Stabilizing NaCl particles with Cd^{2+} in a saturated solution during ex situ PSD measurement

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Abstract

The measurement of a particle size distribution (PSD) of a soluble salt, NaCl, dispersed in a saturated solution using laser light scattering (LLS) is fraught with difficulty since this apparatus and others like it do not have strict temperature control in the sample chamber. A slight increase or decrease in temperature produces conditions where the crystals grow or dissolve spontaneously from or into background solution during PSD analysis. The difficulties introduced in particle size analysis can be overcome by adding 100 ppm $CdCl_2$ to the saturated solution used to disperse the crystals for analysis. The Cd^{2+} ion is known to adsorb on the surface of NaCl in solution, thus inhibiting the crystal growth/dissolution rate by pinning steps of NaCl produced during the crystallization from a NaCl contaminated 38 wt% $CaCl_2$ solution cooled from 70 to 30 °C in a 1.4 liter jacketed-baffled-stirred tank is stabilized so that it can be reproducibly measured with the LLS.

Key words: Crystallization, Particle stabilization, *CdCl*, *NaCl*, PSD, Laser light scattering

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Fig. 1. Pinning of an advancing step by immobile absorbed impurities [3]. Top-down view of a growing layer.

1 Introduction

Cabrera and Vermilyea [1] hypothesized that strongly absorbing, *immobile* impurities can be adsorbed on terraces of crystal surfaces and *pin* steps, thus drastically impeding the step movement relative to that expected without impurities present. The mechanism of pinning and impeding steps has been widely practiced in many metal alloys, e.g., precipitation hardening in aluminum copper and aluminum silver alloys and others [2]. Figure 1 is a schematic picture showing the qualitative effect of immobile impurities on step movement. The step movement, and hence, growth rate, would be halted altogether when the distance (d) between impurities on the surface was $< 2r_c$ apart, where r_c was the medium radius curvature of a step. For spacings greater than this, the step may squeeze past the adsorbed species if the step growth velocity is high enough. The impurity spacing is also called a critical distance, whose magnitude is approximately given by the Gibbs-Thomson critical diameter [1][3].

Recently, use of atomic force microscopy (AFM) to investigate impurity-step interactions [4][5] has shown clear images of the impurity poisoning process of the steps and proved that below a certain supersaturation (σ_d) the crystal exhibits a dead zone where no growth occurs. When the supersaturation (σ) is increased beyond σ_d , the surface begins to grow with a step speed that is weakly dependent on σ . Above a sufficiently high supersaturation ($\sigma^* > \sigma_d$), the step velocity rises rapidly, approaching a linear value with respect to σ . Supersaturation was defined by $\sigma \equiv \Delta \mu/kT = \ln(a/a_e)$, where $\Delta \mu$ is the change in chemical potential per molecule upon crystallization, k is Boltzmann's constant, T is the absolute temperature, and a and a_e are the actual and equilibrium solution activities, respectively.

Based on the underlying assumptions of the model, it appears especially suited

to describing systems containing tailor-made additives or otherwise chemically similar impurities that strongly interact with the product during crystallization. Such impurities characteristically contain functional groups that bear strong structural and chemically resemblance to the host crystalline phase, resulting in strong surface adsorption, high levels of incorporation, and completely blocked growth rate at high concentration.

The use of 100 ppm $CdCl_2$ was chosen to stabilize NaCl particles since Cd^{2+} is known to adsorb on the crystal surface [6][7][8], pinning and immobilizing the steps in the surface of the NaCl crystal. Cadmium was chosen as the divalent impurity because its ionic radius is within five percent of that of sodium [7][8][9][10]. Also the value of σ^* is determined not only by impurity concentration (number of impurity ions per mole of NaCl), but by its type as well. The strongest hindering action was observed with a smaller ionic radius [11]. In the solution containing small amounts of Cd^{2+} and NaCl crystals, the Cd^{2+} ions enter the Na^{+} lattice substitutionally on the surface of NaClcrystals. Since the crystal must be electrically neutral, each divalent impurity ion replaces two sodium ions with the result that an excess concentration of positive ion vacancies equal to the concentration of impurity ion is introduced into the crystal [7]. However, at low enough temperature the concentration of vacancies is so low that the impurity ions are mostly unassociated and permanently fixed at their positions in the lattice. The unassociated impurity ions have no mobility by themselves. However, an impurity ion may move whenever there is an adjacent vacancy into which it can jump, although not otherwise. The use of step pinning Cd^{2+} additive to stabilize NaCl crystals, to measure PSDs using LLS, in nearly saturated solutions undergoing temperature variations that under or super saturate the solution is discussed below.

2 Experiments

2.1 Crystallization Experiments

A feed solution of $CaCl_2$ (38.63 wt%), KCl (1.07 wt%), and NaCl (0.67 wt%) which contains a large amount of crystals at room temperature can be dissolved by heating to 70 °C. To ensure complete dissolution, the solution was maintained at 70 °C for more than 24 hr. Then the solution is fed to the tank and cooled to 30 °C to induce crystallization. The $CaCl_2$ and KCl are soluble at around 30 °C, and NaCl crystallizes out of solution in a continuous stirred tank reactor (CSTR) with four standard baffles radially-directed around the reactor periphery running the length of the reactor's straight side and a Rushton impeller in the middle of reactor. A standard baffle design and detailed baffling information as well as experimental set-up can be found

elsewhere [12][13][14]. The solute concentration of solutions before and after crystallization was determined by atomic adsorption spectroscopy (AAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Also scanning electron microscopy (SEM), energy-dispersive spectrometry (EDS), and X-ray diffraction (XRD) were performed on solid particles for crystal morphology, elementary, and phase analyses.

2.2 Measurement of Particle Size Distribution (PSD)

The PSD was measured with Beckman Coulter $LS230^{TM}$ and verified for the particle shape and size range with an optical microscope and scanning electron microscopy (SEM). The Beckman Coulter $LS230^{TM}$ is a system of multifunctional particle size characterization tool and has an experimental reproducibility of 1%. Initial experiments to find an inert liquid in which to disperse the NaCl particles produced in these crystallization experiments were unsuccessful. Those liquids that allow for particle stabilization against aggregation were ones that also dissolved the particles. Those liquids that were inert (e.g., no dissolution) did not disperse the particles well enough for PSD analysis.

For PSD measurement, a slurry sample ($\sim 10 \ ml$) was taken directly from the reactor to the sample bottle with vacuum pump in a very short time (< 1 s). The temperature was kept constant during sampling to avoid any change in the crystals. This sample was diluted in the LS230 to lower the number density of particles so that light scattering measurement could be made without multiple scattering. A saturated solution at the temperature of the crystallizer was used for dilution. It was prepared by filtering the product of the same crystallization experiment with a 0.2 μm Supor-200 GelmanScienceTM filter making sure that the temperature remained constant. Thus the temperature of the solution and suspension for sampling, diluting, and measuring of sample was kept constant at all times at 30 °C, the same temperature as the slurry in the crystallizer. This is feasible for all of the steps except measurement in the LS230 where the sample is heated by 2 to $5 \,^{\circ}\text{C}$ by the light source and mixer inside the sample chamber. Due to this heating the measurement of the PSD is not stable over a 10-minute period as is shown in Figure 2. The particles tend to dissolve slowly.

To stabilize the PSD measurement cadmium impurities were introduced into the filtrate solution, which was kept at 30 °C by adding precisely determined levels of Cd^{2+} ions in distilled water to the saturated solution placed in the LS230 sample cell before the addition of ~10 ml of the slurry. At a concentration of 100 ppm Cd^{2+} in the final solution, the PSD measurement was stable as shown in Figure 3. In Figure 2 and 3 each of the PSD measurements was



Fig. 2. PSD measurements without addition of $CdCl_2$. Each of the measurements was done for 1 min.



Fig. 3. PSD measurements with addition of $CdCl_2$. Each of the measurements was done for 1 min.

performed for 1 *min*. with a 1 *min*. time interval between measurements. The tri (or quadra) modal form is due to the nucleation, crystal growth, aggregation and breakage in the crystallizer. The measured PSD was validated with SEM (Figure 4) and microscopic photos, which show detailed particle size and morphology, that do not change with time in the cadmium modified saturated solution.



Fig. 4. SEM image of particles showing the crystal habit and size after crystallization at 30 $^{\circ}\mathrm{C}.$

3 Results and Discussion

With the application of Cd^{2+} impurities to stabilize particles during PSD measurement, there was no appreciable change in the PSD measured repeatedly over a 10-minute period. Table 1 shows a comparison of volume mean diameter (D_v) and percentile volume diameters $(D_{v10}, D_{v50}, \text{ and } D_{v90})$ as a function of time to illustrates more clearly the effects of dissolution on the PSD in Figure 2 and 3. Here we see that there is only a 1.1% change in the mean size for the stabilized crystals based upon the differential volume size distribution and a 6.8% change in the mean crystal size for the unstabilized particles over 10 minutes. Note that the reproducibility of the instrument was 1%.

Using this experimental protocol with its step immobilization additive and careful temperature control, accurate particle size distributions can be measured for materials that are unstable due to crystal growth/dissolution from/to the background solution of the light scattering apparatus. We have used this experimental protocol to measure the effluent of a crystallizer for various materials [15]. For practical purposes, particle stabilization with impurities could be a useful industrial practice when particle size measurement is required during crystallization if no inert solvent is available to stabilize the particles. Step immobilizing additives and crystal habit modifiers for other particle systems are tabulated in Myerson's book [16].

4 Conclusions

Measuring the PSD produced by crystallizers is often difficult due to the dissolution or growth of the particles during analysis in traditional light scattering

Table 1

| | | Figure 2 | Figure 3 |
|---------------------|---------|----------------------|-------------------|
| | | (without Cd^{2+}) | (with Cd^{2+}) |
| | 0 min. | 118 | 108 |
| $D_v \; (\mu m)$ | 5 min. | 108 | 106 |
| | 10 min. | 103 | 106 |
| C.V. (%) | | 6.8 | 1.1 |
| | 0 min. | 38.9 | 38.6 |
| $D_{v10} \ (\mu m)$ | 5 min. | 36.9 | 38.4 |
| | 10 min. | 36.1 | 38.3 |
| C.V. (%) | | 3.8 | 0.4 |
| | 0 min. | 114 | 103 |
| $D_{v50}~(\mu m)$ | 5 min. | 104 | 101 |
| | 10 min. | 99.6 | 101 |
| C.V. (%) | | 6.7 | 1.0 |
| | 0 min. | 200 | 184 |
| $D_{v90}~(\mu m)$ | 5 min. | 183 | 181 |
| | 10 min. | 175 | 180 |
| C.V. (%) | | 6.9 | 1.13 |

Comparison of volume statistics (Arithmetic). Summary of 10 measurements. Calculations from 0.04 to 2000 μm . D_v : volume mean diameter. D_{v10} , D_{v50} , and D_{v90} : 10, 50, and 90 percentile volume diameters.

instruments. If an inert liquid can not be found into which the particles can be dispersed the only technique available is to use a saturated solution. Even with dispersion in a saturated solution, the PSD measured can be effected by dissolution or growth of the particles due to slight variations in the temperature of the sample in the instrument. Dissolution and growth of the particles in a slightly under or over saturated solution can be arrested by the addition of step immobilizing additives. These additives effectively stabilize the crystals by opening up a window of saturation where the steps of the surface of the crystal lattice are immobile.

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References

- N. Cabrera and D. Vermilyea, in *Growth and Perfection of Crystals: The Growth of Crystals from Solution*, R. H. Doremus, B. W. Roberts and D. Turnbul (Eds.), (Wiley, New York, 1958).
- [2] D. A. Porter and K. E. Eastering, *Phase Transformations in Metals and Alloys*, (Chapman and Hall, New York, 1992).
- [3] J. P. van der Eerden and H. Muller-Krumbhaar, Formation of Macrosteps Due to Time Dependent Impurity Adsorption, *Electrochimica Acta* **31** (1986) 1007– 1012
- [4] Terry A. Land, Tracie L. Martin, Sergey Potapenko, G. Tayhas Palmore and James J. De Yoreo, Recovery of surfaces from impurity poisoning during crystal growth, *Nature* **399** (1999) 442–445.
- [5] A. J. Malkin, Yu. G. Kuznetsov, and A. McPherson, In situ atomic force microscopy studies of surface morphology, growth kinetics, defect structure and dissolution in macromolecular crystallization, J. Cryst. Growth. 196 (1999) 471–488.
- [6] R. J. Davey, Adsorption of impurities at growth steps, J. Cryst. Growth. 29 (1975) 212–214.
- [7] H. W. Etzel and R. J. Maurer, The Concentration and Mobility of Vacancies in Sodium Chloride, J. Chem. Phys. 18 (1950) 1003–1007.
- [8] R. Kern, Crystal Growth and Adsorption, Growth Cryst. 8 (1969) 3–23.
- [9] C. Kittel, Introduction to Solid State Physics, (Wiley, New York, 1996).
- [10] A. R. Allnatt and Morrel H. Cohen, Statistical Mechanics of Defect-Containing Solids. II. Ionic Crystals, J. Chem. Phys. 40 (1964) 1871–1890.
- [11] L. N. Rashkovich and N. V. Kronsky, Influence of Fe^{3+} and Al^{3+} ions on the kinetics of steps on the {100} faces of KDP, J. Cryst. Growth. **182** (1997) 434–441.
- [12] R. L. Bates, Impeller Characteristics and Power, Chapter 3 in *Mixing: Theory and Practice*, V. W. Uhl and J. B. Gray (Eds.), (Academic Press, New York, 1966).

- [13] Kevin J. Myers, Mark F. Reeder and Julian B. Fasano, Optimize Mixing by Using the Proper Baffles, CEP February (2002) 42–47.
- [14] Byung S. Choi, Bin Wan, Susan Philyaw, Kumar Dhanasekharan and Terry A. Ring, Residence Time Distributions in a Stirred Tank - Comparison of CFD predictions with experiment, I & EC Research Submitted in Nov. 2003
- [15] Terry A. Ring, Fundamentals of Ceramic Powder Processing and Synthesis, (Academic Press, New York, 1996).
- [16] A. S. Myerson, *Handbook of Industrial Crystallization*, (Butterworth-Heinemann, Boston, 2002).