

# Powtech '85

PARTICLE  
TECHNOLOGY

2-53

## **Preface**

These papers were presented at the 11th Powtech Conference held at the National Exhibition Centre, Birmingham in March 1985. Powtech is held annually, alternately in the UK and the Federal Republic of Germany.

The Organizing Committee for the Conference was drawn from the Institution of Chemical Engineers Particle Technology Subject Group. Membership of the Subject Group is open to members and non-members of the Institution of Chemical Engineers and brings together people from a wide range of technological backgrounds with an interest in particle technology.

The papers, which were refereed by the Organizing Committee, cover particle formation, the interaction of solid particles with both liquids and gases and aspects of handling powders in bulk.

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## CRYSTALLIZATION AND DOWNSTREAM PROCESSING INTERACTIONS

A.G. Jones\*

The characteristics of slurries produced from batch and continuous crystallizers and their interaction with downstream separation stages are considered. Crystal size distribution and magma density are predicted from population balance theory and are linked to simple models of solid-liquid separation. The possibilities for controlling the slurry and particle characteristics in order to design and operate these integrated processes are discussed.

Industrial crystallization concerns the formation of particles from solution and their subsequent separation. The physical form of the slurry from a crystallizer can markedly affect the performance of downstream operations such as thickening, filtration and drying. These performance characteristics place demands on crystallizer design and vice versa thus giving rise to important interactions. Crystallization theory has developed to the point where the crystal size distribution (CSD) and slurry density can be predicted for idealized crystallizer configurations from population balance models and the performance controlled by design (1).

The purpose of this paper is to review how this may be linked to simple models of solid-liquid separation and to discuss the possibilities for an integrated approach to industrial crystallization process design and operation.

INDUSTRIAL CRYSTALLIZATION PROCESSES

The "wet-side" of a typical industrial crystallization process is shown schematically in Figure 1. This comprises a crystallizer followed by a thickener, a filter and finally a dryer. Subsequent dry solids processing stages could include such operations as grading, milling, conveying, blending and bagging but will not be considered further here.

The crystal size distribution and solids hold-up are largely determined by the kinetic processes of nucleation and crystal growth coupled with the overall mass balance and the mixing characteristics within the crystallizer. Crystal growth and primary nucleation (common in precipitation) are largely determined by the prevailing level of supersaturation, while it is now well

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established that, since crystals produced in a slurry are normally suspended by an agitator or pump, secondary nucleation (common in crystallization from solution) may be induced and thereby have a deleterious effect on the CSD. Attempts to decrease the vessel volume, e.g. by operation at a higher working level of supersaturation (or shorter retention time), also tend to reduce the mean crystal size.

In subsequent steps the familiar processes of hindered settling and flow through porous media predominate as the liquor is removed in thickeners and filters, etc. Both these processes are strongly influenced by particle and slurry characteristics and may, of course, be enhanced by centrifugal action. Slurries of lower solids content or of finer particles require larger separation vessels. Again, as the crystals become in close proximity, or are subject to mechanical handling, so the possibility of particle breakdown (and also of agglomeration) increases, but these aspects have been studied in much less detail.

Because of these interactions, attempts to economize on crystallizer design can simply add to downstream separation costs, and a balance should be struck (2).

### CRYSTALLIZER PERFORMANCE

#### Theory

Crystal size distributions and solids holdup can be predicted from population balance theory coupled with the overall mass balance (Randolph and Larson (3), as follows.

The general population balance for the well-mixed crystallizer may be summarized as:

$$\frac{\partial n}{\partial t} + \frac{\partial (Gn)}{\partial L} = \frac{Qn}{V} \quad (1)$$

where  $n$  is the number, or population, density of crystals ( $= dN/dL$ ),  $Q$  the volumetric flowrate through the vessel of volume  $V$ .

Given expressions for the crystallization kinetics and solubility of the system, Equation 1 can be solved to predict the performance both of batch crystallizers ( $Q = 0$ ) and of continuous crystallizers, at either steady- or unsteady-state.

The overall linear crystal growth rate,  $G$  ( $= dL/dt$ ), is normally given by an expression of the form:

$$G = k_g \Delta c^g \quad (2)$$

where  $\Delta c$  is a measure of the supersaturation expressed as concentration difference ( $c - c^*$ ).

The nucleation rate ( $= dN/dt$ ) occurs as a boundary condition to Equation 1. Primary nucleation may be expressed theoretically by the relation:

$$J = k_n \exp(-k_n / \log^2 S) \quad (3)$$

where  $S$  is the supersaturation ratio ( $c/c^*$ ). Secondary nucleation may be

correlated by the expression:

$$B = k_b M_T^j \Delta c^b \quad (4)$$

where  $M_T$  is the solids holdup (magma density).

The solubility,  $c^*$ , is often correlated with temperature, e.g. using an expression of the form:

$$c^* = s_0 + s_1 \theta + s_2 \theta^2 \quad (5)$$

The solids holdup is related to the CSD by the integral equation:

$$M_T = \alpha \rho_c \int_0^\infty n(L) L^3 dL \quad (6)$$

and can also be determined by mass balance from the change in solution concentration (see later).

### Control of slurry characteristics

The slurry characteristics of both batch and continuous crystallizers can be controlled by the appropriate design and manipulation of the operating conditions. Some examples are discussed below.

Batch operation. Batch crystallizers are in common use industrially, especially for relatively low tonnage products, but are notorious for producing variable quality crystals, often containing fines which can cause difficulty in subsequent separations. This is a natural consequence of the time varying conditions during operation and the techniques for controlling their performance have been reviewed recently (Tavare et al (4); Jones (5)). Batch-cooling crystallizers, for example, can be controlled by manipulating the cooling rate with time such that as the batch proceeds the supersaturation rate due to cooling balances the crystallization rate on seed crystals, resulting in a controlled cooling curve of the form:

$$\theta(t) = \theta_0 - \phi Y Z (1 + Y Z + Y^2 Z^2 / 3) \quad (7)$$

where  $Y$  is a dimensionless crystal size ( $= (L_P - L_{SO}) / L_{SO}$ ) and  $Z$  is dimensionless time ( $= t / \tau$ ).

Equation 7 indicates that as the surface area of the crystals increases, so can the cooling rate increase (see Figure 2), resulting in a larger mean crystal size and a lower fines content. If nucleation can be neglected, as is assumed here, then the product crystal size is given by:

$$L_P = L_{SO} (M_P / M_{SO})^{1/3} \quad (8)$$

where  $M_{SO}$  is the mass of seed crystals of initial size  $L_{SO}$  and  $M_P$  is the final crystal mass given by:

$$M_P = M_L (c_1 - c_2) \quad (9)$$

where  $c_1$  and  $c_2$  are the initial and final solution concentrations respectively and  $M_L$  is the mass of solvent in the vessel.

For example, for potassium sulphate solutions seeded with crystals of mean size 550  $\mu\text{m}$  the weight-mean size of the product was increased from about 792  $\mu\text{m}$  using natural cooling to about 1031  $\mu\text{m}$  using controlled cooling, and the CV was reduced from about 75% to about 39% (Jones and Mullin (6)).

Similarly, as shown in Figure 3, the fines content (defined here as % < seed size) was reduced from about 24% using controlled cooling to about 9% using fines destruction in addition, resulting in a mean size of about 1380  $\mu\text{m}$  and a corresponding CV of only 29% (Jones et al (7)).

Continuous operation. For higher tonnage materials continuous operation is often the preferred method, offering, as it does, nominally steady production conditions. However, the product stream of continuous mixed-suspension, mixed-product-removal (MSMPR) crystallizers also contains a wide range of crystal sizes. In the simplest ideal case the size distribution is analytically exponential in population density and is given by an expression of the form:

$$n(L) = n^0 \exp(-L/G\tau) \quad (10)$$

and the magma density is given by:

$$M_T = c_i - c_o \quad (11)$$

where  $c_i$  and  $c_o$  are the inlet and outlet solution concentrations respectively.

The coefficient of variation of mass of the CSD from the ideal MSMPR is always 0.5 (i.e. 50%). In order to tighten the distribution in continuous crystallization both fines destruction, as above, and classified product removal, i.e. changing the residence time distribution such that only the largest crystals are withdrawn, are commonly employed. The analysis of these techniques has been summarized by Garside (1), who shows that by their use the CV of the commercial potash data reported by Canning (8) has been reduced to about 35%.

### SEDIMENTATION AND THICKENING

The processes of sedimentation and thickening are conveniently analysed by first considering the settling characteristics of single spherical particles (9).

#### Single particles

The terminal settling velocity of a single particle may be predicted from a force balance and in general terms is given by the expression:

$$u_t = \left[ \frac{4L(\rho_c - \rho_l)g}{3\rho_l C_D} \right]^{1/2} \quad (12)$$

where the drag coefficient,  $C_D$ , is a function of particle Reynolds number,  $Re_p$ . At low particle Reynolds numbers ( $Re_p < 0.2$ )  $C_D$  is given analytically by Stokes' Law whence  $C_D = 24/Re_p$  and:

$$u_t = \frac{L^2(\rho_c - \rho_l)g}{18\mu} \quad (13)$$

Equation 13 applies to fine crystals settling in the laminar regime. In the intermediate range ( $0.2 < Re_p < 500$ ) the drag coefficient is given empirically by  $c_D = 10/Re_p^{0.5}$  and the corresponding terminal settling velocity is (10):

$$U_t = 0.26 \left[ \frac{L^3 (\rho_c - \rho_1) g^2}{\mu \rho_1} \right]^{1/3} \quad (14)$$

For the range  $500 < Re_p < 20 \times 10^3$  Newton's Law applies with  $c_D = 0.44$  and:

$$U_t = 1.74 \left[ \frac{L (\rho_c - \rho_1) g}{\rho_1} \right]^{1/2} \quad (15)$$

Thus over the range of interest the settling rate increases with particle size varying approximately from a quadratic to a square root dependence. Crystals may, of course, deviate significantly from spherical, and for these cases correction factors should be applied.

### Hindered settling

The sedimentation rate of particles in a slurry is hindered by the flow induced by the presence of other particles. Again, analysis of the behaviour of particles of equal size forms a basis for the prediction of particle size distributions.

Monodisperse. The superficial settling velocity,  $u$ , of a particulate slurry of voidage  $\epsilon$  can be estimated from the Richardson and Zaki (11) equation:

$$u = u_o \epsilon^z \quad (16)$$

where  $\epsilon$  is related to the solids holdup and  $u_o$  is almost equal to the sedimentation velocity of a single particle in an infinite fluid. The exponent  $z$  depends on particle Reynolds number varying from about 4.4 at  $Re_p = 1$  to 2.4 at  $Re_p = 500$ .

Polydisperse. Particle size distributions result in segregation by size during sedimentation and consequent zone formation with differing settling rates. Thus Mizra and Richardson (12) extended the R-Z equation above to polydisperse systems. In a further development, a model due to Selim et al (13) accounted for the particle-fluid interaction due to the effect of the fines displaced by the larger, faster settling, particles. The fines increase the effective fluid density and further hinder sedimentation. The basis of this model is depicted graphically in Figure 4 with results for a tertiary suspension shown in Figure 5.

As discussed above, the product of a crystallizer normally contains a whole range of particle sizes and the data in Figure 5 clearly demonstrate the marked difference in the sedimentation rates of fine and coarse particles that may be expected, especially at higher voidages; fine particles being the most difficult to separate.

### FILTRABILITY

The most widely accepted simple models of filtration are those based on Darcy's Law which assume a uniform filter cake:

$$\frac{1}{A} \frac{dV}{dt} = \frac{\Delta p}{r \mu H} \quad (17)$$

where  $r$  is the specific resistance of the filter cake averaged over depth  $H$ . In the capillary model Equation 17 is combined with the Hagen-Poiseuille equation for laminar flow leading to the familiar Carman-Kozeny equation. The specific cake resistance is then given by:

$$r = \frac{K (1 - \epsilon)^2 S_p^2}{\epsilon^3} \quad (18)$$

where  $S_p$  is the specific surface area of the particles and is determined by the particle size distribution and shape, increasing with fines content and deviation from spherical. The bed voidage,  $\epsilon$ , depends on the packing characteristics of the material which are again size and shape dependent. Voidage is normally determined empirically, although simple models have been proposed, e.g. for the ideal case of a distribution of spheres (14). The Kozeny coefficient,  $K$ , is typically  $\approx 5$ , but also varies with particle shape (9).

Thus bed permeability (inverse resistance) strongly depends on the physical form of the particles. Filter cloth resistance can also be affected by the CSD, notably due to cloth blinding by fines.

Recent advances in modern filtration theory are based on the integration of point processes and attempt to account for non-uniform characteristics during the build-up of a filter cake (Willis and Tosun (15); Wakeman (16); Willis et al (17)), but will not be discussed further here.

Schnel et al (18, 19) related the simple filtration model to crystallization kinetics for both batch and continuous precipitation by making the simplifying assumptions of monodisperse and exponential distributions of spherical particles respectively and use of an empirical voidage function. The dependence of filtration resistance on initial supersaturation is depicted in Figure 6, which demonstrates that an increase in  $S$  (defined here as molar supersaturation ratio) results in precipitates of lower filtrability.

Kavanagh et al (20) have shown that increasing the percentage of fines (defined here as  $\% < 40 \mu\text{m}$ ) in slurries of gypsum crystals from 15 to 100% increases the final moisture content after filtration from 15 to 24% w/w. Thus fines would consequently increase the dryer load.

Giorgio and Kern (21) further related the filtrability of paraffin wax crystals to crystal morphology and bed structure and tortuosity as shown in Figure 7. Again, voidage was taken as an independent factor determined empirically. It was also observed that crystal platelets filter more easily than do needles, and addition of a "filter aid" (alkylacrylate polymer) further improved filtrability. This was attributed to the formation of agglomerates of open structure comprising fine crystals of conical habit rather than by improving the filtration process itself.

Thus, these studies again indicate that filtrability and subsequent dryer load are dependent on slurry and particle characteristics and hence crystallization conditions.

CONCLUSIONS

This paper has demonstrated the interactions between crystallization and downstream processing in terms of crystal size distribution and solids holdup. In particular, problems which occur in solid-liquid separation often arise upstream and benefit from attention to control at the crystallization stage. As is well known, the "optimum" slurry for ease of solid-liquid separation (product specification apart) would contain a high solids content of large uniform crystals with an absence of fines. Although this ideal can rarely be obtained on a large scale, there are, nevertheless, now available a number of techniques both to control the form of the particulate slurry from industrial crystallizers and to predict the CSD and magma density from population balance theory. These can then be integrated with models of solid-liquid separation. Further progress will depend on the development of more comprehensive models of crystallization kinetics and fluid-particle interactions.

NOMENCLATURE

- A = cross-sectional area of filter ( $\text{m}^2$ )
- B = number nucleation rate (number/kg solvent)
- c = solution concentration (kg anhydrous substance/kg solvent)
- c\* = equilibrium saturation concentration (kg anhydrous substance/kg solvent)
- $c_D$  = drag coefficient (-)
- $\Delta c$  = supersaturation (concentration driving force,  $c - c^*$ , kg anhydrous substance/kg solvent)
- G = overall linear crystal growth rate (m/s)
- H = bed depth (m)
- $k_g$  = linear growth rate coefficient (Equation 2)
- $k_b$  = secondary nucleation rate coefficient (Equation 4)
- $k_n, k_m$  = primary nucleation rate coefficients (Equation 3)
- K = Kozeny constant (Equation 18)
- L = crystal size, characteristic dimension (m)
- $L_p$  = size of product crystals (m)
- $L_{so}$  = initial size of seed crystals (m)
- $M_h$  = mass solvent in crystallizer (kg)
- $M_p$  = product crystal mass (kg)
- $M_{so}$  = initial mass of seed crystals (kg)
- $M_T$  = solids holdup (kg/kg)
- n = population (number) density (number/m kg solvent)

- N = number of crystals (number/kg solvent)  
 $\Delta p$  = pressure drop ( $N/m^2$ )  
 Q = volumetric flowrate ( $m^3/s$ )  
 $Re_p$  = particle Reynolds number ( $\rho u L/\mu$ )  
 S = supersaturation ratio (mole anhydrous substance/mole solvent)  
 $S_p$  = specific surface area of particles ( $m^2/m^3$ )  
 t = time (s)  
 u = settling velocity (m/s)  
 V = working volume of crystallizer ( $m^3$ ); volume of filtrate ( $m^3$ )  
 Y = dimensionless crystal size,  $(L_p - L_{so})/L_{so}$  (-)  
 Z = dimensionless time,  $t/\tau$  (-)

Greek

- $\epsilon$  = bed voidage (-)  
 $\alpha$  = volume shape factor of crystals (i.e.  $Vol = \alpha L^3$ )  
 $\rho_c$  = crystal density ( $kg/m^3$  crystal)  
 $\rho_l$  = density of liquor ( $kg/m^3$  solution)  
 $\theta$  = solution temperature (K or deg C)  
 $\phi$  = coefficient (Equation 7)  
 $\tau$  = batch time; mean residence time (s)  
 $\mu$  = viscosity ( $Ns/m^2$ )

Exponents

- b = "order" of secondary nucleation (Equation 4)  
 g = "order" of growth (Equation 2)  
 j = holdup dependence of secondary nucleation (Equation 4)  
 n = "order" of primary nucleation (Equation 3)  
 z = exponent in R-Z equation (Equation 16)

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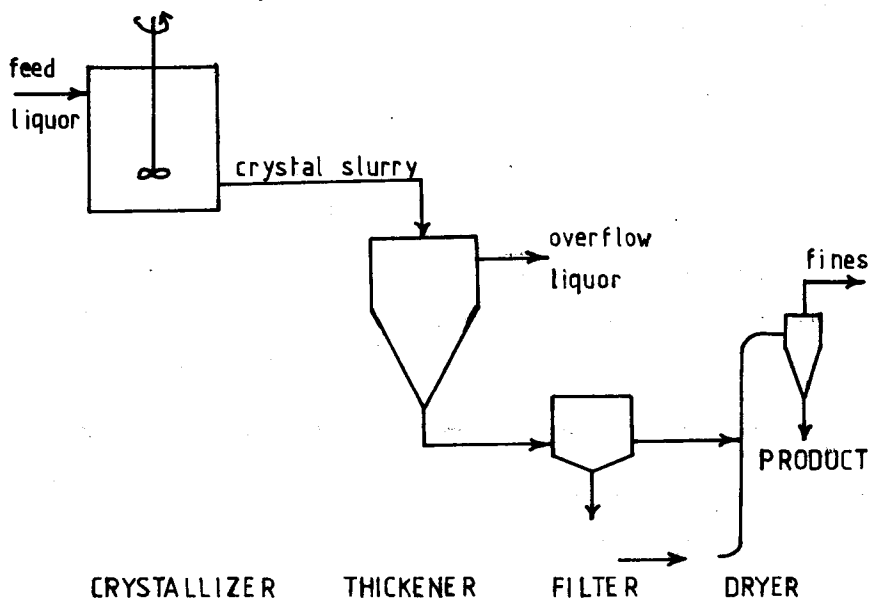


Figure 1 A typical industrial crystallization process (schematic)

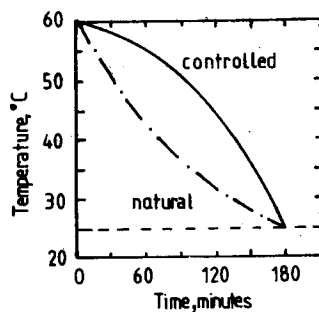


Figure 2 Controlled cooling curve ( $K_2SO_4$  solutions (6))

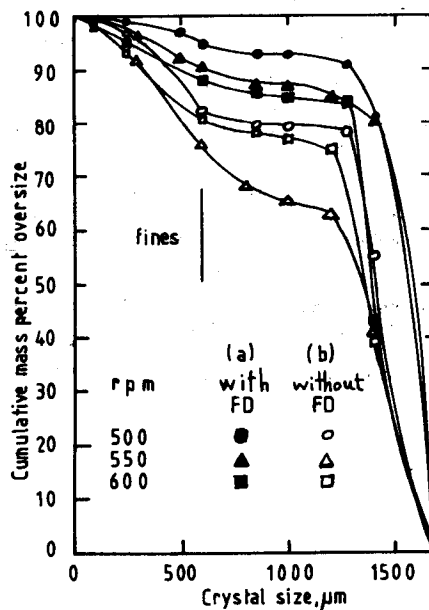


Figure 3 Experimental crystal size distributions ( $K_2SO_4$  crystals (7))

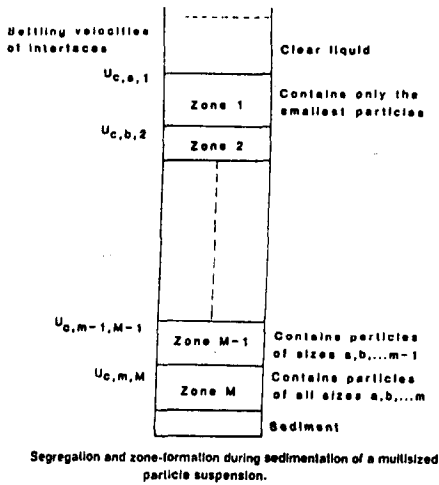


Figure 4 Polydisperse sedimentation (after Selim et al (13))

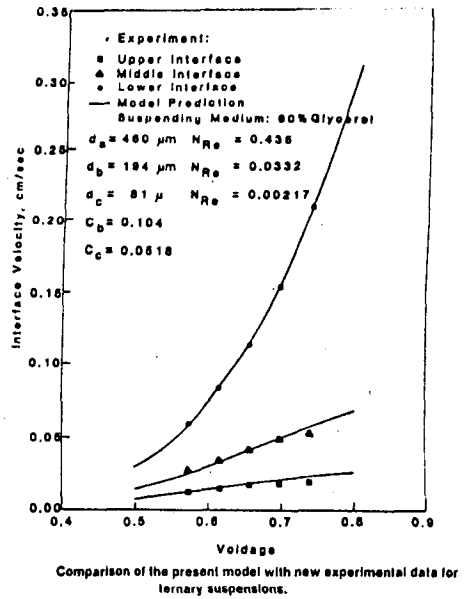


Figure 5 Sedimentation of ternary suspensions (after Selim et al (13))

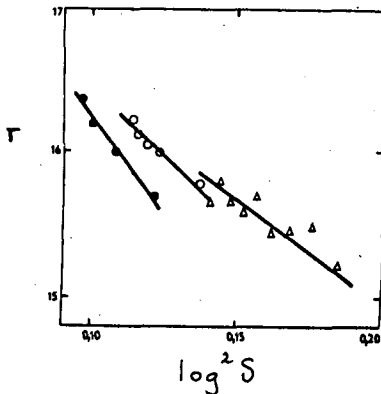


Figure 6 Dependence of filtration resistance on initial supersaturation (after Söhnel et al (19))

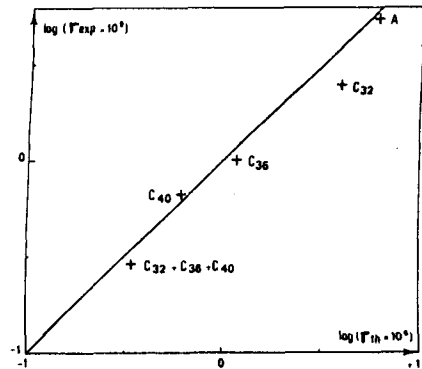


Figure 7 Theoretical and experimental specific filtrabilities (after Giorgio and Kern (21))



PHYSICAL FORM CONTROL OF SOLIDS PRODUCED BY CRYSTALLISATION

R J Davey\*

EXTENDED ABSTRACT

In the industrial preparation of powdered products the unit operation of crystallisation dominates as the major solids forming process. Apart from some plastics (eg polyethylene terephthalate) and certain inorganic and organic products (notably ammonium nitrate and urea) which are solidified from melts, crystallisation from solution is a dominant process for both commodity and speciality chemicals. Table 1 gives some indication of the range of business areas which utilise crystallisation technology.

The objective of any crystallisation process is to achieve a product having desirable physical properties which are often referred to collectively as its Physical Form. These properties are well defined viz.,

1. Crystal Size
2. Crystal Shape
3. Crystalline Phase
4. State of Aggregation
5. Purity

and for each one certain criteria have to be met in order for the product to satisfy both process and product requirements. Thus for example in the full scale production of a pharmaceutical product the solid/liquid separation equipment available may demand the preparation of crystals

\*ICI PLC New Science Group, The Heath, Runcorn