Crystal-Size Distribution and its Interaction with Crystallizer Design

Recent progress in understanding crystallization processes is reviewed, especially with regard to the problem of crystal-size distribution (CSD) and its many interactions with the design, analysis, and operation of crystallizers. This subject is considered from both the researcher's and practitioner's points of view, and special attention is given to the impact of recent theories on crystallizer design and operation.

A generalized theory for the analysis and prediction of CSD, based on population balance mechanics, has been developed and tested over the past decade. Predictive design of CSD is now a possibility with the design techniques presented here and using suitable bench-scale data. Published evaluations of the reliability of design methods utilized in commercial practice would be a valuable asset to the science of crystallization.

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SCOPE

Much work has been done on the problem of crystal-size distribution (CSD) and its relation to crystallizer design and operation. An especially rapid burst of activity in this area has occurred over the last decade. Analytical studies of CSD both reveal the need and provide the means for quantitative measurement of secondary nucleation in realistic well-mixed crystallizers. The population balance theory of CSD provides the unifying link between predictive CSD studies in complex crystallizer configurations and descriptions of crystal growth and nucleation kinetics. Development has proceeded rapidly in both of these areas over the last few years, with each area reinforcing and motivating work in the other.

A mass-based theory rather than population-based theory of crystallizer analysis has emerged from recent work in Europe. Experiments have been developed that yield kinetic information that potentially could be used in either mass-based or population-based crystal-size distribution algorithms. The implications and limitations of these theories are discussed in the text.

The purpose of this review is to outline the advances that have been made in the analysis of crystal-size distribution and crystallization kinetics with particular emphasis on how these studies might influence the design and operation of industrial systems. Mention is made of areas that have received inadequate attention and/or areas where further studies seem appropriate.

CONCLUSIONS AND SIGNIFICANCE

Study of crystallization kinetics and related crystal-size distribution (CSD) has increased understanding of the complex interactions that occur in crystallizers and has opened up new vistas of exploration in crystallization technology. Continued feedback by users of the various analytical modeling techniques and persistent investigation of interphase kinetics are needed to strengthen the underlying knowledge of crystallization technology.

The design and analysis of crystallization processes of the continuous well-mixed suspension type have developed into formal design algorithms which can now be applied in situations of industrial importance. Specific process configurations that can be rigorously modeled include fines destruction, clear liquor advance, classified product removal, vessel staging, and seeding. Such process configurations can be modeled rigorously with a population balance CSD algorithm or, in many cases, with an alternative mass-based formulation. Crystal-size distribution transients and stability can also be evaluated as well as the effects of size-dependent growth rate and suspension-concentration-dependent secondary nucleation. Simulation capabilities have in fact outstripped the ability to physically manipulate and control liquid and solids residence-time distributions in a crystallizing environment.

Secondary nucleation mechanisms represent the dominant seed source in mixed-magma (suspension) crystallizers. Nuclei are formed by crystal-solid collisions, thus guaranteeing a significant interaction between suspension properties and the mechanical design of the crystallizer. Confirmation of this observation is seen in correlations which show the dependence of secondary nucleation kinetics upon agitation and suspension density. Nucleation rate B^0 has been found to be directly proportional to a rate constant k_N (which varies with degree of agitation) and to powers of the suspension density M_T and growth rate G. Power-law kinetics correlations of the form:

$$B^0 = k_N\,(RPM)\,M_T^j\,G^i$$

have proven adequate for correlation of secondary nucleation data in the majority of cases studied. Experimentation *of at least a limited nature, however, is required to* establish crystallization kinetics due to the widely varying nature of different chemical systems and crystallization environments.

Although numerous design methods and kinetic theories to analyze specific crystallizer configurations now exist, no clear-cut guidance has been provided by researchers to choose between crystallizer types and/or modes of operation. Design algorithms for classified and plug-flow crystallizers require considerable strengthening to be of much practical value, and documented case studies of the application of mixed-suspension, mixed-product-removal (MSMPR) design methods, especially for systems employing fines removal, product classification, and staging are needed to further establish the usefulness of MSMPR theory. Suggested fundamental research areas include: (1) interphase kinetic mechanisms, particularly that of secondary nucleation, (2) growth and dissolution (digestion) rates of sub-micron crystals, and (3) formation, migration, and removal of crystal occlusions. With continued improvement of design techniques and the emergence of realistic kinetic models, the practice of crystallization has the potential of becoming a highly developed science.

INTRODUCTION

Crystallization is a commonly used industrial separations and purification technique. If the desired product is an evaporate (or filtrate) rather than the crystalline phase, then the process emphasis is primarily that of separation rather than purification. In either case there is a strong interaction and dependence between both the degree of separation and purification and the particulate nature of the solid phase produced. Fundamental research on the unit operation of crystallization has focused mainly on understanding and predicting the particulate nature of the crystalline phase, recognizing that better knowledge and control of this aspect would permit improvement of the unit operation of crystallization, both as a separations and purification technique.

Specifically, a general theory of crystal-size distribution (CSD) has been advanced and refined. Concomitant experimental and theoretical studies of the kinetics of crystal nucleation and growth rate together with particle mixing, segregation, and classification mechanics were initiated. These particle kinetics and mechanics, together with a unified theory of CSD, permit analysis, evaluation, and prediction of crystallizer performance at levels of operation ranging from bench-scale to commercial production.

A number of excellent books and monographs that present the state-of-the-art in this rapidly moving field have been published since 1960. Reviews by Botsaris et al. (1969) provide quick reference material for many contemporary phases of the subject. Publications by Mullin (1961), Van Hook (1961), and Strickland-Constable (1968) consolidate much of the background material in crystallization fundamentals. *Chemical Engineering Progress Symposium Series Number 121* edited by Estrin (1972), *Number 110* edited by Larson (1971), and an earlier publication, *Number 95*, edited by Palermo and Larson (1969) present compilations of academic and industrial research. Four recent books are of particular interest and provide much of the background material for this review: (1) Randolph and Larson (1971) present techniques for analyzing and designing continuous crystallization processes based on back-mixed crystallizer theory. Extension of population balance concepts to provide insights into crystallization mechanisms is included. (2) Nyvlt (1971) presents theory based on mass-balance ideas and develops design relationships for a wide variety of crystallizers. (3) Bamforth (1965) concerns himself with the practical aspects of crystallization, leaving theoretical matters to others. (4) An international symposium presented by the Institution of Chemical Engineers, London (1969), describes a wide variety of contemporary approaches to analysis of crystallization.

Crystallization can be approached from several points of view; the remarks in this review are primarily confined to solution crystallization and, in particular, to techniques for analyzing and predicting crystal-size distribution. Both process configuration (crystallizer design) and crystallization kinetics (particular to a given system) must be considered to elucidate the CSD problem. Both of these areas will be considered from a researcher's standpoint as well as in light of current industrial practice.

HISTORY

Crystallization is no different from most other unit operations since industrial practice predates analysis of the operation. It is impossible to operate a crystallizer, observing the range of product sizes and shapes and perhaps also product transients, without speculating on the complex physical processes that generate such a product distribution. Who first understood these phenomena and predicted crystal-size distribution may remain one of history's secrets. However, the first analytical work in this area that we are aware of is attributed to R. B. Peet who worked for the American Potash Company on the crystallization of Searles Lake brines. Peet (1931) speculated on the CSD which should be produced in an unseeded, continuous-flow, well-mixed borax crystallizer. He derived an expression for the product weight distribution (which was recognized as a gamma function) and even integrated the distribution to obtain kinetics parameters in terms of moments of the distribution. The results were verified with borax data.

Perhaps without realizing the significance or generality of the work (all physical parameters were assumed to be for the borax system), Peet clearly laid out the rudiments of the mixed-suspension, mixed-product-removal (MSMPR) crystallizer concepts. This work was especially remarkable considering the primitive technical working conditions that existed in the Searles Valley in the 1920s. Unfortunately, the work was never published or fully exploited—even by the originating company. Publishing of novel work is thus seen to be important for acceptance and utilization.

Bransom et al. (1949) detail the first published use of the MSMPR crystallizer to obtain quantitative nucleation and growth rates in a continuous back-mixed slurry. The work was done for RDX explosive using a salting-out water/organic system. Kinetic parameters were obtained from a sedimentation measurement of mass distribution. No mention was made of the possible engineering significance of this technique to obtain design-oriented kinetics or of predicting CSD in other configurations.

Saeman (1956) published the first engineering-oriented study of CSD in continuous mixed-magma crystallizers. This study derived the exponential population and gamma weight distribution of the mixed removal crystallizer and compared them with the classified removal case. The idea of fines removal to increase crystal size was discussed in an engineering context; engineering analysis of CSD dates to this work of Saeman.

The past decade has seen much emphasis on the analysis of CSD in crystallizer configurations of practical interest. Randolph (1962) and Randolph and Larson (1962) identified the crystal population balance as a natural starting point for the study of crystal-size distribution. CSD transients were first investigated in their work. Hulburt and Katz (1963) and Randolph (1964) generalized on the population balance as a fundamental concept in particle mechanics. Spatially back-mixed and distributed forms of the balance, as well as the useful moment transformation, were discussed. From the concepts developed by investigators in the early 1960s, population balance models for increasingly complex flow fields have evolved by relaxing several of the idealizations of the basic well-mixed crystallizer model.

CRYSTALLIZATION KINETICS

The models presented in the previous and following sections are useful for describing a wide variety of crystallizer behavior if parameters describing growth and nucleation kinetics are available and if the assumptions utilized in the development of the generalized models are sound. The problem is to first devise experiments to isolate the parameters of interest and then to relate the experimental environment to an industrial crystallizer regime. Numerous techniques and theories have been devised to measure and analyze crystal growth and, to a far lesser extent, nucleation. Ohara and Reid (1973) present an excellent review and critical analysis (from a chemical engineer's point of view) of the various basic mechanisms proposed for describing crystal growth from solution. They emphasize the need for first asking what are the significant independent variables that control growth and then how can these variables be measured and related to growth. The kinetic parameters for crystal growth and nucleation and the experimental techniques described in this section are based on phenomenological models and, although the parameters in some cases may not be relatable to basic theory, they are satisfactory for design purposes.

Growth Kinetics

Techniques for measuring crystal growth may be categorized as direct or indirect methods depending upon whether crystal growth rate or supersaturation depletion rate is measured. Direct techniques such as single crystal growth experiments or measuring the weight gain of uniform or nonuniform crystal seeds suspended in a supersaturated solution are discussed as are indirect methods that monitor the rate of supersaturation depletion in the presence of seed crystals. Population balance routes to both nucleation and growth rates, wherein the entire crystal-size distribution is measured and parameters extracted, have been alluded to previously and are covered in the subsequent section on nucleation kinetics.

A conventional power law form for the empirical correlation of growth rate data where particle size is not a factor is given as

$$G = k_g s^a \tag{3.1}$$

where the exponent 'a' is usually found to be in the range of one to two. Equation (3.1) is a simple model to utilize and will fit a surprising amount of data; however, it is recognized that the overall resistance to growth rate k_g^{-1} is composed of a diffusion resistance (which becomes negligible at high solution/crystal velocities) and a particle integration resistance at the crystal surface. When growth rate is first order in supersaturation, the overall resistance can be expressed in terms of these two resistances as

$$\frac{1}{k_g} = \frac{1}{k_r} + \frac{\delta(L)}{\mathcal{D}} \tag{3.2}$$

where k_r is the particle integration rate, $\mathcal{D}$ is the solute molecular diffusivity, and $\delta(L)$ is the size-dependent effective diffusion film surrounding the crystal. Marked dependence of crystal growth rate to crystal-size is indicative of diffusion-limited growth. In a well-mixed crystal magma with low supersaturations, growth rate is often independent of crystal-size (McCabe's ΔL-law), and particle integration represents the growth-limiting step. Normally, investigators attempt to establish whether diffusion or surface reaction limits growth and what is the specific form of the growth rate correlation. A number of techniques have been proposed in the literature for growth rate measurements, although fluidized bed experimentation is currently being emphasized.

For solutions that will sustain moderate to high levels of supersaturation (and not all will), useful design insight can be provided by relatively simple laboratory fluid bed experimentation. Fluidized bed crystallizers have been used with success by Rumford and Bain (1960) and Mullin and Garside (1968) to study variables affecting growth rates of crystals. A small quantity of presized and weighed crystals is suspended in an upward flowing stream of supersaturated solution. Direct measurement of crystal weight change or alternately of liquid concentration variation allows crystal growth rate to be determined as functions of solution concentration, solution velocity, supersaturation, impurity level, and crystal size.

Rumford and Bain identified zones of diffusion and reaction rate controlled growth in salt solutions and utilized the metastable limits found in bench-scale fluid bed studies to ascertain process conditions for Oslo-type crystallizer pilot work. Of interest is the observation that it was impractical to start up with saturated solution and evaporate until nucleation occurred. Large numbers of nuclei were formed, and days were required to form a stable fluidized crystal bed.

Mullin and Garside (1968) investigated the growth of both single potash alum crystals and seeded fluidized beds at controlled solution velocity and supersaturation. Excellent agreement of growth rates was found by comparing single crystal and fluidized bed data at similar crystal-size and slip velocities, suggesting that either method can provide meaningful growth rate correlations. Mullin and Garside (1968) also conducted dissolution rate studies with potash alum using fluidized bed apparatus and showed clearly that crystallization and dissolution are not reciprocal processes. Dissolution proceeded between 2 to 4 times faster than growth under comparable driving forces.

Mullin and Bujac (1969) reported indirect growth rate measurements from a closed loop fluidized bed in which they incorporated a recording liquid density meter, making it possible to measure growth rate at various supersaturations in one experiment. Utilizing population balance relationships, Misra and White (1971) obtained growth kinetics by nonuniform seeding of a supersaturated solution and then employed the time-varying particle-size distribution to observe growth dependence on supersaturation.

Nyvlt (1971) reviews direct methods for obtaining crystallization parameters which involve measurement of crystal size or weight change versus time at constant levels of supersaturation, and he discusses indirect methods based on rate of decrease of liquid supersaturation. He states that for the small degrees of supercooling normally found in industrial crystallizers, growth rate increases linearly with supersaturation. Nyvlt's relationship indicates that the reaction kinetics of building ions or molecules into the crystal lattice is usually the rate limiting step rather than diffusion controlled mass transfer as no dependence upon crystal size is indicated in his growth rate expression.

Nucleation Kinetics

Startup and operation of a continuous crystallizer involves several phases. Initially, high levels of supersaturation are generated in an unseeded liquor which causes spontaneous nucleation by either homogeneous or heterogeneous origins. After a solid phase is formed in the vessel, very little supersaturation is necessary to promote sufficient nucleation by secondary mechanisms. The isolation and quantitization of the various types of nucleation mechanisms occurring in an industrial crystallizer have generated considerable activity in recent years. An excellent review of the current state of the art regarding nucleation phenomena has been edited by Estrin (1972).

Most homogeneous nucleation rate expressions are modifications of the Becker-Doering relationship based on the free energy concepts of Gibbs. The Miers nucleation model is a linearized form of the Becker-Doering model and advances the concept of a metastable, but supersaturated, region within which nucleation does not occur. Thus

$$B^0 = k(C - C_M)^i \tag{3.3}$$

where C_M is the metastable threshold of nucleation. In this relationship, k can be a function of temperature but i is not. Heterogeneous nucleation models, based upon the adsorptive properties of trace solid impurities (for example, dust) are modifications of the more general Becker-Doering equation.

Population density from an MSMPR experiment is determined from weight distribution data by the expression

$$n(L) = (M_T \Delta W)/(\rho k_v L^3 \Delta L) \tag{3.4}$$

Semilog plotting of n versus L allows growth rate and population densitity of nuclei to be determined from the idealized MSMPR distribution

$$n = n^0 \exp\{-L/G\tau\} \tag{3.5}$$

Nucleation rate is related to growth rate and population density by the relationship

$$B^0 = \lim_{L \to 0} nG \equiv n^0 G \tag{3.6}$$

Thus, from size distribution analysis of crystallizer product, both nucleation and growth rates are obtained. The relative kinetic order i and the pre-exponential rate constant k_N which are both needed for scale-up computations can be extracted from experimental data if the following models hold:

$$\text{Growth} \quad G = k_g s \tag{3.7}$$

$$\text{Nucleation} \quad B^0 = k_N s^i \tag{3.8}$$

Elimination of s gives

$$B^0 = k_N G^i \quad \text{or} \quad n^0 = k_N G^{i-1} \tag{3.9}$$

From the relationship between n^0 and G one can obtain i, the relative kinetic order. A series of experiments, at equal suspension densities but varying feed rates, provide sufficient information for determination of the relative kinetic order. In principle, the exponent i and the rate constants k_g and k_N could be obtained by directly plotting growth and nucleation rates versus supersaturation. In many crystallizers, however, supersaturation levels are virtually impossible to measure and kinetics are best obtained by analysis of crystal-size distribution. In typical computations, k_N and i represent sufficient kinetic information for scaleup; however, per-pass yield cannot be calculated unless growth and nucleation kinetics are expressed in terms of supersaturation.

Pilot or bench-scale testing to obtain kinetic parameters is usually unavoidable. Randolph and Larson (1971) suggest the use of an MSMPR crystallizer for laboratory determination of both growth and nucleation rates. A laboratory MSMPR is simply a small vessel fitted with a draft tube and agitator operated with continuous feed and mixed discharge. If growth rate is not dependent on crystal size, this technique facilitates simultaneous measurement of both nucleation and growth rate at the same level of supersaturation, agitation, temperature, and suspension density.

Most of the reported MSMPR crystallization kinetics studies utilize the technique of precipitation or salting-out by addition of a third component. This technique eliminates heat transfer and pressure control problems but does not represent the majority of industrial applications. Small-scale MSMPR indirect cooling crystallization units have been tested, but evaporative cooling or evaporative concentration presents rather formidable experimental difficulties in bench-scale equipment. In cases where MSMPR kinetic data have been taken in similar equipment on the same system, good agreement between nucleation data taken with surface cooling and by evaporative cooling was obtained. This result is consistent with recent studies, indicating collision breeding is the dominant source of nuclei in systems rather than spontaneous nucleation.

The validity of kinetic measurements obtained from an MSMPR crystallizer depends upon achieving the constraints assumed in the derivation of the exponential population distribution as well as sampling procedures and treatment. Separation of crystals from mother liquor and accurate determination of crystal-size distribution, especially in the fine size range, can be troublesome. Although these techniques are utilized by industry to characterize crystallizers, most of the published data are from university researchers and represent less realistic systems. A sampling of kinetic orders observed in published studies is shown on Table 1.

Recently, it has been observed that secondary effects such as crystal microattrition can be significant sources of new particles. Youngquist and Randolph (1972) and Randolph and Cise (1972) quantitized the effects of secondary nucleation in a seeded MSMPR crystallizer by direct measurement of the crystal-size distribution in the small size range using a multichannel Coulter counter.

They demonstrated that nuclei are formed by microattrition of seed crystals. Youngquist and Randolph correlated particle nucleation data with the power-law equation

$$B^0 = k_N G^i M_T^j \tag{3.10}$$

with the kinetic parameters $i = 1.2$ and $j = 1.0$. In this equation B^0 was an approximation of nucleation rate taken as the sum of crystal births up to an arbitrary large crystal size. Equation (3.10) has proven adequate for the correlation of nucleation data from numerous systems.

McCabe and Clontz (1971) conducted classic experiments to demonstrate the mechanism of contact nucleation or collision breeding in which a supported crystal in a supersaturated medium was tapped with a gentle impact by a metal rod or another crystal. They reported that nucleation by collision breeding is approximately linear with both contact energy and supersaturation, and they suggest that contact nucleation is an important source of nuclei in heavy suspensions; thus, sliding crystals along sides or bottoms of the crystallizer and direct crystal contact with impellers provide sufficient energy for prolific nucleation. Microscopic attrition might explain some of the characteristics of contact nucleation but should not be affected by supersaturation. However, the mechanisms of microattrition and contact breeding both depend on supersaturation and may be manifestations of the same phenomenon. The emphasis in McCabe's experiments was the elucidation of mechanisms, not the development of kinetic correlations. Recently Ottens et al. (1972) and Bennett et al. (1973) have demonstrated how McCabe's contact mechanism can explain power-law nucleation kinetics observed in mixed-suspension crystallizers.

An alternate technique for determination of nucleation kinetics is described by Nyvlt (1969) and is utilized by Larson and Mullin (1973) to explore the kinetics of nucleation of ammonium sulfate. A brief discussion of the method follows:

Nyvlt describes nucleation rate as

$$M^0 = k_N s^a \tag{3.11}$$

where M^0 is the mass rate of nucleation per unit volume at a small but finite nuclei size. Nyvlt gives no particular physical significance to the nucleation rate order 'a' or to the nucleation rate constant because of the simplifying assumptions utilized in the reformulation of the Becker-Doering equation. Assuming that nucleation rate is proportional to the maximum allowable supersaturation to the 'a' power [Equation (3.11)], and further that mass nucleation rate M^0 is also proportional to the cooling rate b, the following expression is derived:

$$\log b = K + a \log \Delta T_{\max} \tag{3.12}$$

where $\Delta T_{\max}$ is the degree of subcooling at which nucleation occurs. The slope of a log-log plot of b versus $\Delta T_{\max}$ gives the order of nucleation in Equation (3.11).

The value of 'a' determined in this manner was found to decrease with increasing molecular weight, to vary with presence or absence of solid phase, and to exhibit little variation with temperature. Nyvlt also describes a method for determining kinetic order which involves measurement of the induction period elapsing from the instant at which the solution is saturated until crystals first form.

Larson and Mullin (1973) attempt to demonstrate the equivalence of Nyvlt's nucleation parameter 'a' and the power-law nucleation parameter 'i' (from population balance theory). Both parameters typically have low values in the range of 1 to 4. The two different methods of determining nucleation rate gave similar results for a pure ammonium sulfate system but contradictory results where impurities are present.

It would certainly be advantageous to obtain reliable kinetic parameters by shortcutting the laborious data gathering and analysis necessary with the MSMPR technique; however, it is unlikely that the complex mechanisms of secondary nucleation as they exist in a back-mixed crystal suspension could be completely modeled with the simple unseeded batch cooling experiments of Nyvlt.

CRYSTALLIZER SYSTEMS ANALYSIS

Crystallizing systems present rather complex analysis problems since they are characterized by their mode of operation, by the type of crystallizer geometry employed, by how solids and liquid phases are manipulated to control crystal-size distribution, and by whether or not the system is cascaded. The various options available to the designer are briefly discussed, and then attention is focused on system simulation techniques.

The mode of operation referred to in this section is the technique employed to generate supersaturation (and normally a solid phase) from a solution. The most common techniques for creating supersaturation include: (1) indirect cooling, (2) evaporation of solvent, (3) adiabatic vacuum cooling, and (4) salting-out by addition of a component to reduce the solubility of the crystallizing substance. The indirect cooling mode, wherein heat is removed through a heat exchanger wall, is utilized when product solubility is strongly temperature dependent. By contrast, the evaporation technique is suitable for solutions with small or negative temperature dependence. Adiabatic cooling is used for crystals with intermediate types of solubility curves while salting-out is not normally encountered except in experimental laboratory units. The proper mode of crystallization for a given situation is dictated by an analysis of the yield per pass as functions of various modes of operation and economic considerations.

Typical crystallizer configurations are shown on Figure 1. The externally forced-circulation crystallizer with suspension chamber (FCSC) and the simple forced-circulation unit (FC) are typified by high external recirculation and are general purpose crystallizers that can be utilized for either evaporative or indirect cooling modes of operation. The draft tube crystallizer, frequently supplied with an internal baffle to facilitate fines removal and hence the abbreviation, DTB, has high internal recirculation and is suitable for adiabatic cooling, indirect cooling, and medium evaporative loads. Although there are many possible crystallizer geometries, the three types mentioned here have flow patterns which resemble the majority of commercial crystallizers.

For a given crystallization mode and crystallizer vessel geometry, four techniques (in addition to staging) are available to vary the characteristics of a crystallizer suspension. In the generalized CSD algorithm that follows, various functions are included in the model to describe (1) clear liquor advance, (2) product classification, (3) fines withdrawal, and (4) seeding. Average suspension density for MSMPR is fixed by overall mass and component balances, but provision for clear liquor advance allows some control of slurry concentrations. Removal of classified product from a settling leg is commonly encountered as are systems which isolate and dissolve the fines portion of the CSD. Addition of crystal seeds from a recycle stream or with the feed as in a staged system also alter crystallizer CSD.

To analyze a crystallizer system, both steady state

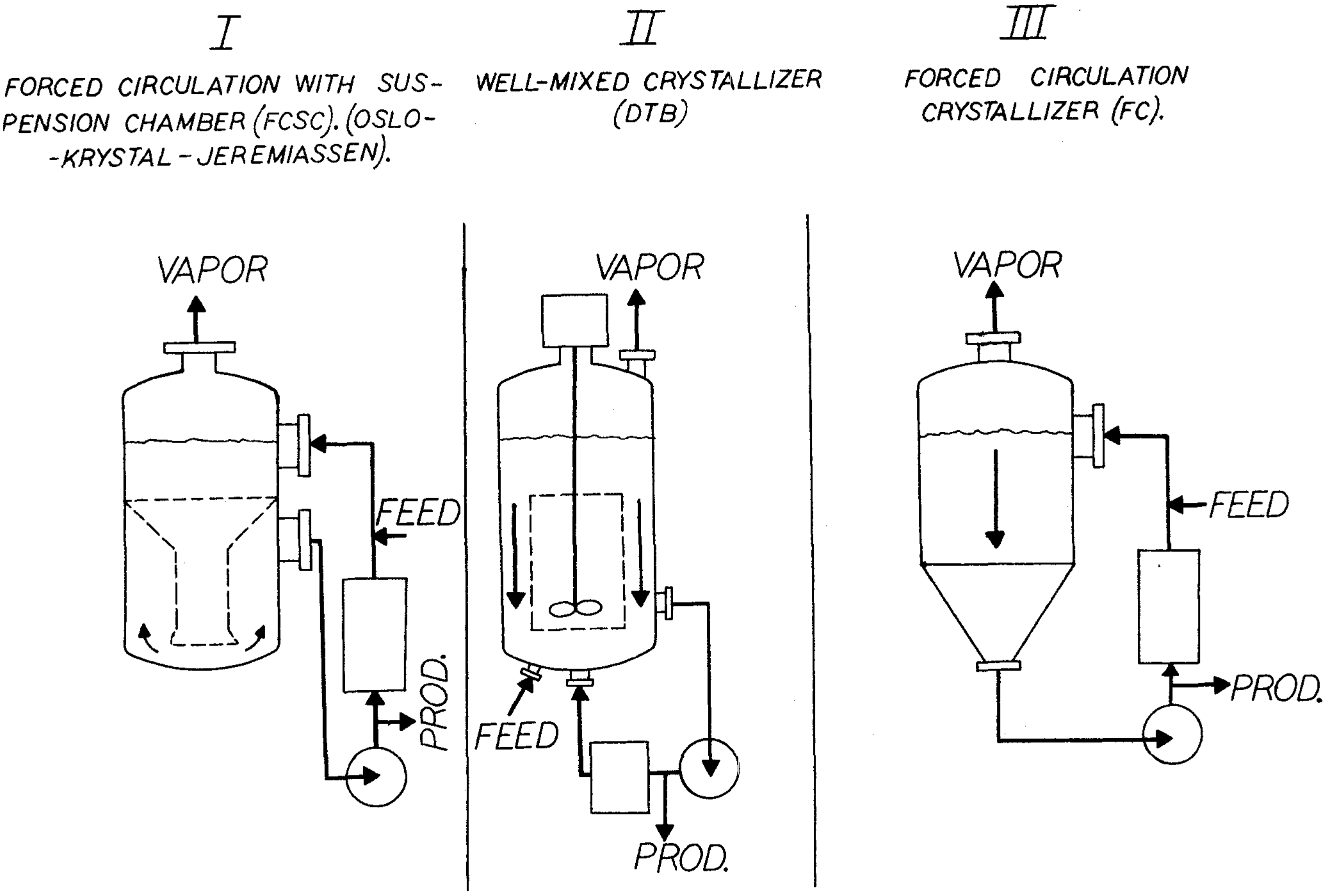

Fig. 1. Typical crystallizer configurations.

and transient CSD behavior must be considered. Algorithms based on the population balance concept are summarized in the following sections. Crystal-size distribution dynamics, which can occur as transients or as inherent instability, are also reviewed. Correlation techniques utilized to characterize CSD from operating units are also given.

Population Balance Algorithms

"As the Lord commanded Moses, so he numbered them . . ."

Numbers 1, v.19

The population, or numbers, balance is the starting point for much of the work in the area of analysis and prediction of crystal-size distribution in crystallization systems. This work is summarized in a recent book by Randolph and Larson (1971). The population balance in particle phase space (phase space is thought of as a linear measure of crystal size plus any spatial dependence of the particle distribution) logically interrelates crystal growth and nucleation kinetics with the particle residence-time distribution which is controlled by process configuration.

Complications arise from the promotion of nuclei formation from secondary sources, that is, crystal/impeller and crystal/crystal interactions; thus, the kinetics of secondary nucleation must be included to complete the process description. Population balance models can be phrased for either a spatially distributed suspension or for a well-mixed crystal suspension with uniform properties. In addition, the size-dependence of the distribution can be integrated out with the moment transformation (Hulburt and Katz, 1964; Randolph and Larson, 1971, Ch. 3) to increase computational efficiency, especially when dynamics are being studied.

For purpose of illustration of the essential physics governing CSD, this review will consider the size-distributed population balance written for a dynamic mixed-suspension of volume V with arbitrary particle withdrawal. Feed streams to the crystallizer contain no crystals. The describing equations are as follows:

Population balance

$$\frac{\partial n}{\partial t} + \frac{G^0\,\partial(g(L)n)}{\partial L} + \frac{Q(L)n}{V} = 0 \qquad (4.1)$$

Mass balance (supersaturation driving forces)

$$\frac{ds}{dt} = \frac{\delta C_i}{\tau} - \frac{s}{\tau} - \frac{\rho G^0 k_a}{2}\int_0^\infty n\,g(L)\,L^2 dL \qquad (4.2)$$

Crystallization kinetics

Growth
$$G = G^0(s)\,g(L) \qquad (4.3)$$

Nucleation
$$B^0 = B^0(s, m_j, RPM, \ldots) \qquad (4.4)$$

In the above equations, supersaturation is given as $s = C - C_s$, nuclei density as $n^0 = B^0/G^0$, and τ is liquid retention time. The solute resource term δC_i includes dissolved solute mass recycle if the crystallizer configuration involves a fines destruction loop. The structure and interrelationship of these equations is illustrated in an information flow diagram, Figure 2. Note the four feedback loops designated (1) to (4). These information feedbacks are unique to crystallization and allow for the possibility

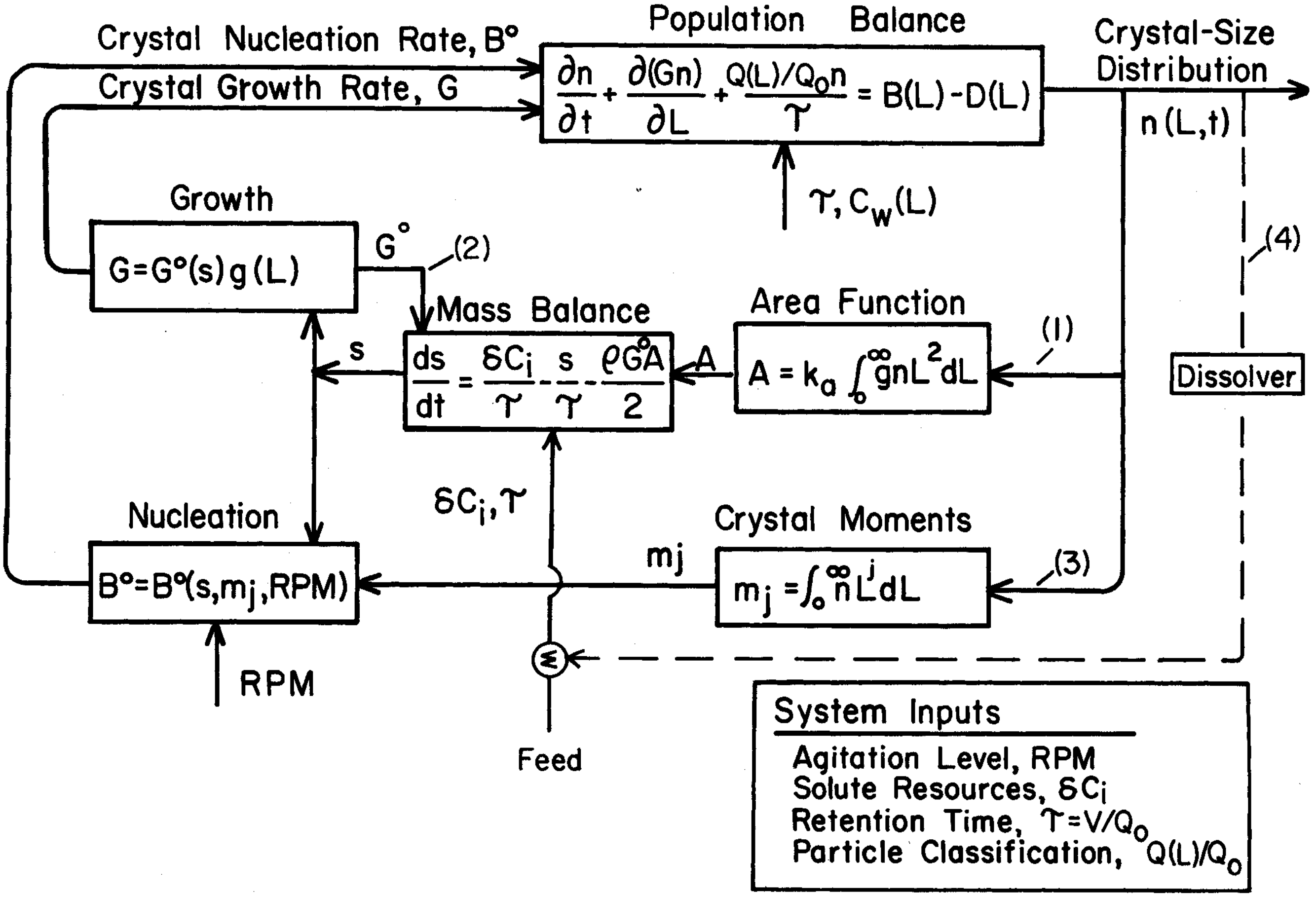

Fig. 2. Information flow diagram showing process interrelationships which determine CSD in mixed-magma crystallizers.

of instability, that is, sustained cycling. Further discussion on these loops will be deferred to the next section on stability.

Equivalent statements of the population balance can be phrased in terms of population or mass distributed about size or particle volume coordinates. Thus, the differential population or mass (per unit volume suspension) could be written in terms of a differential size or particle volume coordinate as

$$dN = n(L)dL$$
$$dN = n(v)dv$$
or
$$dM = m(L)dL \qquad (4.5)$$
$$dM = m(v)dv$$

Any of the distributions formulated above can, of course, be transformed one to the other using the geometrical relationship between size and volume. Of the four possible ways of formulating a distribution function, the population-size form has proved most useful in crystallization applications.

There are two good reasons for choosing the size-dependent population distribution $n(L)$ as an analytical representation of CSD. First, size L, rather than volume v, is used as the dependent variable because the linear growth rate of crystals $G = dL/dt$ is often found to be independent of size in a well-mixed crystal suspension (McCabe's ΔL-law). Second, population, rather than mass, is chosen as the dependent variable as crystal-size distribution is dominated by nucleation at sizes where population is enormous but crystal mass is negligible. These factors are not important in other particulate processes (for example, comminution) where mass-size or mass-volume representation of the distribution is often used.

The equations describing crystal-size distribution have two uses. The equation can be used for determination of kinetic parameters from analysis of experimental distributions from well-defined simple crystallizer configurations. Another use is in the a priori prediction of CSD from known kinetics for realistic crystallizer configurations.

The MSMPR crystallizer illustrates the former use of the CSD equations to obtain quantitative secondary nucleation and growth rate kinetics in realistic mixed-suspension environments representative of industrial practice. For the steady state MSMPR crystallizer with size-independent growth kinetics, the well-known exponential population density distribution is obtained.

$$n = \frac{B^0 \exp\{-L/G\tau\}}{G^0} \qquad (4.6)$$

The simplicity of the MSMPR concept, together with its many experimental verifications, has been the single most important factor in the acceptance of analytical CSD modeling and analysis. Larson and Randolph (1969) detail the use of the MSMPR technique for analysis and correlation of CSD data. Significantly, the MSMPR constraints can be applied at the bench-scale, pilot plant, and production levels, thus providing direct comparisons of crystal kinetics. The MSMPR concept is easy to grasp and can serve as an information channel between research and operating groups (Randolph, 1970).

The second and very practical use of the population balance equations is for analysis and prediction of CSD in crystallizers of complex configurations, assuming kinetics can be modeled. Nuttall (1971) developed a population balance algorithm (referred to as the Mark I CSD simulator) which assumes completely arbitrary residence-time distributions of solids and liquids, size-dependent growth kinetics, and suspension concentration dependent secondary nucleation kinetics. The following equations are solved by this steady state CSD simulator:

Population balance

$$G_0 \frac{d}{dL}(g(L)n) + \frac{Q_0 C_w(L) n}{V} = \frac{Q_i n_i(L)}{V} \qquad (4.7)$$

Mass balance constraint

$$P = \rho k_v Q_0 \int_0^\infty C_p(L) n L^3 \, dL \qquad (4.8)$$

Nucleation kinetics

$$B^0 = k_N M_T{}^j G_0{}^i \qquad (4.9)$$

Growth kinetics

$$G = G_0 g(L) \qquad (4.10)$$

The central program algorithm adjusts G_0 by trial and error until the mass balance constraint is satisfied. The absolute size of crystals produced depends on the nucleation rate and solute resources available; however, to change the form of CSD, one of the four size-dependent functions $n_i(L)$, $g(L)$, $C_w(L)$, or $C_p(L)$ must be manipulated. The size-dependent growth rate function $g(L)$ cannot readily be manipulated, leaving only three designer handles to control the form of the crystal-size distribution. These size-dependent functions, which involve product classification, fines removal, seeding, and clear liquor advance, serve to model a wide variety of process configurations.

Withdrawal function $C_w(L)$. Physically, this is the ratio of volumetric withdrawal of solids at size L compared to total slurry withdrawal. Product classification is modeled when $C_p = C_w > 1$ for product-sized crystals.

Product withdrawal function $C_p(L)$. This function is the ratio of volumetric withdrawal of solids at size L going to product (rather than dissolved and recycled) compared to total slurry withdrawal. Fines dissolving is modeled when $C_w > 1$ for small-sized crystals while $C_p = 1$ for all sizes. Clear liquor advance (growth-type crystallizer) configuration is modeled for $C_p = C_w > 1$ for small crystals.

Seeding function, $n_i(L)$. Seeding can be modeled by specifying an arbitrary input population density n_i. The Mark I simulator calculates n_i from inlet solids concentration and weight distribution M_{Ti} and $W_i(L)$. Staging is a special case of seeding and is modeled when $(n_i)_k = n_{k-1}$.

Growth function, $g(L)$. The size-dependency of growth rate $g(L)$ is normally not a design variable. This function, if different from unity, can be determined from careful analysis of MSMPR data. Classification effects are similar to size-dependent growth rate effects on CSD and the former must be carefully evaluated before discarding in the analysis of abnormal CSD data. Values of $g(L) > 1$ for large sizes widen a distribution while $g(L) < 1$ narrows the distribution. By clever manipulation of supersaturation zones in a crystallizer, it is conceivable that size-dependent growth rate phenomena could be exploited to control CSD to a limited degree.

One has to work with this generalized CSD formulation only a short time to observe that it is difficult to model completely arbitrary CSD forms with the available functions C_p, C_w, and n_{k-1}. Further, the implementation of these functions is sometimes impossible in practice. Clearly, breakthroughs are needed in the ability to separate residence-time distributions of liquid versus solids or solids as a function of size without destroying the operational advantages of the well-mixed suspension or inducing excessive secondary nucleation. As a specific example, development of continuous sucrose pans has been held up

TABLE 1. KINETIC ORDER REPORTED FOR VARIOUS CRYSTAL SYSTEMS[1]

System	Mode of Crystallization	Kinetic order	Comments	Reference
Calcium sulfate/ phosphoric acid	Precipitation	2.6-2.8	Indication that homogeneous nucleation dominates	Amin and Larson (1968)
Ammonium sulfate/ water	Cooling	1.7	No enhancement in crystal size with increased suspension density noted	Chambliss (1966)
Ammonium alum/ water	Cooling	2.1	Strong secondary nucleation effects were noted	Chambliss (1966)
Ammonium alum/ water/ethanol	Salting out	1.0	Increased residence time had no effect on crystal size distribution	Timm and Larson (1968)
Ammonium sulfate/ water/methanol	Salting out	4.0	Increased residence time has moderate effect on CSD	Timm and Larson (1968)
Sodium chloride/ water/ethanol	Salting out	9.0	Increasing residence time strongly affects CSD	Timm and Larson (1968)
Ammonium alum/ water/ethanol	Salting out	2.0	Utilized MSMPR theory to analyze data. Secondary nucleation effects not accounted for	Timm and Larson (1968)
Cyclonite-water/ nitric acid	Precipitation	1.0	Used MSMPR theory to obtain kinetic order	Bransom (1949)

[1] In all cases MSMPR theory was utilized to obtain kinetic order.

by the inability to duplicate the narrow CSD's obtained in batch operation. The production of such narrow distributions in continuous operation would require an unreasonable number of stages (with nucleation totally suppressed in all but the first stage) or extensive size-classification which cannot be implemented in the viscous massecuite.

The so-called "*R-Z* crystallizer model" is flexible enough to model single crystallizers having fines removal, product classification, and clear liquor advance, yet simple enough to permit analytical solutions, and is modeled by employing the following parameter choices in the previous generalized CSD algorithm:

$$\begin{aligned} C_w &= R \quad \text{for } L \text{ in } (0, L_f) \\ C_w &= 1 \quad \text{for } L \text{ in } (L_f, L_p) \\ C_w &= Z \quad \text{for } L \text{ in } (L_p, \infty) \end{aligned} \qquad (4.11)$$

Randolph and Larson (1971, Ch. 8) and Randolph et al. (1973) solve the *R-Z* crystallizer algorithm with production constraint and secondary nucleation kinetics. These analytical equations require a trial-and-error solution for crystal growth rate but can easily be programmed for a desk-top electronic calculator with stored program capability.

CSD Dynamics

CSD dynamics can occur as transients (response to outside disturbances) or as instability. In the latter case the process itself is unstable and sustained cycling of CSD occurs even in the absence of outside disturbances. The possibility for sustained CSD limit cycles exists as noted before because of the unique process feedback in which nucleation and growth rates, which determine CSD, are dependent on the level of driving forces (supersaturation) in the magma. Supersaturation itself is determined by crystal area and hence the current state of CSD. The same dynamic CSD equation can be used to analyze both CSD stability and transients.

Four feedback relationships in self-seeded, mixed-magma crystallizers have been identified (Randolph et al., 1973) and are designated as loops (1) to (4) in the information diagram of Figure 2. These information feedback loops are described as follows:

1. The main information feedback loop in crystallization systems is the CSD/area/supersaturation/growth rate/nucleation rate/CSD relationship shown as loop (1) Figure 2. This is the relationship that has been used by previous investigators in the study of CSD stability.

2. Nested within loop (1) is a growth rate loop, identified as (2), which tends to damp out fluctuations in solute concentration and bring crystallizers with a long holding time to a high yield/low growth rate condition. Hulburt and Stefango (1969) and Lei et al. (1971) have shown that in a Class I (variable yield) system, loop (2) aggravates the tendency toward cycling caused by the primary feedback, loop (1).

3. Recent studies of secondary nucleation indicate that nucleation rate is suspension-concentration dependent and can be correlated to leading moments of the parent seed distribution. Thus, another process feedback, shown as loop (3), exists due to the mechanisms of secondary nucleation. Randolph and Larson (1971, p. 231) show that suspension-dependent nucleation kinetics correlated to the first or fourth moment of the CSD have little effect on CSD stability in the Class II (high yield) MSMPR crystallizer. CSD stability is slightly increased when nucleation rate is proportional to a power of the suspension density (Randolph et al., 1973).

4. Nuttall (1971) considers the recycle of dissolved fines as another information feedback shown as loop (4). If this recycle is neglected in stability analysis, fines removal at finite size (significant mass recycle) is predicted to totally stabilize CSD (Randolph et al., 1973). Nuttall illustrates the destabilizing effect of dissolved fines recycle in a rigorous numerical simulation of a cycling crystallizer with fines destruction and classified product removal.

The study of CSD stability has proceeded much like the study of CSD design algorithms, namely each of the restrictive assumptions in the Class II (high yield) MSMPR model were successively relaxed. Randolph (1962) derived the result that the nucleation/growth rate sensitivity parameter $i = \dfrac{d(\log B^0)}{d(\log G)}$, must be less than 21 for stability in the Class II MSMPR crystallizer, thus indicating that only a nucleation discontinuity could result in CSD cycling for such a system. Hulburt and Stefango (1969) studied Class I (variable yield) and Class II (high yield) crystallizers with clear liquor overflow. Lei, Shinnar, and Katz (1971), using the same crystallizer system equations, studied the similar effects of fines removal. In both of these studies, large values of the nucleation sensitivity parameter were required to cause CSD cycling. Sherwin, Shinnar, and Katz (1969) studied an idealization of the classified product crystallizer and showed that product classification severely destabilizes CSD and might reasonably account for CSD cycling. In a recent study Randolph et al. (1973) examined the classified product crystallizer with fines removal, considering fines mass recycle and suspension-dependent nucleation kinetics (three of the four feedback loops in Figure 2). Only product classification can reasonably account for low nucleation sensitivity cycling. None of the previous studies predict cycling if the nucleation kinetic parameters typically observed in MSMPR tests are valid unless some degree of product classification occurs. In conclusion, systems with only fines removal are stable unless excessive fines dissolving forces supersaturation into a region of homogeneous nucleation (nucleation discontinuity); systems employing product classification, either with or without fines removal, can become unstable.

Crystal-size distribution transients depend on the nature of the outside disturbance. Timm (1968) presents transients in an MSMPR salting-out crystallizer following a step change in throughput. Reasonable agreement between experimental observations and theoretical calculations was obtained. Transient CSD calculations can be used with confidence to evaluate the likely effect on CSD of major process upsets. One practical guideline that has resulted from CSD transient simulation is that a period of about ten retention times under steady operation is necessary to come to a complete steady state CSD in an MSMPR crystallizer. This result has been experimentally verified many times. A transient period of six retention times is often sufficient if population densities at the larger sizes is disregarded.

Characterization of CSD in Operating Systems

Several authors report attempts to compare performance of crystallizers on the basis of a measure of the mean or most probable particle size plus a parameter that characterizes the width of the size distribution. Crystal-size distribution is frequently described by mean aperture (MA), which gives the sieve aperture in microns through which 50% by weight of the sample passed and the coefficient of variation (CV), which is defined as $\text{CV} = \sigma/\bar{L} \times 100$. A working definition for CV that is easier to apply and is often used is given as $\mathrm{CV} = 100 \dfrac{L_{84\%} - L_{16\%}}{2L_{50\%}}$. For agitated crystallizers (MSMPR), CV typically ranges from 30 to 50. Classifying crystallizers have CV's of 20 or less.

Although plots of CSD on log-probability paper frequently show nonlinearity, this technique is often utilized in industry to characterize crystal distributions. This method of data presentation is reportedly widely used in the beet and cane sugar industry for description of crystalline products. There are no solutions to the population balance CSD equations to indicate that weight distribution should be of log-normal form, although this is often a good approximation. An alternate method for correlating CSD is to employ the two-parameter Rosin-Rammler relationship:

$$W(L) = 100 \exp \{-(L/\overline{L})\}^{\gamma} \qquad (4.12)$$

where γ is a measure of crystal uniformity and $\overline{L}$ is the statistical mean particle size. $W(L)$ is the oversized fraction in weight percent.

Bennett (1962) computed coefficient of variations and mean apertures for industrial data obtained from forced circulation, draft-tube-baffle, and Oslo-type crystallizers. He found that the theoretical distributions of Saeman (1956) and Bransom (1964) did not adequately describe large-scale data for either mixed or classified suspensions. Matz (1966) correlated most of Bennett's reported data by utilizing the Rosin-Rammler (R-R) relationship. He found that γ varied from 1.9 to 4.7 in the R-R equation. Witte and Voncken (1971) compared both the R-R and the CV methods of describing particle-size distributions. They recognized that each method is characterized by two parameters, one describing average particle size and the other describing width of the distribution. Witte and Voncken observed that industrial data are usually quite well represented by the R-R method and favor this technique.

It should be emphasized that all of the two-parameter CSD models discussed above are merely descriptive and have no predictive value unless the empirical parameters can be correlated with operating conditions and/or process configuration. By comparison, population balance models have the process configuration and system kinetics nested in the equations and are useful for predictive studies, if information defining the system kinetics is available.

INDUSTRIAL PRACTICE

A considerable amount of skepticism is naturally expressed by crystallization practitioners concerning the unbridled use of parameters generated in well-controlled small-scale equipment to predict performance of industrial-scale crystallizers. Many factors contribute to the nonideal behavior of industrial crystallizers, and not all of these can be easily explained. This section first reviews available design models and then examines a cross section of reported pilot- and industrial-scale experimental endeavors that attempt to analyze the vagaries of industrial crystallization.

Design Models

Few really useful design procedures for industrial crystallizers have existed until recently. Randolph (1971) reviews and comments on the progression of crystal distribution analysis which includes modeling of fines removal (Randolph, 1963), product classification (Saeman, 1956; Randolph, 1965; Han and Shinnar, 1968), clear liquor advance (Randolph, 1965; Hulburt and Stefango, 1969), size-dependent growth rate (Bransom, 1960; Abegg et al., 1968; Canning and Randolph, 1967), crystal fracture (Randolph, 1969), and staging (Randolph, 1965; Larson and Wolff, 1971). Table 2 is a compilation of crystallizer design studies reported in the literature and shows the diversity of crystallizer configurations and analytical treatments now available to the designer.

Some of the design models presented assume that the parameters are obtained by independent laboratory measurement; others are formulated in such a way that parameters are extracted directly from bench- or pilot-scale crystal-size distribution data. In either case, the recent trend is to describe the kinetics by phenomenological equations. Although not totally satisfactory, this approach overcomes the formidable obstacles of describing growth and nucleation from a molecular standpoint and has resulted in the development of useful techniques for describing and analyzing industrial crystallization operations.

As evident from Table 2, the well-mixed crystallizer has received much recent attention. Manipulation of mixed-suspension bench-scale or pilot data to obtain sufficient kinetic data for scale-up to well-stirred industrial units has been described in detail in the literature. The success of this design procedure depends upon the closeness of approaching steady-state back-mixed conditions in the industrial unit and the accuracy of the designer in predicting primary and secondary nucleation effects in a large operating unit.

Randolph and Larson have focused their attention on representation of a population balance for the MSMPR crystallizer and then generalized the mathematical treatment to include the many techniques for varying crystal residence time inside the crystallizer as formalized by the algorithms of the first part of section 4. Crystallizer dynamics can also be rigorously analyzed using the population balance technique. Randolph and Larson (1971) show how crystal-size distributions in complex crystallizer configurations can be expressed in terms of functionals of the crystal distribution obtained in a well-mixed crystallizer. Table 2 summarizes many of these studies. For the special case of growth not a function of crystal size, that is, McCabe's Delta Law holds, and defining n^0 as the population density of embryo size crystals (and assuming the size of these crystals to be close to zero), the well-known MSMPR exponential population distribution for a perfect mixed-suspension crystallizer holds. Power-law forms for nucleation/growth rate kinetics were used in their development. These empirical forms are given as

$$n^0 = k_N G^{i-1} \qquad \text{Magma-independent secondary nucleation} \qquad (5.1)$$

or

$$n^0 = k_N G^{i-1} M_T^{j} \qquad \text{Magma-dependent secondary nucleation} \qquad (5.2)$$

and have often proven useful in the correlation of secondary nucleation data. In principle, the relative nucleation/growth rate kinetic order i can be obtained simply by varying mean crystal residence time. Thus, sufficient kinetic information for scale-up can be obtained directly from bench-scale crystal-size distributions. Once kinetics can be described for a particular system, calculations can be carried forward, working through mass balance relationships to describe a wide variety of situations.

Crystallizers that attempt to classify crystals in a suspension chamber (Oslo-Krystal-Jeremiassen) present rather difficult analysis problems and have not been

TABLE 2. CRYSTALLIZER DESIGN MODELS

Crystallizer type	Treatment/comments	Investigators
1. Continuous stirred tank	Mixed product withdrawal	Saeman (1956), Randolph (1965), Bransom (1964), Nyvlt (1971), Randolph and Larson (1971)
Continuous stirred tank	Product classification	Saeman (1965), Sherwin et al., Nyvlt (1971), Randolph and Larson (1971)
Continuous stirred tank	Fines dissolution	Randolph and Larson (1971)
Continuous stirred tank	Initial seeding	Randolph and Larson (1971)
Continuous stirred tank	Clear liquor advance	Randolph and Larson (1971)
Continuous stirred tank	Combination of above	Randolph and Larson (1971)
2. Batch stirred tank	Cooling or isothermal evaporation	Nyvlt (1971)
Batch stirred tank	Initial seeding	Nyvlt (1971)
Batch stirred tank	Controlled nucleation	Nyvlt (1971)
Batch stirred tank	Variable volume—(constant growth)	Randolph and Larson (1971)
3. Classifying crystallizer (Krystal-Oslo)	Initial seeding	Bransom (1964), Nyvlt (1971), Pulley (1962)
4. Parallel flow crystallizer	Supersaturated feed (no additional supersaturation)	Nyvlt (1971)
5. Continuous stirred tanks in series	Nucleation in first stage (no additional nucleation)	Robinson and Roberts (1957), Randolph and Larson (1962), Nyvlt (1971), Randolph and Larson (1971)
Continuous stirred tanks in series	Nucleation at same rate in all stages (Equal volume stages)	Nyvlt (1971), Randolph and Larson (1971)
Continuous stirred tanks in series	Allocated production and retention times	Randolph (1965), Randolph and Larson (1971), Wolff and Larson (1971)
6. Others		
Combined classifying and stirred		Nyvlt (1971)
Double crystallizers—twinned		Nyvlt (1971)
Combined classification and staging	Gives maximum narrowing of CSD	Randolph et al. (1968)

treated analytically as extensively as have well-mixed vessels. Pulley (1962), in a three-series article, presented equations analyzing the hydraulics and crystallization characteristics of a fluidized bed of crystals seeded by crystals at the top and suspended in an upward flow of supersaturated liquor, namely, application to the Krystal crystallizer. His assumptions were: no nuclei formation in the suspended crystal bed, no attrition or agglomeration, ideal fluidized bed, plug flow of liquid, crystal growth rate linear with supersaturation, and growth not a function of crystal size. Subsequently, he developed equations characterizing a dense fluidized bed. Minimum crystal size, seed crystal feed rate, and supersaturation depletion ratio are design choices and must be specified. The weakness of Pulley's design procedure is the arbitrary nature of selecting seed crystal rates and supersaturation depletion. Assumption of no nucleation from secondary sources within the suspension is also a gross simplification.

Application of well-stirred crystallizer concepts to segregated crystallizers is dubious, although it is being done. It is difficult to imagine a forced-circulation or a compartmented crystallizer performing wholly back-mixed; however, with very high recirculation rates this could be disputed. Other types of analysis for classifying crystallizers seem more appropriate, and Pulley (1962) analyzed the problem by assuming ideal classification in the suspension chamber. These design procedures are difficult to apply since they require independent determination of linear crystal growth rate (and associated rate constant), minimum nuclei size, nuclei formation rate, and maximum permissible liquid supersaturation. Alternately, the entire deviation of residence-time distribution from the MSMPR case due to particle classification in the bed can be accounted for as a deviation from the ideal mixed-suspension with nonideal removal (Randolph and Larson, 1971, Ch. 8).

Bransom (1964) developed equations describing an ideal classifying crystallizer. Allowing the growth rate dependence on crystal size to be either zero or first order and assuming the amount of supersaturation decay, he showed that for high supersaturation depletion and first-order growth rate dependence on crystal size, a greatly increased holdup was required. Bransom also concluded that for a fixed-volume crystallizer, nucleation rate control is critical and that the maximum inlet supersaturation is fixed by its effect on rate of nucleation. He also remarked that secondary mechanisms must be considered as sources of nuclei; these mechanisms are not yet thoroughly understood.

A recent publication by Nyvlt (1971) presents the derivation and use of design equations for a wide variety of crystallizers. Many of these design equations, he claims, have been utilized successfully in industrial crystallizer design. Nyvlt does not interrelate growth and nucleation kinetics but handles them as separate effects, nor does he account for secondary nucleation phenomena in the nucleation kinetics expression. The following equation derived from mass balance considerations formed the basis for the development of his design relationships:

$$\epsilon \frac{ds}{dt} = s^* - k_1 A_1 s - k_2 s^a \qquad (5.3)$$

where the first term on the right s^* represents the rate of supersaturation generation due to cooling, evaporation, etc., and the second and third terms are models representing depletion rate of supersaturation by growth and nucleation, respectively. Linear crystal growth rate G is related to the coefficient of crystal growth k_1 by the relationship:

$$G = \frac{2k_1 s}{\rho} \qquad (5.4)$$

Equation (5.3) is an unsteady state supersaturation balance and is utilized with a linear growth rate expression to derive relationships describing mean crystal size for a wide variety of steady and unsteady state crystallizer operations. Kinetic parameters k_1 and k_2, surface area A_1, and 'a' must be obtained from independent laboratory experiments. The minimum stable nuclei size also appears in many of Nyvlt's equations and must be determined experimentally. If one has these parameters, crystal distribution can be computed for a wide variety of situations. Nyvlt makes no claim to present an exact description of the crystallization process but suggests that his models are sufficient to reduce substantially the risks involved in designing crystallization equipment.

The design theories presented for mixed and classified crystallizers do not clearly indicate the preferred mode of crystallization, that is, cooling versus evaporation, where a choice exists. Nyvlt has included consideration of the method by which supersaturation is generated in his development but has not expanded this treatment into guidelines for choosing the preferred technique. In the same vein, guidance for selection of crystallizer configuration must also be deduced by the designer. Nyvlt claims that the throughput of an ideal classified-suspension crystallizer is appreciably lower than a mixed-suspension crystallizer but admits that common practice includes provision for excess fines removal and suspension circulation, thus giving higher performance.

Because of the difficulty of accurate parameter determination and the anomalous behavior of many large-scale crystallizing systems, crystallizers designed from first principles are rare. A theoretical framework now exists, however, and explanation of crystallizer behavior can in many cases be given a scientific basis.

The MSMPR crystallizer, exemplified by the draft-tube-baffle (DTB) design can be modeled with reasonable confidence. The well-known crystal population distribution has been verified in numerous systems and can be used for design as well as for back-calculating fundamental crystallization parameters; nevertheless, careful bench-scale to pilot-scale to industrial size kinetic analysis is rare in the reported literature. An exhaustive investigation of the closeness of fit of experimental data to predict crystal-size distribution for crystallizers with fines dissolution and/or classified product withdrawal is needed.

Analysis of Operating Systems

Use of mathematical models for designing industrial crystallizers has lagged other chemical processing operations because of the complexities of rationally describing and interrelating growth and nucleation kinetics with the process configuration and mechanical features of the crystallizer. Crystallizers have traditionally been designed by scale-up of pilot- or bench-scale data, taking care to control supersaturation levels and to maintain similar crystal residence time, vessel configuration, and hydraulic regimes. System kinetics, even though controlling the ultimate crystal-size distribution, were thought to be subjects better relegated to the laboratory and were rarely used for crystallizer design. This section reviews published literature describing operation of large scale or pilot crystallizers where authors have attempted to qualify or, in some cases, quantify the behavior exhibited.

Bennett and Van Buren (1969) utilized the mixed-suspension population balance equation with the expression $n^0 = k_N M_T{}^j G^{i-1}$ to compare experimental urea crystallization data from large (25,000 gal.) and small (200 gal.) DTB units against 12,000 and 175 gal. forced-circulation units. Surprisingly, he found that the kinetic order i was less than unity and concluded that mechanical stimulus and attrition are, in fact, controlling the intrinsic nucleation rate. (If nucleation excursions are caused by extraneous factors not accounted for in a nucleation kinetics correlation, mass balance constraints will force a value of $i = -3$ in the correlation.) Increasing residence time in such systems does not result in larger crystals since nucleation due to secondary effects dominate and since lowering of supersaturation driving forces decreases growth rate more than nucleation. Bennett (1969) reported the use of the population balance technique to obtain nucleation rate data for a continuous forced-circulation sugar crystallizer. Sugar solutions are relatively difficult to nucleate, and Bennett measured nucleation rate variation caused by the mechanical stimulus of the circulation pump and internal stirrer.

Canning (1971) depicts the usefulness of the population density plot as a tool in analyzing industrial crystallizer data. Canning encountered and identified the following causes of deviations from the ideal well-mixed crystallizer: (a) Differential fines dissolution: Intentional or unintentional fines dissolution causes upward curvature in the small crystal end of the population density versus particle size curve; in effect, this represents lower than average fines growth rates. (b) Diffusion limited growth: When growth is a function of particle size (generally attributed to diffusion limited growth rates), the population density plot will be distinctly convex downward. (c) Classification: Intentional or unintentional classification of product will cause a downward break in the population density plot at the large particle end. (d) Crystal breakage: A concave downward plot is theoretically obtained if crystal breakage is a significant factor. Screening and particle counting difficulties, such as screen blinding and particle agglomeration or attrition, may also contribute to unusual forms of CSD population curves.

Ayerst et al. (1969) conducted a study of a pilot-scale forced-circulation evaporative crystallizer. A MSMPR model was utilized for analyzing the data from their forced-circulation unit. A growth rate model of the form

$$G = k_1 s^m (L_m)^z \qquad (5.5)$$

was utilized in their analysis. Size distribution was characterized by two parameters, L_m the crystal size after one mean residence time and z the crystal growth dependence on mean particle size. The parameter L_m was found experimentally, and z was back-calculated. The parameter z was found to be very small, between -0.2 and 0.1. Computed curves agreed quite well with experimental data. They claim product crystals from a forced circulation crystallizer follow a size distribution which is in agreement with MSMPR theoretical distribution and can be effectively described by mean aperture and coefficient of variation. Coefficients of variation (CV) were mainly within the range of 45 to 56%. They admit the difficulty in designing for a desired crystal distribution from first principles because of the difficulty in predicting values of independent variables, such as supersaturation and slurry density.

Laurich (1969) emphasizes the importance of designing to avoid excessive nucleation from occurring in the first place. He notes that with flat or inverted solubility curves fine crystals cannot be destroyed by segregation and that dissolving and nuclei control must be by supersaturation control. Also, controlling CSD by nuclei dissolving may place undue strain on system auxiliaries—particularly in cooling-type applications. Laurich claims the objectives in crystallizer design are: (a) control of degree of supersaturation, (b) sufficient contact time to desupersaturate solution, and (c) sufficient residence time for crystal growth.

Nauman and Szabo (1971) describe the steady state performance of a continuous crystallizer with nonselective fines destruction, for example, by withdrawal, heating, and returning a portion of the magma. When crystal and mother liquor densities are similar, segregation of fines by elutriation techniques is not possible and differential dissolution is a technique utilized to remove excess nuclei; however, their analysis contradicts their observation in showing a detrimental effect on crystal growth by utilizing a nonselective fines trap. Nauman (1971) analyzed the usefulness of a selective fines trap and concluded it can give dramatic improvement in crystallizer performance. He suggests an explanation of the phenomena is that fines dissolution in effect allows operation at higher supersaturations than might otherwise be possible. The observed usefulness of nonselective fines removal could be explained if crystal dissolution rate were a strongly decreasing function of increased crystal size. This is consistent with the known variation of particle solubility with size.

Caldwell (1961) in his discussion of draft-tube-baffle crystallizer operation emphasizes that crystal-size distribution is strongly influenced by removal of excess nuclei or fines, by circulation of growing crystals to the zone where supersaturation is produced, and by maintenance of a high solids density in circulation. Data are presented revealing a moderate dependence of crystal-size distribution upon suspension solids concentration. Caldwell also points out that another potential source of nucleation occurs at the feed location and that care must be taken to properly enter feed material. He states that heat transfer occurs more quickly than mass transfer and that the hotter stream may nucleate excessively when added to a colder stream. The benefits of starting up a crystallizer with established suspension solids density is also discussed.

Palmer (1969) determined coefficient of variations for crystallizers with suspension chambers (Oslo/Krystal) and indicated that either classified ($CV \cong 20$) or mixed ($CV \cong 50$) crystal-size distributions could be obtained depending on the mode of operation of the Oslo unit. If a high proportion of crystals circulate, Palmer claims that well-mixed (MSMPR) conditions are approached. Operation at low capacity and large crystal sizes indicate near-classified suspension operation. Palmer states that precise calculation of classified-bed crystallizer performance is not practicable, that optimal designs for similar systems have gradually evolved from experience, and that the basis of industrial designs is necessarily semi-empirical.

Witte and Voncken (1971) observed that flow patterns in an Oslo crystallizer disturb the classification action in the base. They claim that insufficient classification results in small crystal production. In fact, this effect must be attributed to some other phenomenon (for example, poor supersaturation distribution, excess secondary nucleation, poor removal of fines, etc.) as classification per se can be shown to always lower the mean size produced compared to MSMPR operation. Witte and Voncken modified the base section of the bed so that two separate beds were formed, each with a fairly intense circulation pattern. They reported that larger and more uniform crystals were produced after the modification.

Houghton (1965) reviewed nucleation, growth, and size-distribution theories. He discussed several types of commercial crystallizers with respect to their ability to provide a proper environment for production of large crystals. Among these were circulating magma, forced circulation, and circulating liquor crystallizers. Houghton claims that mixed-suspension, small-scale results can be extrapolated more accurately than forced circulation data. Also, he stated that pilot-plant data obtained by skilled personnel provides the best guide to full-scale design.

Lidster (1969) reported an interesting and candid case study involving selection of industrial crystallizer suppliers and operation of the equipment supplied by the successful bidder. Lidster emphasizes the difficulties that may follow the design of a crystallizer unless designed and built on pilot-plant data by experienced designers. He concluded that in all things, and crystallization in particular, there is no substitute for knowledge and experience.

In unpublished reports Union Carbide (1967) conducted bench- and pilot-scale tests using ammonium sulfate solutions to test procedures for analysis, scale-up, and operation of crystallization processes. Crystallization of ammonium sulfate from water solution was first studied in a bench-scale 2-liter-cooling, continuous, well-mixed crystallizer. Slurry density and residence times were varied and population density data obtained by sieve analysis. A high variance in the nucleation rate was obtained in the bench-scale apparatus, making determination of kinetic order unreliable; however, at fixed slurry concentrations, plots of growth rate and nucleation rate versus production rate (which is a measure of supersaturation) were represented by linear and second-order relationships, respectively. The data from small vessel tests showed dramatically the advantage of operating at a high solids concentration.

The crystallization of ammonium sulfate was then studied in a 70-gal. circulating suspension, draft-tube crystallizer. An attempt to duplicate the cooling crystallization mode of operation was unsuccessful because of gradual fouling of the cooling surfaces; thus, the evaporative mode was utilized. A simplex experimental design procedure was used with slurry density, temperature, residence time, and feed concentration as independent variables. Measured responses included production rate, crystal growth rate, and nucleation rate. It was observed that neither the operating temperature nor the feed concentration had much effect on the size distribution of the product. This would be expected in a Class II (high yield) back-mixed system. Plots of growth and nucleation rates both varied linearly with production rate, and nucleation rate appeared to be an increasing function of slurry density. Strong secondary nucleation effects were evidenced in the evaporative crystallizer that were not present in the bench-scale apparatus.

Kern (1973) reported the kinetics of an unspecified chemical system in well-mixed miniplant and in pilot-plant equipment. He utilized the indirect cooling crystallization mode of operation in the bench-scale equipment and evaporative mode in the large. Contrary to the remarks in the preceeding paragraph, the kinetics of this system were unchanged by varying equipment size or mode of generating supersaturation; thus, the use of kinetic parameters generated in small-scale equipment can be reliably used for scale-up computations. (The kinetics of the industrial scale crystallizer have not yet been determined.)

The ability to predict crystal behavior in complex systems is ahead of our ability to manipulate crystal and liquid residence time. Generalizations of the MSMPR equations have been made to predict CSD with arbitrary process configurations and kinetics; however, there is no guarantee that a required process residence-time distribution can be physically implemented in order to produce a given customized product CSD. Size distribution in cascaded crystallizers, for example, multiple effect evaporators, can be computed if kinetic parameters are known or assumed. No investigator, however, has reported comparative data showing the applicability of utilizing these kinetic parameters for predicting complex crystallizer behavior. And no definitive technique exists for predicting size-dependent growth rates in systems that exhibit strong diffusion controlled crystal growth. If the specific size-dependency of growth rate is known, the effect on crystal-size distribution in a given crystallizer configuration can be computed. Quantitization of secondary nucleation effects in industrial crystallizers is rapidly moving forward, but much is yet to be learned concerning the complex mechanisms that create nuclei.

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NOTATION

A_1 = surface area of crystals per unit volume
a = nucleation rate order in Equation (3.11)
B^0 = nucleation rate
$B(L)$ = particle birth function at size L
b = rate of cooling
C = solute concentration
δC_i = solute resource term in Equation (4.2)
$C_p(L)$ = withdrawal function
C_s = saturation concentration
$C_w(L)$ = withdrawal function
CSD = crystal-size distribution
CV = coefficient of variation
$\mathfrak{D}$ = solute molecular diffusivity
$D(L)$ = particle death function at size L
G = linear particle growth rate
G^0 = growth rate dependence on supersaturation
$g(L)$ = crystal growth rate of size L
i = nucleation sensitivity parameter
j = suspension density sensitivity parameter
K = constant in Equation (3.12)
k_a = shape factor relating area to size squared
k_g = constant in growth rate equation
k_r = particle integration rate constant
k_N = constant in nucleation kinetics equation
k_v = volumetric shape factor
L = particle size
$\overline{L}$ = arithmetic mean particle size
L_m = crystal size after one mean residence time
$\delta(L)$ = size dependent diffusion film
M = cumulative crystal weight distribution
MSMPR = mixed-suspension, mixed-product-removal
M^0 = mass rate of nucleation
m_j = jth moment of population distribution
N = cumulative crystal number distribution
n = population density of crystals at size L
n^0 = population density of zero size crystals (nuclei)
P = crystal production rate
Q = volumetric feed and discharge rate
$Q(L)$ = withdrawal rate of crystals of size L
R = index of volumetric flow through fines system
s = supersaturation defined as $C - C_s$
s^* = rate of supersaturation
ΔT = degrees of supercooling
$\Delta T_{\max}$ = maximum allowable supercooling
t = unit time
V = crystallizer volume
v = particle volume
W = dimensionless cumulative mass distribution
ΔW = weight fraction crystals in size range ΔL
Z = index of volumetric flow-through product classification system
z = crystal growth dependence on crystal size [Equation (5.5)]

Greek Letters

γ = measure of crystal uniformity, Equation (4.12)
ρ = particle density
τ = holding time
σ = standard deviation
ϵ = factor defined by material balance

Subscripts

0 = outlet stream
i = inlet stream
T = total quantity

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Bubble-Free Expansion of Gas-Fluidized Beds of Fine Particles

Five different fine powders with average particle size of about 100 microns or smaller were fluidized with air over their respective bubble-free ranges of fluidization. Photographs taken through the front transparent wall of the column showed that the beds contained cavities and microchannels whose sizes were of the same order of magnitude as the particle size. It is shown that interparticle van der Waals and capillary forces play an important role in the bubble-free expansion of small particles. Measurements of bed expansion and average particle drag coefficients are consistent with the proposed role of interparticle forces.

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SCOPE

Fine catalytic powders, less than 100μm in size, are widely used in industry for fluid bed operations because of their high contact areas and favorable heat transfer rates. Contrary to beds of coarser materials, beds of fine particles can be bubble-free fluidized over a considerable range of superficial velocity and expanded to voidages as high as 0.60 to 0.65 before bubbles appear. This expansion of the dense phase may affect solids mobility in the bed, gas exchange processes, and particle renewal at heat transfer surfaces.

The problem of whether a bed of particles fluidizes in a particulate or aggregative manner has long been of concern to chemical engineers (Wilhelm and Kwauk, 1948; Trawinski, 1953). It has been suggested (Anderson and Jackson, 1964) that aggregative fluidization results from the instability of the state of uniform fluidization to small perturbations. However, Molerus (1967) has shown that not all gas fluidized beds are unstable, especially for low voidages, fine particles and low particle to fluid density ratios. The range of bubble-free fluidization found for particles smaller than about 100μm (Davies and Richardson, 1966; Rietema, 1967; Geldart, 1967; Rowe, 1969) is in general agreement with this conclusion. Very fine particles do not show particulate behavior, however (Baerns, 1966). Instead, heavy channeling prevails, probably because of pronounced interparticle forces.

The work described in this paper is an extension of earlier work (Massimilla et al., 1972) aimed at elucidating the structure and mechanisms of bubble-free gas fluidized beds.

CONCLUSIONS AND SIGNIFICANCE

Previous conclusions (Massimilla et al., 1972) regarding bubble-free fluidization of cracking catalysts have been shown to be valid for a number of different powders. In particular, it has been shown that bubble-free fluidized beds contain cavities and microchannels. Particles show little mobility, and average drag coefficients were higher and permeabilities lower than for comparable liquid fluidized beds. Expansion of beds of fine particles occurs primarily by the nucleation and growth of cavities or particle defects.

The above mode of bed expansion has been explained by considering the role of interparticle forces, in particular, van der Waals and capillary forces. These forces act to stabilize cavities and microchannels. The cavity growth mechanism of bed expansion probably occurs because of a broad distribution of interparticle forces due