SECONDARY NUCLEATION OF K-ALUM BY MINIMUM SIZE SEEDS IN A STIRRED VESSEL

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Secondary nucleation rate of K-alum was studied by adding controlled amounts into a stirred vessel. Change in number of produced nuclei against the elapsed time was observed by direct counting, and the results were featured by slight increase in number at the initial stage, followed by rapid increase in constant elapsed time specified by the particular supersaturation. The existence of a definite size to contribute to following nucleation was recognized, and this size was minimum for secondary nucleation and correlated with supersaturation. Minimum size was proposed as a new effective factor on the secondary nucleation rate, and secondary nucleation rate per unit surface of crystals near minimum size was correlated with supersaturation and agitation rate in the stirred vessel. Secondary nucleation rate in the stirred vessel was also discussed in comparison to that in the fluidized bed. The primary nucleation in the stirred vessel and latent period for the produced nuclei to grow to minimum size to contribute to following nucleation were also discussed.

Introduction

Recent studies of secondary nucleation have been focused on determination, correlation and mechanism; for example, nucleation rate in Mixed Suspension Mixed Product Removal (MSMPR)⁷⁾, nucleation rate correlated with size or growth rate^{8,9)}, contact nucleation owing to impact energy⁹⁾ and nucleation by fluid shear²⁾.

Determination of secondary nucleation rate in the fluidized bed was reported in our previous paper¹¹⁾. This method was characterized by counting crystals grown from secondary nuclei in the supersaturated solution passed through seed crystals bed, and secondary nucleation rate was correlated with supersaturation and Reynolds number. A new design method was also presented, keeping the Oslo type of crystallizer in mind.

The study of secondary nucleation in a mixed type of crystallizer appears to be difficult because the agitation effect in the fluid state is complicated and following-nucleation induced by seed crystals grown from produced nuclei is effective. Among them, same work was reported on the contribution of birth nuclei to following-nucleation. Cayey and Estrin²⁾, and Rousseau and *et al.*¹⁰⁾ reported the existence of a definite size for nucleation in aqueous solution of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

This study was carried out in recognition of the minimum size effect on secondary nucleation rate in a stirred vessel in the original method, using the results of our previous work¹¹⁾. A feeding method of sec-

ondary nuclei was devised: controlled secondary nuclei were fed from the fluidized bed into the stirred vessel. Change in number of nuclei produced was measured against the elapsed time on direct counting, and minimum size to contribute to following-nucleation was measured and correlated with the supersaturation, from the overall growth rate and the time at which a rapid increase in number was observed. Using total crystal surface calculated from minimum size, secondary nucleation rate per unit crystal surface near minimum size was obtained and correlated with supersaturation and agitation rate. Many reports on secondary nucleation rate per unit volume of a crystallizer have been presented. But in this paper, the secondary nucleation rate was expressed per unit crystal surface on the basis of consideration that secondary nuclei were produced by fluid shear, and minimum size was reported as a new factor in secondary nucleation rate.

1. Experimental Methods

1.1 Measurement of produced nucleus

The apparatus is shown in Fig. 1. The stirred vessel (8) set in the thermostat bath (1) to give the same temperature as in the seed bed, is 110 mm in diameter and 130 mm in depth, and the paddle type of agitator is 40 mm in length and 15 mm in width.

An aqueous solution of potassium alum was circulated through the dissolution tank (2), feed tank (3), and head tank (4). When the solution was dissolved sufficiently in this flow, circulation flow was changed by passing through flow meter (5), heat exchanger (6), the fluidized bed (7), and the dissolution tank (2). Solution was supersaturated by heat exchanger (6).

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Fig. 1 Schematic diagram of experimental apparatus

Fig. 2 Correlation between overall growth rate and supersaturation

Table 1 Operational conditions

Supersaturation ΔC [kg-mol/m ³]	0.0292–0.0450
Dimensionless supersaturation s [—]	1.06–1.11
Operation temperature T_{op} [°C]	30 ± 0.05
Agitation rate n_r [rpm]	300–800

After steady state, sieved seed crystals ($-14+28$ mesh) were fed into the fluidized bed. When the seed bed height grew twice the initial one, one liter of supersaturated solution containing a known number of secondary nuclei separated from seed crystals, was fed from the top of the fluidized bed (7) into the stirred vessel (8). As soon as feed operation was completed, the agitator was started at a fixed revolution rate. Every five minutes, ten milliliters of solution was taken as sample. At this time, no crystallites were observed. The sampling cell was immersed in the thermostat bath for a few hours at the fixed operational temperature. Nuclei appeared in the cell, grew to visible size and were counted. In the sampling cell of the initial stage, crystallites were of uniform size and dispersed on the bottom surface, but in the solution sampled after some elapsed time, fine crystals were recognized among the large uniform crystals. In

every cell, thousands of crystals were counted in the defined volume. The number of produced nuclei per liter solution (number/l) was obtained. On the other hand, the following two tests, A and B, were carried out to determine primary nucleation. In these tests, one liter of supersaturated solution with supersaturation range from 0.0292 to 0.057 (Kg-mol/m³) was fed into the stirred vessel without adding seeds in the fluidized bed.

In test A, the vessel was immersed in the thermostat bath for a few hours, but no trace of crystals were observed. Nucleation owing to feed solution was not observed. Test B was carried out to determine primary nucleation owing to agitation effect. In this test, ten milliliters of solution was taken as sample every five minutes, after nuclei free solution was fed into the stirred vessel. Size distribution and number of crystals in the cell was observed.

Overall growth rate of seed crystals in the stirred vessel was obtained from size change of seeds after a certain elapsed time, by taking photographs before inducing following-nucleation. When photographs were taken after inducing following-nucleation, the size of seeds was measured with difficulty owing to the size distribution. At the taking of the final photograph, crystal size distribution was within a few percent, and size was considered to be almost uniform.

Desupersaturation was determined from the weight of suspended crystals at the end of individual test runs and was within 0.5 to 5% of supersaturation of the initial solution. Effect of suspension density on secondary nucleation was not observed in these experiments. It was estimated from small suspension density such as 0.1 to 2 Kg/m³, though the detailed determination was not carried out. The operational conditions are shown in Table 1.

2. Results and Discussion

2.1 Overall growth rate of crystals in the stirred vessel

In the photographs, crystals were almost of uniform size in the sampling cell, and correlation of crystal size against elapsed time is proportional. Overall growth rate of relatively small seeds (from 10μ to 100μ) in the stirred vessel, was calculated from the slope. In Fig. 2, overall growth rate of small seeds was plotted against supersaturation, and Eq. (1) was obtained.

$$r_a = 2800 \times (\Delta C)^{5/3} \quad (1)$$

Within the experimental range as shown in Table 1, little effect of agitation was observed.

Comparison of the overall growth rate shown above with that of seeds in the fluidized bed and of fixed seed in piston-flow of supersaturated solution, is also shown in Fig. 2²⁾, as the dotted line in the former¹¹⁾

and dot-dash line^{1,11}) in the latter. Power of supersaturation in the stirred vessel is same as in the fluidized bed. The value of overall growth rate of small seed (10 to 100 μ) in the stirred vessel is almost same range as that of fixed seeds, but smaller than that of seeds (1000 to 2000 μ) in the fluidized bed.

2.2 Minimum size of seeds to contribute to following secondary nucleation

Number of produced secondary nuclei per liter solution is plotted against the elapsed time from the start of agitation, as parameter of supersaturation. Some typical results for this are shown in Fig. 3 at 640 rpm. Introduced secondary nuclei were differed from one another because those separated from seeds in the fluidized bed were different owing to operational supersaturation. These typical correlations were characterized by broken lines with various angles. In the initial stage, only slight increase in number was observed, but in the latter stage after the constant elapsed time, rapid increase in number was observed. The gradual straight line is thought to be due to primary nucleation, because this slope is in accordance with that in the result of test B at the same degree of supersaturation and agitation. In Fig. 3, the result of test B at each supersaturation level is shown as a dotted lines. From the data of test B, it is also shown that the number of primary nuclei is small, and that the time at which number of produced nuclei began to increase rapidly is same in each tests at fixed supersaturation. Consequently, fine crystals turned out not to effect secondary nucleation before they grew to a certain size. This meant that the existence of minimum size was recognized and the uniform secondary nuclei fed from seeds fluidized bed, grew to minimum size before contributing to following-nucleation as the model explained in Fig. 4. Rapid increase in number of nuclei at the several minutes elapsed as in Fig. 3, can readily be understood by this model for secondary nucleation.

Minimum size was calculated from product of overall growth rate in Fig. 2, by the time at which rapid increase started at the fixed conditions, and was plotted against the supersaturation in Fig. 5. Therefore, Eq. (2) was obtained, though these plots were somewhat scattered.

$$L_{min} = 0.35(\Delta C)^{-5/3} \quad (2)$$

The scattering was not correlated with agitation rate of the impeller and suspension density of crystal. The value of minimum size of K-alum was 120 μ at supercooling of 3°C in this study. On the other hand, that of $MgSO_4 \cdot 7H_2O$ was reported to be from 180 to 190 μ at the same degree of supercooling by Estrin²⁾ and Rousseau¹⁰⁾. The fact that minimum size was not much different between these systems is interesting and might be expected to be studied in the near future.

Fig. 3 Change in number of produced nuclei against the elapsed time at 640 rpm

Fig. 4 Schematic diagram of secondary nucleation mechanism in these tests

Fig. 5 correlation of minimum size against supersaturation

2.3 Secondary nucleation rate by minimum size seeds

Secondary nucleation rate per unit volume of solution N_s (number/l·sec), was calculated from the steep slope in Fig. 3, and primary nucleation is neglected as explained in the previous section. Secondary nucleation is considered to be induced by crystal over the minimum size. The shape of crystallites having minimum size is properly octahedral, and surface shape factor is $2\sqrt{3}$. Therefore, total crystal surface

Fig. 6 Effect of agitation on secondary nucleation rate

Fig. 7 Effect of supersaturation on secondary nucleation rate

Fig. 8 Correlation of secondary nucleation rate with agitation and supersaturation

area, a_{tot} , is calculated by Eq. (3), when crystal in the vessel is uniform minimum size.

$$a_{tot} = n_{tw} \times (L_{min})^2 \times 2\sqrt{3} \quad (3)$$

n_{tw} is number of crystal at the time corresponding to the broken point. Secondary nucleation rate per unit surface induced by minimum size crystals, f' (number/cm²·sec), is calculated from dividing N_s by a_{tot} in Eq. (4).

$$f' = \frac{N_s}{a_{tot}} \quad (4)$$

Secondary nucleation rate f' is plotted against agitation rate as parameter of supersaturation in Fig. 6, and Eq. (5) was obtained.

$$f' \propto (n_r)^3 \quad (5)$$

Secondary nucleation rate f' is plotted against supersaturation as parameter of agitation rate in Fig. 7, and Eq. (6) was obtained.

$$f' \propto (\Delta C)^{3.3} \quad (6)$$

In Fig. 8, secondary nucleation rate f' is plotted against $(\Delta C)^{3.3} \times (n_r)^3$, for making sure of the power number. This correlation becomes a straight line with 45° slope in log-log plot, and Eq. (7) was obtained.

$$f' = 6 \times 10^{-4} (\Delta C)^{3.3} (n_r)^3 \quad (7)$$

When Eq. (7) is compared with Eq. (8) in the fluidized bed reported before¹¹⁾, power of supersaturation in the stirred vessel

$$f' = 10 (\Delta C)^{3.3} (Re)^{2.5} \quad (8)$$

is equal to that in the fluidized bed. Power of agitation rate n_r is same as the one reported by de Jong⁴⁾, and a little larger than that of Reynolds number in Eq. (8). The value of f' in the stirred vessel is from 1 to 10 (number/cm²·sec), and the same extent as in the fluidized bed at the same supersaturation.

Effect of suspension density has been reported by Larson⁵⁾ and Randolph⁶⁾, and correlation of contact nucleation with suspension density was presented in the range of suspension density from 20 to 40 kg/m³. In this experiment, suspension density is small (0.2–2.0 kg/m³), and the data was not correlated against suspension density. Since these data were correlated against the seed surface, nuclei seem to be produced mainly by washing-effect from surface due to fluid shear and contact nucleation might be not much effective. In the fluidized bed, similar phenomena seem to occur, and the produced nuclei are mainly due to fluid shear near crystal surface, in spite of large suspension density.

In this manner, effect of minimum size was observed in the stirred vessel, but it was not observed in the fluidized bed recently reported in the previous¹¹⁾ paper, for the reason that secondary nuclei separated from seeds were brought out before becoming minimum size.

2.4 Time required to grow to minimum size

The time required to grow to minimum size is expressed by T_w . Compared with data in this study, T_w is also recognized to be the elapsed time at which rapid increase in number of nuclei started in Fig. 3. On the other hand, latent period, τ , was proposed by Mullin⁶⁾ as the elapsed time at which the decrease of supersaturation was found by sudden promotion of

crystallization rate since the seed crystal was introduced into the supersaturated solution. Though T_w is not exactly same as τ because of difference of observation, their physical meaning may be almost the same. And also T_w is proposed from the assumption that secondary nucleation occurs as soon as the seed crystal is contacted with supersaturated solution. Therefore, the concept of T_w does not conflict with zero waiting time for secondary nucleation in the previous paper¹¹⁾.

T_w values obtained in this study were plotted against the supersaturation as in Mullin's paper⁶⁾ and Fig. 9 was obtained. Their correlation became Eq. (9).

$$T_w = 1.2 \times 10^{-4} (\Delta C)^{-10/3} \quad (9)$$

Equation (9) is easily understood to be obtained by dividing Eq. (2) by Eq. (1) from the definition above, and is independent of agitation rate of agitator as same as the correlation of minimum size in the experimental range of Table 1.

Conclusion

Known-number of secondary nuclei separated from seeds in the fluidized bed were fed into the stirred vessel and secondary nucleation rate of K-alum was studied. By means of measurement of produced nuclei, the minimum size for nuclei to contribute to following nucleation was correlated with supersaturation as Eq. (2). Minimum size was proposed as a new factor for correlating secondary nucleation rate. Using this minimum size, secondary nucleation rate per unit crystal surface near minimum size was correlated with supersaturation and agitation rate as Eq. (7). T_w , the time required for nuclei to contribute to following-nucleation was also discussed.

Nomenclature

a_{tot}	= total crystal surface	[m ²]
ΔC	= supersaturation	[kg-mol/m ³ H ₂ O]
f'	= secondary nucleation rate per unit crystal surface	[number/cm ² ·sec]
L_{min}	= minimum size	[μ]
N_s	= secondary nucleation rate per unit volume of solution	[number/l·sec]
n	= number of produced nucleus per unit

Fig. 9 Effect of supersaturation on T_w

	volume of solution	[number/l]
n_{tw}	= n at the time of T_w	[number/l]
n_r	= agitation rate	[rpm]
Re	= Reynolds number	[—]
r_a	= overall growth rate of small crystals in the stirred vessel	[μ/min]
s	= dimensionless supersaturation	[—]
T_{op}	= operational temperature	[°C]
T_w	= the time required for nucleus to grow to minimum size to contribute to following nucleation	[min]
τ	= latent period	[min]
θ	= the elapsed time from the beginning of agitation	[min]

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