Part 2:

TRANSIENT CRYSTAL SIZE DISTRIBUTION
CHAPTER 2

MONTE CARLO SIMULATION OF TRANSIENT CRYSTAL SIZE DISTRIBUTION IN A CONTINUOUS CRYSTALLIZER USING THE ASL MODEL

2.1 Introduction

The classical analysis of crystal size distribution (CSD) in a continuous mixed suspension mixed product removal (MSMPR) crystallizer is based on several hypotheses. A very important assumption is the constant growth rate of the crystals known as McCabe's delta $L$ law. However, there is ample evidence that growth rate is a function of size in some systems. GARSIDE et al., (1976, 1990) have shown that the following mechanisms contribute to size-dependent growth:

(i) The effect of crystal size on solubility (the Gibbs-Thomson effect) is such that the solubility increases with decreasing size of a crystal. This mechanism holds for crystals smaller than 10 $\mu$m.

(ii) The growth rate increases with decreasing size if it is diffusion controlled. These effects are rarely seen.
(iii) Size-dependent surface integration kinetics is strongly influenced by dislocation density that increases with crystal size.

(iv) Increasing slip velocity with larger crystals leads to increase in the growth rate.

RANDOLPH and LARSON (1971) derived the population balance equation (PBE) of unseeded system or at least a system which has no crystals in the input large enough to be in the size range under consideration and this is given by,

$$\frac{d(Gn)}{dL} + \frac{n}{\tau} = 0 \quad (2.1)$$

If an appropriate model for $G(L)$ is available, it can be used in Eq. (2.1) to predict the expected number distribution of crystals obtained from a continuous crystallizer. For practical purposes, one is not usually interested in the number distribution but in the distribution of mass, which can be obtained from the third moment of the distribution. But a functional relationship for $G(L)$ will render the mathematical treatment of the higher moments of the distribution difficult (BAUMANN and Voigt, 1984).

Important exceptions to McCabe’s growth rate model have been noted by BRANSOM (1960), CANNING and RANDOLPH (1967), and ABEGG et al. (1968). They have all proposed different models to account for the effect of crystal size on
the growth rate. In the present work, ASL model (ABEGG et al. (1968) for size-dependent growth rate has been employed in conjunction with exponential residence time distribution to forecast the CSD in a continuous potassium carbonate crystallizer. Both the transient and steady state CSDs are simulated using the MC technique.

Various researchers have attempted transient CSD modelling in a continuous crystallizer. For example, JAGER et al. (1991) estimated the nucleation kinetics from CSD transient of a continuous crystallizer while WEN et al. (1993) studied the transient CSD of zeolite-A. However, owing to the complexity in PBE their analysis is restricted to simple cases of residence time modelling. The other important factors such as growth rate dispersion, size-dependent growth, shape factor dispersion and change in nucleation rate cannot be taken into account. In the analysis of transient CSD, the traditional PBE approach yields a number distribution, which would tally with that of Saeman (1956), and RANDOLPH and LARSON (1962) under simplified condition. Although there is a need for obtaining mass fraction distribution of crystals under transient condition, a lack of mathematical tool has been the major impediment. Further, to simplify the commonly used mixing models, the influence of dispersion and variation in nucleation rate is ignored.

SEN GUPTA and DUTTA (1989) first showed that MC simulation is a very powerful tool for simulation of steady state CSD in continuous crystallizer. They obtained CSD as cumulative mass fraction under various dispersion effects and
under the rigid conditions of a continuous MSMPR crystallizer, the model matches very well with the analytical CSD obtained from the equation proposed by Saeman (1956) and Randolph and Larson (1962). Sen Gupta and Dutta (1990a) further extended this model to forecast transient CSD in a crystallizer when dispersions in growth rate, birth size and shape factor take place concurrently.

Dey and Sen Gupta (1994) used MC simulation technique to deal with steady state analysis of a continuous potassium carbonate crystallizer together with size-dependent growth by incorporating the ASL model. The present contribution concerning the analysis of transient CSD is an extension of their work.

2.2 The simulation scheme

The model is based on the generation of random residence time from a known RTD. In this case, one of the several existing models for size-dependent growth is used for the interpretation of kinetic data. According to the ASL model crystal growth is given by Eq. (1.68) and (1.69) which on integration yields

\[
L = G_o \tau \left( 1 + \frac{T(1-b)}{\tau} \right)^{\frac{1}{1-b}} - 1
\]  

(2.2)

The fundamental assumptions underlying the model are:
(i) The growth rate depends on the crystal size according to the ASL model.

(ii) Residence time of a crystal is exponentially distributed with mean residence time as the one given by LEVENSEIPL (1975), i.e., Eq. (1.11), which gives

\[ T = -\tau \log(RND) \]  
(2.3)

The basic equations describing any crystal (say \( i \)th. crystal) in a continuous MSMPR crystallizer are therefore taken to be the following:

Residence time: \( T_i = -\tau \log(RND) \)  
(2.4)

Diameter: \[ L_i = G_o \tau \left[ 1 + \frac{T_i(1-b)}{\tau} \right]^{1-b} - 1 \]  
(2.5)

Mass: \[ W_i = K_i \rho L_i \]  
(2.6)

In this work, the shape factor is assumed to be a constant that equals one. The sample nucleation rate is assumed to be 1000 nuclei/min. The suggested algorithm is based on the earlier work of DEY and SEN GUPTA (1993a). Appendix II.1 outlined the program and sample results (Experiment No. 1) for generating the transient CSD employing the Microsoft Visual Basic Version 3 software.
2.3 Results and discussion

ŠKRTIĆ et al. (1989) have described the growth rate characteristics of potassium carbonate in a continuous MSMPR crystallizer by the ASL model. The values of different parameters used in the simulation are taken from their work and are listed in Table 1.10. Residence times are generated from Eq. (2.4) while the corresponding diameter and mass are obtained from Eq. (2.5) and Eq. (2.6) respectively. Each crystal, according to its size, is classified into 16 classes.

The number distribution and cumulative mass fraction of the crystals are computed at intervals of 1 min. Table 2.1 shows the number distribution of crystal at selected time intervals for Experiment No.1. The corresponding cumulative mass fraction of the crystals is shown in Figure 2.1 for each time interval. It was observed in the present case that after 160.83 min, there was very little change in the crystal population in the individual size classes. So, it can be assumed that steady state is reached by this time where 16546 crystals are obtained in the sieve size under consideration. For the purpose of comparing this result with the steady state runs of DEY and SEN GUPTA (1994 and 1993a) the same number of crystals were taken as the sample size. The algorithm also uses the same set of equations described earlier, and in addition, the experimental CSD reported by ŠKRTIĆ et al. (1989) is inserted in Figure 2.1. The agreement between theory and experiment confirms the validity of the proposed scheme.
Figures 2.2, 2.3 and 2.4 show the cumulative mass fraction of the crystals at
selected time intervals for Experiment Nos. 2, 3 and 4 respectively. The time
required to reach steady state and the sample size at the corresponding time for all
the experiments are summarized in Table 2.2.

For steady state runs, the sample sizes from Table 2.1 are used in MC
simulation using the algorithm reported by DEY and SEN GUPTA (1994 and 1993a).
The results obtained from the transient CSD simulation for the four experiments
approach the steady state values after 10τ, and these are in consistent with the steady
state runs and the experimental results of ŠKRTIČ et al. (1989).

2.4 Conclusions

Transient and steady state CSDs in a continuous crystallizer for size-dependent
growth rate are predicted. The crystal growth rates are described by the ASL model
and the agreement between prediction and available data confirms the validity of the
model. In the absence of any specific information on the distribution function of
shape factor, it is assumed to be one. The sample nucleation rate was taken as 1000
nuclei/min for calculation purposes.

Monte Carlo simulation provides the cumulative mass distribution of the
crystals, which is mathematically difficult by usual moment transformation of
population balance. The present scheme is also attractive due to its simple algorithm and easy implementation on a personal computer. However, the MC simulation shows oscillation in CSD’s that is an inherent drawback of this method.
### Table 2.1 Number distribution of crystal for Experiment No.1

<table>
<thead>
<tr>
<th>size in mm [-]</th>
<th>56.29</th>
<th>104.54</th>
<th>160.83</th>
<th>steady state</th>
</tr>
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<tr>
<td>0.074</td>
<td>14105</td>
<td>14117</td>
<td>14098</td>
<td>14000</td>
</tr>
<tr>
<td>0.163</td>
<td>1739</td>
<td>1781</td>
<td>1775</td>
<td>1865</td>
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<tr>
<td>0.200</td>
<td>134</td>
<td>248</td>
<td>234</td>
<td>259</td>
</tr>
<tr>
<td>0.231</td>
<td>-</td>
<td>118</td>
<td>136</td>
<td>119</td>
</tr>
<tr>
<td>0.281</td>
<td>-</td>
<td>106</td>
<td>116</td>
<td>132</td>
</tr>
<tr>
<td>0.325</td>
<td>-</td>
<td>78</td>
<td>73</td>
<td>63</td>
</tr>
<tr>
<td>0.400</td>
<td>-</td>
<td>55</td>
<td>50</td>
<td>45</td>
</tr>
<tr>
<td>0.470</td>
<td>-</td>
<td>24</td>
<td>36</td>
<td>30</td>
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<tr>
<td>0.555</td>
<td>-</td>
<td>12</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>0.655</td>
<td>-</td>
<td>-</td>
<td>11</td>
<td>8</td>
</tr>
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<td>0.785</td>
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<td>-</td>
<td>2</td>
<td>7</td>
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<tr>
<td>0.924</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>2</td>
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<tr>
<td>1.072</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>2</td>
</tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.548</td>
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<td>-</td>
</tr>
<tr>
<td>1.848</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>15978</td>
<td>16539</td>
<td>16546</td>
<td>16546</td>
</tr>
</tbody>
</table>

### Table 2.2 Summary of MC simulation (transient state) for each experiment

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Time required to reach steady state (min)</th>
<th>Sample size at steady state</th>
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<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>230.00</td>
<td>23672</td>
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<td>3</td>
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<td>4</td>
<td>506.67</td>
<td>51289</td>
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</table>
Figure 2.1 Cumulative mass fraction at different residence time for Experiment No. 1
Figure 2.2 Cumulative mass fraction at different residence time for Experiment No. 2
Figure 2.3: Cumulative mass fraction at different residence time for Experiment No. 3
Figure 2.4 Cumulative mass fraction at different residence time for Experiment No. 4