# **Crystallization and Precipitation Engineering**

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## Abstract

New computational techniques for the analysis and design of systems for the manufacture of particulate crystals have become available, and the more complex precipitation processes whereby crystallization follows fast chemical reactions have also been analysed more deeply. This progress has been aided by the growing power of the population balance and kinetic models, CFD and mixing theory, respectively. These aspects are selectively reviewed and areas requiring further progress are identified.

Keywords: crystallization, precipitation, population balance, CFD, scale up

## 1. Introduction

Crystallization from solution is a core technology in major sectors of the chemical process and allied industries. Crystals are produced in varying sizes ranging from as small as a few tens of nanometers to several millimetres or more, both as discrete particles and as structured agglomerates. Well-established examples include bulk and fine chemicals and their intermediates, such as common salt, sodium carbonate, zeolite catalysts and absorbents, ceramic and polyester precursors, detergents, fertilisers, foodstuffs, pharmaceuticals and pigments. Applications that are more recent include crystalline materials and substances for electronics devices, healthcare products, and a wide variety of speciality applications.

Thus, the tonnage and variety of particulate crystal products worldwide is enormous, amounting to possibly more than half the product of the modern chemical industry. The economic value, social benefit and technical sophistication of crystal products and processes are ever increasing, particularly in the newer high added value sectors of global markets. This places yet greater demands on the skill and ingenuity of the scientist and engineer to form novel materials of the required product characteristics and devise viable process engineering schemes for their manufacture (Jones, 2000).

Previously a largely empirical art, the design of process systems for manufacturing particulate crystals has now begun to be put on a rational basis, and the more complex precipitation processes whereby crystallization follows fast chemical reactions have also been analysed more deeply. This progress has been aided by the growing power of the population balance and kinetic models, computational fluid dynamics, and mixing

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theory. This not only increases understanding of existing processes but also enhances the possibility of innovative product and process designs, and speedier times to market.



Figure 1: Calcite and vaterite crystals

The process engineering goal for crystallization systems is to develop generic scale up methodologies to integrate across the length scales - from the formation of primary crystals to industrial scale plant operation. In this selective review, particular attention is paid both fundamental to the mechanisms of mixing and the formulation of computer aided mathematical methods for scale up, whilst emphasising throughout the continuing need for careful yet efficient practical experimentation to collect

basic data; the latter being essential in order to discriminate between competing theories, to inform and validate process models, and to discover the unexpected. Substantial progress has been made in integrating CFD with particulate process models but because of the extra dimensionality, however, there remain substantial challenges.

# 2. Particulate Crystal Characteristics

Crystallization is an important separation process that purifies fluids by forming solids. Crystallization is also a particle formation process by which molecules in solution or vapour are transformed into a solid phase of regular lattice structure, which is reflected on the external faces. Crystallization may be further described as a self-assembly molecular building process. Crystallographic and molecular factors are thus very important in affecting the shape (habit), purity and structure of crystals, as considered in detail by, for example, Mullin (2001) and Myerson (1999). Here the internal crystal structure and external particle characteristics of size and shape are considered, which are important indicators of product quality and can affect downstream processing, such as solid-liquid separation markedly. Solid particles have a distinct form, which can strongly affect their appearance, product quality and processing behaviour. Larger particles separate out from fluids more quickly than fines and are less prone to dust formation whilst smaller particles dissolve more rapidly. Real particles (Figure 1) are rarely exactly the same form as each other and irregular particles have many individual dimensions - they are in fact 'multi-dimensional', together with shape and size distributions giving rise to the corresponding problem of mathematical dimensionality (Kaye, 1986), and some simplification of the problem is usually in order.

## 3. Fluid-Particle Transport Processes

The formation and subsequent solid-liquid separation of particulate crystals from solution normally involves alternate periods of suspension and sedimentation during which they experience relative fluid-particle motion. Similarly, solid matter may change phase from liquid to solid or vice versa. New particles may be generated or existing ones lost eg. in crystallizers or mills. They may be separated from fluids by flow through vessels eg. settlers, thickeners or filters. Thus both the liquid and solid phases are subject to the physical laws of change: continuity (for conservation of both mass and particle) and flow (solid through liquids and liquid through particle arrays etc.).

#### **3.1 Conservation Equations**

Conservation is a general concept widely used in chemical engineering systems analysis. Normally it relates to accounting for flows of heat, mass or momentum (mainly fluid flow) through control volumes within vessels and pipes. This leads to the formation of conservation equations, which, when coupled with the appropriate rate process (for heat, mass or momentum flux respectively), enables equipment (such as heat exchangers, absorbers and pipes etc.) to be sized and its performance in operation predicted. In analysing crystallization and other particulate systems, however, a further conservation equation is required to account for particle numbers. This is known as the population balance. It is another transport equation that when coupled with the corresponding rate processes for particle formation (nucleation, growth, agglomeration etc.) enables crystallizers to be sized and their performance to be predicted in terms of not only mass yield but also its particle size distribution, n(L, t).

The conservation equation for mass (continuity equation) is given by:

$$\frac{D\rho}{Dt} + \rho \nabla \mathbf{v} = 0 \tag{1}$$

The analogous population (number) balance is given by:

$$\frac{\partial n}{\partial t} + \nabla(\mathbf{v}_i n) + \nabla(\mathbf{v}_e n) - B + D = 0$$
<sup>(2)</sup>

with the internal velocity  $v_i$  and the external velocity  $v_e$ . In this context the internal coordinate space specifies the characteristics of the particle, while the external co-ordinate space refers to the position of the particle in the physical space (Randolph and Larson, 1988). The internal velocity therefore describes the change of particle characteristic eg. its size, volume or composition, and the external velocity the fluid velocity in the crystallizer. The population balance is a partial integro-differential equation that is normally solved by numerical methods, except for special simplified cases. Numerical solution of the population balance for the general case is not, therefore, entirely straightforward. Ramkrishna (1985, 2000) provides a comprehensive review. Hounslow et al. (1988), Hounslow (1990), Hostomský and Jones (1991), Lister et al. (1995), Hill and Ng (1995) and Kumar and Ramkrishna (1996a,b) present numerical discretization schemes for solution of the population balance and compute correction factors in order to preserve total mass and number whilst Wójcik and Jones (1998a) evaluated various methods. Gelbard and Seinfeld (1978), Nicmanis and Hounslow (1998), Wulkow et al (2001) and Rigopoulos and Jones, 2003a) propose alternative finite element methods with improved precision and reduced computational time.

The momentum (Navier-Stokes) equation for incompressible flow with constant viscosity is given by:

$$\rho \frac{D \mathbf{v}}{D t} = \rho \mathbf{g} - \nabla p + \mu \Delta \mathbf{v}$$
<sup>(3)</sup>

This set equations is valid for both laminar and turbulent flow; for the latter the system of equations can be closed using turbulence models. Unfortunately, however, these require an excessive amount of computation to resolve all turbulence scales by direct numerical simulation (DNS). Shortcuts with variable levels of detail have been developed, ranging from the commonly used in engineering turbulent viscosity-based approaches such as the k- $\varepsilon$  (Launder and Spalding, 1972) to the much more accurate Large Eddy Simulation (LES, see e.g. Pope, 2000), which, though sparingly used today, may become the industry standard in the future.

#### 3.2 Computational Fluid Dynamics (CFD)

Computational Fluid Dynamics (CFD) is the numerical analysis of systems involving transport processes and solution via by computer simulation. Manninen and Syrjänen (1998) modelled turbulent flow in stirred tanks and tested and compared different turbulence models. They found that the standard k- $\varepsilon$  model predicted the experimentally measured flow pattern best. Rielly and Marquis (2001) highlight that even a stirred tank is actually very inhomogeneous fluid mechanical environment, where the relevant mean-flow and turbulence quantities may vary by orders of magnitude throughout the vessel, especially around the impellor zone, as illustrated in Figure 2.



Figure 2: CFD of an agitated vessel.

It is clear therefore that the 'well-mixed' assumption commonly used for the modelling of crystallization processes will lead to significant errors on the rates of growth, nucleation and agglomeration and consequently on the crystal size distribution. In these cases knowledge of the solid concentration distribution, as well as knowledge of local velocities, shear rates and energy dissipation rates would be needed for design purposes, process development and scale-up. For dense suspensions as employed typically in industry two and four-way couplings

need to be taken into account (Kuipers and van Swaaij, 1997). Models for such interactions exist and some of these have already been implemented into commercial CFD codes but, due to the lack of validation, their viability and reliability in the case of stirred vessels is still to be fully tested.

A preliminary attempt was performed by Brucato et al. (2002), aimed at using current standard CFD modelling techniques to predict the phenomenon of the formation of a clear liquid layer in the upper region of a stirred vessel at high solids loading. Simulation results show an encouraging agreement with experimental data.

#### 3.3 Mixing Effects and Scale up

Crystallization systems frequently exhibit high levels of supersaturation around the points where it is generated, such as at cooling surfaces, evaporation interfaces and where two or more liquid reactants are brought into contact. Attainment of uniform conditions throughout the reactor volume therefore becomes difficult and this mixing problem becomes magnified as the scale of operation increases, and can be particularly pronounced in fast precipitation systems. Attempts have therefore been made both to predict the effects of such imperfect mixing on crystallizer performance and to engineer alternatives reactor configurations in order to minimise the problem.

Wei and Garside (1997) studied the precipitation of barium sulphate using Computational Fluid Dynamics (CFD) assuming perfect micromixing within each cell. It was shown, however, the computational demand often increases enormously even for very simple reactor geometries. Using a different approach, Van Leeuwen (1998) developed a compartmental mixing model for modelling precipitation processes based on the engulfment theory developed by Baldyga and Bourne (1984a to c). Mixing parameters between the feed and the bulk zone from the flow characteristics in the reactor are obtained and subsequently moments and mean sizes of the precipitate calculated.

Several mesomixing and micromixing models have been proposed to describe the influence of mixing on chemical reactions on the meso- and molecular scale. Most of them fall into one of three categories discussed by Villermaux and Falk, 1994. Baldyga et al. (1995) proposed the meso time constant defined by:

$$t_{meso} = A \frac{\varepsilon_{avg}}{\varepsilon_{loc}} \frac{Q^{\frac{1}{3}}}{N^{\frac{4}{3}} d_s}$$
(4)

which can be was used to model mesomixing in a stirred tank by including the term  $\varepsilon_{avg}/\varepsilon_{loc}$  to take different feed point positions into account. The inverse of the time constant tmeso (mesomixing) can be interpreted as a transfer coefficient for mass transfer by convection. Micromixing is regarded as turbulent mixing on the molecular level. It comprises the viscous-convective deformation of fluid elements, followed by molecular diffusion (Baldyga and Poherecki, 1995). Baldyga et al., 1995 and Baldyga et al., 1997 proposed a characteristic timescale for micromixing based on Kolmogoroff's microscale of eddy lifetime:

$$t_{micro} = 17.3 \times \left(\frac{\nu}{\varepsilon_{loc}}\right)^{1/2}$$
(5)

The inverse of the time constant  $t_{micro}$  (micromixing) can be interpreted as a transfer coefficient for mass transfer by diffusion. Baldyga and Bourne (1999, Chapter 14) present considerations in relation to choosing an adequate model of mixing for modelling precipitation processes. Micromixing effects are present only at high concentrations with correspondingly low values of the time constants for precipitation compared to time constants for mixing.

#### 3.4 Probability Density Function (PDF) methods

Baldyga and Orciuch (2001) studied the precipitation of barium sulphate from unpremixed feed in a two-dimensional tubular precipitator (pipe  $2m \times 0.0320$  m i.d.). Crystal size distribution is predicted using a Beta PDF (Probability Density Function) adapted from Balyga and Orciuch (1997) incorporating a turbulent population balance, and the turbulent mixing model implemented in a k- $\varepsilon$  CFD code (Fidap 8.5). Baldyga and Orciuch (2001) conclude that their method enables the particle size distribution to be predicted effectively when compared with experimental data in the absence of aggregation. Figure 3 gives an example of the crystal size distribution; both measured and calculated using both the full model and that which neglects concentration fluctuations. The difference is clearly observed; predicted and measured distributions agree better for the full model. The effect of mixing should be better observed at still larger concentrations.



Figure 3: Crystal size distributions (Baldyga and Orciuch, 2001)

Falk and Schraer (2001) similarly present a PDF model of precipitation reactors. The micomixing model considered is the interaction and exchange with the mean (IEM). Precipitation reactions are nucleation, growth and aggregation. Based on Monte Carlo simulations, the method is able to produce, at any point in the flow, reactants concentration and supersaturation fields, and the particle size distribution field, by the simple moments method. The main advantage claimed for the method is its capability to treat multi-dimensional (viz. size, morphology, chemical properties, etc)

population balances as efficiently as it treats high dimensional PDF. The PDF code is again coupled with a k- $\varepsilon$  CFD code (FLUENT) to calculate the flow in the absence of two-phase effects. Typical integration times are reported to be several hours on a PC.



Figure 4: SFM due to Villermaux (1989)



Figure 5: Precipitation process scale-up methodology (After Zauner and Jones, 2000a,b)

Zauner and Jones (2000a,b) presented a short cut compartmental methodology for predicting precipitate particle properties and mean size based on a hybrid Segregated Feed Model (SFM, Figure 4) coupled with the population balance.

The reactor is divided into three zones: two feed zones  $f_1$  and  $f_2$  and the bulk *b*. The feed zones exchange mass with each other and with the bulk as depicted with the flow rates  $u_{1,2}$ ,  $u_{1,3}$  and  $u_{2,3}$ respectively, according to the time constants characteristic for micromixing and meso-mixing.

The methodology used to scale up a precipitation process is depicted in Figure 5.

The fluid dynamic parameters, i.e. the local specific energy dissipation around the feed point, can be obtained either from Computational Fluid Dynamics (CFD) or from Laser Doppler Anemometry measurements. In the compartmental Segregated Feed Model, the population balance is solved and the particle properties of the final product are predicted. As the model contains only no physical and phenomenological parameters, it can be used for scale-up.

The model predicts the influence of mixing on particle properties and kinetic rates on different scales for a continuously operated reactor and a semibatch reactor with different types of impellers and under a wide range of operational conditions. The precipitation kinetics for nucleation, growth, agglomeration and disruption have to be determined from laboratory-scale experiments (Zauner and Jones, 2000c).

#### 3.5 Model validation

In order to validate the predictions of the theoretical analysis based on the SFM, Zauner and Jones (2000a,b) studied the effect of reactor scale (capacity) on the precipitation of calcium oxalate and calcium carbonate, respectively.



Figure 6: Semi-batch precipitation of CaOx (After Zauner and Jones, 2000a)

#### 3.6 Gas-liquid reactor modelling

dissipation is predicted by the model, consistent with experimental observations (Figure 6). Small particle sizes obtained at low energy inputs are probably a result of local zones with very high levels of supersaturation and therefore high nucleation rates. At high values of energy input, in contrast, breakage might act as a size-reducing process, leading to smaller particles.

A maximum in particle size with energy

The performance of gas-liquid reactors relies on the combined outcome of multiphase fluid dynamics, interfacial mass transfer and chemical reactions. The detailed, simultaneous analysis of the above phenomena is out of reach given the currently available computing power, partly because they take place at different scales. Furthermore most of these phenomena are non-linear, and empirical models cannot be extrapolated too far from the set of design parameters and operating conditions under which they were extracted. The direct application of CFD to chemical processes faces several obstacles. The coupling of fluid dynamics with complex and often non-linear chemical reaction and precipitation systems results in a steep increase of computational time (Al-Rashed and Jones, 1999), which prohibits the use of this approach for reactor scale-up purposes. Recently, 'hybrid' approaches have emerged as an alternative.



Figure 7: Mapping of a CFD grid into a compartmental network and virtual tracer experiment (left to right: volume fraction, mean velocity profile (m/sec) and dimensionless scalar concentration). (After Rigopoulos and Jones, 2003b).

In these methods, CFD is employed only for hydrodynamic simulation, while the chemical phenomena are resolved in a custom-built compartmental model. Bauer and Eigenberger (1999) used a 'zone model' to study a bubble column reactor; Bezzo, Macchietto and Pantelides (2000) developed an interface of communication between the gPROMS modelling software and a commercial CFD code. Rigopoulos and Jones, 2001 made predictions using a population balance coupled to a cell model with backflow. Rigopoulos and Jones (2003b) have proposed that the quantification of mixing is accomplished through averaging the flow and concentration profiles resulting from a CFD flow field calculation and a computational ('virtual') tracer experiment i.e. computation of the dispersion of a passive scalar using a CFD code (Figure 7). The flow and scalar concentration fields that result from CFD are subsequently used to derive a compartmental model, on which the chemical reactions are superimposed. The generalised compartmental model was introduced, a network of compartments with many degrees of freedom that may be tailored to accommodate the main features of the flow field and turbulent mixing. A mapping of the CFD grid into a generalised compartmental model is constructed whereby the chemical calculations can be efficiently carried out. Owing to its CFD origins, it retains the essential features of the equipment geometry and flow field.



*Figure 8: Particle size distribution from precipitation (Rigopoulos and Jones, 2003c)* 

#### **3.7 Microcrystallizers**

In further work, Rigopoulos and Jones (2003c) studied modelling of semibatch agglomerative precipitation of  $CaCO_3$  in a bubble column, which produces nano-structured, micron-sized crystal agglomerates. The evolution of the process was adequately reproduced in terms of particle size distribution (Figure 8), but it was concluded that more fundamental work on mixing and precipitation kinetics is required to obtain quantitative agreement.

The synthesis of powders with controlled shape and narrow particle size distribution is increasingly a major challenge for the chemical industry. It has been shown that whilst the conventional mixed suspension crystallizer is versatile and flexible in operation, the size distribution of the product is often far from ideal from either the downstream units or customer viewpoints. It can also give rise to difficulty on scale up since the required power input to maintain perfect mixedness is difficult to attain. Plant scale product is often of differing characteristics in crystal shape, size distribution and degree of agglomeration to that obtained from the laboratory scale. In order to overcome these limitations, several alternative configurations have been proposed eg. impinging jets, spinning discs and micro-crystallizers.



Figure 9: a) SFTR technique b). Vaterite crystals. (Courtesy www.bubbletube.com).

Lemaître et al. (1996, 1997), for example, conceived a new tubular micro reactor, known as the Segmented Flow Tubular Reactor (SFTR), which operates in the plug flow regime (Figure 6). The SFTR avoids the mixing problems encountered in batch reactors leading to inhomogeneous reaction conditions and resulting in broad particle size distributions. Narrower particle size distributions, enhanced control of particle morphology, polymorph selectivity and better stoichiometry control are the claimed advantages of the SFTR process.

# 4. Conclusion

Combined population balance and kinetic models, computational fluid dynamics (CFD) and mixing theory enable prediction and scale up of crystallization and precipitation systems. Though these hybrid approaches represent essentially a compromise, their lifetime is likely to be quite long, as the full CFD solution at each node awaits a radical breakthrough in computer technology. Simultaneously, alternatives to conventional agitated vessels are beginning to emerge.

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