

Modelling of Neodymium Oxalate Precipitation by the Method of Classes

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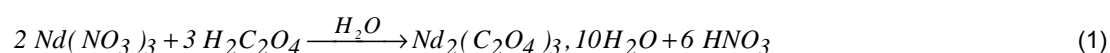
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Oxalic precipitation is usually used in nuclear industry to process radioactive wastes and recover actinides from a multi-component solution. To facilitate the development of experimental methods and data acquisitions, actinides are often simulated 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 under various operating conditions, especially in nuclear environment in which experiments are limited.

The aim of this article is to describe the modelling approach of neodymium oxalate precipitation in a continuous MSMPR (Mixed Suspension Mixed Product Removal). Primary nucleation, crystal growth and agglomeration are taken into account in the model. Thermodynamic effects are modelled 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 population balance of the particulate suspension is solved by the method of classes. The particle sizes predicted by the model 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:



The modelling approach is based on experimental acquisitions for the thermodynamic and kinetic laws and on a numerical model using a specific method of classes to calculate the crystallite and the loose agglomerate population balances taking into account nucleation, growth and agglomeration. When agglomerates are loose, the solution is expected to be in contact with all the 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. Two population balances are therefore considered: one for the crystallites which can nucleate and grow and another one for the agglomerates created by the crystallites collisions and sticking.

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 related to the solubility product P_s , 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).

Under stoichiometric conditions, the supersaturation becomes:

$$S = \gamma_{\pm} \left(\frac{3}{2} \right)^{3/5} \left(\frac{1}{P_s} \right)^{1/5} (C_{Nd,0} - 2C_c) \quad (3)$$

with $C_{Nd,0}$ the initial neodymium concentration after the reagent mixing and C_c the solid concentration in the suspension. The solid concentration C_c is determined from the crystallite 3rd moment μ'_3 , calculated from the discretized population, the crystallite volume shape factor ϕ_v (0.06), the crystallites density ρ_c (2420 kg.m⁻³) and the solid molar mass M_c (732.6 g.mol⁻¹):

$$C_c = \frac{\phi_v \rho_c}{M_c} \mu'_3 \quad (4)$$

2.2 Nucleation

Homogeneous primary nucleation is a fast process relative to mixing; therefore the reagents have to be rapidly mixed in order to achieve a spatially homogeneous supersaturation. Experimental runs, used for the determination of the nucleation rates R_N , 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).

$$R_N = A_{\text{hom}} \exp\left[-\frac{67600}{RT}\right] \exp\left[-\frac{187}{(\ln S)^2}\right] \quad S > 50 \quad 293 \text{ K} < T < 333 \text{ K} \quad (5)$$

where R is the ideal gas constant (8.31 J mol⁻¹ K⁻¹) and $A_{\text{hom}} = 3 \times 10^{31} \text{ m}^{-3} \text{ s}^{-1}$

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 , expressed in meters per second, can be written as:

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

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 (expressed in cubic meters per second):

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

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

3. Experimental study of neodymium oxalate continuous precipitation

All experimental runs are carried out in a continuous MSMPR precipitator until reaching a 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.

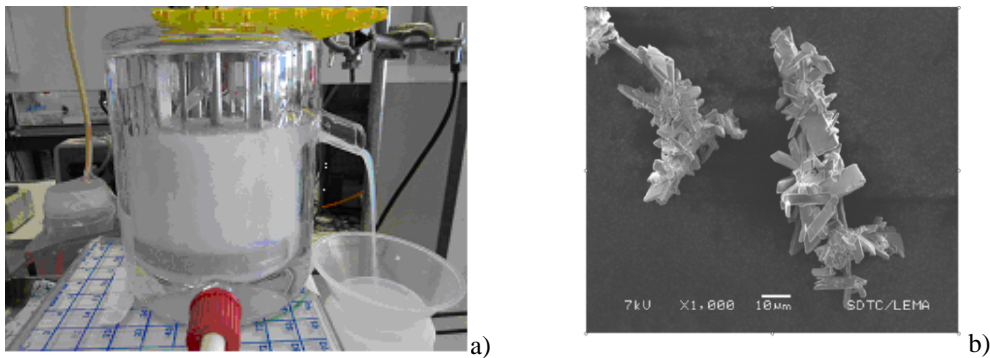


Figure 1: a) 200 mL precipitator. - b) SEM observation of neodymium oxalate agglomerates

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 τ , defined as the ratio between the reaction volume and the reactant flow rates, 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 (see Table 1). This latter can be computed thanks to the rate of kinetic energy dissipation as follows:

$$\dot{\gamma} = \sqrt{\frac{\varepsilon}{\nu}} \quad (8)$$

$$\varepsilon = \frac{N_p N^3 D^5}{V} \quad (9)$$

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
$C_{Nd,0}$	mol.m ⁻³	142.2	142.2
$C_{Ox,0}$	mol.m ⁻³	213.7	213.7
$\bar{\dot{\gamma}}$	s ⁻¹	362	1024

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 size $L_{4,3}$ are ranging between 41 and 65 μm and decrease when the mean shear rate increases.

4. 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). This model was, firstly, formulated in steady state conditions and solved by the method of moments (Gaillard et al., 2012). A transient version of this model, closing the set of equations by quadrature and providing a reconstruction of the particle size distribution, was then used in a previous study (Gaillard et al., 2013). This study emphasizes the resolution of the two population balances by a highly accurate discretization scheme of the particle size range by the method of classes.

The transient evolutions of the number of particles, N'_k , per unit of suspension in a k th cell, of size width ΔL_k , of the crystallite population are given by:

$$\frac{dN'_k}{dt} + \frac{N'_k}{\tau} = 0^k R_N + \frac{1}{\Delta L_k} \left[F(G_{k+1/2}) - F(G_{k-1/2}) \right] \quad (10)$$

Where $F(G_{k+1/2})$ and $F(G_{k-1/2})$ represent the edge fluxes, due to growth, which are calculated by a 3rd order resolution scheme (Koren, 1993), primary nucleation occurring only at the smallest discretized particle size.

And those of the loose agglomerates N_k can be written as:

$$\frac{dN_k}{dt} + \frac{N_k}{\tau} - \frac{N'_k}{\tau} = B_k - D_k \quad (11)$$

where B_k and D_k correspond to the birth et death terms due to agglomeration. Those terms are discretized thanks to the numerical scheme of (Litster et al., 1995) which was improved by (Wynn, 1996).

Taking into account the expression of the supersaturation ratio (Eq. 3), the primary nucleation rate (Eq. 5), the crystal growth rate (Eq. 6) and the agglomeration kernel (Eq. 7), the sets of equations for the crystallites (Eq. 10) and agglomerates (Eq. 11) are solved by a 2nd order semi-implicit method.

5. Results

In this study, the crystallite and agglomerate population balances have been discretized in 70 classes ranging from 1 micron to about 220 microns. The geometric progression between to cells is $2^{1/3}$. Finer discretizations have been also tested, leading to similar results.

The evolutions of the volume mean size, L_{43} , and of the concentrations are presented on Figure 2.

The concentrations keep increasing during the whole experiment and a steady state is reached after about 4 mean residence times (Figure 2a) whereas the particle size distribution of the agglomerates need a little more time to get to its the asymptotic value, see Figure 2b for the volume mean sizes and Figure 3 for the volume fractions. The evolution of the volume mean size is accurately predicted during the transient (Figure 2b). In fact, the whole distribution of the particle size is also well determined, as can be seen in Figure 3 for the stationary states related to the 2 stirring rates.

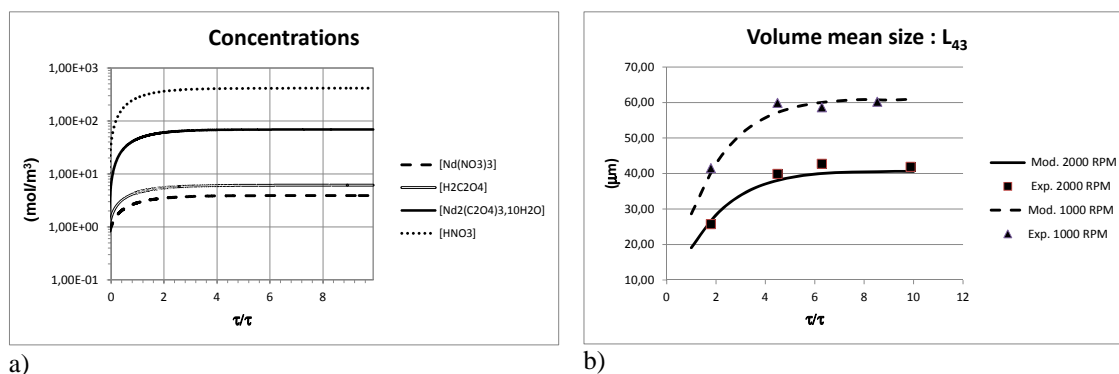


Figure 2: a): Concentrations - b): Volume mean sizes

The volume fractions of the steady state experimental distributions and the calculated ones at 2,4,6,8 and 10 mean residence times are compared in Figure 3. The values at the last three mean residence times are almost overlapping.

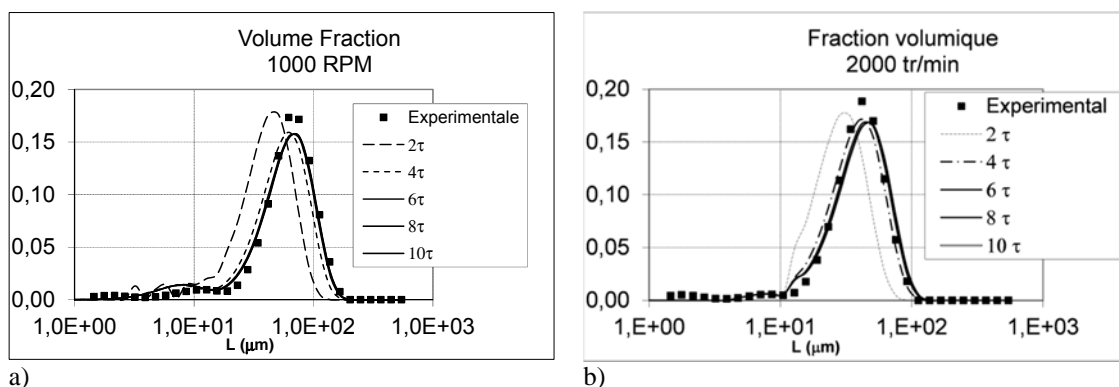


Figure 3: Comparison of experiments (squares) and calculations (lines): a): 1000 RPM. - b): 2000 RPM

The steady-state, of the particle sizes, is reached after approximately 6 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.

Good agreements have been also found for other operating conditions.

6. Conclusion

Observing the formation of loose agglomerates for the precipitation of neodymium oxalate, a transient model based on two population balances, one for the crystallites and one for the agglomerates has been derived.

Those two population balances are solved by discretization of the particle size domain thanks to a high resolution scheme including the 3rd order Koren scheme for the growth of crystallites and the Litster method for the agglomeration terms. The comparison of the predicted distributions with the experimental ones shows a good agreement, both at the steady state and during the transient, which validates the model.

The concentrations of the reactants and of the products is reached after 4 mean residence times, faster than the one of the particle size distribution which requires about 6 mean residence times.

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