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

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J.Ph. Gaillard [a] – S. Lalleman [a] – M. Bertrand [a]– E. Plasari [b]

a CEA, Nuclear Energy Division, RadioChemistry & Process Department, French Alternatives Energies and Atomic Energy Commission, F-30207 Bagnols sur Cèze, France

b Reaction and Chemical Engineering Laboratory, Université de Lorraine, 1 rue Granville BP 20451, 54001 Nancy, France

Introduction

- Oxalic precipitation :
  - to deal with radioactive waste and recover the actinides lanthanides → To facilitate the development of experimental methods
- Modelling approach:
  - Experimental → 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

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

[6]

$1{,}16 \cdot 10^{-14}\ mol^5 \cdot mol^{-5}$

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

0,06 ; 2420 kg·m^{-3} ; 732,6 g·mol^{-1}

Particle concentration

Homogeneous primary nucleation

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

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

[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

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

$S > 61$

$293K < T < 333K$

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

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

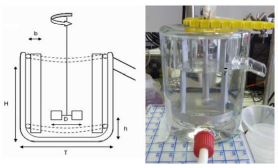
[7]

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

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**



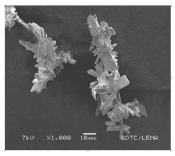
H = T \\ D = T/3 \\ h = T/3 \\ b = T/10

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

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

Nucleation ; Growth ; Source

Elementary particles

- 3rd order scheme of Koren [4]

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

Birth ; Death

- scheme of Litster [5]

Loose agglomerates

Quadrature of Moments

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

Nucleation ; Growth ; Source

for k= 0,1,2, …,2n-1 [10]

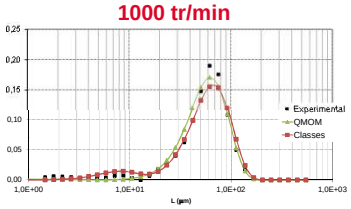
$$\frac{d\mu_k}{dt} + \frac{\mu_k}{\tau} = \frac{\mu'_k}{\tau} + \frac{\beta}{2}\sum_{i=1}^{n} w_i \sum_{j=1}^{n} w_j \left(L_i^3 + L_j^3\right)^{k/3} - \frac{\beta}{2}\sum_{i=1}^{n} w_i L_i^k \sum_{j=1}^{n} w_j$$

Birth ; Death

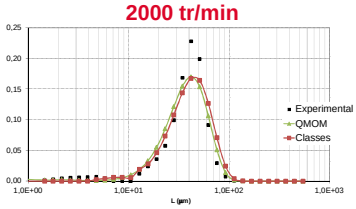
Main results

- Comparison of volume fractions at 5 τ

1000 tr/min

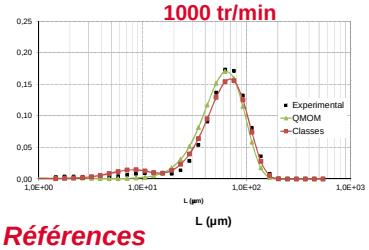


2000 tr/min

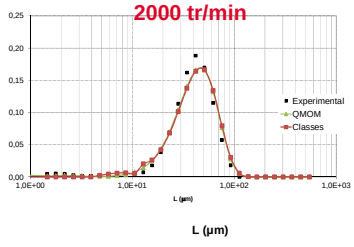


- **Crystal size distributions → Experimental vs. Predicted**
- Comparison of volume fractions at steady state

1000 tr/min



2000 tr/min



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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CEA, Nuclear Energy Division
RadioChemistry & Process Department
30207 Bagnols sur Cèze, France

French Alternatives Energies and Atomic Energy Commission
Centre de Marcoule | BP17171 | 30207 Bagnols-sur-Cèze Cedex
T. +33 (0)4 66 79 18 77 | F. +33 (0)4 66 79 60 27