Contact Nucleation from Aqueous Potash Alum Solutions

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INTRODUCTION

Crystal growth and nucleation rates in continuous mixed suspension, mixed product removal (MSMPR) crystallizers may be determined using the population balance technique developed by Randolph and Larson (1971). This technique predicts the steady state population density for an ideal MSMPR crystallizer to be

$$n(L) = n^{\circ}\exp(-L/GT)$$

On a semilogarithmic plot this equation predicts a linear relation between the crystal population density and size when certain assumptions are made. These assumptions include size-independent growth, equal growth for all crystals (i.e., no growth rate dispersion), and near zero size nuclei formation. However, evidence from MSMPR crystallization experiments [e.g., Garside and Jančić (1979) for potash alum] has shown that orders of magnitude more crystals are present in the small crystal sizes ($<50 \times 10^{-6}$m) than are predicted by this relation. Therefore, one or more of the assumptions may be in error.

EXPERIMENTAL

Photomicroscopic contact nuclei experiments were conducted with the potash alum-water system. The experimental apparatus and technique conform closely to those described in Berglund and Larson (1982) with one exception. The nucleation cell in the present study was modified to allow a constant flow of supersaturated solution over the contact nuclei. This modification guards against the supersaturation depletion that would eventually occur in a stagnant cell. As a result, this permits continued observation of nuclei to larger sizes than those previously studied with the stagnant cell arrangement. A schematic diagram of the cell is pictured in Figure 1.

All solutions and parent crystals were prepared with Fisher Scientific reagent grade potash alum. A parent crystal grown by slow evaporation was epoxied to the contact rod prior to filling the cell. The solution was supersaturated by lowering the temperature with the constant temperature water. (An undercooling of about 4 K in each run allows comparison of the results.) In order to purge the cell of nuclei that may have been formed during start-up and to slightly dissolve the parent crystal, the cell temperature was raised above the saturation temperature. The solution was then cooled and the parent crystal allowed to grow. After a short growth period and at steady state flow, the contact nuclei were formed by sliding the parent crystal across the glass cover slip. The potash alum solution was pumped through the cell at a maximum flow rate that would not disturb the nuclei. Subsequently, the nuclei were photographed at timed intervals during the experiment.

To determine crystal growth rates, film negatives were first projected onto a sheet of paper and the crystal outlined. Each length chosen as the characteristic growth dimension was the perpendicular distance between parallel edges of the projected outline. However, as the crystal grew, its shape and the number of edges changed due to the different growth rates of the various faces. Therefore, the choice of characteristic length was dictated by the presence of the same parallel edges in successive photographs during the experiment. Since length versus time plots were consistently linear, it was not considered necessary to measure more than two lengths on each crystal. Actual lengths were calculated by comparing the projected lengths with the projection of a scale that had been photographed at the same magnification. Characteristic growth dimensions in this study are analogous to the face growth rates incorporated in the Burton-Cabrera-Frank crystal growth model. The slopes represent the average growth of two faces; therefore, crystal growth rates were calculated by dividing the slopes by 2.

Evidence that a crystal in the cell experienced constant supersaturation as long as it remained relatively isolated is illustrated in run 4 (Figures 2a and 2b). In Figure 2a the slopes of the lines, and therefore the growth rates, were initially constant and then underwent an abrupt change. Photographs show several crystals growing closer to this crystal as the experiment progressed. However, the growth rates of a crystal isolated from neighboring crystals did not change during the same run (Figure 2b). Therefore it may be assumed that mass transfer constraints in the immediate vicinity of the crowded crystals were the cause of the growth decline and not overall cell supersaturation depletion.

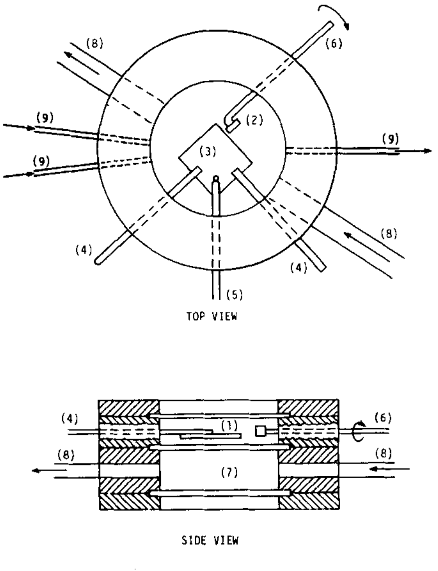

Figure 1. Schematic diagram of nucleation cell with the features: (1) chamber containing solution; (2) parent crystal; (3) glass cover slip where parent crystal is slid; (4) support rods for glass cover slip; (5) thermistor; (6) movable rod holding parent crystal; (7) chamber containing constant temperature water; (8) water inlet and outlet; (9) solution inlet and outlet (top view only).

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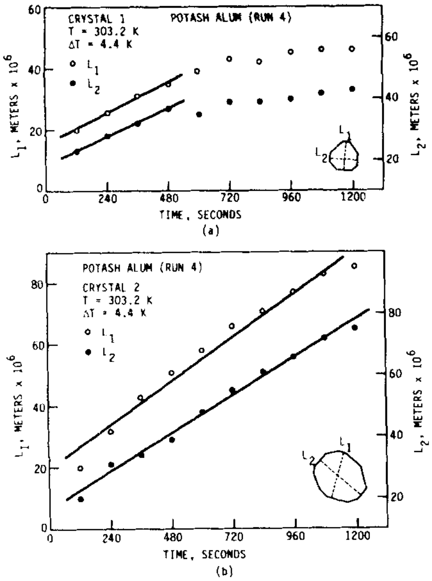

Figure 2. Characteristic lengths vs. time for potash alum contact nuclei formed and grown at 303.2 K with 4.4 K undercooling. A schematic of the crystal and characteristic lengths are shown.

RESULTS AND DISCUSSION

Length vs. time plots are presented in Figure 3. A summary of experimental results is presented in Table 1. First, it is evident, and confirmed by high correlation coefficients, that a linear relation exists between the characteristic length and time. The assumed linearity is best illustrated by Figure 3 where the experiment ran for 130 min, crystal length reached 500 micron, and the correlation coefficient was 0.999. Since the slope of the line is proportional to the growth rate, the linearity suggests size-independent growth. This agrees with Garside's (1979) observations of initial time-independent growth for potash alum. However, he noted apparent time-dependent growth as the growing crystal changed shape, a phenomenom that definitely was not present in this study. The lines are also characterized by different slopes. This indicates a distribution of growth rates among the individual crystals and a distribution among the faces of the crystals.

A third feature to be noted is the variation in the intercept that corresponds to an extrapolated initial size. This linear behavior and distribution of initial sizes have been observed in other contact nuclei experiments. Some examples are the sucrose-water system (Shanks and Berglund, 1985), citric acid monohydrate-water system (Berglund and Larson, 1982), and the KNO_3-water system (Berglund et al., 1983).

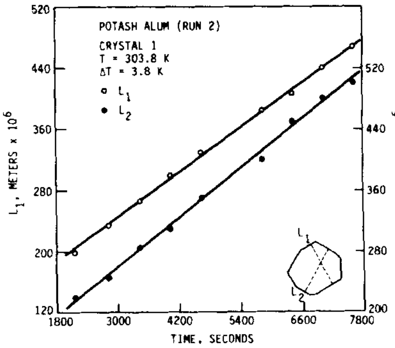

Figure 3. Characteristic lengths vs. time for potash alum contact nuclei formed and grown at 303.8 K with 3.8 K undercooling. A schematic of the crystal and characteristic lengths are shown.

The size-independent growth observations in this study do not agree with Garside and Jančić's (1976) assertion of size-dependent growth for potash alum. This assertion was based on interpretation of Coulter Counter data from batch crystallization experiments. The attendant cumulative numbers versus size plot seems to indicate increasing growth rate with increasing crystal size. However, it has been shown by Berglund and Larson (1982) in contact nucleation experiments that the same plot may result when the individual crystal growth rates are constant but a distribution of growth rates is present. This suggests that analysis of Coulter Counter data may be subject to conflicting interpretations. That is, growth rate dispersion may be interpreted as size-dependent growth.

Garside and Jančić (1976) note that size-dependent growth may result from solution impurities, mechanical stress, or crystal collisions. The present study, though, does not include the effect of crystal interactions, impurities, or involve a stirred suspension, all factors that could alter results. Further study is necessary to verify fully the appropriateness of comparing results from photomicroscopic and stirred suspension experiments.

CONCLUSIONS

Potash alum contact nuclei grow at a size-independent rate in a system where flow does not result in crystal collisions. Both initial size and growth rate distributions are present for contact nuclei of potash alum. Curvature in semilogarithmic population density-size

TABLE 1. LINEAR REGRESSIONS PERFORMED ON EXPERIMENTAL RESULTS

Run	Crystal Number	Solution Temp., K	Under-Cooling, K	Growth Rate* (Slope/2), m/s × 10^8 G_1	G_2	Initial Size** (Intercept), m × 10^6 L_{o1}	L_{o2}	Correlation*** Coefficient C.C.$_1$	C.C.$_2$
1	1	303.6	4.0	1.9	1.7	16	15	0.990	0.972
	2	303.6	4.0	3.0	3.3	34	32	0.995	0.992
	3	303.6	4.0	3.5	4.9	55	42	0.995	0.998
2	1	303.8	3.8	2.4	2.7	99	99	0.999	0.999
3	1	303.9	3.7	2.4	2.6	21	21	0.996	0.992
	2	303.9	3.7	3.9	3.8	10	15	0.999	0.997
4	1	303.2	4.4	2.1	1.9	16	19	0.996	0.999
	2	303.2	4.4	3.0	2.6	19	16	0.986	0.995
5	1	303.6	4.0	2.1	1.6	13	13	0.998	0.996

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* Growth rate based on characteristic length specified in subscript.

** Extrapolated initial size of characteristic length specified in subscript.

*** Correlation coefficient from linear regression performed on characteristic length specified in subscript.

plots from continuous potash alum crystallization studies may be due to growth rate dispersion and not size-dependent growth.

ACKNOWLEDGMENT

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NOTATION

G = linear crystal growth rate, $1/t$
L = characteristic crystal size, 1
n° = zero size crystal population density, $\#/1 \cdot 1^3$
$n(L)$ = crystal population density, $\#/1 \cdot 1^3$
T = retention time, t

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