Modelling neodymium oxalate precipitation with a moment approach and a Chebyshev quadrature spline reconstruction

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Abstract

This paper deals with the modelling of the precipitation of decahydrated neodymium oxalate from experimental data. The model takes into account the kinetic laws of primary nucleation, crystal growth and agglomeration and is based on two population balances, one for the crystallites and one for the particles. The population of particles is solved using a quadrature moment approach and then reconstructed by splines using an algorithm proposed by Chebyshev. The particle sizes predicted, at steady state for different experimental conditions, are in very good agreement with the experimental measurements.

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1. Introduction

Oxalic precipitation is applied to process radioactive wastes or to 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. In this study, the precipitation of neodymium oxalate achieved by mixing solutions of neodymium nitrate and oxalic acid according to the precipitation reaction (1) is chosen as the working system:

\[
2 \text{Nd(NO}_3\text{)}_3 + 3 \text{H}_2\text{C}_2\text{O}_4 \xrightarrow{H_2O} \text{Nd}_2(\text{C}_2\text{O}_4\text{)}_3 + 10\text{H}_2\text{O} + 6\text{HNO}_3
\]

(1)
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 particle population balances taking into account nucleation, growth and agglomeration. A reconstruction of the size distribution of the particles is then carried out using an algorithm due to Chebyshev and compared with the experimental distribution to validate the global approach.

### Nomenclature

- \( a \) activity in solution, \( \text{mol.m}^{-3} \)
- \( C_{\text{Nd,0}} \) initial concentration of neodymium nitrate in the reactor after mixing, \( \text{mol.m}^{-3} \)
- \( C_{\text{Cr,0}} \) initial concentration of oxalic acid in the reactor after mixing, \( \text{mol.m}^{-3} \)
- \( G \) crystal growth rate, \( m.s^{-1} \)
- \( I \) ionic strength, \( \text{mol.m}^{-3} \)
- \( L \) particle size, \( m \)
- \( L_{4.3} \) mean volume diameter of particles, \( m \)
- \( m_j \) \( j \)th moment of the particle size distribution, \( m^j \)
- \( m'_j \) \( j \)th moment of the elementary particle size distribution, \( m'^j \)
- \( N \) stirring rate, rpm
- \( P_s \) solubility product, \( \text{mol}^5 \text{.m}^{-15} \)
- \( R \) ideal gas constant, \( J.mol^{-1}.K^{-1} \)
- \( R_N \) nucleation rate, \( m^{-3}.s^{-1} \)
- \( S \) supersaturation ratio
- \( T \) temperature, \( K \)
- \( \beta \) agglomeration kernel, \( m^3.s^{-1} \)
- \( \gamma_s \) mean activity coefficient
- \( \dot{\gamma} \) mean shear rate, \( s^{-1} \)
- \( \phi(L) \) particle population density, \( m^{-6} \)
- \( \lambda \) particle size, \( m \)
- \( \tau \) mean residence time, s

### 2. Determination of the kinetic laws

The driving force of the precipitation process is given by the supersaturation ratio which can be expressed using the mean activity coefficient \( \gamma_s \) and the total concentrations of species as follows:

\[
S = \sqrt[5]{\frac{a_{\text{Nd}}^2 \times a_{\text{C}_2\text{O}_4}^3}{P_s}} = \sqrt[5]{\frac{[\text{Nd}]_P^2 \times [\text{C}_{2\text{O}_4}]_P^3}{P_s}}
\]

where \( S \) is the supersaturation ratio, \([\text{Nd}]\) and \([\text{C}_{2\text{O}_4}]\) the concentrations of neodymium and oxalate constitutive ions, i.e. the total concentrations in solution without taking into account the distribution of these ions in different complexes. The mean activity coefficient \( \gamma_s \) is calculated using the Bromley method [1].

The primary nucleation, crystal growth and agglomeration kinetics of the neodymium oxalate are experimentally determined over a wide range of concentrations and temperatures according to phenomenological approaches.
2.1. Nucleation

According to the classical nucleation theory, the primary nucleation rate can be expressed as follows:

\[ R_N = A_N \exp\left[-\frac{B_N}{(\ln S)^2}\right] \]  

(3)

where \( R_N \) stands for the number of nuclei formed per unit volume and time. \( A_N \) and \( B_N \) represent the nucleation kinetic parameters to be determined.

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. That is why, experimental runs are performed in a specific apparatus patented by the French Atomic Energy Commission and AREVA [2], shown in Fig. 1. This apparatus allows the reagent mixing state at molecular scale to be controlled. Using the chemical test “iodide-iodate” [3], it has been shown to achieve very efficient micromixing, which occurs in less than one millisecond.

![Fig 1: Apparatus for the determination of primary nucleation: photo and principle description](image)

The principle of this apparatus is based on the Nielsen’s method [4]. The reagent solutions are rapidly mixed by a crossbow mechanism in a small tube (2 mm diameter and 10 cm length) in which a high supersaturation is achieved and the nucleation process occurs. At the outlet of the tube, the flow is instantaneously diluted into a large volume of mother liquor to get a drop in supersaturation. Nucleation process is therefore stopped and nuclei formed into the nucleation tube can grow slowly until they reach a detectable size range to be analyzed in a particle size analyzer. Agglomeration phenomena are avoided by adding gelatin (2 g/L) into the dilution volume. The nucleation rate can be easily deduced from the total number of nuclei formed in the nucleation tube [5]. This latter is estimated using the particle size distribution. Numerous of experiments have been performed with different supersaturation ratios and temperatures to fit equation (3). The homogeneous nucleation rate of the neodymium oxalate is expressed as the classical theory proposed by Volmer and Weber [6]:

\[ R_N = 3 \times 10^{31} \exp\left[-\frac{67600}{RT}\right] \exp\left[-\frac{187}{(\ln S)^2}\right] \]  

(4)

\[ 273 \text{ K} < T < 323 \text{ K} \]

2.2. Crystal growth

The crystal growth rate \( G \) is generally linked to the driving force by a power law:
\[ G = k_g s^g \]  \hspace{1cm} (5)

where \(k_g\) and \(g\) are the crystal growth kinetic parameters to be determined, \(s\) stands for the absolute supersaturation.

The crystal growth kinetic law is 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, nucleation and agglomeration being negligible. The originality of the method is to follow the growth of the solid phase by tracking the evolutions in the liquid phase. As soon as, the oxalic acid is injected, the neodymium consumption in solution is continuously monitored thanks to a recirculation loop by spectrophotometric measurements in a 10 cm-cell. The inlet of the loop is equipped with a filter of a 2μm-porosity to stop particles. Experimental runs are performed in a batch glass tank reactor stirred by a marine propeller. The experimental set up principle is shown on Fig. 2.

![Experimental set-up for the crystal growth study](image)

From the decrease of the neodymium concentration in solution (see Fig. 2), the kinetic parameters can be identified [5]. The crystal growth rate \(G\) is linked to the driving force as follows:

\[
G = 2.9 \times 10^{-6} \exp\left(-\frac{14000}{RT}\right)(P_S)^{1/2} \left(S^{-1}\right) \hspace{1cm} (6)
\]

The crystal growth process is controlled by the surface integration into the crystal lattice, thanks to a screw dislocation mechanism [7].

### 2.3. Agglomeration

Agglomeration phenomena of neodymium oxalate crystals are studied using a method adapted to loose agglomerates and fully detailed in [8]. Experiments are carried out in a continuous perfectly mixed precipitator where nucleation, growth and agglomeration occur simultaneously. Knowing primary nucleation and crystal growth rates, the mathematical treatment of experimental crystal size distributions leads to the neodymium oxalate agglomeration kernel:

\[
\beta = 2.55 \times 10^{-7} I^{-0.70} S_{fract}^{-0.24} \exp\left(-\frac{40900}{RT}\right) \hspace{1cm} (7)
\]
3. Experimental investigations of neodymium oxalate continuous precipitation

All experimental runs are carried out in a continuous Mixed Suspension Mixed Product Removal (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 Fig. 3a. 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 baffles’ width b are as follows: H=T, D=T/3, h=T/3, b=T/10.

Precipitation experiments are performed by mixing a neodymium nitrate solution with an oxalic acid solution under stoichiometric conditions according to Eq. (1). The mean residence time is 66.8 s in order to reach high supersaturation ratio values of about 200. Experiments are carried out at 20°C in identical chemical conditions, for two different shear rates. This one, assumed to be constant in the MSMPR precipitator, is calculated from the mean energy dissipation.

![Fig. 3. a) 200 mL MSMPR precipitator. - b) SEM observation of neodymium oxalate agglomerates](image)

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

<table>
<thead>
<tr>
<th>Run</th>
<th>21</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>rpm</td>
<td>1000</td>
</tr>
<tr>
<td><em>C</em>&lt;sub&gt;Nd,0&lt;/sub&gt;</td>
<td>mol.m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>142.2</td>
</tr>
<tr>
<td><em>C</em>&lt;sub&gt;Ox,0&lt;/sub&gt;</td>
<td>mol.m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>213.7</td>
</tr>
<tr>
<td><em>γ</em></td>
<td>s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>362</td>
</tr>
<tr>
<td><em>L</em>&lt;sub&gt;4,3&lt;/sub&gt;</td>
<td>μm</td>
<td>65</td>
</tr>
</tbody>
</table>

4. Precipitation model

Scanning Electron Microscopy (SEM) observations oxalates point out the formation of loose agglomerates (see Fig. 3b). In such a case, during precipitation, the solution is in contact with all elementary particles which make up the agglomerates, so that they can grow in the same way as single crystals in the suspension. This result leads us to develop a specific method, to solve the population balance, which distinguishes the behaviors of elementary particles (crystallites) from the particles [8].
The moments of the elementary particle population, at steady-state, are given by:

\[ m^j_\tau = \frac{j! R_n(G\tau)^j}{\tau} \quad \text{for } j=0,1,2, \ldots, 2n-1 \]  

(8)

And those of the particles can be expressed as follows:

\[ \frac{m^j_\tau - m^j_\tau'}{\tau} = \frac{1}{2} \int_0^\infty \left( (L^3 + \lambda^3)^{1/3} - L' \right) \beta(L, \lambda) \varphi(L) \varphi(\lambda) dL d\lambda \]  

(9)

\[ \beta(L, \lambda) \] is the frequency of the collisions between particles of sizes \( L \) and \( \lambda \) that are successful in producing a particle of volume \( L^3 + \lambda^3 \).

The set of equations for the particles (Eq. 9) is solved using a quadrature closure based on the Chebyshev algorithm [9]. The moments are used to reconstruct the particle population density, \( \varphi(L) \), by a spline approximation of degree \( m \) with \( n \) distinct knots:

\[ s_{n,m}(L) = \sum_{j=1}^{n} p_j (L_j - L)^m \quad \text{with} \quad u_i = u(H(u)) \]  

(10)

Where \( H \) is the Heaviside step function and so that the moments are preserved:

\[ \int_0^\infty s_{n,m}(L) L^j dL = \mu_j = \int_0^\infty \varphi(L) L^j dL \quad \text{for } j=0,1, \ldots, 2n-1 \]  

(11)

The coefficients \( (p_j) \) and knots \( (L_i) \) are calculated from a three-term recurrence relation using the Chebyshev algorithm adapted from [9], this moment preserving spline approximation reconstruction is detailed in the appendix A.

5. Results

The steady-state is reached after approximately 10 residence times. 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 and volume mean sizes \( L_{4,3} \) ranging between 41 and 65 mm.

![Volume Fraction](image)

Fig. 4. Comparison of experiments (squares) and calculations (lines): a) Run 21 : 1000 rpm. - b) Run 18 : 2000 rpm
Taking into account the expression of the supersaturation ratio (2), the primary nucleation rate (4), the crystal growth rate (6) and the agglomeration kernel (7), the sets of moment equations for the crystallites (8) and particles (9) are calculated. The reconstruction of the particle size distribution, from the 6 first calculated moments (9), is then performed. The volume fractions of the experimental and reconstructed distributions, for the operating conditions presented in Table 1, are compared in Fig. 4.

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 moments calculated are used to reconstruct the size distribution thanks to an algorithm due to Chebyshev and a spline approximation. The comparison with the experimental distributions shows very good agreement. The model is expected to be used to optimize industrial processes and facilitate the design of future installations.

Acknowledgements

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References

Appendix A. Moment-preserving spline approximation reconstruction

Substituting (10) into (11) yields, since \( L_i > 0 \) to:

\[
\sum_{j=0}^{n-1} p_j \int_0^L L^j (L_i - L)^m \, dt = \int_0^L \varphi(L) dL, \quad j=0,1,\ldots,2n-1
\]  

(12)

The left hand side can be seen, through \( m \) integrations by parts, as:

\[
\sum_{j=1}^{n} p_j \int_0^L L^j (L_i - L)^m \, dt = \frac{m!}{(j+1)(j+2)\ldots(j+m+1)} \sum_{i=1}^{n} p_i L_i^{j+m+1}
\]  

(13)

The Right Hand Side (RHS), is similarly transformed by \( m+1 \) integrations by parts.

Assuming:

(i) \( \varphi \in C^{m+1}(\mathbb{R}_+), \)

(ii) the first \( 2n \) moments of \( \varphi \) exist,

(iii) \( \varphi^{(j)}(L) = o(L^{-2n-j}) \) when \( L \to \infty, j=0,1,2,\ldots,m \)

We infer the convergence of the integral of the right hand side of (14):

\[
\int_0^L \varphi(L) dL = \frac{(-1)^{m+1}}{(j+1)(j+2)\ldots(j+m+1)} \int_0^L \varphi^{(m+1)}(L) dL
\]  

(14)

Comparing (13) and (14), we see that (14) is equivalent to:

\[
\sum_{j=1}^{n} (p_j L_i^{m+1}) L_i^j = \frac{(-1)^{m+1}}{m!} L_i^{m+1} \varphi^{(m+1)}(L) L_i^j dL, \quad j=1,2,\ldots,2n-1
\]  

(15)

Since the integrals of the RHS of (15) converge, these equations state that the \( L_i \) are the nodes and that the \( p_j L_i^{m+1} \) are the weights of the \( n \)-point Gauss quadrature for the measure \( \frac{(-1)^{m+1}}{m!} L_i^{m+1} \varphi^{(m+1)}(L) dL \).

Comparing again (13) and (14), we have:

\[
\sum_{j=1}^{n} (p_j L_i^{m+1}) L_i^j = \frac{(j+1)(j+2)\ldots(j+m+1)}{m!} \int_0^L \varphi(L) L_i dL, \quad j=1,2,\ldots,2n-1
\]  

(16)

\[
= \frac{(j+1)(j+2)\ldots(j+m+1)}{m!} \mu_j = \xi_j, \quad j=1,2,\ldots,2n-1
\]  

(17)

The three-term recurrence relation of the classical Chebyshev algorithm is applied to the modified moments \( \xi_j \) defined by the RHS of (17) to compute the nodes and weights of the quadrature which also uniquely determine the coefficients of the spline approximation \( (p_i, L_i) \).