Comparison of the method of classes and the quadrature of moment for the modelling of Neodymium Oxalate Precipitation

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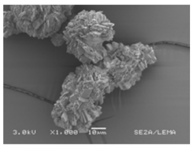
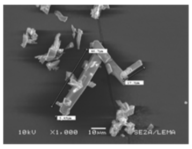
Introduction

- **Oxalic precipitation** :
  - to deal with radioactive waste and recover the actinides lanthanides → To facilitate the development of experimental methods
- **Modelling approach**:
  - Experimentation ➔ Thermodynamics + kinetics & numerical methods

[1] [2] [7] [4] [5]

$Nd_2(C_2O_4)_3 \cdot 10\ H_2O$ obtained for precipitation different conditions





$$2\,Nd(NO_3)_3 + 3\,H_2C_2O_4 \xrightarrow{H_2O} Nd_2(C_2O_4)_3 \cdot 10\,H_2O + 6\,HNO_3$$

Thermodynamics et kinetic laws

- Supersaturation ratio (S) → **The driving force of the precipitation process**
- Kinetic laws of **nucleation**, cristal growth and **agglomeration = f (S)**

Bromley's method

$$S = \boxed{\gamma_{\pm}} \left(\frac{C^2_{Nd^{3+}} C^3_{C_2O_4^{2-}}}{\boxed{Ps}} \right)^{1/5}$$

[6]

$1{,}16 \cdot 10^{-14}$ mol⁵·mol⁻⁵

$$\boxed{C_c} = \frac{\boxed{\phi_v}\boxed{\rho_c}}{\boxed{M_c}} \mu'_3$$

Particle concentration

0,06 — 2420 kg·m⁻³ — 732,6 g·mol⁻¹

Homogeneous primary nucleation

$$\boxed{R_N} = 3{,}10^{31} \exp\left[-\frac{67600}{RT}\right] \exp\left[-\frac{187}{(LnS)^2}\right]$$

$S > 50$ $\quad 293K < T < 333K$

[1] [8] [9]

Crystal growth

$$\boxed{G} = 2{,}9\,10^{-6} \exp\left[-\frac{14000}{RT}\right] (Ps)^{1/5} (S-1)$$

$293K < T < 333K$

[2] [3]

Agglomeration

$$\boxed{\beta} = 2{,}55\,10^{-7} \cdot I^{-0{,}70} \cdot S \cdot \dot{\gamma}^{-0{,}24} \exp\left[-\frac{40900}{RT}\right]$$

$S > 61$

$293K < T < 333K$

$45 s^{-1} < \dot{\gamma} < 1024 s^{-1}$

$600 mol \cdot m^{-3} < I < 2100 mol \cdot m^{-3}$

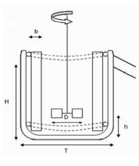
[7]

$$\dot{\gamma} = \sqrt{\frac{\bar{\varepsilon}}{\nu}} \qquad \bar{\varepsilon} = \frac{Np \cdot N^3 \cdot D^5}{V}$$

Experimental Study

MSMPR

- **Continous precipitation until steady state**
  - **V = 200 ml**
  - **Temperature = 20° C**
  - four stainless steel baffles
  - stainless steel four 45° pitched blade turbine° → **Np = 1,5**



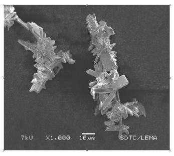
H = T \\ D = T/3 \\ h = T/3 \\ b = T/10

Continuous experiments

- Short mean residence time ≈ **1 min** → **high S**
- **Constant agglomeration kernel : β**
- Scanning Electron Microscopy → **crystal size distributions**

	N tr/min	$C_{Nd,0}$ mol·m⁻³	$C_{Ox,0}$ mol·m⁻³	s⁻¹	$L_{4,3}$ µm
Run 1	1000	142,2	213,7	362	65
Run 2	2000	142,2	213,7	1024	41

MEB observations of Loose agglomerates



Two population balances

Method of classes

$$\frac{dN'_k}{dt} + \boxed{\frac{N'_k}{\tau}} = 0^k \underbrace{\boxed{R_N}}_{\text{Nucleation}} + \frac{1}{\Delta L_k} \underbrace{\boxed{\left[F(G_{k+1/2}) - F(G_{k-1/2})\right]}}_{\text{Growth}}$$

Elementary particles

- **3rd order scheme of Koren [4]**

Source

$$\frac{dN_k}{dt} + \frac{N_k}{\tau} = \boxed{\frac{N'_k}{\tau}} + \underbrace{\boxed{B_k}}_{\text{Birth}} - \underbrace{\boxed{D_k}}_{\text{Death}}$$

- **scheme of Litster [5]**

Loose agglomerates

Quadrature of Moments

$$\frac{d\mu'_k}{dt} + \boxed{\frac{\mu'_k}{\tau}} = 0^k \underbrace{\boxed{R_N}}_{\text{Nucleation}} + \underbrace{\boxed{k G \mu'_{k-1}}}_{\text{Growth}}$$

for k= 0,1,2, …,2n-1 [10]

Source

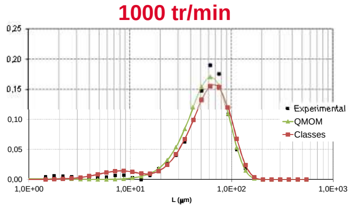
$$\frac{d\mu_k}{dt} + \frac{\mu_k}{\tau} = \boxed{\frac{\mu'_k}{\tau}} + \underbrace{\boxed{\frac{\beta}{2} \sum_{i=1}^{n} w_i \sum_{j=1}^{n} w_j (L_i^3 + L_j^3)^{k/3}}}_{\text{Birth}} - \underbrace{\boxed{\frac{\beta}{2} \sum_{i=1}^{n} w_i L_i^k \sum_{j=1}^{n} w_j}}_{\text{Death}}$$

Main results

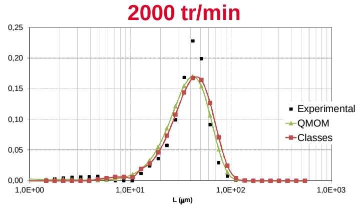
- **Crystal size distributions → Experimental vs. Predicted**

- Comparison of volume fractions at 5 τ

1000 tr/min

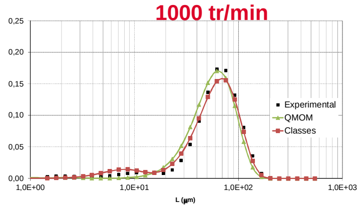


2000 tr/min



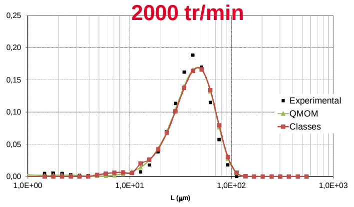
- Comparison of volume fractions at steady state

1000 tr/min



L (µm)

2000 tr/min



L (µm)

Conclusions

- Kinetic laws (R_N, **G** et **β**) and **loose agglomerates** from experimental runs
- Two population balance models : solved by the **Method of classes** and **QMOM**
- Both methods compared well with experimental data during transient and at steady state
- **QMOM** requiered much less computational effort and is preferentially used with the reconstruction method detailed in [10]

Références

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