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

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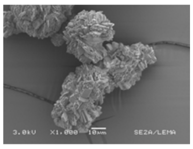
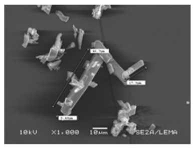
## Introduction

- **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)**

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

Bromley's method → $\gamma_{\pm}$ [6]; $Ps$ = 1,16·10$^{-14}$ mol$^5$·mol$^{-5}$

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

$C_c$: Particle concentration; $\phi_v$ = 0,06; $\rho_c$ = 2420 kg·m$^{-3}$; $M_c$ = 732,6 g·mol$^{-1}$

### Homogeneous primary nucleation

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

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

[1] [8] [9]

### Crystal growth

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

$293K < T < 333K$

[2] [3]

### Agglomeration

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

$S > 61$

$293K < T < 333K$

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

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

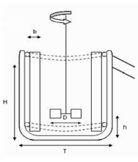
[7]

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

## 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**



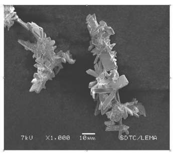

H = T \\ D = T/3 \\ h = T/3 \\ b = T/10

### 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

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

(Source: $\frac{N'_k}{\tau}$; Nucleation: $R_N$; Growth: $F(G_{k+1/2}) - F(G_{k-1/2})$)

**Elementary particles**

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

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

(Source: $\frac{N'_k}{\tau}$; Birth: $B_k$; Death: $D_k$)

- **scheme of Litster [5]**

**Loose agglomerates**

### Quadrature of Moments

$$\frac{d\mu'_k}{dt} + \frac{\mu'_k}{\tau} = 0^k R_N + kG\mu'_{k-1}$$

for k= 0,1,2, …,2n-1 [10]

(Source: $\frac{\mu'_k}{\tau}$; Nucleation: $R_N$; Growth: $kG\mu'_{k-1}$)

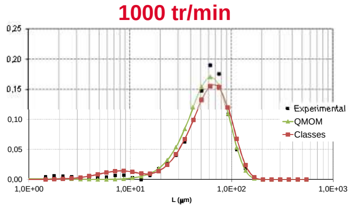
$$\frac{d\mu_k}{dt} + \frac{\mu_k}{\tau} = \frac{\mu'_k}{\tau} + \frac{\beta}{2}\sum_{i=1}^{n} w_i \sum_{j=1}^{n} w_j (L_i^3 + L_j^3)^{k/3} - \frac{\beta}{2}\sum_{i=1}^{n} w_i L_i^k \sum_{j=1}^{n} w_j$$

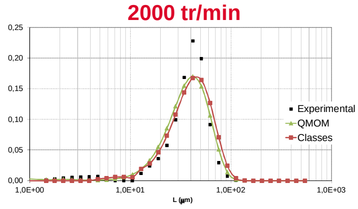
(Source: $\frac{\mu'_k}{\tau}$; Birth; Death)

## Main results

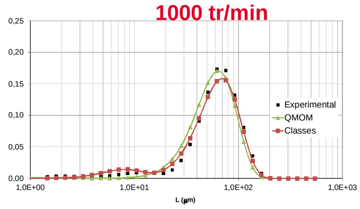
- **Crystal size distributions → Experimental vs. Predicted**

- Comparison of volume fractions at 5 τ

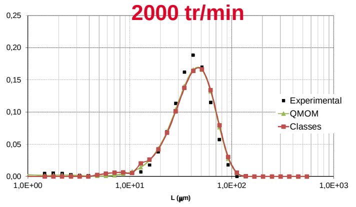



- Comparison of volume fractions at steady state




L (µm)




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]

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