

# Population Balance as a Tool in Analyzing Continuous Crystallizer Design

Thomas F. Canning

Kerr-McGee Chemical Corp.  
Trona, Calif.

## ABSTRACT

*Considerable progress has been made in the past decade in achieving an analytical description and understanding of crystallization processes through application of the population balance concept. A review of the application of the population balance in understanding crystallization is presented.*

*The size distribution of the crystal product (CSD) is generally of prime importance in the selection, design and modification of continuous industrial crystallizers. It is the interaction of crystallizer operating and design parameters upon both nucleation and growth rates that determines the resulting product CSD. Without knowing the effects of crystallizer parameters on both nucleation and growth, it is not possible to predict the effects upon CSD with confidence. Usually it is the sensitivity of nucleation to operating conditions that makes prediction from theoretical principles difficult. Current research is concentrating on secondary nucleation mechanisms. Each crystallization system is likely to respond differently to the empirical tried and true techniques developed in the past for correcting CSD problems. However, through application of the population balance, the needed kinetic data can be readily obtained in small, continuous bench-scale equipment operated over the same range of conditions and with the same feed materials as the full-scale crystallizer, whether new or existing. The methods for collecting the necessary kinetic data and for using the data to design new crystallizers or to modify existing crystallizers are reviewed.*

*Kinetics of the NaCl-ethyl alcohol system reported in the literature are used to illustrate methods for tailor-making a size distribution.*

## INTRODUCTION

The selection, design or modification of industrial crystallizers is most frequently determined by a need to con-

trol the crystal size distribution (CSD) of the product. The standard chemical engineering approach of applying heat and material balances cannot provide sufficient information to predict crystallizer product CSD. Since CSD is nothing more than the relationship between crystal numbers and sizes, some method of accounting for crystal numbers and sizes in a crystallizer would be desirable. Such a method has been derived by a number of people as far back as 1931 (Peet, 1931; Bransom, 1949; Saeman, 1956; and Robinson and Roberts, 1957). Then, about ten years ago the numbers balance was further dignified as a population balance and refined as a tool for describing crystallization systems (Randolph and Larson, 1962). Now, with energy, material and number balances and with appropriate rate equations, a crystallization system can be fully defined and equipment designed confidently to produce a desired CSD.

The preceding sounds as if crystallization technology were fully developed, but certain incompletely known factors still preclude complete understanding. Among these remaining complicating factors are such devious phenomena as multicrystal growth, agglomeration, chemical effects including habit modification, mechanical and other effects influencing nucleation, and multifarious other factors peculiar to individual systems. In spite of the many factors precluding complete understanding, the population balance provides a theoretical basis for a better understanding of crystallization and for a practical means of scale-up and design.

## THE POPULATION BALANCE

In an operating crystallizer the individual crystals remain as single, identifiable particles (as long as agglomeration and crystal cleavage are minor or nonexistent). The crystals may grow or even diminish in size in the case of a dissolver but will remain as individual particles. If a

suitable representation of the rate of appearance of new crystals or disappearance of older crystals is available, it is possible to keep a running account of all particles in the crystallizer. Such an accounting is called a population balance and as with heat and material balances results in a mathematical expression that characterizes some aspect of the system. The population balance then is useful in characterizing the size distribution of crystals in suspension. In order to get from a simple accounting of numbers to size distribution, growth rate,  $G$ , must be included.

### Population density

The mathematics of formulating a population balance in terms of a "continuous" variable representing a distribution of discrete particle is greatly simplified by introducing a statistical density function called the population density. This is a difficult term to visualize but represents the number of crystals in a given size range. Graphically, as in Figure 1, population density is merely the slope of the cumulative numbers vs size curve.

### The MSMPR crystallizer

The simplest crystallization system for applying the population balance is one comprised of a well-agitated vessel which is supplied with a solids-free stream at a continuous, steady rate and from which is removed at a continuous, steady rate a product stream having a crystal size distribution and solids concentration exactly the same as that in the crystallizer. This then is the ideal mixed

suspension, mixed product removal (MSMPR) crystallizer upon which the population balance concept has been based (Randolph and Larson, 1962, 1965 and 1971). Now, in addition to these conditions, if the crystallizer has been operating long enough at constant conditions to be at steady state, if crystals of all sizes grow at the same rate (McCabe's  $\Delta L$  Law holds) and have the same shape and if no gross crystal breakage occurs, then the population balance is given by the simple exponential equation

$$n = n^0 \exp(-L/G\tau) \quad (1)$$

where  $L$  = crystal size, the screen mesh size through which a crystal just passes, in microns.

$G$  = growth rate, microns/min.

$\tau$  = drawdown time, mins.

$n^0$  = nuclei population density, no./cm. crystal size/cm.<sup>3</sup> mother liquor, the boundary value of  $n$  at  $L = 0$ .

$n$  = population density at  $L$ , same units as  $n^0$

For a crystallizer that approaches the above constraints, the relationship between crystal size and population density,  $n$ , can be determined from a screen analysis of a representative slurry sample taken from the crystallizer operated long enough for the CSD to be at steady state. For each screen fraction the population density can be determined by:

$$n = \frac{\Delta W}{\Delta L} \frac{M_T}{\rho_c K_L (\bar{L})^3} \quad (2)$$

where  $\Delta W$  is the weight fraction of crystals found in the screen fraction  $\Delta L$  expressed in cm.,  $M_T$  is slurry density, in gms solids/cm.<sup>3</sup> mother liquor,  $\rho_c$  is the crystal density in gms/cm.<sup>3</sup>,  $K_L$  is a shape factor previously defined by McCabe and Stevens (1951), and  $L$  is the arithmetic mean crystal size in the screen fraction in cm.

If the logarithm of  $n$  is plotted against  $L$ , the resulting population density plot will be a straight line as in Figure 3. From the slope of the line,  $m = \frac{-1}{G\tau}$ , the growth rate can be determined (after converting to natural logarithms) by

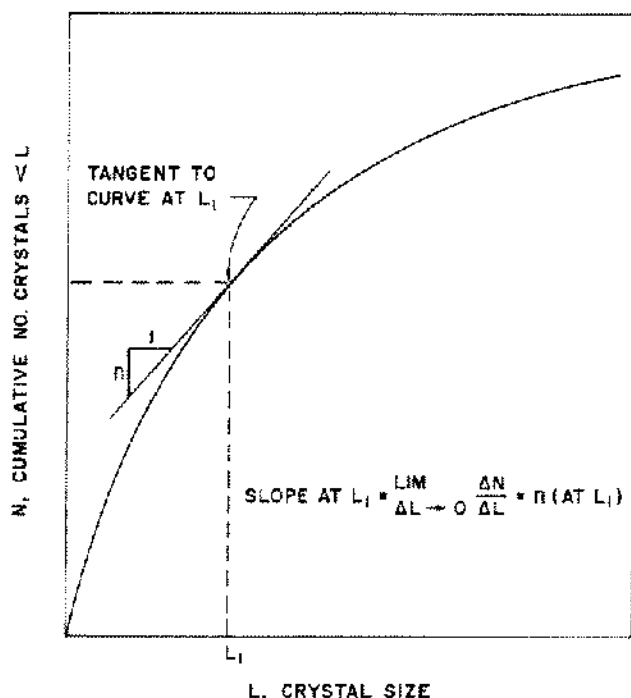


Figure 1. Cumulative Crystal Numbers Plot.

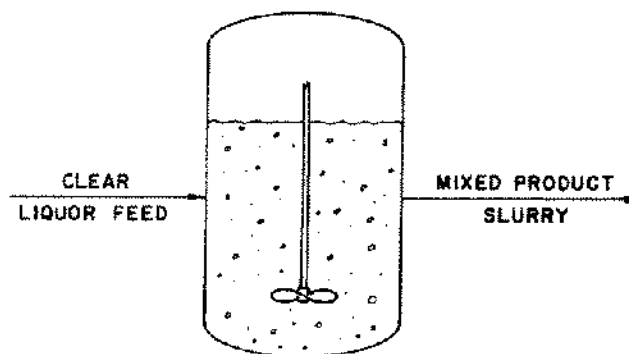


Figure 2. Ideal Continuous Crystallizer.

$$G = -1/m\tau \quad (3)$$

The product of  $n^\circ$  and  $G$  in consistent units is the actual nucleation rate,  $B^\circ$ , no./min./cm.<sup>3</sup>.

The intercept at  $L = 0$  is the nuclei population density,  $n^\circ$ . Thus, Equation (1) is completely defined.

The population density plot thus obtained is a very useful representation of the CSD obtained from an MSMR crystallizer. Other methods of graphically representing a CSD, such as direct plotting of screen analysis data on normal or log-normal probability paper, are useful in comparing CSD's qualitatively but cannot be used for anything but cut and try experimentation.

### Nucleation kinetics

A single population density plot characterizes in a convenient form the CSD obtained from a crystallizer but represents only a single point and tells nothing about the CSD at other conditions. Something must be known of the crystallization kinetics of the system. Crystallization kinetic data needed are the relationships between operating variables and both growth and nucleation rates. The population balance provides a means of determining growth and nucleation rates *simultaneously*. It is important that the effects of operating variables upon *both* nucleation and growth rates be known for anything to be learned concerning the effects of those variables upon product CSD. The driving force for crystallization is supersaturation, that incremental amount of solute remaining in solution above equilibrium solubility. It has been well established theoretically and experimentally that both nucleation and growth rates are individually and simultaneously influenced by

supersaturation. Growth rate has been shown to be a linear function of the second power of supersaturation. Nucleation, on the other hand, is a function of supersaturation raised to a power that is highly variable, ranging from 0 to +9 and higher for precipitation systems. The variability is due to the sensitivity of nucleation to a variety of factors also dependent upon supersaturation. The nucleation rate referred to here is the net rate of formation of particles that influences the product CSD and includes many effects other than homogeneous nucleation. If supersaturation could be measured precisely, nucleation and growth rates could be related directly to supersaturation. Supersaturation, however, is usually at such low levels that accurate measurement is difficult and usually impossible. Further, except for those few systems where supersaturation levels are high enough to affect the solute material balance, knowledge of the precise supersaturation is not necessary. Since both growth and nucleation rates are related to the same supersaturation they can be related to each other by a power function of the form

$$B^\circ = k_n G^i \quad (4)$$

or if nuclei population density is used

$$n^\circ = k_n G^{(i-1)} \quad (5)$$

where  $k_n$  and  $i$  are constants.

The constants  $k_n$  and  $i$  can be determined by obtaining experimental values of  $n^\circ$  and  $G$  at different supersaturations. A series of tests can be run in continuous laboratory bench-scale, pilot plant or commercial scale equipment keeping all conditions including feed composition constant except feed rate. Changes in feed rate change the drawdown time and hence supersaturation.

A convenient way of determining  $i$  is to plot  $n^\circ$  vs  $G$  on log-log paper. The slope of the line (it should be straight) will be  $(i - 1)$ . Some recent data developed at the University of Texas for NaCl salted out of brine with ethyl alcohol (Koros, 1972) has been reproduced in Figure 4 to illustrate. For the data of Figure 4 the kinetic equation was determined to be

$$n^\circ = 1.059 \times 10^7 G^{0.72} \quad (6)$$

The value of  $i$ , the nucleation sensitivity, provides a good indication of which direction the slurry residence time or drawdown time should be changed to obtain a desired change in CSD. Figure 5 illustrates in relative terms the effect increasing drawdown time would have on product CSD for crystal systems having various  $i$  values. For example, for a crystallizer system where  $i = 2$  normally producing a product with an average crystal size of 149 microns (100 mesh, U.S. Sieve Series), a six-fold increase in drawdown would result in an increase in product CSD to an average crystal size of 210 microns (70 mesh). Depending upon the specific objective, this increase may or may not be attractive. At any rate, either six times as

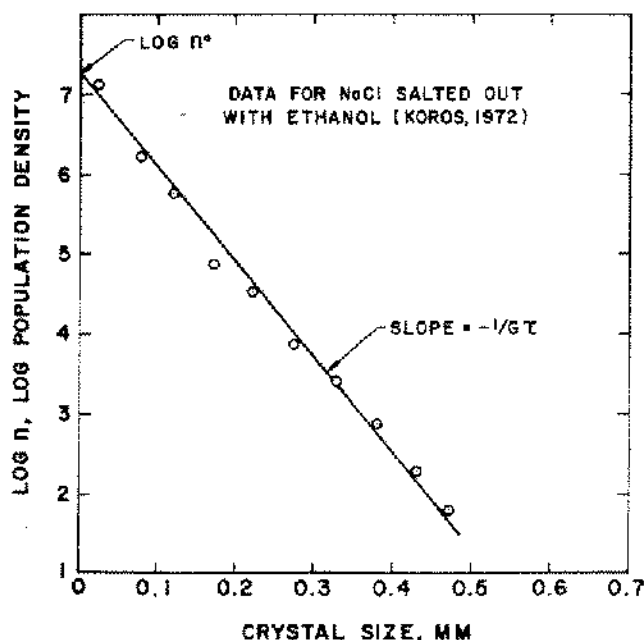


Figure 3. Ideal Population Density Plot.

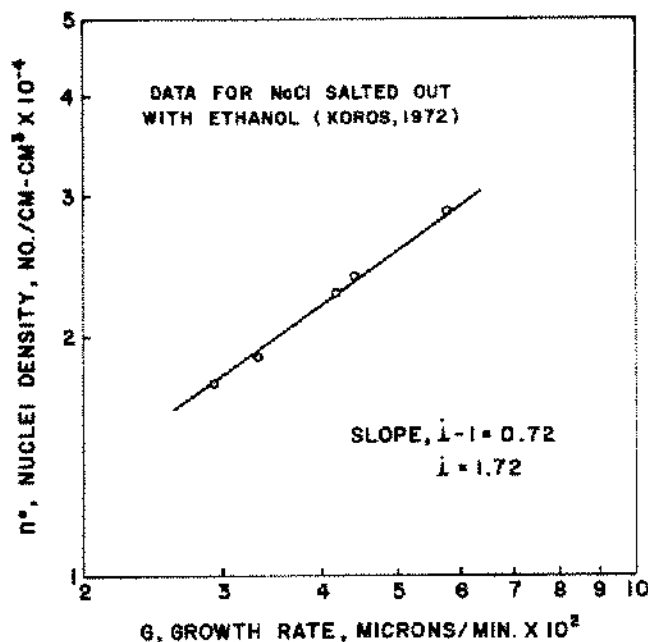


Figure 4. NaCl Nucleation Kinetics.

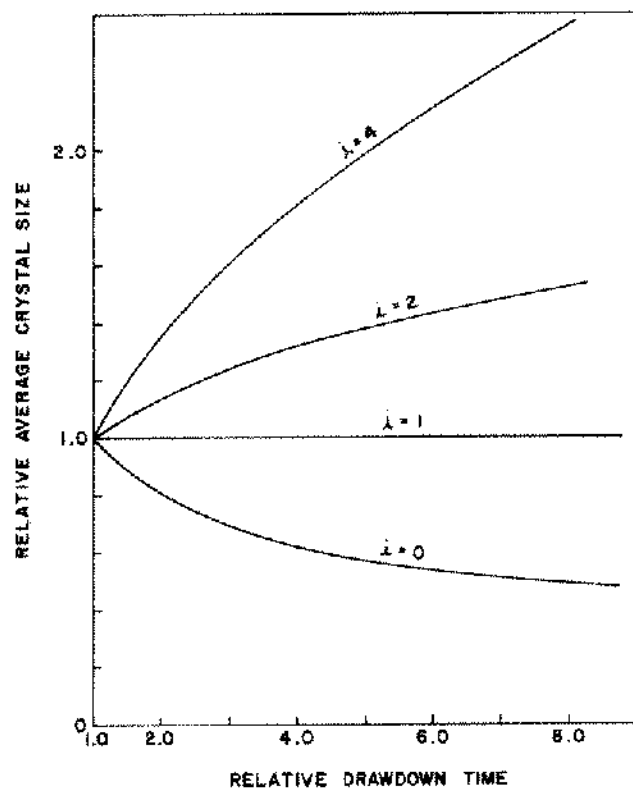


Figure 5. Effect of Drawdown Time on Product CSD at Various Nucleation Sensitivities.

much crystallizer volume must be supplied to maintain production capacity or the feed rate, and hence capacity, must be reduced to one-sixth.

In general, if  $i = 1$ , product CSD will remain unchanged with changes in drawdown. If  $i > 1$ , larger crystals will be obtained by increasing drawdown time. For the rather rare case where  $i < 1.0$ , larger crystals can be obtained by reducing drawdown times.

For some applications a change in drawdown time may be a practical means of attaining a desirable change in CSD. Drawdown time can be increased by either adding crystallizer volume with a fixed feed rate or by reducing feed rate with a fixed crystallizer volume. In most commercial processes, however, production rate is of utmost importance, so that an increase in drawdown in an existing crystallizer for the most general case where  $i > 1.0$  cannot be tolerated.

### APPLICATION TO CRYSTALLIZER DESIGN

The application of the principles discussed thus far can be illustrated through a hypothetical example. Assume that an actual crystallizer has been in operation in which sodium chloride is being salted out of an aqueous solution through addition of ethyl alcohol with a normal drawdown time of 25 minutes. The kinetic data obtained by Koros and coworkers (1972) summarized in Figure 4 and Equation (6) are assumed to have been obtained from our hypothetical crystallizer. Management has requested that the product CSD be changed to approach that for granulated vacuum pan salt as reported by Kaufmann (1960). We shall then consider the changes that must be made to the system to attain the desired new CSD.

The application of ethanol to salt out NaCl is probably not an economical or practical one for such a low-priced product but serves well for illustration. Also, some liberties have been taken with the data reported by Koros (1972) to simplify the discussion. First, the effects of varying agitation were removed by using only low turbulence data. Low turbulence with complete crystal suspension is consistent with good crystallizer design practice. Second, residual NaCl supersaturation was assumed to be negligible in the overall material balance. Their experiments demonstrated this to be an incorrect assumption, but is being made here to simplify the calculations for the following illustrative examples.

#### The simple mixed crystallizer

Generally, the objective in changing a product CSD is first to make it coarser and then to obtain more of the production within a narrow screen range reducing both the percentage of the large and the fine screen fractions. The exponential distribution obtained from the simple mixed crystallizer described above is usually too broad to meet narrow screen cuts. Shifting the CSD obtained from

a mixed crystallizer by changing the drawdown time as described above can reduce either the percent fines or coarse but in doing so will make the other end of the distribution even farther from the desired range. For the NaCl-ethanol system, an increase in drawdown time from 25 to 200 minutes would result in the CSD change shown in Table I. While the average size has been increased from 147 to 203 microns, it is apparent that the CSD would still be far smaller than the desired granulated vacuum pan salt. To make even this modest change required either an eight-fold increase in crystallizer volume or an eight-fold reduction in feed rate.

TABLE I  
Effect of an 8-Fold Drawdown Time Change on CSD

Drawdown Time, Min. Dominant Crystal Size, $L_d$	25 Min. 147 Microns	200 Min. 203 Microns	Granulated Vacuum Pan Salt
Cum. % Retained on			
10	—	—	0.0
20	—	0.2	2.4
30	0.2	2.4	28.4
40	2.9	13.3	61.6
50	14.7	36.1	81.2
60	25.3	49.5	93.7
70	37.9	62.7	97.0
80	51.5	73.2	—
100	64.0	81.9	—
Pass	36.0	18.1	3.0

It is quite apparent that increasing drawdown time produces only a modest improvement in CSD at a great sacrifice in capital or operating cost.

This example serves to illustrate two points: (1) Changing the supersaturation driving force by changing the drawdown time in a mixed crystallizer is not a particularly effective way of altering the product CSD. (2) The simple exponential distribution obtained from a mixed crystallizer is undesirable in those cases where a narrow screen cut range is required.

A convenient way of characterizing the narrowness of a distribution is provided by the coefficient of variation, C.V., which is defined as the ratio of the standard deviation to the mean on a weight basis.

$$C.V. = \frac{\sigma}{\bar{X}} \cdot 100 \quad (7)$$

For a single-stage, mixed crystallizer the product CSD will have a C.V. = 50. For many crystalline products appearance and handling properties are improved with a narrow CSD or C.V. less than 50. Table salt, for example, has a C.V. less than 20 with better than 90% between 40 and 60 mesh. To produce a salt of this size and C.V. would obviously require more drastic measures than provided by simple changes in drawdown time in a single mixed crystallizer.

Such other methods as increasing the operating temperature, reducing agitation to the minimum required for complete crystal suspension and other methods of changing the effective nucleation rate might raise the overall CSD but the C.V. would remain at 50. Four general methods are available for narrowing the CSD to reduce the C.V.: 1) batch crystallization, 2) crystallization in a multistage system with crystallizers arranged in series, 3) fines removal and/or destruction, and 4) classified product removal. The latter three methods are commonly used alone or in combination to narrow industrial CSD's. Batch crystallization will not be considered here.

### Staged crystallizers

In the case of serially staged crystallizers with nucleation occurring only in the first stage, Randolph and co-workers (1968) have shown that 22 stages would be required to obtain a C.V. of 20. In addition, the CSD, although narrower in range, would be much finer than from a single stage of the same total volume. For this paper, only fines removal and classified product removal will be considered further.

These two methods of narrowing a product CSD have been well-known and practiced for many years. However, they have been applied in empirical ways that have not always produced the desired results. Through use of kinetic data obtained by application of the population balance, fines removal and product classification systems can be specified to provide the necessary control of crystal numbers to approach a given product CSD much more closely than old empirical methods. It should be made clear that the population balance has introduced no new equipment or techniques, only the technology for better design and control of existing ones.

### Fines removal

Fines removal and/or destruction effectively increases the average particle size by removing a fraction of the smallest crystals thus reducing the number of crystals available to grow to product size. By reducing the number of crystals upon which the total crystallizable mass can grow, each remaining crystal must grow larger to accommodate the total mass to be crystallized. Since the area available for growth has been reduced, supersaturation will rise slightly to force the system to a higher growth rate and nucleation rate. More fine crystals must be removed than are created by the additional nucleation caused by the higher supersaturation for fines removal to effectively increase CSD. The nucleation sensitivity  $i$  is important in determining the fraction of fines it is necessary to remove.

A variety of ways are available for accomplishing fines removal and/or destruction including wet external classifiers, internal classifiers and external heating or cooling loops. For the NaCl-ethanol system another fines destruc-

tion method is available: distillation of ethyl alcohol. The size at which removal and/or destruction must occur and the fraction of the total number up to that size that must be removed are important in selecting the type of equipment to be used.

Fines destruction can be applied to the process wherein NaCl is produced by salting out with ethanol. Again assuming the CSD for granulated vacuum pan salt is desired, the largest size and the fraction to be destroyed that will provide the desired CSD can be determined. Without going into the mathematics, a classification size,  $L_c = 74$  microns and destruction of 70% of the crystals  $\leq L_c$  would produce the CSD shown in Table II. If the % of fines destroyed is increased to 90%, the CSD approaches the desired one more closely with more oversize being produced. Practically, a 90% destruction rate would require a circulation rate through the fines destruction device ten times the feed rate. In most systems this might be excessive.

A better way of comparing the two CSD's is by means of a population density plot as in Figure 6.

TABLE II  
Effect of Fines Destruction on CSD

Drawdown Time Classification Size Destruction Rate Cum. % Retained on	25 Min. 74 Microns 70% Calculated Product CSD's	25 Min. 74 Microns 90% Calculated Product CSD's	Granulated Vacuum Pan Salt
20	0.4	13.9	2.4
30	5.4	36.7	28.4
40	21.4	62.8	61.6
50	46.8	82.0	81.2
60	59.6	88.1	93.7
70	70.2	92.1	97.0
80	79.7	95.0	—
100	86.3	96.8	—
Pass	13.7	3.2	3.0

The break in the curve represents the change in drawdown time for the crystals smaller than that represented by the breakpoint. For example, the break at 74 microns (.074 mm) represents the classification size at which fines destruction was taking place. The crystals smaller than 74 microns are retained, on the average only 2.5 minutes before being removed and destroyed. The crystals larger than 74 microns are retained the nominal drawdown time of 25 minutes. The difference between the two curves shows how much the two CSD's differ.

If the percent destroyed were reduced to 88% at a 74 micron cut size, the two curves would coincide above 74 microns.

For practical purposes, the application of fines destruction to our hypothetical process provides a CSD close enough to the desired CSD. The excess +20 mesh fraction could be handled by means of a scalping screen, but for completeness coarse classification will be considered. The

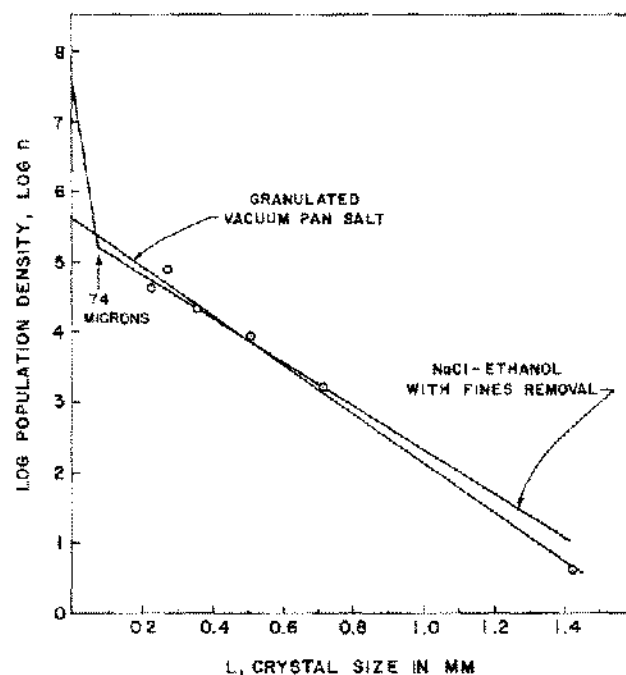


Figure 6. CSD Obtained with Fines Removal.

+20 mesh fraction could be reduced by adding a coarse classification device which would remove the coarse crystals as soon as they reached some critical size.

#### Classified product removal

Coarse classification could be accomplished in practice through use of wet screens, rake classifiers, cones, or similar devices. These devices would serve to separate the coarse crystals from a circulating loop above some design classification size. The crystals smaller than the classification size would follow the liquor. That is, the fine crystals would report to the oversize along with the entrained mother liquor in the same ratio of solids to mother liquor as in the feed to the classifier. In effect, their residence time would not be altered. The coarse crystals would be removed at a higher rate thus reducing their retention time.

Mathematically this additional step was added to the model of the NaCl-ethanol system to predict the effect on product CSD. The results are presented in Table III and plotted in Figure 7.

Obviously this is not a perfect fit and further adjustment of the coarse cut size and rate of removal would be necessary to approach the optimum for duplicating the vacuum pan salt CSD. The large number of trial and error calculations required can best be solved by computer. Suitable computer programs are available to do this job.

#### Crystallizer configuration

The crystallizer system required to produce a NaCl CSD approaching that of vacuum pan salt by salting out with ethanol would appear schematically like that shown

TABLE III

Effect of Fines Destruction and Coarse Classification

Drawdown Time	50 Min.
Fines Classification Size	149 Microns
Destruction Rate	80%
Coarse Classification Size	500 Microns
Recirculation Rate	50%

Cum. % Retained on	Calculated CSD	Granulated Vacuum Pan Salt
20	1.3	2.4
30	16.3	28.4
40	53.8	61.6
50	75.0	81.2
60	81.6	93.7
70	86.1	97.0
80	89.0	—
100	90.8	—
Pass	9.1	3.0

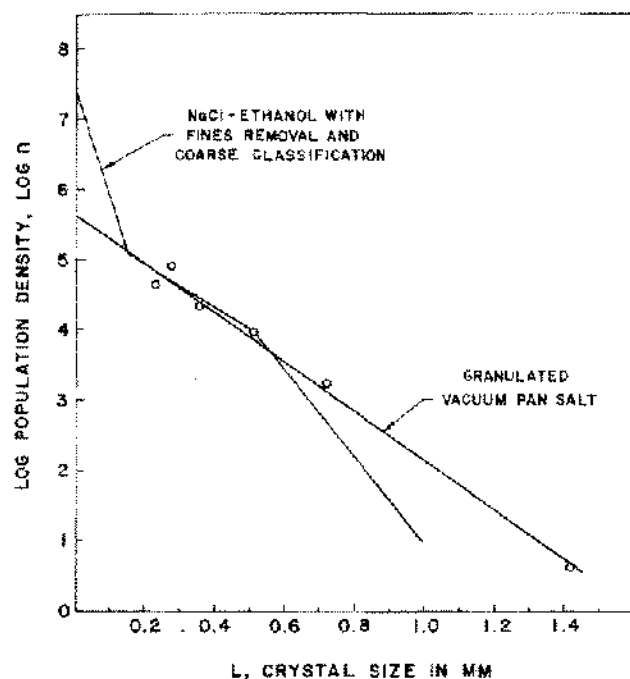


Figure 7. CSD Obtained with Fines Removal and Coarse Classification.

in Figure 8. Most single unit commercially available crystallizers do not have the flexibility to handle the classification requirements of the proposed system. Such a system would have to be custom designed and built. The components are not expensive, however, and with sufficient design data of the type described here design of such a unit is quite feasible.

### SUMMARY

The population balance approach provides a much more rigorous method of attacking crystallizer design

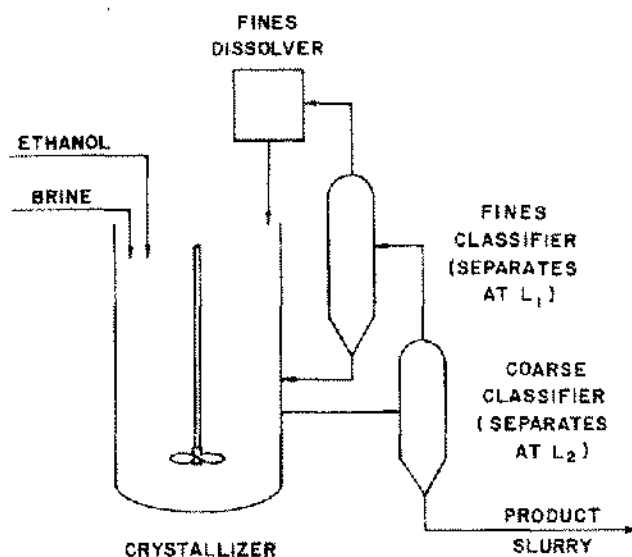


Figure 8. Schematic Crystallizer System for the NaCl-Ethanol Process.

problems than has been available in the past. Through an example, the application of population balance to the design of an NaCl crystallizer in which NaCl is crystallized from brine by salting out with ethanol is demonstrated. While perhaps of little commercial importance, the example is adequate for demonstration. The mathematics involved in the analysis has been purposely omitted for simplicity of presentation. Adequate discussions of the mathematics have been presented elsewhere (Randolph and Larson, 1962, 1965 and 1971).

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