STUDY OF AGGREGATION IN BARIUM SULPHATE PRECIPITATION

D. L. Marchisio¹, A. A. Barresi, M. Garbero, M. Vanni and G. Baldi
Dip. Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino,
C.so Duca degli Abruzzi 24, 10129, Torino, Italy

Barium sulphate precipitation has been widely studied in the last decades. This reactive system has attracted much attention since it represents a realistic test reaction for studying interaction between mixing and fast reactions. Experimental evidences showed that mixing is responsible for generating super-saturation and plays an important role in the competition between nucleation and crystal growth. Moreover besides crystal growth another size-enlargement process exists: aggregation. Aggregation takes place in two steps, first particles must be brought into close proximity by a transport mechanism, and then depending on the balance between attractive and repulsive forces particles may adhere or not. Inter-particle forces are caused by Van der Waals attraction and double layer repulsion. In the case of barium sulphate precipitation double layer repulsion is likely caused by specific ion adsorption and differential solution of ions. In this work the role of aggregation during barium sulphate precipitation is investigated by using a continuous tubular reactor. The effect of ion concentration, ion excess, and turbulence on the Crystal Size Distribution (CSD) and crystal morphology is investigated. Results showed the strong role of ions excess in determining the final aggregation rate. Eventually a modelling approach is presented and applied to the case study.

1. EXPERIMENTAL SET-UP

Barium sulphate precipitation was studied in a continuous tubular reactor with a single jet configuration. The tubular reactor is 2.1 m long and has an internal diameter of 1 cm. The jet is positioned on the reactor axis and is made of a small pipe (ID=1mm and OD=1.5 mm). The two reactants were separately fed in the small tube and in the annular region. Distilled water and analytical grade reagents were used to prepare barium chloride and sodium sulphate solution.

The CSD was measured by using a laser particle analyser (Coulter LS 230) on-line, in the outflow of the tubular reactor, and off-line, on samples taken at the reactor outlet. During off-line measurements the CSD was monitored with time and part of the samples were filtered and prepared for Scanning Electron Microscope (SEM) observation. The inlet velocity in the annular region was kept equal to 1 m/s, because of on-line measurements constrains, so that macroscopic Reynolds number was equal to 10,000. All the experiments were carried out with a ratio between the velocity in the feed stream in the nozzle and the feed stream in the annular region (VR) equal to one.

¹ Current affiliation: Dept. of Chem. Eng., Iowa State University, 3131 Sweeney Hall, Ames IA, 50011, U.S.A.
Three different series of experiments were carried out. We will indicate with $A$ the reactant fed in the nozzle and with $B$ the reactant fed in the annular region. In the first series of experiments (case 1) barium chloride was fed in the nozzle and sodium sulphate in the annular flow. Barium sulphate concentration was kept at a constant value ($c_{A0}=34 \text{ mol/m}^3$) whereas the concentration of the reactant fed in the annular region was varied in order to keep the concentration ratio ($\alpha=c_{B0}/c_{A0}$) within the range 0.01-3.00. In the second series (case 2) the feed positions were inverted and sodium sulphate was fed in the nozzle and barium chloride in the annular region but still with $c_{A0}=34 \text{ mol/m}^3$ and $\alpha$ within 0.01 and 3.00. The experiments in the last series (case 3) were carried out with barium chloride in the nozzle and sodium sulphate in the annular region and with $0.01<\alpha<3.00$ but with $c_{A0}=341 \text{ mol/m}^3$.

2. EXPERIMENTAL RESULTS

In Fig. 1 the CSDs at the reactor outlet with barium chloride fed in the nozzle $c_{A0}=34 \text{ mol/m}^3$ (left) and sodium sulphate fed in the nozzle $c_{A0}=34 \text{ mol/m}^3$ (right) at different concentrations of the co-reactant fed in the annular region (and thus different values of reactant ratio $\alpha$) are reported (on the left for barium chloride fed in nozzle and on the right for sodium sulphate fed in the nozzle). As it is possible to see in all the cases investigated the CSDs are mono-modal and the mean crystal size ranges from about 0.5 to 1.5 $\mu$m. If the mean crystal size is plotted against the concentration ratio ($\alpha$) or the co-reactant concentration $c_{B0}$ a shallow maximum is detected. In fact, being the reactant fed in the nozzle the limiting one and being kept at a constant concentration ($c_{A0}=34 \text{ mol/m}^3$), increasing the co-reactant concentration ($c_{B0}$), the mean crystal size first increases, because of the enhanced growth rate, but then decreases because of the transition of the nucleation rate into the homogeneous region. It is interesting to note that in all the cases investigated if sodium sulphate is fed in the nozzle particles are smaller (and thus probably higher in number density). If samples are taken and monitored with time the CSD evolution can be investigated. In Fig. 2 the CSD evolution for two cases (barium chloride fed in the nozzle) are reported. At low co-reactant concentration the main changes in the CSD seem to be caused by crystal growth, whereas at higher concentration aggregation starts to play an important role. These considerations are confirmed by SEM observation (see Fig. 3). At low concentration the crystals are regular and well-shaped. Increasing the reactant concentration crystal growth goes under diffusion control and crystals become dendritic. A further increase in the reactant concentration causes the transition to homogeneous nucleation and the total particle number density increases of several order of magnitude,
allowing aggregation to take place. Moreover, aggregation seems to be influenced by reactant feeding modes. This behaviour can be explained in terms of particle stability (Bramley et al., 1997).

Suspended particles interact depending on the balance between attractive and repulsive forces. A useful indication on the dispersion stability is the Point of Zero Charge (PZC), which is the ion concentration when the surface charge is null and repulsion forces vanish. For barium sulphate this condition is reached with a strong excess of sulphate ions (which is verified when barium chloride is fed in the nozzle). It can thus be inferred that in this case, in the early stages of nucleation, due to high value of total particle number density and strong instability, nuclei have a high tendency to aggregate, reducing the total particle number density and thus producing larger crystals. Moreover, once formed these crystals have a higher tendency to aggregate as proved by comparison of crystal morphology and CSDs in case 1 and 2. In the last case investigated barium chloride was fed in the nozzle and sodium sulphate in the annular region with $c_{A0}=314 \text{ mol/m}^3$ and with $c_{B0}=3.14-1000 \text{ mol/m}^3$. In this case reactant
concentrations were so high that the reaction was always complete at the reactor outlet and in all the cases investigated the CSDs were multi-modal.

In Fig. 4 the mean crystal size is reported against the co-reactant concentration. The maximum detected in the previous two cases is not observed here since, in this range, an increase in the co-reactant concentration causes only a decrease in particle size. In this case aggregates are constituted by monomers of about 0.1 \( \mu \text{m} \) that after aggregation form stable agglomerates of about 1 \( \mu \text{m} \).

3. PRECIPITATION MODEL

The experimental data presented in this work have been used to validate different modelling approaches. The model is Computational Fluid Dynamics (CFD) based (Baldyga and Orciuch, 2001; Marchisio et al., 2001); with this approach the governing equations (continuity, Navier-Stokes, and scalar transport) are solved in a finite-volume code. Several commercial CFD codes exist, such as Fluent and CFX. The tubular reactor has been modelled by using the standard \( k - \varepsilon \) model with standard wall functions, and the computational grid is a 2D grid under the assumption of axial symmetry. When dealing with turbulent flows and fast reactions (such as precipitation reactions) the CFD approach need a closure model due to mixing at the molecular level. This can be done using different approaches and one of the most popular is the presumed Probability Density Function (PDF) method. According to it, the PDF of each scalar is assumed to follow a particular functional form. In this work the finite-mode PDF approach was used, in which the PDF is represented by a finite set of delta functions (or modes). If three delta functions are used the representation is reported in Fig. 5 and the set of transport equations that needs to be solved is as follows:

\[
\frac{\partial p_1}{\partial t} + \frac{\partial}{\partial x_1}\left( \langle x_1 \rangle p_1 \right) = \frac{\partial}{\partial x_1} \left( \Gamma \frac{\partial p_1}{\partial x_1} \right) + \gamma_1 \left( p_1, \langle x_1 \rangle \right),
\]

\[
\frac{\partial p_2}{\partial t} + \frac{\partial}{\partial x_1}\left( \langle x_1 \rangle p_2 \right) = \frac{\partial}{\partial x_1} \left( \Gamma \frac{\partial p_2}{\partial x_1} \right) + \gamma_2 \left( p_1, \langle x_1 \rangle \right),
\]

\[
\frac{\partial \langle x_1 \rangle}{\partial t} + \frac{\partial}{\partial x_1}\left( \langle x_1 \rangle \langle x_1 \rangle \right) = \frac{\partial}{\partial x_1} \left( \gamma_3 \langle x_1 \rangle \langle x_1 \rangle \right) + \gamma_4 \left( \langle x_1 \rangle, \langle x_1 \rangle \right),
\]

where \( p_1 \) and \( p_2 \) are the probabilities of modes 1 and 2 and \( \langle x_1 \rangle \) is the weighted mixture fraction for mode 3, \( \langle x_1 \rangle_1 \) and \( \langle x_1 \rangle_2 \) are the local mixture fraction for modes 1 and 2, and where the micro-mixing rates \( \gamma \) and \( \gamma_3 \) are determined in order to force the mixture fraction variance to decay following the correct transport equation. Each delta function can be thought of as an Environment in which each computational grid of the domain is
divided. In this case for example, Environments (or modes) 1 and 2 contain unmixed reactants and due to micro-mixing they mix together generating Environment (or mode) 3 in which reaction and particle formation takes place (Fox, 1998).

The other issue that needs to be addressed in the investigation of precipitation is the population balance. This is a continuity statement written in terms of the CSD function. Several approaches exist such as, the Discretised Population Balance (DPB) approach, the Moment Method (MM) and the Monte Carlo (MC) method. The first method (DPB) is based on the discretisation of the internal coordinate that can be particle length or volume (Vanni, 2000) whereas the last one (MC) is based on a stochastic simulation which involves a population of particles (Smith and Matsoukas, 1998). Both the approaches require a strong computational effort and are not suitable to CFD applications. When using the MM the internal coordinate is integrated out and the population balance is solved through the moment of the CSD (Hulburt and Kats, 1964):

\[
\frac{\partial m_k(x,t)}{\partial t} + \sum_i \left( u_i \frac{\partial m_k(x,t)}{\partial x_i} - \frac{1}{\Gamma_k} \frac{\partial}{\partial x_i} \left( \Gamma_k \frac{\partial m_k(x,t)}{\partial x_i} \right) \right) = 0^k J(x,t) + k G m_{k-1}(x,t) + B_k(x,t) - D_k(x,t)
\]

where \( m_k \) is the \( k \)-th moment of the CSD, \( J \) is the nucleation rate, \( G \) is the molecular growth rate, and the birth and death terms of aggregation can be written as

\[
B_k(x,t) = \frac{\beta_o}{2} \int_0^\infty \int_0^\infty n(\lambda_x,t) \left( u^i + \lambda^i \right)^{k+1} n(u;\lambda_x,t) du d\lambda \approx \beta_o b_k m_0 m_k
\]

\[
D_k(x,t) = \frac{\beta_o}{2} L^k n(L_x,t) \int_0^\infty \int_0^\infty n(\lambda_x,t) d\lambda dL \approx \beta_o m_0 m_k
\]

where \( \beta_o \) is the size-independent aggregation kernel and \( b_k \) is a numerical constant (Marchisio et al, 2002a). This method has been lately applied in its standard formulation, giving acceptable agreement with experimental data. In Fig. 6a model

![Fig. 5. Finite-mode representation of the PDF.](image)

![Fig. 6. Precipitation model results: (a) \( c_{in} = 34 \text{ mol/m}^3 \) barium chloride fed in the nozzle (circles) and sodium sulphate fed in the nozzle (squares), continuous line: model predictions; (b) \( c_{in} = 341 \text{ mol/m}^3 \) barium chloride fed in the nozzle (square), dashed line: model predictions without aggregation, continuous line: model predictions with aggregation.)](image)
predictions are compared with experimental data for $c_{\text{A0}} = 34$ mol/m$^3$ with barium chloride fed in the nozzle and sodium sulphate fed in nozzle and for $c_{\text{A0}} = 341$ mol/m$^3$ with barium chloride fed in the nozzle. As it is possible to see the agreement is quite good. At high concentration (Fig. 6b) the role of aggregation is much stronger, in fact including aggregation in the model the agreement is improved. However, in this case the agreement is still not satisfactory and the contribution of turbulent motions to the aggregation rate must be included. This task requires the use of size-dependent aggregation kernels, and cannot be handled by using the standard MM. In this case use of the Quadrature Method of Moments (QMOM) is suggested (McGraw, 1997). This approach can be seen as an extension of the MM in which the closure problem (i.e., the source terms for lower-order moments transport equations are written only in terms of lower-order moments themselves) is solved by means of a quadrature approximation (Gordon, 1968).

4. CONCLUSIONS

The experimental campaign showed that barium sulphate precipitation is strongly influenced by aggregation and mixing (also at the molecular level at high concentrations). Ion excess plays an important role in determining aggregation efficiency and likely influences also nucleation and growth rates. A modelling approach needs to accurately describe mixing and solid evolution. This can be done coupling CFD with a micro-mixing sub-grid-scale model and with the population balance. Micro-mixing can be successfully modelled using a presumed PDF approach which in comparison with the full PDF approach (Fox, 1996) requires less computational efforts. The population balance can be modelled with the standard MM or with the QMOM which has been lately validated for simultaneous nucleation, growth and aggregation problems (Marchisio et al., 2002b, 2002c).

ACKNOWLEDGEMENTS - The research has been partially supported by an Italian National Research Project (PRIN – Analysis and modelling of solid-liquid mixing processes).

6. REFERENCES

Vanni, M., 2000, J. Colloid Interface Sci., 221, 143.