

PRECIPITATION KINETIC PARAMETER ESTIMATION

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Abstract

The aim of the Bayer refinery precipitation circuit is to maximise product yield whilst meeting product quality constraints, particularly product size. In order to optimise the precipitation circuit it is important to have a good understanding of the processes of growth, agglomeration, and nucleation; and to build mathematical relationships for these processes into precipitation circuit population balance models. A mathematical model has been developed that is capable of estimating the precipitation growth (G), nucleation (B_u), and agglomeration (β_0) kinetic parameters from batch experimental data. These kinetic parameters are required for solving the population balance equation, which is the cornerstone of precipitation circuit population models. The method is primarily based on work conducted by Bramley *et al.*¹, Litster *et al.*², and Wynn³.

Introduction

Gibbsite precipitation is a complicated system, with the processes of growth, agglomeration, and nucleation occurring simultaneously. Investigating the kinetics of growth, agglomeration, and nucleation requires the ability to extract kinetic information from precipitation reaction data in which these processes are occurring simultaneously. Kinetics estimation techniques are based on population balance models. These models take the form of an integro-partial differential equation, which, for a batch process, is given below in equation 1.

Eqn 1

$$\frac{\partial n(L,t)}{\partial t} + G \frac{\partial n(L,t)}{\partial L} = B_u \delta(L - L_1) + B(L,t) - D(L,t)$$

where $n(L,t)$ is the number based size distribution, t is time and L is the characteristic size of particles. The rate of particle growth is described by G , which, as written in equation 1, is the size independent linear growth rate and is defined as dL/dt . To account for the movement of particles into the field of view of the particle size analyser a 'source function'¹, B_u , is introduced. B_u is the rate of appearance of particles entering the first size interval, L_1 , of the particle size analyser and is related to the nucleation rate. δ is the Dirac delta function.

The terms $B(L, t)$ and $D(L, t)$ describe the agglomeration kinetics, and represent the rate of appearance and disappearance of particles due to agglomeration. For size independent agglomeration they are defined as

Eqn 2

$$B(L,t) = \frac{\beta L^2}{2} \int_0^L \frac{n([L^3 - \lambda^3]^{\frac{1}{3}}, t) n(\lambda, t)}{(L^3 - \lambda^3)^{\frac{2}{3}}} d\lambda$$

Eqn 3

$$D(L,t) = \beta n(L,t) \int_0^\infty n(\lambda, t) d\lambda$$

where β is the agglomeration kernel, or agglomeration rate constant. The agglomeration kernel is a measure of the frequency of collisions between crystals of sizes L and λ that are successful in producing an agglomerate, and is defined as

Eqn 4

$$\beta = \beta_0 \times f(L, \lambda)$$

where β_0 is a function of operating conditions such as liquor composition, temperature and shear rate. The second factor, $f(L, \lambda)$, is some function of size and, in general, reflects the mechanism thought to have caused agglomeration (e.g. gravitational settling, shear etc.). For size independent agglomeration systems $f(L, \lambda) = 1$.

Kinetics estimation refers to the determination of the growth, nucleation, and agglomeration kinetic parameters within the population balance model (G , B_u , and β respectively). A suitable kinetics estimation technique identified by Queensland Alumina Limited (QAL) is that developed by Bramley *et al.*¹. The purpose of the work conducted at QAL has been to apply the Bramley method to Bayer gibbsite precipitation, particularly to lab-scale batch precipitation reactions.

CSIRO have developed a method to extract growth (G), agglomeration (β), and nucleation (B_u) kinetics from batch experiments, which was subsequently used in the AMIRA P521 series of projects. However, the project sponsors do not have free access to the kinetics estimation procedures developed, as CSIRO claim that the techniques were developed separately to the AMIRA projects. Due to the cost of having experimental data analysed by CSIRO, QAL decided to develop the techniques in house.

Experimental

Batch precipitation experiments were conducted in QAL's laboratory precipitation reactors using synthetic liquors and Alcoa C31 hydrate as seed material. A total of 6 experiments were conducted under the same conditions to allow development of the experimental procedures.

A large batch of Alcoa C31 hydrate was washed with hot distilled water, and once dry, riffled into 1 kg identical batches for use in the experimentation. This hydrate was then used both for making synthetic liquors and as a seed material in the precipitation experiments.

Synthetic liquors were made to the following composition:

- A/C = 0.7
- Caustic = 200g/L
- C/S = 0.83

The required amounts of analytical grade NaOH pellets and Alcoa C31 hydrate were added to ~2L of distilled water. This mixture was heated and allowed to lightly boil until all of the hydrate had dissolved (~1.5 hours). The liquor was then allowed to cool before being vacuum filtered through a GF/C filter paper.

Sodium carbonate solution was made by dissolving the required amount of analytical grade Na_2CO_3 powder into ~1.5L of distilled water. Once dissolved, the solution was vacuum filtered through a GF/C filter paper.

The two solutions were then mixed together, and made up to 5.5L with distilled water. Upon mixing the solutions, often it was observed that very fine nuclei auto-precipitated. When this was

observed the liquor was re-filtered through a GF/C filter paper, before being added to the precipitation reactor.

All precipitation simulations were conducted in a lab-scale batch reactor. The main features of this reactor are:

- A total volume of 5.5L
- Precise temperature control ($\pm 0.1^\circ\text{C}$) via operation of a water jacket
- Overhead impeller agitation, including a draft tube complete with baffles

Batch precipitation reactions were conducted in the lab-scale reactors at the following conditions:

- Liquor composition = As above
- Temperature = 80°C
- Seed Charge = 45g/L
- Agitation Rate = 450 rpm
- Initial Volume = 5L

The necessary volume of synthetic liquor was added to the precipitation reactor, and allowed to reach the experimentation temperature (~ 1 hour) before a pre-heated allotment of C31 hydrate was charged to begin the precipitation reaction.

Samples were taken from the reactor at $t = 0, 5, 15, 30, 40, 50, 60, 75, 90$ and 120 minutes. At each time point the following samples were taken:

- 10mL sample for particle size analysis
- 10mL sample syringe filtered for ACS titration using the Metrohm automatic titrater
- 10mL sample for solids concentration

The 10mL sample for particle sizing was taken with a 5mL Eppendorf pipette and added to 240mL of milliQ water. From this solution two 5mL samples were taken and each added to 195mL of isoton (electrolyte used for coulter counter). These two solutions were then analysed on the Coulter Counter Multisizer III in "volume mode", with five separate 2mL samples analysed from each solution. These "runs" were checked for consistency against each other before summing each particle size distribution (PSD) to give the final size distribution for that time point in the precipitation experiment.

The 10mL sample for solids concentration is filtered through a millipore filtration set-up using a $0.7\mu\text{m}$ filter paper before being rinsed thoroughly with $\sim 200\text{mL}$ of distilled water, ensuring that no material is left on the funnel walls. The filter paper is then carefully removed to ensure that no solids are lost before being placed in a 60°C oven to dry.

Results and Discussion

Experimental Results

Figure 1 below shows the evolution over time of the PSD during the batch reaction due to the precipitation phenomena of growth, agglomeration, and nucleation. From $t = 0$ to $t = 30$, while the supersaturation is high, agglomeration appears to be the main contributor to the change in the PSD shape, growth then dominates for the remainder of the batch test. True nucleation is not observed, as any nuclei produced are smaller than the minimum measurable size using the $280\mu\text{m}$ orifice on the coulter counter ($5.6\mu\text{m}$).

Figure 2 below shows the change in the total number of particles with time during the batch reaction. Initially the total number of particles increases (i.e. from $t = 0$ to $t = 15$); it is believed that this is a result of particles smaller than the minimum measurable size agglomerating and growing into the size measurement region. Evidence of this is observed in Figure 1, with the increase in numbers from $t = 0$ to $t = 5$ occurring over a relatively wide

size range ($5.6\mu\text{m}$ to $\sim 12\mu\text{m}$). If the minimum measurable size were to be $10\mu\text{m}$, the data would show a significant increase in numbers from $t = 5$ min to $t = 15$ min; it is likely that a similar phenomenon occurs below the current minimum size of $5.6\mu\text{m}$. After this initial increase the total number rapidly decreases as particles agglomerate, the total numbers then becomes steady as the solution supersaturation and agglomeration kinetics reduce.

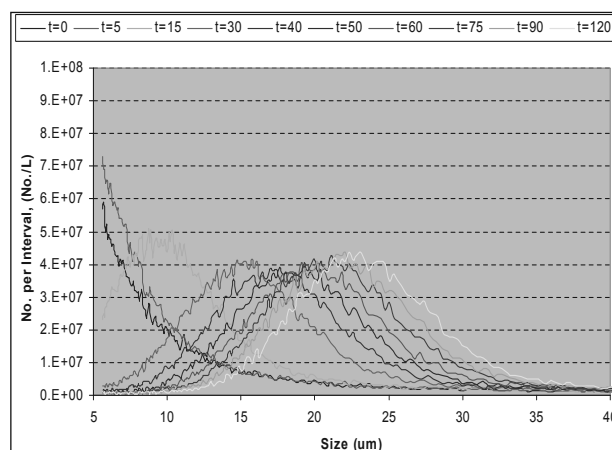


Figure 1. PSD Evolution During a Batch Precipitation Reaction

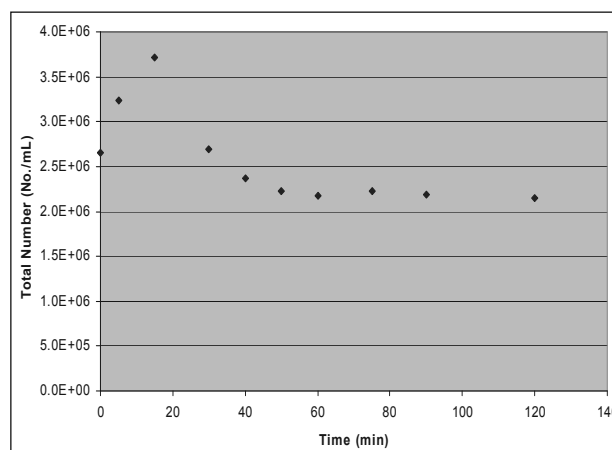


Figure 2. Total Number vs Time in a Batch Precipitation Reaction

A key requirement for the kinetics estimation procedure is to determine the rate of change of crystal mass within the system. As such the mass balance during each batch reaction is monitored and checked for consistency. Mass balances are calculated from the solids concentration, liquor titration, and particle size distribution at each sample time (Figure 3). It is clear from Figure 3 that there is agreement between mass of solids determined from the titration and the measured solids concentration. However, the coulter calculated mass is consistently lower than the other measurements, which is consistent with an issue with sampling the larger particles within the system (i.e. the particles containing the mass).

The data presented in Figure 3 is from the third batch precipitation test. It was noticed during sub-sampling for the coulter measurement that some (only a very small percentage) of the particles were not being suspended (and hence not sampled). Ensuring that the impeller was close enough to the bottom of the baffled beaker to provide sufficient agitation rectified this. In the initial two batch tests, the solids measurement was consistently higher than that calculated from the liquor titration and also exhibited much greater variation. This was rectified by:

- Ensuring that a sufficiently large volume of water was used to rinse the solids and filter paper to remove any residual liquor, and
- Taking care in removing the filter paper such that no solids were lost.

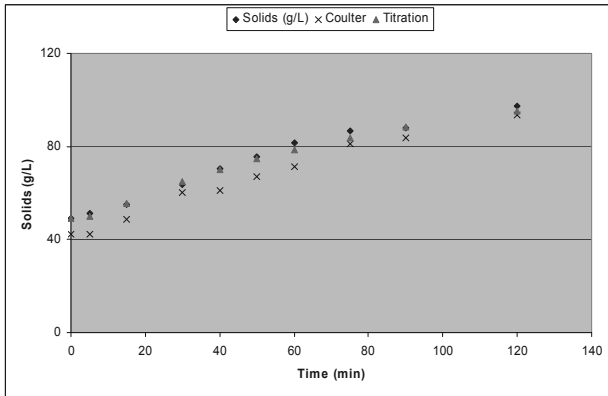


Figure 3. Mass Balance Consistency Between Solids Content Calculated from Solids, PSD, and Titration Data

Experimental Reproducibility

To date a total of 6 batch experiments have been completed, and during this time significant improvements have been made in the experimental method to improve experimental reproducibility. The initial batch experiment is excluded from the reproducibility analysis due to the poor quality of data obtained.

Figure 4 below shows the experimental reproducibility for the particle size obtained after 120 min of precipitation. The reproducibility in the desupersaturation curves is presented below in Figure 5, showing very little variation between the repeat experiments.

The caustic concentration over time for the 5 repeat experiments is shown in Figure 6. It is clear that the variation observed between experiments is due to the difficulty in achieving the aim initial caustic concentration; after $t = 0$ the caustic increases similarly for each repeat experiment.

Figure 7 shows the measured solids content with time for 4 of the repeat experiments (17 Mar data is excluded as this was prior to the improved method for solids measurement). It is clear that the solids concentration is generally consistent between the repeat batches and variation can be explained by errors in achieving the aim start solids concentration and in poor washing of the solids and filter paper.

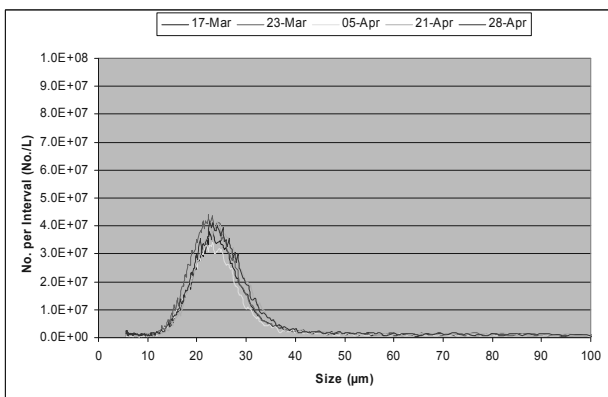


Figure 4. Reproducibility of PSD's After 120min for the 5 Repeat Experiments

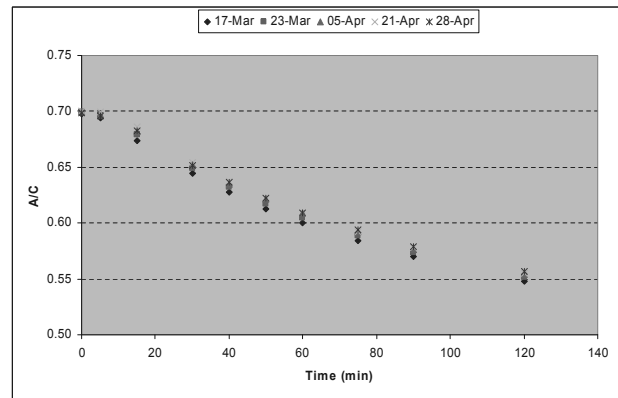


Figure 5. Reproducibility of the Desupersaturation Curves for the 5 Repeat Experiments

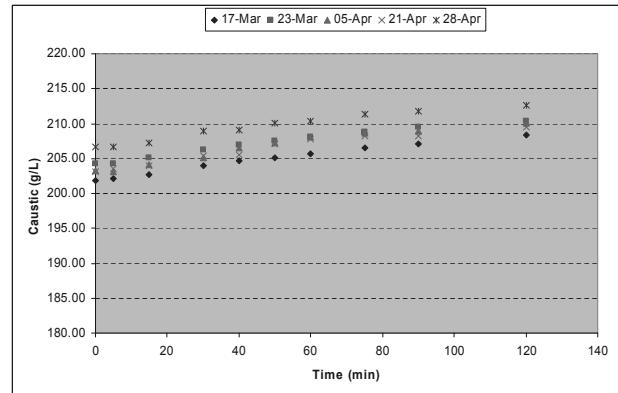


Figure 6. Reproducibility of the Liquor Caustic Concentration for the 5 Repeat Experiments

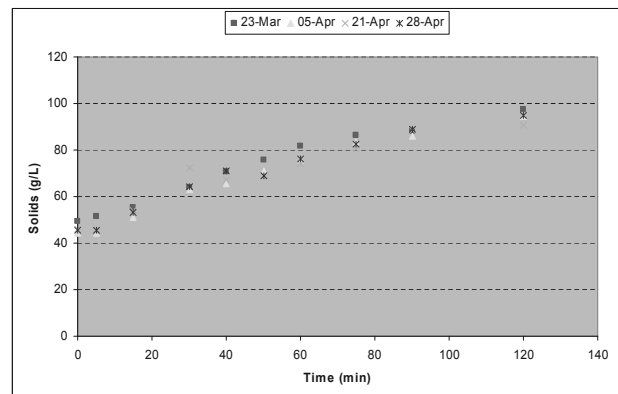


Figure 7. Reproducibility of the Measured Solids Content for the 5 Repeat Experiments

Kinetics Estimation Procedure and Results

The kinetics estimation procedure has been developed using a combination of the Bramley method¹ for kinetics estimation and the work conducted by Litster *et al.*² and Wynn³ on discretisation of the population balance. The procedure for obtaining the kinetics estimates from the experimental data will be outlined in the following sections.

1. Particle Size Distribution Conversion

The first step in the estimation procedure is to convert the size distribution reported by the Coulter Counter, which can use either a linear or logarithmic spacing for the size intervals, to a size distribution that uses a geometric progression to determine the size intervals^{2,4}. The ratio of the geometric progression, r , is determined by:

$$\text{Eqn 5 } \frac{1}{r} = 2^{3q}$$

where q is an integer; the larger q , the finer the PSD discretisation. Figure 8 below shows the raw coulter PSD as compared to the converted PSD, the size interval conversion smoothes most of the noise from the raw coulter data.

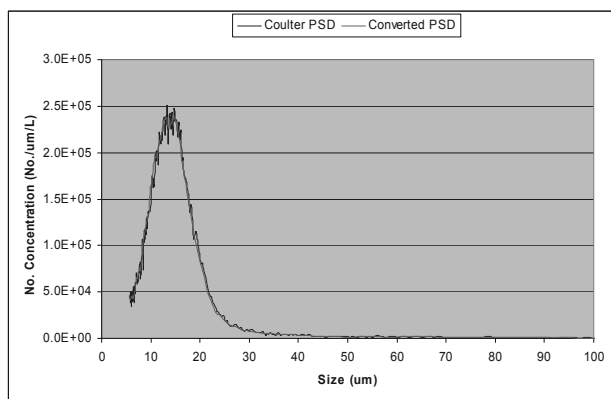


Figure 8. Comparison between the Normalised No. Concentration for Coulter and Converted PSD

Determination of the Moments of the Distribution

After the Coulter size distributions have been converted, as described above, the moments of the size distributions are calculated at each experimental time point. The k^{th} moment for a discretised size distribution is defined by:

$$\text{Eqn 6} \quad m_k = \sum_{i=1}^{\infty} L_i^k \cdot n_i$$

where L_i is the mean particle size of the i^{th} size interval, and n_i is the number of particles in the i^{th} size interval. The moments used in the kinetics estimation procedure are:

- The zeroth moment, μ_0 , which is the total number of particles
- The second moment, μ_2 , which is proportional to the total area of particles
- The third moment, μ_3 , which is proportional to the total volume of particles

The other property of the converted PSD used in the kinetics estimation method is the number of particles in the first size fraction (N_1), which is simply recorded from the converted size distribution at each time interval.

2. Determining the Rate of Change of μ_0 , μ_3 , and N_1

The next step in the procedure is to calculate the rate of change of the zeroth moment, the third moment and the number of particles in the first size fraction. This is the most critical step in getting reasonable kinetic parameter estimates. There are two methods that have been used to determine the rate of change:

- 1 Fit a natural cubic spline function to each set of data and evaluate the derivative of the function at each time point
- 2 Fit a model to the data using a least squares minimisation, and evaluate the derivative of the model function at each time point

In practice it is best to use a combination of the two methods as they both have their positives and negatives.

Natural cubic spline

Positives

- A natural cubic spline program can easily be coded into a macro in visual basic to fit the spline to the data, evaluate the derivative, and output the derivative at the experimental times.

Negatives

- The spline has to pass through every single experimental data point, and as such, experimental error in the data can cause significant errors in the calculation of the derivative (see Figure 9 below).
- When there are very small changes in the data (e.g. 0th moment at $t > 50$ min in Figure 10 below), small experimental variation can cause swings between positive/negative derivatives, which in turn introduces error into the kinetic estimates.

Model Fitting

Positives

- More robust to random experimental variation, as the model doesn't need to pass through every data point.

Negatives

- More complex than a cubic spline. Need to determine the right form of model equation to fit the data.
- An equation form may not exist that fits the experimental data.
- Differentiation of the model equation may be difficult for complex model equation forms.

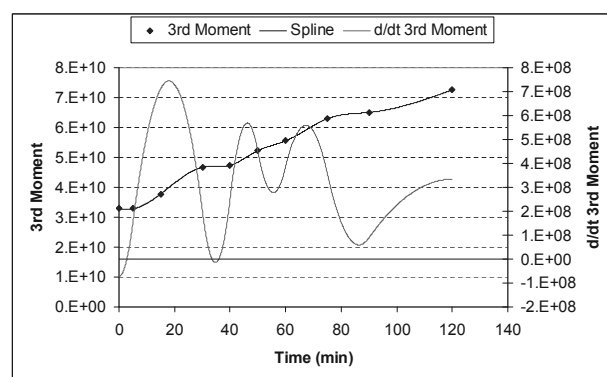


Figure 9. Natural Cubic Spline Fit to Experimental 3rd Moment Data

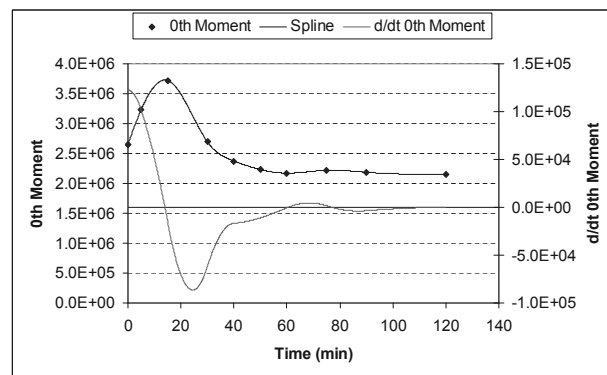


Figure 10. Natural Cubic Spline Fit to Experimental 0th Moment Data

3. Determination of Kinetic Parameters

Once the rate of change of each of μ_3 , μ_0 , and N_1 has been determined at each sample time, the kinetic parameters (G , B_u , β_0) can be found by solving 3 simultaneous equations:

$$\text{Eqn 7} \quad \dot{\mu}_0 = \beta_0 \Phi_0 + B_u$$

$$\text{Eqn 8} \quad \dot{\mu}_3 = G \Phi_3 + B_u \bar{L}$$

$$\text{Eqn 9} \quad = G \Phi_2 + \beta_0 \Phi_1 + B_u$$

The derivation of these equations is detailed in Bramley *et al.*¹, and Φ_0 , Φ_1 , Φ_2 , and Φ_3 are determined by the following equations and can be calculated from the particle size distribution data^{2,3}:

Eqn 10

$$\Phi_0 = \sum_{n_{eq}} (B_1 + B_2 + B_3 + B_4 - D_1 - D_2)$$

Eqn 11

$$\Phi_1 = -N_1 \sum_{j=1}^{n_{eq}} f(\bar{L}_1, \bar{L}_j) N_j$$

Eqn 12

$$\Phi_2 = \frac{2}{(1+r)\bar{L}_1} \left(\left(1 - \frac{r^2}{r^2-1} \right) N_1 - \frac{r}{r^2-1} N_2 \right)$$

Eqn 13

$$\Phi_3 = \frac{2}{(1+r)\bar{L}_1} \left(\left(1 - \frac{r^2}{r^2-1} \right) N_1 - \frac{r}{r^2-1} N_2 \right) \bar{L}_1 + \sum_{i=2}^{n_{eq}} \frac{2}{(1+r)\bar{L}_i} \left(\frac{r}{r^2-1} N_{i-1} + N_i - \frac{r}{r^2-1} N_{i+1} \right) \bar{L}_i$$

Where,

Eqn 14

$$B_1 = \sum_{j=1}^{i-S_1} f(L_{i-1}, L_j) N_{i-1} N_j \frac{2^{\left(\frac{j-1}{q}\right)}}{2^q - 1}$$

Eqn 15

$$B_2 = \sum_{p=2}^q \sum_{j=i-S_{p-1}}^{i-S_p} f(\bar{L}_{i-p}, \bar{L}_j) N_{i-p} N_j \frac{2^{\frac{j-i+1}{q}} - 1 + 2^{\frac{-(p-1)}{q}}}{2^q - 1}$$

Eqn 16

$$B_3 = \frac{1}{2} f(\bar{L}_{i-q}, \bar{L}_{i-q}) N_{i-q}^2$$

Eqn 17

$$B_4 = \sum_{p=1}^{q-1} \sum_{j=i+1-S_p}^{i+1-S_{p+1}} f(\bar{L}_{i-p}, \bar{L}_j) N_{i-p} N_j \frac{-2^{\frac{(j-i)}{q}} + 2^q - 2^q}{2^q - 1}$$

Eqn 18

$$D_1 = \sum_{j=1}^{i-S_1+1} f(\bar{L}_i, \bar{L}_j) N_i N_j \frac{2^{\frac{(j-i)}{q}}}{2^q - 1}$$

Eqn 19

$$D_2 = \sum_{j=i-S_1+2}^{n_{eq}} f(\bar{L}_i, \bar{L}_j) N_i N_j$$

Eqn 20

$$S_p = \ln t \left[1 - \frac{q \ln(1 - 2^{-p/q})}{\ln 2} \right]$$

n_{eq} is the total number of size fractions used to describe the particle size distribution and $f(\bar{L}_i, \bar{L}_j)$ is the size dependency term in the agglomeration kernel (eqn 4 above) and is equal to 1 for size independent agglomeration.

Solving the simultaneous equations at each sample time point for G, Bu, β_0 and gives the growth, nucleation, and agglomeration kinetics as a function of time during the batch test (Figures 11, 12, and 13 below).

Validation of the Estimates by Solving the Population Balance Equation

A batch precipitation model has been developed which uses a 4th order Runge-Kutta technique to numerically solve the population balance equation for $n(L, t)$. The model needs the following inputs:

- An initial particle size distribution and supersaturation
- The growth, nucleation and agglomeration kinetic parameters as a function of supersaturation (this is done by

fitting a model to the kinetic estimates with the experimental supersaturation at each of the sample times)

The model then uses the second moment of the PSD (proportional to surface area) and the growth rate to determine the amount of gibbsite precipitated during the time step. The model can then calculate the supersaturation at the end of the time step, which is then used to calculate the kinetic parameters at the new time point. The calculated particle size distributions (i.e. $n(L, t)$) are compared against those obtained experimentally, and any significant deviations indicate poor kinetic estimates. Figure 14 and Figure 15 below show the model predicted particle size distributions (at t=40min and t=120min) using the t=30 experimental data as initial conditions and the kinetic estimates determined above versus the experimental particle size distributions.

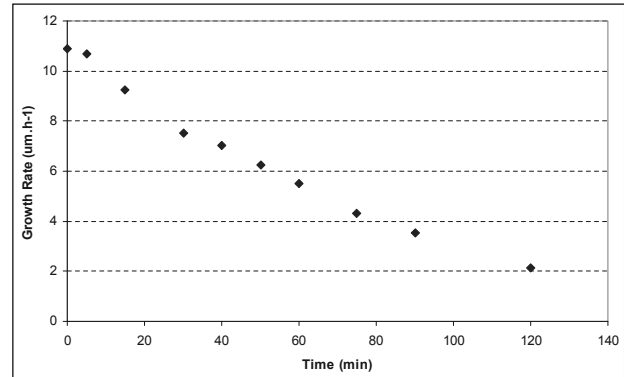


Figure 11. Growth Rate Estimates

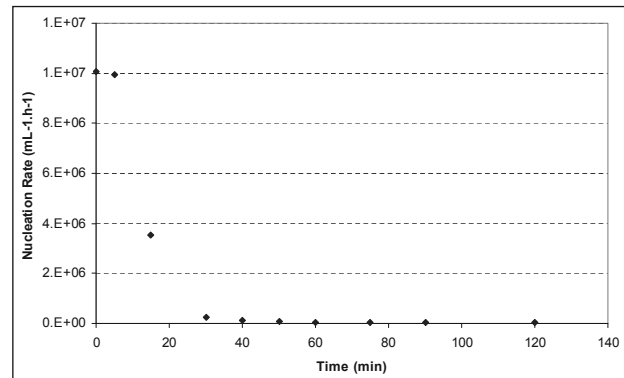


Figure 12. Nucleation Rate Estimates

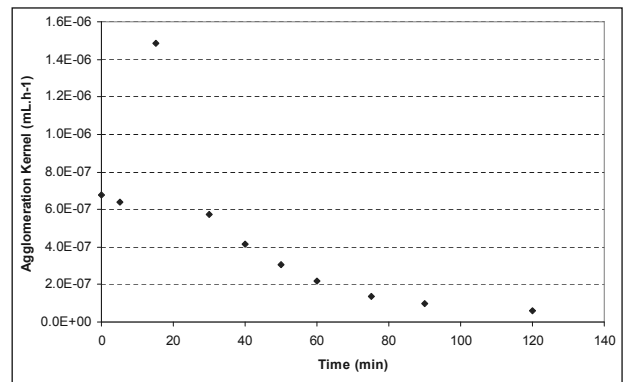


Figure 13. Agglomeration Kernel Estimates

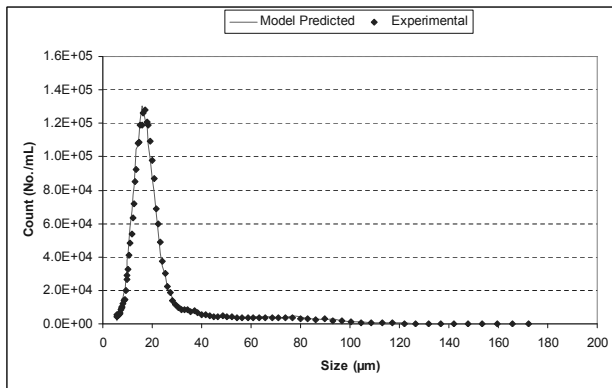


Figure 14. Model Predicted Vs Experimental PSD for t=40 min

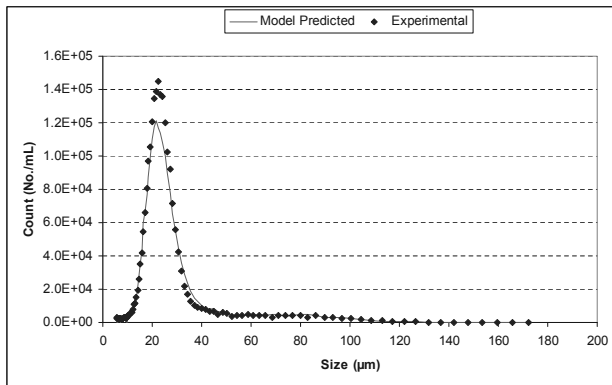


Figure 15. Model Predicted Vs Experimental PSD for t=120 min

Conclusions

A mathematical model has been developed that is capable of estimating the precipitation growth (G), nucleation (Bu), and agglomeration (β_0) kinetic parameters from batch experimental data. These kinetic parameters are required for solving the population balance equation. The steps are:

- Conduct a batch experiment, collecting samples over the duration of the simulation for liquor composition, solids concentration, and particle number size distribution
- Check for mass balance consistency using the 3 analyses
- Convert the raw particle size distributions into the correct form for analysis
- Calculate the zeroth and third moments (μ_0 and μ_3) and the number of particles in the first size interval (N_1) of the converted PSD's
- Determine the rate of change of μ_0 , μ_3 , and N_1 at each of the sample times
- From the PSD at each sample point, calculate the values of the coefficients Φ_0 , Φ_1 , Φ_2 , and Φ_3
- Solve the system of 3 simultaneous equations for the kinetic parameters G, B_u , and β_0
- Check the validity of the estimates by solving the population balance equation using the values of G, B_u , and β_0 and comparing the predicted PSD with the experimental PSD

References

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