STIRRING AND MIXING EFFECTS IN AGGLOMERATIVE PRECIPITATION

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<u>Summary</u> Precipitation of a solid product from liquid ionic solutions includes mixing, fast chemical reaction, nucleation, growth and agglomeration of crystals. At high supersaturation precipitation is dominated by agglomeration of particles that are much smaller than the Kolmogorov microscale. Modeling of particle agglomeration includes effects of bulk fluid motion, Brownian diffusion (both with hydrodynamic interaction), colloidal forces and mixing. Mixing determines chemical environment of colliding particles.

INTRODUCTION

Consider the complex process of agglomerative precipitation of solid products from two liquid ionic solutions A and B:

$$A^{n+} + B^{n-} \rightarrow C\downarrow \tag{1}$$

involving instantaneous (mixing controlled) chemical reaction, subsequent crystallization of the product (i.e. nucleation and growth of crystals) and its agglomeration. At low supersaturation there are usually negligible effects of agglomeration, and the crystals size distribution is mainly affected by competition between nucleation and growth of crystal, which results from the competition between creation and consumption of supersaturation. Supersaturation is created by mixing controlled chemical reaction, and is consumed by precipitation; it also decreases due to mixing with the less supersaturated environment. At high supersaturation the process is dominated by agglomeration. Modeling of the agglomerative precipitation process requires a complete knowledge of the spatial distribution of instantaneous, local concentrations of all ions and molecules involved in the process and resulting distribution of supersaturation. Supersaturation distribution determines the local rates of nucleation and growth of particles and affects strongly agglomeration process; effect on agglomeration results from the fact that the supersaturated solution supplies material necessary to bond colliding particles and form agglomerates. Local concentrations determine also electrical interaction between small colloidal particles, because most particles in aqueous media are charged, and resulting repulsion force depends on solution composition. Identification of concentration distributions requires application of mixing models. In what follows PDF approach is used to model mixing, whereas the agglomeration rate is expressed as the product of expressions describing collision rate and probability of agglomeration.

THEORY AND MODELLING OF AGGLOMERATION

Collision of particles

We consider small particles of collision diameter smaller than the Kolmogorov length microscale. We further assume that particles are so small that their relaxation time is much smaller than the Kolmogorov time microscale. Under such assumptions the effect of inertial forces on the micro-motions of the fluid and particles can be neglected and the creeping flow can be assumed. New formed nuclei have the size of the order of nanometer and they grow due to crystal growth and agglomeration up to several micrometers size. Hence, to follow nucleation, growth and agglomeration of particles, one needs to model simultaneously the perikinetic (Brownian diffusion), orthokinetic (convective transport due to fluid motion) as well as an intermediate regime of collision and to include effects of the colloidal forces on relative particle velocity. The model applied in this work is based on the convective-diffusion equation for the probability of finding two particles at a given relative position, similarly as in models presented in ref. [1, 2]. The Batchelor-Green [3] relation is used for the relative particle velocity, and the turbulent flow at scales smaller than the Kolmogorov microscale is represented by assuming an axisymmetrical extensional flow with the mean value of an extension rate given by Batchelor [4]. The tensor of Brownian diffusion is expressed using the method of Batchelor [5] and the hydrodynamic functions $A(\rho,\lambda)$, $B(\rho,\lambda)$, $G(\rho,\lambda)$, $H(\rho,\lambda)$ that describe the disturbance of the ambient fluid velocity by presence of two colliding particles are determined by solving analytically the Stokes and continuity equations following the method proposed by Lin et al. [6]. For a very small distance between particles instead of an exact analytical solution the near-contact asymptotics are used following O'Neill and Majumdar [7]. The colloidal interaction forces that induce particle velocity in the radial direction result from attractive and repulsive potentials; the potentials are calculated from equations proposed by Hamaker and Hogg respectively. The repulsive potential is identified with the diffuse layer potential and calculated from the Gouy-Stern-Grahame double layer model [8] using the surface potential resulting from the Nernst equation. The Nernst equation shows that composition of the solution including ionic strength and ion concentration affects the surface potential the resulting collision rate. This means that also mixing, by affecting concentration distribution, has indirect effect on the agglomeration rate. Fig. 1 presents distribution of the pair probability function computed for spherical particles. One can see increased concentration of small particles in the neighbourhood of the larger one; this results from slowing down of particles due to action of both repulsive forces and hydrodynamic interactions. Once the pair probability function distribution is determined, the collision rate constant (collision kernel) can be computed by integrating the particle flux over the entire particle surface.
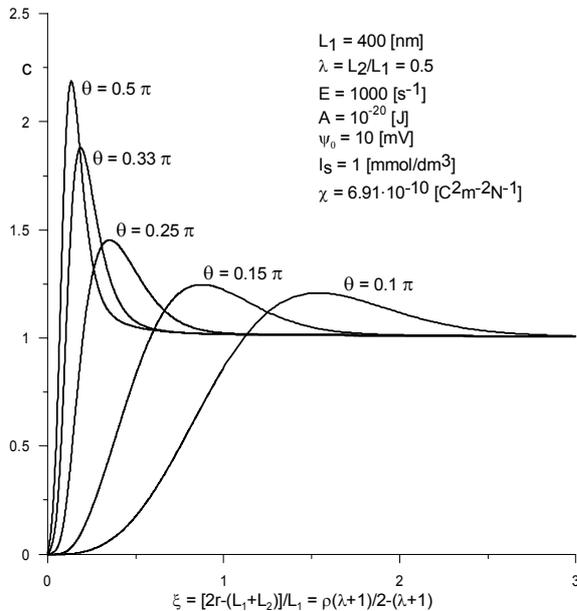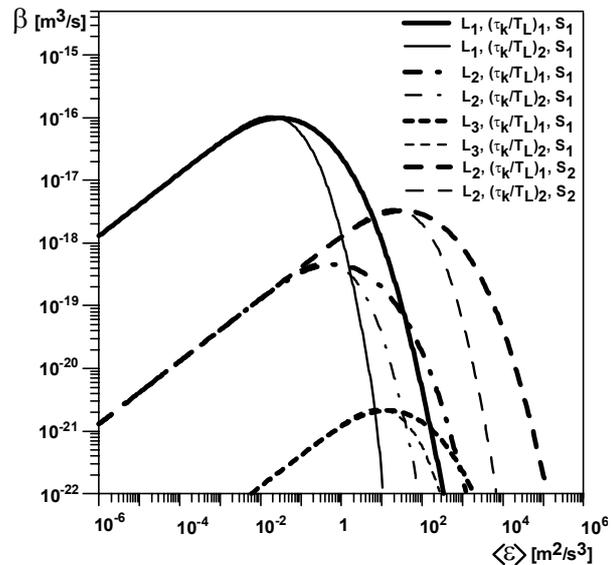
Fig.1.Pair probability function distribution

Fig.2. Effect of the rate of energy dissipation $\langle\varepsilon\rangle$ on the rate of aggregation. $L_1 = 10^{-6}$ m, $L_2 = 10^{-7}$ m, $L_3 = 10^{-8}$ m, $(\tau_k/T_L)_1 = 10^{-4}$, $(\tau_k/T_L)_2 = 0.01$, $S_1 = 2800$, $S_2 = 14400$.

Probability of agglomeration

In the previous section the collision rate of particles was modeled. However, especially in the case of large particles not every collision leads to agglomeration. That is why the concept of agglomeration probability has to be introduced. Agglomeration probability function expresses probability that during particle collision there will be enough time to build the crystalline bridge strong enough to resist the hydrodynamic stresses generated by turbulence.

In this presentation the probability of agglomeration is related to the fine scale structure of turbulence and expressed using multifractal formalism; we apply to this end the Lagrangian approach worked out by Borgas [9]. The multifractal model of turbulence is used as the subgrid closure for the rate of strain and related stresses when the RANS based CFD code is used to simulate the process. Multifractal formalism enables prediction of the form of the agglomeration probability function that is specific for each collision kernel, which distinguishes presented method from the other ones applying presumed forms of this function.

RESULTS AND CNCLUSIONS

The model predicts that the process of agglomeration is scale dependent, which means the scale-up methods employing the constant value of the rate of energy dissipation in the systems of different size that are used by chemical engineers are of limited universality. Fig. 2 illustrates this feature of agglomeration observed in the case of orthokinetic agglomeration in homogeneous, isotropic turbulence for particles of size L_i, in the solution of supersaturation S_i and for two different values of the ratio of the Kolmogorov time microscale τ_K to the Lagrangian time macroscale T_L. The time scale ratio reflects effect of the scale of the system on the process. The agglomeration model was combined with the PDF method for modeling mixing and linked to the CFD code. The computations were carried out with the CFD package Fluent 6 employing the k-ε model. Results of computations were compared with experimental data obtained for barium sulphate precipitation carried out in the 4 m long tubular reactor of diameter equal to 0.0320 m for the pipe Reynolds number varied from 40000 to 70000. The model predicts trends observed in experiments.

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