

#### Greek Letters

- $\tau$  = time constant, s  
 $\tau_D$  = effective time delay constant in Equation (13), s  
 $\tau_1$  = first time constant in Equation (13), s  
 $\tau_2$  = second time constant in Equation (13), s  
 $\phi$  = phase angle, radians  
 $\omega$  = angular frequency, radians/s

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# Impurity Effects in Continuous-Flow Mixed Suspension Crystallizers

The crystallization of NaCl in the presence of  $Pb^{++}$  as an impurity in a continuous, mixed suspension, mixed product removal (CMSMPR) crystallizer was investigated. The results indicated that nucleation and growth rates as well as the dominant crystal sizes can be correlated by simple power functions of impurity concentration. The exponents are constants independent of the impurity concentration, thus permitting the prediction of nucleation rates, growth rates and size distributions at various concentrations of that impurity. This model was shown to apply also to other crystallizing systems.

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#### SCOPE

Additives have been used extensively in crystallization practice. They are often added in very small concentrations in supersaturated solutions in order to retard the nucleation of new crystals, to affect the growth rate of existing crystals, to change their habit (or form), and to improve

the quality of the product through the formation of well-formed crystals.

An important practical question is whether or not one can predict the effect a particular impurity would have on a given crystallizing system; or the opposite question: If a particular effect is desired which impurity should be selected? These questions are far from being answered. The selection of an impurity continues to be an art.

The next best thing, however, would be to be able to predict the effect an impurity would have when used at

\* The terms additive and impurity will be used interchangeably in this paper.

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a particular concentration from data taken at another impurity concentration. There were indications from previous works (Botsaris and Reid, 1967) that such a prediction would be feasible. In these works it was shown that growth rate data of single seed crystals, taken at certain impurity levels, could be extrapolated and used to predict growth rates at different impurity concentrations.

In the present work this idea was tried in a continuous, mixed suspension mixed product removal (CMSMPR) crystallizer. The important parameter in such a crystallizer is the size distribution of the crystal product. This is determined by the interaction of the rate of birth of the crystals (the so-called "nucleation rate") and the rate with which they increase (the so-called "growth rate"). Certain impurities affect both rates and thus affect the size distribution of the crystals.

These effects are sometimes unwelcome, especially when the crystallizing system is associated with random variation of impurities. However, the controlled introduction of certain appropriate impurities provides an additional in-

dependent variable for the operation of a continuous crystallizer. In a CMSMPR crystallizer there are three variables over which one may have control: The temperature, the concentration of the entering solution, and the flow rate, that is, the residence time (for a constant volume of the crystallizer). The last is the one which is usually varied. Whether or not the use of controlled amount of impurities can provide a variable as or more effective than the residence time was one of the questions treated by this work.

The main objectives, however, of this work were to determine the effect of a particular impurity on the nucleation and growth rates and consequently on the size distribution of the crystal product, to express these effects quantitatively, and finally to show that these quantitative expressions were useful in predicting nucleation rates, growth rates, and size distributions at various concentrations of that impurity.

The crystallizing system employed was sodium chloride in aqueous solution, salted-out by ethanol. Lead ions ( $Pb^{++}$ ) were the added soluble impurity.

## CONCLUSIONS AND SIGNIFICANCE

In this work two independent variables were varied: the residence time  $T$  and the impurity ( $Pb^{++}$ ) concentration  $C_i$  in the stream entering the crystallizer. The measured parameter was the steady state crystal size distribution of the crystal product obtained from each run. Following well established procedures, the nucleation rate  $J$  and the growth rate  $r$  of the crystals inside the continuous crystallizer were calculated from these measurements.

The most important conclusions can be summarized in the two correlations, which were deduced from the experimental data.

$$\frac{r_1}{r_2} = \left( \frac{T_1}{T_2} \right)^p \left( \frac{C_{i1}}{C_{i2}} \right)^q \quad (I)$$

$$\frac{J_1}{J_2} = \left( \frac{T_1}{T_2} \right)^p \left( \frac{C_{i1}}{C_{i2}} \right)^{q'} \quad (II)$$

where 1 and 2 refer to two different experimental conditions. The significant finding is that  $p$ ,  $q$ , and  $q'$  were independent of the impurity concentration. These correlations indicate that when the exponents are known one can estimate nucleation and growth rates at one experimental condition from their values at another.

Another way to view the correlations (I) and (II) is the following: they indicate that for example in a logarithmic

graph of growth rate versus  $C_i$  parallel lines of constant  $T$  are obtained (see Figure 2) while in a logarithmic graph of  $r$  versus  $T$ , parallel lines of constant  $C_i$  are obtained (see Figure 3). It is sufficient to know one line in each graph to be able to draw any other line in either graph and thus predict the growth rate at any other  $C_i$  and  $T$ . The same, of course, is true for the nucleation rate  $J$ .

It was also demonstrated in this work that data for other crystal-impurity systems which were recently reported in the literature (Shor and Larson, 1971) fit also Equations (I) and (II). The values, however, of the exponents  $p$ ,  $q$  and  $q'$  were different. It should be noted that power function empirical correlations similar to (I) and (II), relating the nucleation and growth rates to other variables, like suspension (slurry) density, have been proven very useful in crystallization practice (Larson, Timm, and Wolff, 1968).

The data have also shown that, for at least certain crystallizing systems, a reasonable change in impurity concentration can accomplish the same results in terms of crystal size distribution as a reasonable change in residence time. This is particularly useful when changes in production rates (that is, residence times) are undesirable or when changes in residence time are ineffective. The correlations suggested by the data of this study will provide valuable guidelines in these particular cases.

## BACKGROUND

### From the Population Balance Theory

Relations which can apply to a continuous mixed suspension, mixed product removal (CMSMPR) crystallizer include:

1. An expression for the crystal size distribution:

$$n = n^0 \exp \left( - \frac{L}{rT} \right) \quad (1)$$

2. An expression for the suspension density:

$$M_T = 6\rho K_V n^0 (rT)^4 \quad (2)$$

3. A relation between nucleation and growth rates:

$$J = rn^0 \quad (3)$$

4. An expression for the dominant particle size

$$L_D = 3rT \quad (4)$$

The assumptions incorporated in the development of the above equations are well known (Randolph and Larson, 1962; Murray and Larson, 1965).

### Kinetic Expression for Growth Rates

A power form dependence of the growth rate (that is, the rate of the increase of a linear dimension of the

crystal) on supersaturation has been extensively employed (empirical correlation) (Randolph and Larson, 1971)

$$r = k_r S^m \quad (5)$$

#### Kinetic Expression for Nucleation Rates

The classical homogeneous nucleation theory of Volmer-Becker-Doering (Zettlemoyer, 1969) could provide a kinetic expression. However, various experimental evidence indicate that the formation of a new nucleus in mixed suspension crystallizers is drastically affected by the solid interfaces existing in the suspension. These interfaces may be foreign surfaces belonging to the container, the impeller, and to the microscopic dust particles and lead to heterogeneous nucleation, or they may belong to the crystallizing species crystals already in suspension and lead to secondary nucleation. The heterogeneous nucleation has been actually discussed extensively in the past, while the secondary nucleation has only recently attracted considerable attention. In mixed suspension crystallization, nucleation is suspected to be almost totally of the secondary type. [See Botsaris and Denk (1972) for a recent review of the pertinent mechanisms of secondary nucleation proposed]. Unfortunately, very little information on the quantitative rate of nucleation under conditions resembling such collective nucleation mechanism have been reported. The only way to overcome the present gap between theory and practice is to establish a pure phenomenological model of a kinetic process without studying and describing the actual kinetic mechanism.

A number of investigators have followed this approach in order to study the effect of the crystals present in the suspension on the nucleation rate. For instance, Larson, Timm, and Wolff (1968) proposed that the suspension density  $M_T$  could be employed as the parameter which characterizes the effect of the solute solids on the nucleation rate. Then they showed that, for at least their system (potassium alum), a simple power function could describe the effect of both supersaturation and suspension density on the nucleation rate:<sup>\*</sup>

$$J = k_m M^j S^h \quad (6)$$

combining Equation (6) with Equations (5) and (3) we obtain

$$n^0 = k_M M_T^j r^{i-1} \quad (7)$$

For the case of constant suspension density, Equation (7) can be simplified to

$$n^0 = k_{N'} r^{i-1} \quad (8)$$

From (8) the well known conclusion is evident: A log  $n^0$  versus log  $r$  plot will yield the so-called relative kinetic order  $i$ .

Combining now Equation (7) with Equation (2) and using also Equation (4), we obtain the following equations:

$$\frac{r_1}{r_2} = \left( \frac{T_1}{T_2} \right)^{\frac{-4}{i+3}} \left( \frac{M_{T1}}{M_{T2}} \right)^{\frac{1-j}{i+3}} \quad (9)$$

$$\frac{L_{D1}}{L_{D2}} = \left( \frac{T_1}{T_2} \right)^{\frac{i-1}{i+3}} \left( \frac{M_{T1}}{M_{T2}} \right)^{\frac{1-j}{i+3}} \quad (10)$$

$$\frac{n_1^0}{n_2^0} = \left( \frac{T_1}{T_2} \right)^{\frac{-4(i-1)}{i+3}} \left( \frac{M_{T1}}{M_{T2}} \right)^{\frac{4j+i-1}{i+3}} \quad (11)$$

Equations (9), (10), and (11) may be used to predict the effects of suspension density on the crystallizer performance (at constant residence time) or the effect of residence time (at constant suspension density).

In this investigation a similar phenomenological approach<sup>\*</sup> was considered for investigating the effect of impurities on crystallizer performance. This approach led to power form correlations which are analogous to Equations (9), (10), and (11) and contain the concentration  $C_i$  of impurities in the entering stream of the crystallizer in the place of suspension density  $M_T$  of the latter equations.

The crystallizing system employed was the one also used by other investigators in the past: sodium chloride in a CMSMPR salting-out crystallizer. Ethanol was the salting-out agent and lead ions ( $Pb^{++}$ ) the added impurity.

#### EXPERIMENTAL PROCEDURE

The isothermal CMSMPR salting-out crystallization system designed by Murray and Larson (1965) was used in this study. The details of the crystallization system can be found therein. The crystallizer was a 5.5 liter cylindrical, plexiglass vessel with a draft tube, three baffles, and a stirrer. An automatic liquid level controller was used to regulate an intermittent discharge pump operated at relatively high frequency to maintain constant liquid level and ensure mixed product removal. The stirrer shaft used was with two impellers, the small one in the middle of the crystallizer and the large one near the bottom of the crystallizer; their actions were sufficient (1800 rev./min.) to make the crystallizer content well-mixed.

Feed solutions were prepared by dissolving a predetermined weight of NaCl in a known volume of distilled water, (33g. NaCl/100 ml  $H_2O$ ). The solute concentration of the feed solution was checked by evaporating a sample and weighing the solid residue. Known amounts of the ionic impurity solution of  $PbCl_2$  (expressed in ppm, that is, moles  $PbCl_2/10^6$  moles NaCl) were prepared and added to the feed tank of the NaCl solution. To perform an experiment, known amounts of NaCl- $PbCl_2$  solution was charged to the crystallizer, agitation was established and then the required volume of the ethanol was rapidly added, (salt solution: ethanol = 4:1). The two feed streams were started and controlled at their proper flow rates. The crystal suspension was allowed to approach steady state, about 10 residence times being required, as indicated by constant suspension density and crystal size distribution for at least 3 residence times. The final samples were taken at about 15 residence times, well after the steady state had been reached.

The magma samples were removed from the crystallizer through a submerged sample tube. The location of the submerged tube in the crystallizer did not present any problem. Different sampling positions resulted in the relatively same crystal size distributions. The rate of withdrawal was rapid to prevent classification. The total volume of the sample was recorded and the crystals were separated from the mother liquor by suction filtering through a fritted, Buchner type funnel of 40 $\mu$  pore size and then washed and dried. The dried crystals were analyzed by screening analysis using U.S. Standard 3-in. testing sieves of the following standard mesh sized: 20, 25, 30, 40, 50, 70, 80, 100, 140, 200, 325. To check reproducibility of the crystal size distribution at least two samples were taken for screening analysis.

The NaCl and  $PbCl$  used in this study were all ACS Certified Grades (Fisher Scientific Co.). The salting-out agent was 98% ethanol. Distilled water was used to dissolve the solute.

<sup>\*</sup> Other investigators (Cayey and Estrin, 1967) used the total crystal surface area as the parameter characterizing the effect of solute solids. Recently, however, Margolis (1971) has shown that when  $j = 1$ , the same data could be correlated equally well by an equation containing either the suspension density or the total crystal surface area.

<sup>\*</sup> The mechanism by which impurities affect nucleation and growth rates was ignored. For a discussion of the mechanism(s) see Ohara and Reid (1973).

TABLE 1. EXPERIMENTAL DATA

$C_{Pb^{++}}$ moles $Pb^{++}/10^6$	$M_T \times 10^{-2}$ g/ml	$r$ mm/hr	$n^0 \times 10^{-7}$ no/mm	$J \times 10^{-7}$ no/hr	$L_D^0$ mm	
						$T$ hr
1	0.25	1.37	0.336	2.30	0.772	0.252
	0.50	1.39	0.202	1.15	0.252	0.303
	0.75	1.42	0.156	0.68	0.106	0.351
5	0.25	1.41	0.261	4.60	1.210	0.198
	0.50	1.38	0.152	2.40	0.566	0.228
	0.75	1.41	0.115	1.55	0.176	0.258
10	0.25	1.42	0.202	8.80	2.000	0.151
	0.50	1.41	0.132	4.80	0.634	0.198
	0.75	1.42	0.099	3.00	0.298	0.213
30	0.25	1.40	0.186	18.00	3.350	0.140
	0.50	1.39	0.108	9.80	1.508	0.162
	0.75	1.42	0.084	6.30	0.508	0.188
100	0.25	1.39	0.121	60.00	7.930	0.091

\* Calculated from Equation (4).

## EXPERIMENTAL VARIABLES

The variables studied included only the residence time  $T$  and the impurity level in the feed solution  $C_i$ . Their values were

$T$ , min,	15, 30, 45
$C_i$ , ppm (mole $PbCl_2/10^6$ moles NaCl)	1, 5, 10, 30

All other variables were maintained constant: The experiments were run at room temperature ( $26.5 \pm 1^\circ C$ ) and constant agitation rate (1800 rev/min.). The suspension densities remained practically constant under the experimental conditions of the study ( $0.0140 \pm 0.002$  g/ml suspension). This constancy of the suspension density is implied throughout the presentation and discussion of the results of the investigation, even when it is not explicitly mentioned.

## EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

### Nucleation and Growth Rates Obtained at a Given Impurity Concentration (Suspension Density Constant)

The customary procedure for obtaining nucleation and growth rate values from the crystal screen-analysis data was followed.

For each impurity concentration, experiments were performed at three different residence times. The steady state population density data for each residence time were represented on a  $\log n$  versus  $L$  plot.\* An ideal behavior of the crystallizing system was assumed [that is, that Equation (1) applies] and a straight line was fitted through the data points. There were certain deviating points, and in other cases a slight concave upward curvature was observed which would indicate either crystal classification or size dependent growth rate. The curvature, however, was not consistent throughout the data, and its magnitude was such that it made the assumption of ideal behavior adequate for our purpose (that is, the development of an empirical equation). Additional evidence for the ideal or near ideal behavior of the crystallizing system is presented below in section 5.2. In addition, previous work with the same crystallizing system (Timm and Larson, 1968) has demonstrated that the growth rate was not size dependent.

The best straight lines through the experimental points were constructed under the constraint of conservation of mass at steady state, that is Equation (2). Thus, the

straight lines were adjusted until the calculated suspension density from Equation (2) agreed with that obtained experimentally.

From the slope and the intercept of the straight lines in the above plots the growth rate  $r$  and nuclei density  $n^0$  were estimated [see Equation (1)]. The data are summarized in Table 1.

The values of  $r$  and  $n^0$  from these plots are used in Figure 1. According to Equation (8) a straight line should be obtained for a constant impurity concentration. The data indicate that these straight lines are actually parallel. This leads to the important conclusion that the relative kinetic order  $i$  did not change with impurity levels in this study. ( $i = 2.40$ ). Shor and Larson (1971) arrived at the same conclusion for different systems ( $KNO_3-Co^{++}$  and  $KNO_3-Cr^{+++}$ ) in a recent paper.

### Variation of Nucleation Rates, Growth Rates, and Size Distributions with Impurity Levels

The same data used for the construction of Figure 1 could be also used for making a plot of the growth rate  $r$  versus impurity concentration  $C_i$  as well as [using also Equation (3)] for making a plot of nucleation rate  $J$  versus  $C_i$ . These plots, containing lines of constant residence time  $T$ , are presented in log-log form in Figure 2, where good straight line relationships are observed. This result suggests a power function dependence of both nucleation and growth rate on impurity concentration. In addition, since the straight lines are parallel, it can be also concluded that the exponent is a constant independent of the impurity concentration. In other words at constant residence time and constant suspension density, the nucleation and growth rates may be correlated with impurity concentration as follows:

$$\frac{J_1}{J_2} = \left( \frac{C_{i1}}{C_{i2}} \right)^{0.48} \quad (12)$$

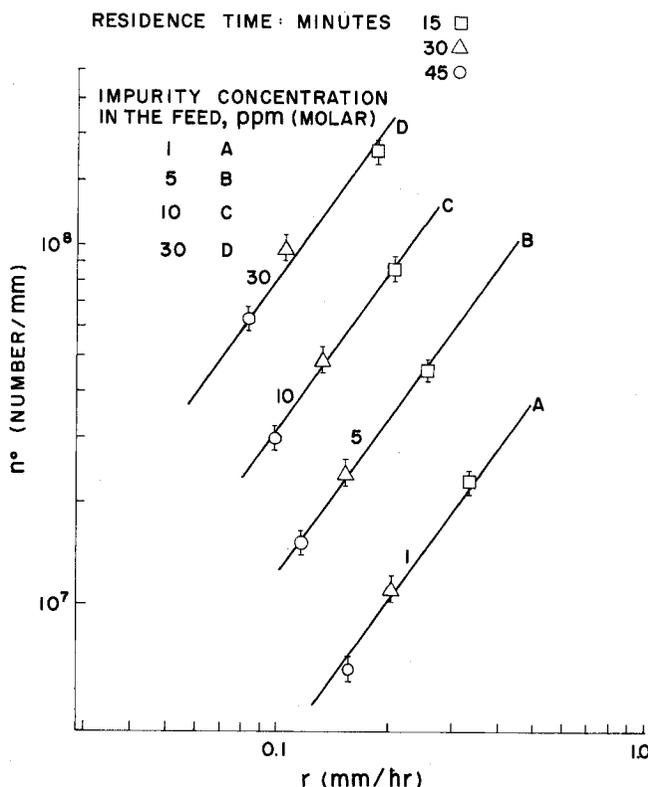


Fig. 1. Nuclei population density ( $n^0$ ) versus growth rate ( $r$ ) at constant suspension density and constant impurity level.

\* The complete data can be found in Liu (1970).

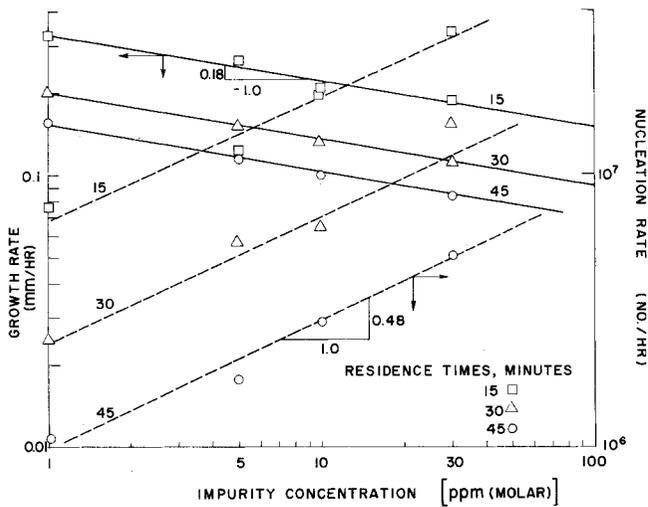


Fig. 2. Effect of impurity level on the nucleation rate and growth rate at constant suspension density and constant residence time.

$$\frac{r_1}{r_2} = \left( \frac{C_{i2}}{C_{i1}} \right)^{0.18} \quad (13)$$

Also in view of Equation (4)

$$\frac{L_{D1}}{L_{D2}} = \left( \frac{C_{i2}}{C_{i1}} \right)^{0.18} \quad (14)$$

The practical implications of the above results will be discussed next.

## DISCUSSION

### Practical Implications of the Experimental Results: Comparison with Results of Shor and Larson (1971)

The significance of the finding that the relative kinetic order  $i$  is independent of impurity level can be demonstrated by the plots of the values of  $r$ ,  $J$  versus  $T$  (Figures 3, 4). Straight lines of constant impurity concentration are obtained. These lines are parallel, which is in agreement and in a way confirms Equations (9) and (11). These equations, when applied for the case of constant suspension density  $M_T$ , indicate that the exponent in the power form equations relating  $r$  and  $n^0$  to residence time  $T$  are functions only of  $i$ . A similar plot of  $\log L_D$  versus  $\log T$  will give also straight and parallel lines (Liu, 1970).

The values of  $i$  obtained from the slopes of the lines in Figures 3 and 4 range from 2.40 to 2.55 (from Figure 1,  $i = 2.40$ ).

Figures 3 and 4 together with Figure 2 provides the basis for the most important conclusion of this study. It concerns the prediction of nucleation and growth rates (and consequently the prediction of crystal size distribution) for any impurity concentration from data taken at two different impurity concentrations. More specifically, let us take growth rate prediction as an example: once one of the growth rate lines in Figure 2 [or equivalently the exponent in Equation (13)] has been determined (by taking data at at least two different impurity levels), it is sufficient to know only one of the lines in Figure 3 to be able to draw the rest.

It should be noted that Figure 2 is sufficient for predicting growth rates  $r$  at any impurity level but only at the residence times of 15, 30, and 45 min. Figure 3, however, is needed for the prediction of  $r$  at any residence time.

A similar procedure can obviously be followed for the

prediction of nucleation rates from Figures 2 and 4.

The question arises whether or not the behavior exemplified by Figure 2 is limited to the studied crystallizing system NaCl-Pb<sup>++</sup>. In a recent study (Shor and Larson,

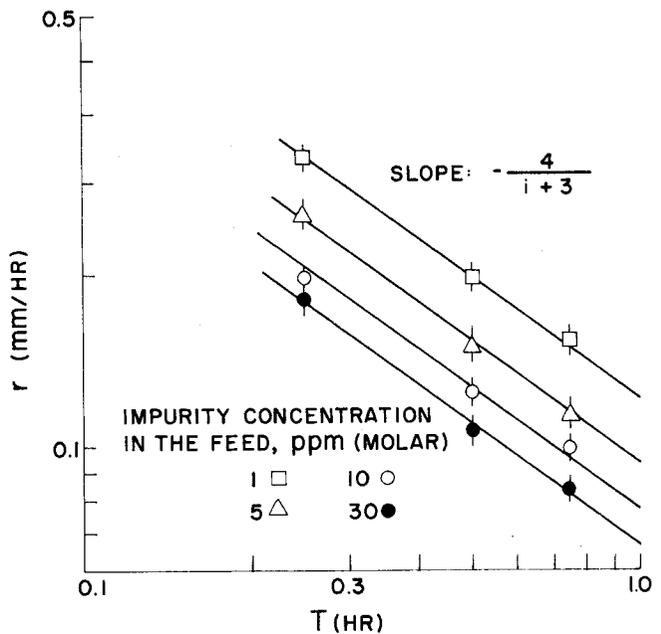


Fig. 3. Effect of resident time ( $T$ ) on steady state growth rate ( $r$ ) at constant suspension density and constant impurity level.

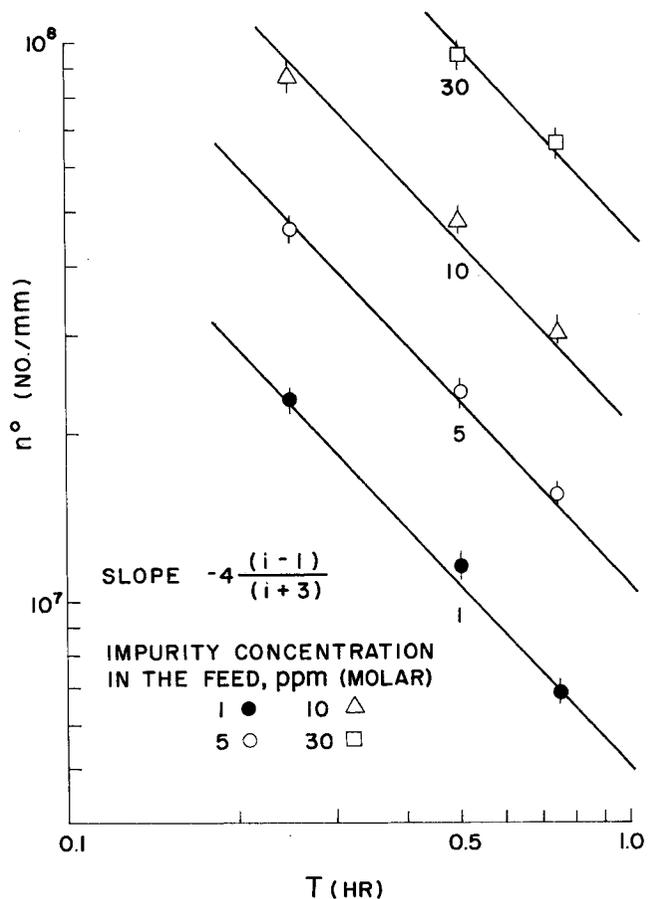


Fig. 4. Effect of residence time ( $T$ ) on steady state nuclei population density ( $n^0$ ) at constant suspension density and constant impurity level.

1971) nucleation and growth rate data were presented for the system  $\text{KNO}_3\text{-Co}^{++}$ .

These data were replotted by us in a log-log form as shown in Figure 5. It is evident that the straight lines are parallel, that is, a similar power function dependency of nucleation and growth rates on the impurity concentration is indeed observed. The same was found true (Liu, 1970) for the data of the  $\text{KNO}_3\text{-Cr}^{+++}$  system, which were reported by the same authors. One should note, however, at least three important differences in the above studies. First, Shor and Larson observed their results by changing the impurity level in the feed solution with only one order of magnitude variation (for example, from 0.5 to 4.0 g. of  $\text{CoCl}_2/100$  ml of  $\text{KNO}_3$  solution, corresponding to 0.082 to 0.656 moles of  $\text{CoCl}_2$  per mole of  $\text{KNO}_3$ ), while in the present study the impurity level in the feed solution has been varied by two orders of magnitudes in most cases. Second, in the study of Shor and Larson the effect of impurities was less pronounced than that of the residence time. This is obvious for the case of the growth rate. For the nucleation rate, it can be seen that an increase of the  $\text{Pb}^{++}$  concentration in the system  $\text{NaCl-Pb}^{++}$  from 1 to 10 ppm will have about the same effect on this rate as the change of the residence time from 30 to 15 min. For the system  $\text{KNO}_3\text{-Co}^{++}$ , on the other hand, the same increase in the impurity concentration will have a smaller effect on the nucleation rate than the change of the residence time from 15 to 30 min. This indicates that  $\text{Co}^{++}$  ions are not as effective for  $\text{KNO}_3$  as  $\text{Pb}^{++}$  are for  $\text{NaCl}$ , which is consistent with the incorporation characteristics of these crystals.  $\text{Co}^{++}$  were not incorporated in the  $\text{KNO}_3$  crystals (Shor and Larson, 1971) while  $\text{Pb}^{++}$  is strongly incorporated in the  $\text{NaCl}$  crystals (Yamamoto, 1939).

The third difference concerns the direction in which

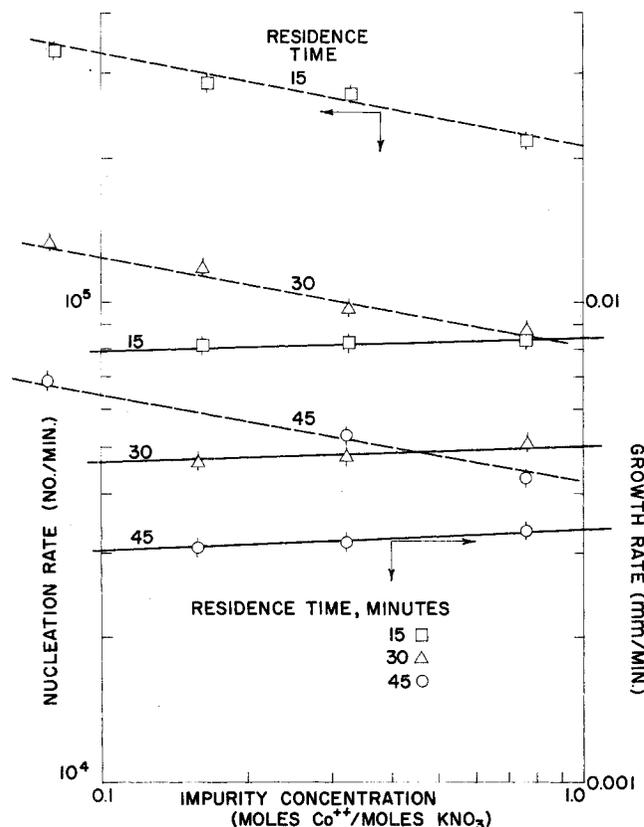


Fig. 5. Effect of impurity level on the nucleation rate and growth rate at constant residence time,  $\text{KNO}_3\text{-Co}^{++}$  system.

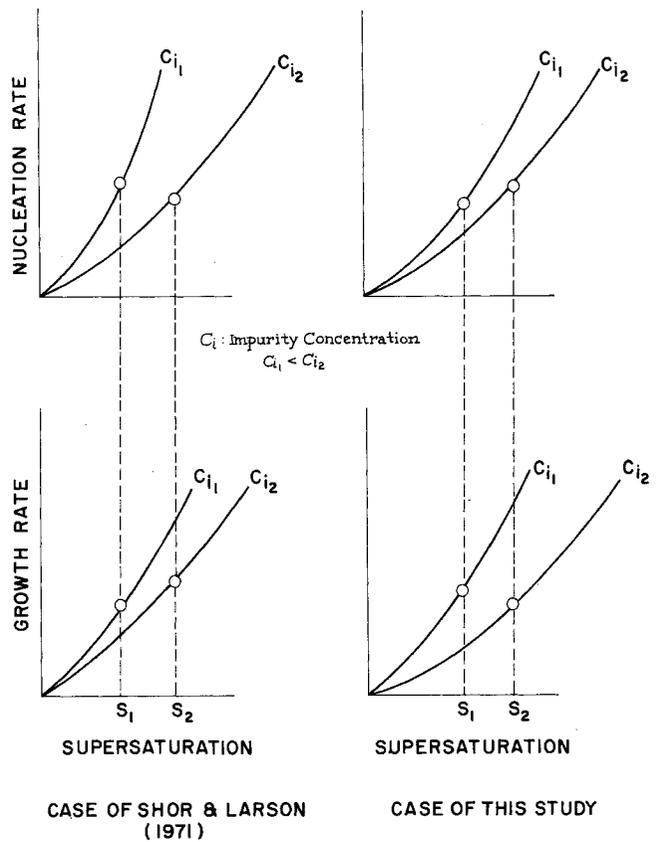


Fig. 6. A comparison of the effects of increasing impurity concentration in two systems.

the rates changed with increasing impurity level. In the case of  $\text{NaCl}$  crystals the growth rate decreased and the nucleation rate increased with increasing impurity ( $\text{Pb}^{++}$ ) concentration. Just the opposite was true, however, for potassium nitrate; the growth rate increased and the nucleation rate decreased with increasing impurity ( $\text{Co}^{++}$ ) concentration.

The fact that in the above studies the impurity affects the nucleation and growth rates in opposite directions is not inconsistent with the well known notion that dissolved impurities as a rule reduce both the nucleation and growth rates. The implication in the latter is that the supersaturation remains constant. In the case of CMSMPR crystallizers, however, an increase in impurity concentration will shift the steady state supersaturation to a different value. In the new supersaturation the nucleation rate may be lower or higher. Under the operating conditions of the CMSMPR crystallizer used in both the above studies (practically constant suspension density) the growth rate should then be higher or lower correspondingly.

This is best demonstrated schematically in Figure 6. This graph provides also an explanation for the difference between the two systems mentioned above.

In all cases the increase in impurity concentration from  $C_1$  to  $C_2$  will shift the nucleation and growth rate curves to the right. This is consistent with the observations that under constant supersaturation addition of an active impurity will decrease both the nucleation and growth rates. In the CMSMPR crystallizer on the left side (Shor and Larson) the supersaturation may increase from  $S_1$  to  $S_2$ ; this will result in lower nucleation rate but higher growth rate. The opposite will happen in the crystallizer of the right side of Figure 6 (this study).

As a final point of interest, it should be mentioned that the power dependency of the growth rate on additive con-

centration has already been demonstrated from experimental results on the growth of single crystals from impure solutions under conditions of constant supersaturation (Botsaris and Reid, 1967; Shah, 1969).

### Control of Crystal Size Distribution by Introducing Appropriate Ionic Impurities

The results suggest that the use of ionic materials such as  $PbCl_2$  as additives adds one more useful independent variable in the control of crystal size distribution. This variable could be very convenient whenever no change in residence time (that is, no change in production rate) is desirable, provided, of course, that the impurity or additive affects appreciably the nucleation and growth rates, as in the  $NaCl-Pb^{++}$  system. It will also be useful for the cases ( $i = 1$ ) in which a change in residence time has no effect on crystal size.

Additives have always been used for such purpose in the art of industrial crystallization (Garret, 1959). This investigation provides the quantitative basis for a more effective use of them.

The practical implication of the quantitative results in Figure 2 can be illustrated by Figure 7 where an example of crystal size distribution variation for two different impurity levels is given. As the concentration increases, the dominant particle size decreases [see also Equation (14)]. One should note the agreement between theoretical [calculated from Equation (4)] and experimental dominant particle size shown in Figure 7; this provides some evidence for the ideal behavior of the crystallizing suspension used in this study.

### CONCLUSIONS

1. The relative kinetic order  $i$  of  $NaCl$  crystallizing in a CMSMPR crystallizer remained constant and independent of the concentration of the  $Pb^{++}$  impurity.

2. At constant residence time and constant suspension density, the nucleation and growth rates of  $NaCl$  as well as the dominant particle size can be satisfactorily correlated by a simple power function of impurity concentration. The exponents are constants independent of the impurity concentration.

3. The applicability of conclusion 2 to other systems was demonstrated using data previously reported.

4. Conclusions 1 and 2 point to a way of predicting nucleation and growth rates at various impurity concentrations from data taken at another impurity concentration.

5. Additives can be helpful in changing crystal size distribution without affecting production rates.

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### NOTATION

- $C_i$  = impurity concentration, moles impurity/moles crystallizing species  
 $J$  = nucleation rate, no/hr\*  
 $k_r, k_m, k_M, k_N$  = proportionality constants  
 $K_V$  = volume shape factor of crystals, Equation (2)  
 $L$  = average crystal size, mm, Equation (1)  
 $L_D$  = dominant particle size, mm, Equation (4)

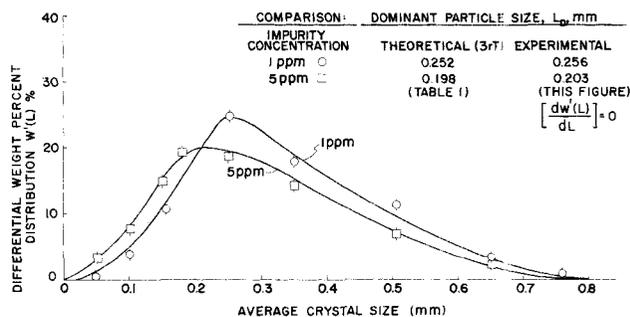


Fig. 7. Differential weight % distribution vs. average crystal size.

- $M_T$  = suspension density, mass of crystals suspended in a given volume of magma, g/ml suspension  
 $n$  = crystal population density, no/mm<sup>3</sup>  
 $r$  = linear crystal growth rate, mm/hr  
 $S$  = supersaturation  
 $T$  = residence time, hr  
 $W'$  = dimensionless differential weight percent distribution  
 $\rho$  = density of crystals, g/(mm)<sup>3</sup>  
 Subscript "0" refers to steady state value  
 Subscript "1", "2" refer to different operating conditions  
 Superscript "0" refers to nuclei

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\* The variables  $n$  and  $J$  were calculated throughout this paper on the basis of 1 ml volume.

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