

# Contact Nucleation in Salt Crystallization

R. C. Bennett

Swenson, Division of Whiting Corporation  
Harvey, Illinois

## ABSTRACT

*The change in crystal size of the evaporator pan salt with changes in circulation pump speed are explained from the standpoint of modern crystallization theory for tests run in pilot scale equipment.*

## INTRODUCTION

The production of sodium chloride, potassium carbonate, sugar (Bennett, 1969), urea (Bennett and van Buren, 1969), sodium sulfate and many other inorganic and organic chemicals is commonly achieved in forced circulation crystallizers employing either adiabatic or controlled evaporation. The distinction between an evaporator and a crystallizer may seem somewhat arbitrary in many situations however, for purposes of this discussion, an evaporator which produces a solid phase at constant temperature by means of evaporation will be called an evaporative-crystallizer.

Since 1962 the theoretical size distribution (Randolph and Larson, 1962) of the product expected from a forced circulation crystallizer has been derived assuming only that the crystallizer is thoroughly mixed, producing the equilibrium size distribution and that the growth follows the Delta L law of McCabe. The Amer. Inst. Chem. Engineers (AIChE) has published three bound volumes of papers dealing with various aspects of the theoretical crystal size distribution under various conditions in crystallization equipment. These are symposium volume Numbers 95, 110, and 121. Drs. Randolph and Larson, the earliest workers in this field, have written an excellent book which contains most of the important theoretical information. Chapter 4 deals particularly with the type of equipment discussed here.

Drs. Randolph and Larson (1971) developed the concept of a numbers balance to deal with systems of this

general type. They introduced the concept of a term called population density,  $n$ , which represents the number of particles per unit length per unit volume of slurry. For an unseeded, forced circulation crystallizer operating without product classification this population density is:

$$n = n^0 e^{-L/GT} \quad (1)$$

where  $G$  equals the growth rate and  $T$  equals the retention time, which for a system of this type is the volume divided by the discharge rate. The nucleation rate can be calculated directly from this information and is:

$$B^0 = n^0 G \quad (2)$$

For this system a plot of the natural log of the population density versus  $L$  for a representative sample should be a straight line. The intercept at size  $L = 0$  is  $n^0$ . The slope of the line  $= -1/GT$ . It is important to recognize that this straight line indicates that the assumed conditions are fulfilled. Deviations from this line do not invalidate the basic concept of the population balance, but indicate the nature and extent of the deviations.

While the particle size distribution may be calculated from the population density it is perhaps more useful to recognize that the coefficient of variation for a forced circulation system operating at equilibrium should be 50%. The coefficient of variation C.V., is defined as

$$CV = \frac{PD_{16} + PD_{84}}{2PD_{50}} \times 100 \quad (3)$$

The particle diameters (PD) are the intercepts corresponding to the cumulative weight plotted on a log probability scale. It is important to point out that in this discussion we are talking about the coefficient of variation in a crystallizer where there is not a classified discharge.

In salt equipment it is quite common to include a pendant elutriation leg beneath the crystallizer which classifies the discharge product. Such a leg distorts the crystal size distribution both in the body and out of the leg.

It is also important to point out that in the relations discussed above the crystal size distribution is characterized as a function of the growth rate, nucleation rate and retention time. These theoretical relations do not include the effects, if any, of the crystallizer on the nucleation or growth rates.

In a previous paper (Bennett, 1962) the results of a large number of systems were reported along with their coefficients of variations. In general these coefficients were lower than the 50% expected in a theoretical mixed suspension system of the forced circulation type. Attrition and segregation during growth in the actual equipment were given as the probable causes for the deviations.

Historically (Young, 1911; Buckley, 1951) nucleation was known to be caused by mechanical shocks in supersaturated solutions. The mechanical effects of changes in circulating pump speed and the introduction of ultrasonic energy (Van Hook, 1961) into a crystallizer which is supersaturated can cause increased nucleation with many products. Experiments by the author confirmed that sodium chloride was susceptible to nucleation from both of these causes.

In 1969, McCabe and his co-workers (Clontz and McCabe, 1971) at North Carolina State University reported before the AIChE on a phenomena which they called contact nucleation. They were able to measure, by very clever experimental procedures the actual number of nuclei produced by striking a crystal with a hammer under controlled conditions. They also measured the nuclei produced by contact when striking two crystals together under controlled conditions. Not only was the degree of supersaturation in the solution flowing past the crystal measured, but also determined were the actual striking force and the area of contact. From this they developed relations which basically indicated that the number of nuclei per contact when a crystal is struck by an anvil is proportional to the energy of contact and the supersaturation. A similar finding was made when crystals are struck with crystals except the degree of nucleation was higher. Based on this work it is clear that some technique for taking into account the probable number of contacts between the crystals themselves and between the impeller and the crystals which are pumped through it must be incorporated into the theoretical equations which describe nucleation in a mixed suspension system. Based on the physics of the problem it seems reasonable that the nuclei formed by contact will be proportional to the total number of particles in the system weighed by the appropriate size factor which influences the input stress.

In the following development, assume a forced circulation evaporative-crystallizer operating at steady state and

constant temperature wherein the temperature rise through the heat exchanger is sufficiently low so that little or no dissolving of fine crystals in the magma pumped through the heat exchanger occurs. If the feed is a saturated, or slightly unsaturated solution, without seed crystals, the total number of particles created should be equal to the algebraic sum of the birth rate due to homogeneous and secondary mechanisms. Algebraically this may be expressed as in equation 4:

$$B_o = B_{ss} + B_e + B_c \quad (4)$$

The term  $B_e$  is used to denote nuclei created due to crystal-impeller contacts and the term  $B_c$  to denote crystal-crystal contacts.  $B_{ss}$  is the homogeneous nucleation rate due to supersaturation driving forces. Among these influences it seems safe to assume, based on much industrial experience, that the nuclei created due to homogeneous nucleation in a well-designed commercial machine is relatively low. The two remaining terms deal with crystal-crystal contact and crystal-impeller contact. In most systems the velocity with which two crystals can strike each other is low simply because movement of particles within the liquor phase is severely restricted by viscous drag. The upper limit of such velocities, even with relatively large granular crystals is in the order of 0.5 ft/second (fps). The expected impact velocity of crystals with metal parts, however, is much higher. Normal pumping velocities range from about 3 fps to 10 fps and it is likely that particles being pumped would experience either glancing or direct blows with impact velocities of this magnitude. Axial flow pumps used for circulation in a crystallizer of this type have tip speeds that range from about 20 to 60 fps. Clearly crystal-impeller contacts from this source should have the most pronounced influence on the nucleation as suggested by recent secondary nucleation mechanism studies by McCabe.

### CRYSTAL-IMPELLER CONTACTS

The number of particles created by contact with the impeller per unit time will be proportional to the number of passes the slurry makes through the pump per unit time times the number of particles per unit volume weighed by an appropriate size factor representing the energy of impact. Assume that the growth rate is proportional to the supersaturation in the case under consideration and the energy per contact is simply the energy required to accelerate the particle to the impeller tip velocity. We define the following terms.

$$\overline{TO} \frac{(\text{Seconds})}{(\text{Turnover})} = \frac{\text{Gal. Crystallizer Volume}}{\text{Gal./min. Circulation Rate}} \times 60 \quad (5)$$

$$\frac{\text{Pump Passes}}{\text{Hr.}} = \frac{3600 \text{ sec./hr.}}{\overline{TO} \text{ sec/turnover}} \quad (6)$$

The equation proposed by McCabe may be simplified to the form:

$$P_i = K G (1/2 m_i \overline{\Delta u}^2) a_i/a_i^{1/2} = \rho k G (\overline{\Delta u})^2 L_i^4 \text{ particles/contact} \quad (7)$$

Where  $P_i$  is the number of secondary nuclei created per crystal-impeller contact of a crystal of size  $L_i$ . The highest velocity in the system is assumed to be the tip of the circulating pump impeller. If the tip of the impeller strikes a crystal whose movement is axial with respect to the pipe entering the pump then the maximum striking energy is proportional to the tip speed squared (TIPS)<sup>2</sup>.

The total generation of nuclei would then be found by summing the collisions of all particles over size range  $\Delta L$  in the suspension. The number of crystals of size  $L_i$  in a differential size range  $dL$  is given as  $n(L)dL$ . Thus the contribution to total nucleation of crystals of size  $L_i$  would be given as

$$dB_e = K \left( \frac{3600}{TO} \right) \rho G (\Delta u^2) L_i^4 n(L) dL \quad (8)$$

And for all sizes in the distribution assuming the collision velocity is proportional to tip-speed gives:

$$B_e = K_e \left( \frac{3600}{TO} \right) (\overline{TIPS})^2 G \rho \int_0^\infty n L^4 dL \quad (9)$$

Or, recognizing the integral term as the fourth moment of the distribution,

$$B_e = k \rho G \left[ \frac{TIPS^4}{TO} \right] m_4 \quad (10)$$

A mixed suspension, mixed production removal crystallizer (MSMPR) which is theoretically expected is:

$$m_4 = \int_0^\infty n L^4 dL = 4! n^0 (GT)^5 \quad (11)$$

Therefore

$$B_e = k n^0 \rho G \left[ \frac{TIPS^4}{TO} \right] (GT)^5 \quad (12)$$

but since

$$L_D = 3GT \quad (13)$$

for this distribution

$$B_e = k n^0 \rho G \left[ \frac{TIPS^4}{TO} \right] L_D^5 \quad (14)$$

These equations derived by the writer based on the results of McCabe's mechanistic studies, indicate that secondary nucleation caused by impeller-crystal collisions should correlate with approximately the first power of the

driving force (as represented by the growth rate  $G$ ) the fourth moment of the parent distribution and at least the square of the impeller tip speed.

In a later paper McCabe (Johnson et al., 1972) found that nuclei generated per impeller contact was proportional to supersaturation and contact pressure only up to certain levels. Beyond that point increases in supersaturation or increased contact pressure did not increase the number of nuclei generated. This critical point may be close to the level of contact energy generated with NaCl on this scale of test equipment. McCabe's work was with epsom salts and, therefore, the critical point, if it exists, would not be expected to be the same for the different systems. This observation would predict powers of the quantity  $(TIPS^2/TO)$  lower than that expected by equation. In this limiting case the number of nuclei generated per contact with the impeller would be independent of the impeller speed as well as crystal size, however, the number of contacts would be proportional to the number of particles present times the number of trips they make through the pump per unit time. Thus the crystal-impeller collision nucleation would be expected to correlate as

$$B_e = \frac{k m_0}{TO} \quad (15)$$

Depending on the level of input energy the nucleation from impeller contacts would be expected to be a function of tip speed to powers ranging from 0 to 3. The third power is introduced because

$$\left( \frac{1}{TO} \right) \quad (16)$$

is proportional to TIPS (tip speed) in a fixed geometry system where the speed is varied.

## CRYSTAL-CRYSTAL CONTACTS

For a complete derivation of the McCabe type contact nucleation applied to this system see Bennett, Fiedelman and Randolph (1973). The derivation is complex and leads to the conclusion that crystal-crystal nucleation is probably of such a small order of magnitude in this system that it can be neglected.

## EXPERIMENTAL

The applicability of the previous equations was demonstrated in a mixed suspension-mixed product removal crystallizer similar to that shown in Figure 1. In a series of three tests the crystallizer was operated at constant temperature, retention time and slurry density. The tip speed of the circulating pump was set at different values by a varied speed drive. The equipment was not shutdown during the test program and changes in the drive speed

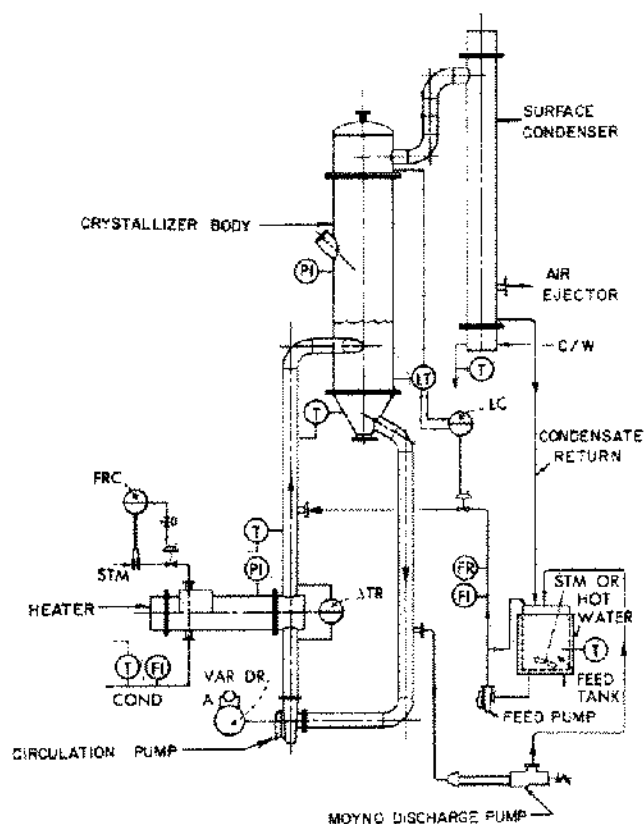


Figure 1. Diagram of Crystallizer.

were made while the unit was in operation. Later a series of 6 additional tests were performed at different retention times and slurry densities to confirm and amplify the data reported as tests 1, 2 and 3. The material crystallized was sodium chloride from a water solution. The feed was prepared by dissolving commercial sodium chloride (without additives) in Lake Michigan water. A summary of the operating conditions during the test program is shown in Table I. The operating temperature of 161°F. was chosen to be sure the growth was linear with supersaturation as outlined by the work of Rumford and Bain (1959).

Shown in Figure 2 are the equilibrium size distributions for the various tips speeds used. These distributions represent a narrower than ideal distribution for a forced circulation crystallizer and do not plot as straight lines on a log  $n$  versus  $L$  plot. The calculated C.V.'s range from 22.2 to 23%. The C.V. for an ideal forced circulation crystallizer of this type should be 50%. The nucleation rate, the nuclei population density and the total number of particles per liter can be calculated from this distribution by extrapolating a straight line on the plot of log  $n$  versus  $L$  through the three largest sizes in the distribution which represent 85% or more of the mass of the product (Fig. 3). However, it is important to recognize that these properties as well as the mass per unit volume and mean size all calculated using the idealized distribution form will not be exact; these properties depend upon the form of the distribution. Nucleation rate and growth rate values calculated from

TABLE I

Summary of operating condition for NaCl Nucleation Study

Test Number	1	2	3	4	6	7	9	10
Date	10/14/71	10/14/71	10/15/71	4/18/72	4/20/72	4/20/72	4/21/72	4/21/72
Pump Speed—RPM	450	675	525	680	530	676	529	675
Tip Speed—Ft/Min.	1350	2020	1580	2040	1590	2038	1587	2025
Sec/Turnover	53	25	28	25	28	24	32	29
Retention Time—Hrs.	1.90	1.82	1.80	1.0	2.5	2.5	1.95	1.95
Slurry Density—GM/L	90	116	90	70	185	190	167	179
(TIPS) <sup>2</sup> /TO	$3.44 \times 10^4$	$1.63 \times 10^5$	$8.92 \times 10^4$	$1.67 \times 10^5$	$9.02 \times 10^4$	$1.71 \times 10^5$	$7.87 \times 10^4$	$1.47 \times 10^5$
Product Size (Ave.) Tyler								
+ 35	20	2	5	16	7.5	1.0	10	6.0
+ 48	75	45	60	62	63	52	59	50.6
+ 65	95.5	89	92.2	90	92	91	92	88
+100	99.3	97.6	98.5	96.76	98.5	98.8	98	95.4
+150	99.7	99.55	99.6	98.53	99.6	99.7	99.7	99.8
+200	99.9	99.85	99.88	98.97	99.8	99.9	99.9	99.9
$\ln n^0$ (Extrapolated)	18.799	23.0	21.226	19.6	22.2	22.75	22.1	22.8
$B_1^0$ (Extrapolated), no/cc-sec	1.84	60.3	14.3	6.3	20.9	50.9	34.1	59.7
Growth Rate, G, mm/hr.	0.0457	0.0227	0.0313	0.0704	0.0172	0.0204	0.0311	0.0270
$B_2^0 \equiv \sum \frac{N_L}{\tau}$ no./cc-sec	0.3213	0.7246	0.456	1.89	0.83	0.77	0.815	1.049
$B_2^0 \equiv \sum \frac{N_L}{\tau}$ (> 150 mesh), no./cc-sec.	0.215	0.512	0.32	0.495	0.53	0.606	0.625	0.854

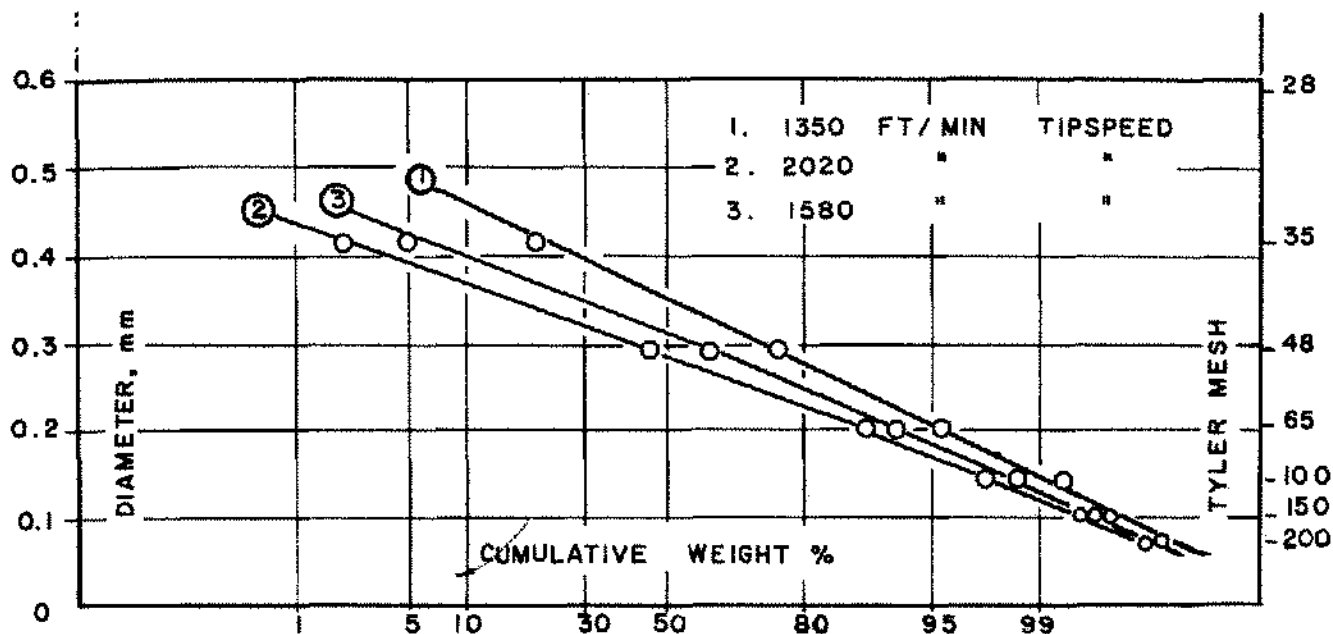
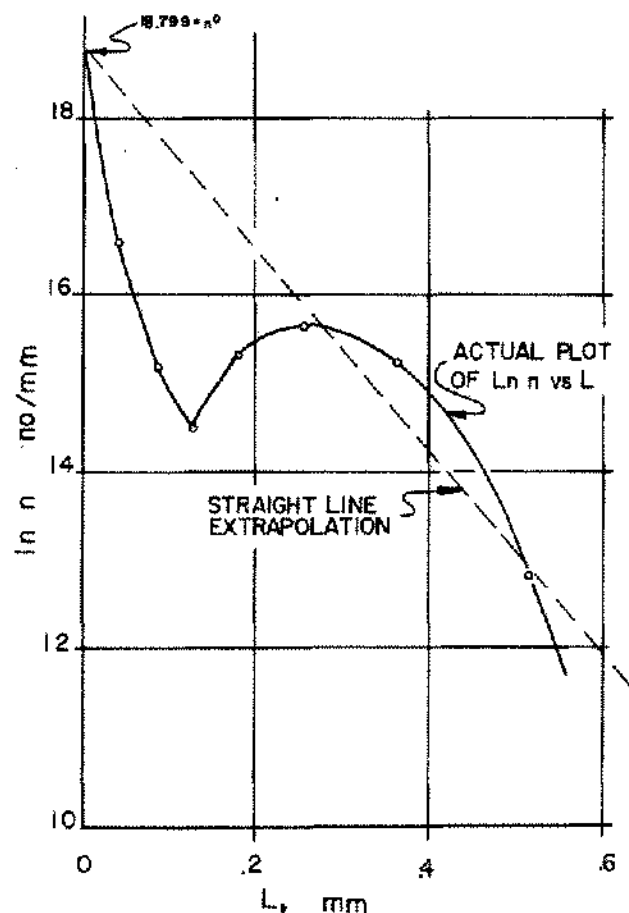


Figure 2. Cumulative NaCl CSD from a forced circulation crystallizer.

Figure 3. Plot of  $\ln n$  versus  $L$ .

this straight line extrapolation of the data are shown in Table I. In this particular case, the ideal distribution completely fails to predict the distribution at the finer sizes. While there are alternative methods for determining the nucleation rate, as will be discussed later, the growth rate calculated by the above technique was used in all correlations. Figure 4 shows the nucleation rate  $B_T$  obtained by this correlation versus tip speed of the circulating pump. The data show a steep increase in nucleation rate for a small change in circulating pump speed.

The crystallization driving forces (as represented by the growth rate,  $G$ ) and circulation rate were changed during these runs. Thus, no correlation of  $B_T$  values is possible without using a multiple regression of all significant factors that change during the runs. The data in Figure 4 is presented to qualitatively illustrate the strong dependence of apparent nucleation rate of the circulating pump RPM. Figure 3 is typical of most of the data from these runs. This plot of  $\log n$  versus  $L$  shows a curved line rather than a straight line which would be expected from MSMPR theory. In this particular case the curve has an "S" shape which unexpectedly shows a dip in the range of 0.1 to 0.15 mm. The change in form of the plot of  $\log n$  versus  $L$  due to size dependent growth rates has been the subject of several papers.

Because of the deviation in the population density from the expected MSMPR form there are serious problems in arriving at a suitable definition of nucleation rate which can be used for confirmation of the theoretical equations presented earlier. One alternative method of calculating the nucleation rate in an MSMPR unit under steady con-

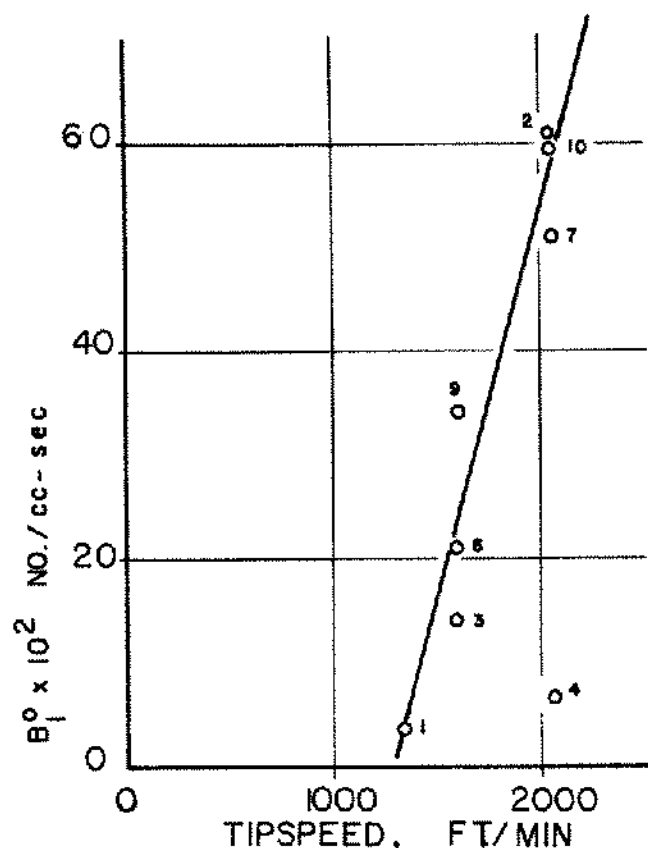


Figure 4. Apparent nucleation rate calculated by extrapolation of three CSD data points.

ditions is to divide the total number of particles per unit volume by the retention time. Thus we define  $B_2^0$  as

$$B_2^0 = \frac{\sum N_L}{t} = \frac{\int_0^\infty n dL}{t} = \frac{m_0}{t} \quad (17)$$

Table I lists the calculated  $B_2^0$  values.

In Figure 5  $B_2^0$  values are plotted against tip speed for the various runs. It can be seen that in runs of the same slurry density (1, 2 and 3) this results in a straight line change with tip speed. In runs of higher slurry density (9 and 10) there is a similar relation. Unfortunately, the data from runs 7, 6 and 4 do not fit neatly into this arrangement. Examination of the data indicates that variations of the population density in the smaller sizes appear to cause a difference as can be seen from Figure 3 for run 1. The number of particles in the sizes below 150 mesh contribute very largely to the total number of particles. Since these two fractions only account for about 0.3% of the total mass of the sample it is apparent that inclusion of these last few screen sizes introduces the probability that large errors in the calculated nucleation rate can occur during screening and weighing of the samples. The simplest way to obviate this difficulty is to include only the particles greater than 150 mesh in size thus calculating an equivalent

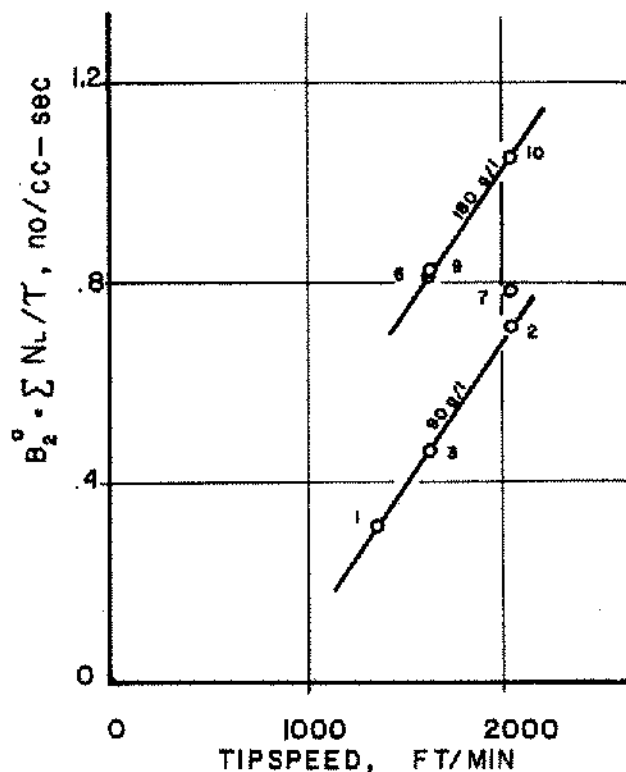


Figure 5. Nucleation rate versus tip speed.

number rate representative of the particular conditions. This technique was used and, therefore, the  $B_2^0$  values listed in Table I represent only the number of particles greater than 150 mesh. These values were used on subsequent kinetics correlations.

It is felt that the  $B_2^0$  values are more representative of the NaCl system than the  $B_1^0$  values for the purpose of illustrating kinetics calculation forms, due to the extreme deviation of particle distribution from the MSMPR form. However, method 1 ( $B_1^0$  and  $G$  values from the extrapolation on a  $\ln n$  versus  $L$  curve) was used to obtain a measure of the driving forces (given by  $G$ ) in the system. Neither  $B_1^0$  nor  $B_2^0$  exactly represents the nucleation rate in this system.

Randolph and Cise (1972) postulated that a size dependent variation in growth rate-supersaturation kinetics relationship can result in a variable particle washout rate of nuclei relative to the product-sized crystals as a function of retention time. As a crystallizer retention is varied the overall driving forces change, thus changing the relative log-population decay rate given by  $1/GT$  between large and small crystals. This effect appears superficially as a smaller-than-expected increase or decrease in apparent nucleation rate as a function of time increases and results in a lower (or negative) apparent dependency of nucleation rate on the driving forces,  $G$ . This effect has been widely observed in the interpretation of nucleation rate

data from MSMR crystallizers. In order to suppress the distortion of the results at differing retention times, a linear regression analysis was performed for runs 1, 2, 3, 9 and 10 which are essentially at the same retention time of 1.8–1.95 hours. The results of this analysis for  $B_2'$  values are given as follows:

$$B_2' = 5.4 \times 10^{-8} \left[ \frac{TIPS^2}{TO} \right]^{.97} m_4^{0.84} G^{0.98} \quad (18)$$

Where  $r^2 = 0.998$  and F-ratio equals 173. Even though there was only one degree of freedom in the variable fit the T-test levels suggest that  $(TIPS^2/TO)$  and  $m_4$  variables are significant at the 86 and 95% confidence levels, respectively. G values which varied only slightly for the constant retention runs were not significant in the correlation. The  $r^2$  correlation coefficient and F-ratio indicate that a correlation among these variables does exist although the high degree of fit is probably fortuitous due to the limited number of data.

Note that the coefficients on the corresponding variables approach unity as one would expect based on equation 10. Thus, the assumptions underlying equation 10 appear valid in this case. The less than unity coefficient of the variable term  $m_4$  also indicated that nucleation was caused by crystal-impeller (or crystal-wall) impacts rather than crystal-crystal collisions.

## DISCUSSION OF RESULTS

This paper attempts to show through derivations the reasonableness of expressing the McCabe type secondary nucleation using empirical power-law nucleation kinetics expressions as currently practiced. In addition mechanical design features of a crystallizer are incorporated into the kinetics expression. The sodium chloride system used in the testwork has a poor fit in terms of crystal size distribution, however, this is probably the result of the high level of nucleation in the system caused by mechanical effects. Because of the deviation from the ideal form, the definition of nucleation rate which is used in this system becomes somewhat arbitrary.

Although the relations developed were specifically aimed at an axial flow pump which is the common type of pump used in this equipment the actual test unit had a centrifugal pump and, therefore, sliding type crystal-impeller contact may have predominated over the direct impact contacts developed during the theory. Preliminary data from large scale installations indicate that the level of nucleation in this work with the centrifugal pump is probably far greater than the level of nucleation in large equipment with axial flow pumps.

The data analysis in this paper assumes that the source of secondary nucleation is essentially due to crystal-impeller contacts. While it is possible to have contacts due to impingement of slurry on metal surfaces within the

crystallizer, such as at elbows and tubesheets, the velocity of such contacts would be proportional to the tip speed and would also correlate as linear functions of the particle population. Thus crystal-metal caused secondary nucleation would correlate like, and be included with, the more likely crystal-impeller source. The number and intensity of the impingements will vary with the system layout. If this impingement type contact were indeed a significant source of nuclei then scale-up of a system of this type would prove most difficult. Assuming that crystal-impeller contacts represent the predominant source of nuclei, then a constant ratio of

$$\left[ \frac{TIPS^2}{TO} \right] \quad (19)$$

should be maintained in scale-up of equipment.

## CONCLUSIONS

1. The commonly held impression that nucleation is increased by higher circulating pump speed seems justified.
2. The greatest source of nuclei in a sodium chloride forced circulation crystallizer is the circulating pump.
3. The log n versus L curve for the sodium chloride system deviates greatly from an ideal distribution.
4. Sodium chloride crystals of small size (under 0.1 mm) grow more slowly than larger crystals, however, the growth rate apparently falls off again at much larger particle sizes due to attrition thus producing a narrow weight distribution. The data for different runs must be compared at constant retention time to avoid differences in relative washout rate between fine and coarse crystals. This difference in washout rate would be accounted as an apparent change in nucleation rate with retention time and lower than expected dependency on supersaturation.
5. McCabe's contact nucleation mechanism adequately explains the correlations reported in this paper.
6. Scale-up tests or translation of test data in this type of system should be done at constant  $(TIPS^2/TO)$  values using the same slurry density and retention time. Acceptable levels of retention time would be determined by factors other than particle size, i.e., fouling rate, crystal purity, crystal appearance.

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