

Study of Neodymium Oxalate Precipitation in a Continuous Mixed Suspension Mixed Product Removal

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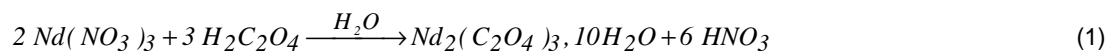
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Oxalic precipitation is used in the nuclear industry. To facilitate the development of experimental methods and data acquisitions, actinides are often simulated using lanthanides, thereby gaining experience in harmless conditions. Precipitation reactions being highly sensitive to many operation parameters, modelling appear to be a very effective tool to predict the evolutions of the system subjected to various operating conditions, especially in nuclear environment in which experiments are limited.

The aim of this article is to describe the modelling approach and its application to the neodymium oxalate precipitation in a continuous MSMPR (Mixed Suspension Mixed Product Removal). The model takes into account the kinetic laws of primary nucleation, crystal growth and agglomeration. Thermodynamic effects are taken into account through activity coefficients which are calculated using the Bromley model. For the nucleation study, experimental runs have been performed in a specific device that allows a micromixing time less than a millisecond. The homogeneous nucleation rate follows the Volmer-Weber equation. The crystal growth rate is first order with respect to the supersaturation and controlled by the surface integration into the crystal lattice according to a screw dislocation mechanism. The agglomeration kernel has been found to be independent of the crystal size. The particle sizes predicted for two different mean shear rates are in good agreement with the experimental measurements.

1. Introduction

Oxalic precipitation is applied to process radioactive wastes and to recover actinides. To facilitate the development of experimental methods, actinides are often simulated using lanthanides. In this study, the precipitation of neodymium oxalate achieved by mixing solutions of neodymium nitrate and oxalic acid according to the precipitation reaction (Eq. 1) is chosen as the working example:



The modelling approach is based on experimental acquisitions for the thermodynamic and kinetic laws and on a numerical model using a specific method of moments to calculate the crystallite and the loose agglomerate population balances taking into account nucleation, growth and agglomeration (Lalleman et al., 2012b). When agglomerates are loose, the solution is in contact with all elementary crystals forming the agglomerate; therefore they can grow in the same way as free elementary crystals in the suspension. According to microscopic observations, neodymium oxalate precipitations lead to the formation of such loose agglomerates. This is why, two population balances are considered: one for the crystallites which can be born and grow, another one for the agglomerates created by the crystallites collisions and sticking. A reconstruction of the size distribution of the loose agglomerates is then carried out using an algorithm due to Chebyshev and compared with the experimental distributions to validate the global approach.

2. Thermodynamic and kinetic laws

2.1 Supersaturation ratio

The expression of the supersaturation ratio, S , appears in the kinetics rates of nucleation, growth and agglomeration and is linked to the solubility product P_S ($1.16 \cdot 10^{-14} \text{ mol}^5 \cdot \text{m}^{-5}$), the mean activity coefficient γ_{\pm} and the concentrations as follows:

$$S = \gamma_{\pm} \left(\frac{C_{Nd^{3+}}^2 C_{C_2O_4^{2-}}^3}{P_S} \right)^{1/5} \quad (2)$$

The mean activity coefficient γ_{\pm} is calculated using the Bromley method (Lalleman et al., 2012a).

The solid concentration C_C is determined from the crystallite 3rd moment μ'_3 , the crystallite volume shape factor ϕ_v (0.06), the crystallites density ρ_c ($2420 \text{ kg} \cdot \text{m}^{-3}$) and the solid molar mass M_c ($732.6 \text{ g} \cdot \text{mol}^{-1}$):

$$C_c = \frac{\phi_v \rho_c}{M_c} \mu'_3 \quad (3)$$

2.2 Nucleation

Homogeneous primary nucleation is a fast process relative to mixing and the reagents have to be rapidly mixed in order to achieve a spatially homogeneous supersaturation. Therefore, experimental runs, used for the determination of the nucleation rate, have been performed in a specific apparatus patented by the French Atomic Energy Commission and AREVA (Bertrand et al. 2004a), based on the stop-flow method (Nielsen, 1964). Experiments have been performed with different supersaturation ratios and temperatures T to fit the classical theory proposed by Volmer and Weber (1926).

$$R_N = 3 \times 10^{31} \exp\left[-\frac{67600}{RT}\right] \exp\left[-\frac{187}{(\ln S)^2}\right] \quad S > 50 \quad 293 \text{ K} < T < 333 \text{ K} \quad (4)$$

2.3 Crystal growth

The crystal growth kinetic law has been determined using a neodymium nitrate solution charged with a high amount of neodymium oxalate particles with an adjusted distribution. A small volume of oxalic acid is rapidly added so that the mass that precipitates doesn't exceed 5 % of the initial crystal mass. Under these conditions, the crystal growth is the predominant process (Bertrand et al., 2004b). From the decrease of the neodymium concentration in solution, monitored by spectrophotometric measurements, the kinetic parameters can be identified (Bertrand et al., 2004b). The crystal growth rate G can be written as:

$$G = 2.9 \times 10^{-6} \exp\left(-\frac{14000}{RT}\right) (P_S)^{1/5} (S - 1) \quad 293 \text{ K} < T < 333 \text{ K} \quad (5)$$

The crystal growth process is controlled by the surface integration into the crystal lattice, thanks to a screw dislocation mechanism (Burton et al., 1951).

2.4 Agglomeration

Knowing the nucleation and crystal growth kinetics, the experimental agglomeration study has been carried out in a continuous MSMPR precipitator (Lalleman et al., 2012b) where nucleation, growth and agglomeration occur simultaneously. The determination of the agglomeration kernel takes into account the influence of the supersaturation ratio, the shear rate $\dot{\gamma}$, the temperature and the ionic strength (I). The mathematical treatment of experimental crystal size distributions leads to the following agglomeration kernel:

$$\beta = 2.55 \times 10^{-7} I^{-0.70} S \dot{\gamma}^{-0.24} \exp\left(-\frac{40900}{RT}\right) \quad S > 61 \quad 293 \text{ K} < T < 333 \text{ K} \quad (6)$$

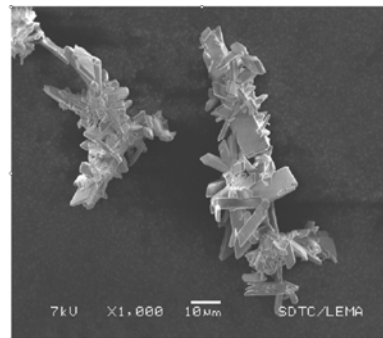
$$600 \text{ mol.m}^{-3} < I < 2100 \text{ mol.m}^{-3} \quad 45 \text{ s}^{-1} < \dot{\gamma} < 1024 \text{ s}^{-1}$$

3. Experimental study of neodymium oxalate continuous precipitation

All experimental runs are carried out in a continuous MSMPR precipitator until reaching the steady-state. This precipitator is a 200 mL cylindrical glass tank reactor, equipped with a heating jacket and four stainless steel baffles, as shown in Figure 1a. It is stirred by a stainless steel four 45° pitched blade turbine. The ratio between the tank diameter T, the impeller diameter D, the height h and the baffle width b are as follows: H=T, D=T/3, h=T/3, b=T/10.



a)



b)

Figure 1: a) 200 mL precipitator. - b) SEM observation of neodymium oxalate agglomerates

Precipitation experiments are performed by mixing a neodymium nitrate solution with an oxalic acid one under stoichiometric conditions according to (Eq. 1). The mean residence time is about 1 minute in order to reach high supersaturation ratios. Experiments were performed at 20°C with identical feeding concentrations, for two different shear rates. This latter is assumed to be homogeneous in the whole reactor and its mean value can be computed thanks to the rate of kinetic energy dissipation as follows:

$$\dot{\gamma} = \sqrt{\frac{\varepsilon}{\nu}} \quad (7)$$

$$\varepsilon = \frac{N_p N^3 D^5}{V} \quad (8)$$

where ε is the mean kinetic energy dissipation rate, ν is the kinematic viscosity, N_p is the power number (1.5 for a four 45° pitched blade turbine), N is the stirrer speed, D its diameter and V is the suspension volume.

Table 1: Operating conditions and parameters obtained during the precipitation experiments

Run		1	2
N	RPM	1000	2000
$C_{Nd,0}$	mol.m ⁻³	142.2	142.2
$C_{Ox,0}$	mol.m ⁻³	213.7	213.7
$\bar{\gamma}$	s ⁻¹	362	1024
$L_{4,3}$	μm	65	41

Slurry samples are then collected at the precipitator outlet and analyzed using a laser diffraction particle sizer analyzer (Malvern Mastersizer) to get the steady-state experimental particle size distributions. The size distributions are relatively narrow. The volume mean sizes $L_{4,3}$ is ranging between 41 and 65 μm and decrease when the mean shear rate increases.

4. Population balances

4.1 Crystallites and agglomerates population balance

Scanning Electron Microscopy observations of neodymium oxalates emphasize the formation of loose agglomerates (see Figure 1b). In such a case, the solution is in contact with all elementary particles which constitute the agglomerates, so that they can grow in the same way as single crystals in the suspension. This observation leads to the development of a specific model, based on two population balances one related to the elementary particles (crystallites) and one for the agglomerates (Lalleman et al., 2012b).

The transient evolutions of the first 2n moments, μ'_k , of the crystallite population are given by:

$$\frac{d\mu'_k}{dt} + \frac{\mu'_k}{\tau} = 0^k R_N + jG\mu'_{k-1} \quad \text{for } k=0,1,2, \dots, 2n-1 \quad (9)$$

And those of the loose agglomerates, μ_k can be written as:

$$\frac{d\mu_k}{dt} + \frac{\mu_k}{\tau} - \frac{\mu'_k}{\tau} = \overline{B}_k - \overline{D}_k \quad (10)$$

where \overline{B}_k and \overline{D}_k represent the birth et death terms due to agglomeration.

$$\overline{B}_k = \frac{1}{2} \sum_{i=1}^n w_i \sum_{j=1}^n w_j (L_i^3 + L_j^3)^{k/3} \beta(L_i, L_j) \quad (11)$$

$$\overline{D}_k = \frac{1}{2} \sum_{i=1}^n w_i L_i^k \sum_{j=1}^n w_j \beta(L_i, L_j) \quad (12)$$

β is the agglomeration kernel, which was found to be independent of the size for neodymium oxalates, therefore $\beta(L_i, L_j) = \beta$ which is calculated using (Eq.6).

w_i and L_i are the weights and abscissa of the quadrature of the moments calculated thanks to the Chebyshev algorithm (Gautschi,2004) by definition:

$$\mu_k = \sum_{i=1}^n w_i L_i^k \quad (13)$$

4.2 Reconstruction of the particle size distribution

The moments of the loose agglomerates (Eq. 10) are used to reconstruct the particle population density, $\varphi(L)$, by a spline approximation, $s_{n,m}$, of degree m with n distinct knots:

$$s_{n,m}(L) = \sum_{i=1}^n p_r (L_r - L)_+^m \quad \text{with } u_+ = u H(u) \quad (14)$$

where H is the Heaviside step function and so that the moments are preserved:

$$\int_0^{\infty} s_{n,m}(L) L^k dL = \mu_k = \int_0^{\infty} \varphi(L) L^k dL \quad \text{for } k=0,1, \dots, 2n-1 \quad (15)$$

The coefficients (p_r) and knots (L_r) are calculated from a three-term recurrence relation using the Chebyshev algorithm adapted from (Gautschi, 2004). This moment preserving spline approximation reconstruction is detailed in the appendix of (Gaillard et al., 2012).

5. Results

Taking into account the expression of the supersaturation ratio (Eq. 2), the primary nucleation rate (Eq. 4), the crystal growth rate (Eq. 5) and the agglomeration kernel (Eq. 6), the sets of moment equations for the crystallites (Eq. 9) and agglomerates (Eq. 10) are solved by a 4th order adaptive Runge–Kutta method. The evolution of the concentrations is calculated from equations (Eq. 3) and (Eq. 1).

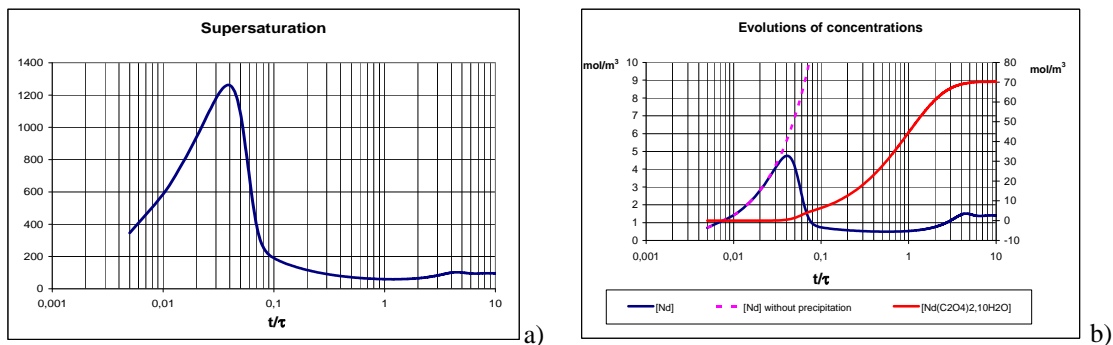


Figure 2: a): Supersaturation ratio - b): Evolution of concentrations

Under the loose agglomerate model, the supersaturation ratio is controlled by the evolution of the population of the crystallites through the mechanisms of nucleation and growth. Due to a very low solubility product, the supersaturation ratio quickly rises up to a value of 1,260 after about 3 s ($t / \tau \sim 0.04$), see Figure 2a, τ being the mean residence time. This generates a high level of primary homogenous nucleation. During this first phase, the rate of change of the neodymium concentration, as shown in figure 2b (blue line), is equal to the one calculated in considering only the contribution of inputs and outputs due to flow (pink dotted line). Then, the growth of these numerous elementary particles has the supersaturation decreasing rapidly and finally stabilizing between 80 and 100. The concentration of the neodymium oxalate keeps increasing up to a value of 70 mol/m^3 , which is reached after about 3 mean residence times.

The reconstruction of the particle size distribution, from the 6 first calculated moments (Eq. 10), can be performed. The volume fractions of the steady state experimental distributions and reconstructed size distributions at 2,4,6,8 and 10 mean residence times are compared in Figure 3.

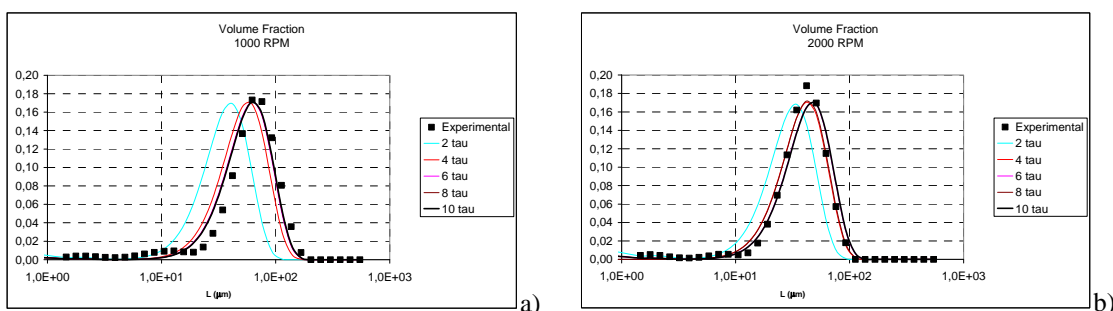


Figure 3: Comparison of experiments (squares) and calculations (lines): a): 1000 RPM. - b): 2000 RPM

The steady-state is reached after approximately 10 residence times. The sizes of the particle predicted at steady state, for the 2 stirring rates, are in very good agreement with the experimental measurements. Other operating conditions have been also studied, yielding to satisfactory agreements between experimental and calculated particle size distributions.

6. Conclusion

From kinetic laws acquired for nucleation, growth and agglomeration by fitting experiments and observing the formation of loose agglomerates, a model based on two population balances using the moment approach, has been applied to neodymium oxalate precipitation. The calculated moments are used to reconstruct the size distributions thanks to an algorithm due to Chebyshev and a spline approximation. The comparison with the experimental distributions shows a good agreement which validates the model.

Acknowledgements

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