR-FTIR monitored experiments performed in impure media offered a means of investigating differences between SNP and IISP.

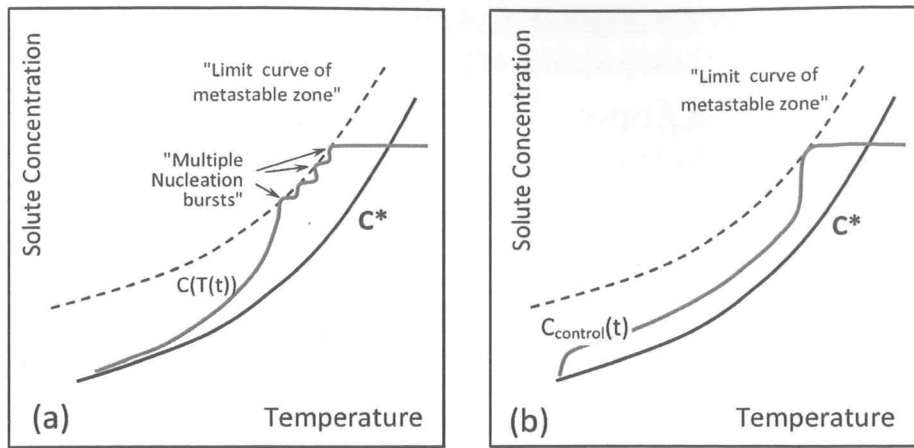


Figure 1. Effect of excessive cooling rate on the development of cooling crystallization, after Griffiths<sup>1,2</sup> (a) Uncontrolled cooling (b) Controlled cooling leading to limited nucleation events during the crystallization process.

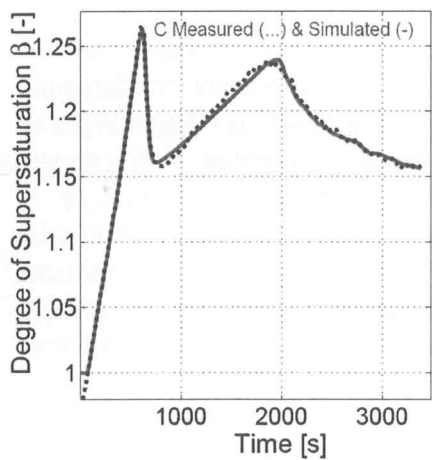


Figure 2. Measured and simulated supersaturation profiles during the batch cooling crystallization of AO with dissolved NiSO<sub>4</sub> (0.02 wt-%)

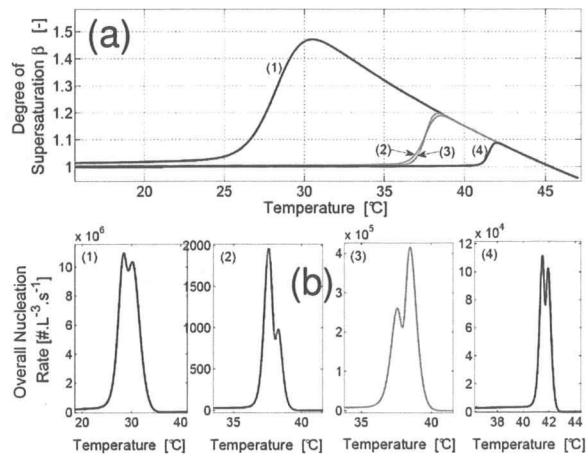


Figure 3. (a) Simulated supersaturation and (b) nucleation profiles for random kinetic parameters (solubility curve of AO in water)

Figure 2 shows that IISPs can be observed when the crystallization takes place in impure solvent. In order to examine whether such profiles can happen in pure solvents,  $2 \cdot 10^5$  random batch cooling operations were simulated on the basis of “standard” crystal growth and primary and secondary nucleation models. While SNPs occur frequently (1/3 of the simulations exhibit dynamic behaviors exemplified in Fig.3), successive nucleation peaks were never found to lead to supersaturation bumps like the ones in Fig.1a<sup>6</sup>.

The nucleation and growth kinetic models used for simulating the experimental data in the presence of impurities were similar to the previous ones, except Kubota-Mullin’s model used to represent pinning inhibition mechanisms induced by the presence of impurities. As Fig.2 shows, the fit between the model and the experiments fit is really satisfactory.  $2 \cdot 10^4$  simulations were again carried out with random values of the involved parameters: primary, secondary nucleation rates, crystal growth rates and

parameters of the unsteady-state impurity adsorption mechanism. Many IISPs behaviors like in Fig. 2 were obtained with varying kinetic parameters<sup>6</sup>. Due to the lack of place, additional examples of IISP curve are not given here, but it can be outlined that up to 4 supersaturation bumps can be reproduced through simulation

A second dynamic feature of the PBE simulation of inhibited crystallization –assuming negligible attrition/breakage, and aggregation/agglomeration occur– deserves to be examined. As Fig.4A shows, simulations of pure systems show a monotonous decrease of the final particle sizes of crystals nucleated at increasing times. The situation is more complex with inhibition effects: Fig.4b shows that identical sizes can characterize particles generated at different moments of the batch process. Despite its major consequences, such mathematical feature is usually not considered in the design of temperature control systems, even though impurities are unavoidably present in industrial mother liquors.

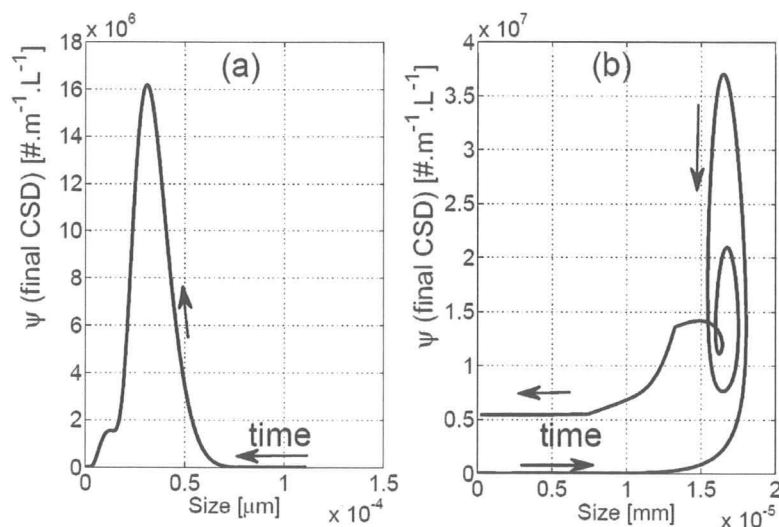


Figure 4. Time variations of sizes and particle numbers for batch crystallizations performed (a) without and (b) with inhibitions effects.

Indeed minute amounts of impurities in solution can tremendously affect the development of crystallization and the quality of its product. Yet, almost all academic modeling and control studies dealing with crystallization engineering assume pure solute/solvent systems: this obviously raises a very serious question. The present paper therefore aims at showing that the problem of improving the CSD through advanced temperature control is probably more complex than usually assumed. In order to improve its performances in industrial context, future control design should account for the specific complex dynamic features of crystallization in impure media. To illustrate this assertion, examples of the detrimental effect of impurities on the efficiency of temperature controlled CSD will be presented.

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