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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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Abstract

Oxalic precipitation is generally used in the nuclear industry to deal with radioactive waste and recover the actinides from a multicomponent solution. To facilitate the development of experimental methods and data acquisitions, actinides are often simulated using lanthanides, gaining experience more easily.
The purpose of this article is to compare the results achieved by two methods for solving the population balance during neodymium oxalate precipitation in a continuous MSMPR (Mixed Suspension Mixed Product Removal). The method of classes, also called discretized population balance, used in this study is based on the method of Litster. Whereas, the Quadrature Method of Moment (QMOM) is written in terms of the transport equations of the moments of the number density function. All the integrals are solved through a quadrature approximation thanks to the product-difference algorithm or the Chebyshev algorithm. Primary nucleation, crystal growth and agglomeration are taken into account. Agglomeration phenomena have been found to be represented by a loose agglomerates model. Thermodynamic effects are modeled by activity coefficients which are calculated using the Bromley model. The sizes of particles predicted by the two methods are in good agreement with experimental measurements.

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Keywords: Precipitation; modelling ; method of classes ; quadrature method of moment

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1. Introduction

In this study, the precipitation of neodymium oxalate, achieved by mixing solutions of neodymium nitrate and oxalic acid, is chosen as the working system (1):

$$2\ Nd(NO_3)_3 + 3\ H_2C_2O_4 \xrightarrow{H_2O} Nd_2(C_2O_4)_3 10H_2O + 6\ HNO_3 \quad (1)$$

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 agglomerates. The population balance is solved either by the method of classes or the method of the quadrature of moments. The results obtained with these two methods are then compared to the experimental ones.

2. Precipitation models

2.1. Kinetic laws

Primary nucleation, crystal growth and agglomeration kinetics of neodymium oxalate during precipitation are experimentally determined over a wide range of concentrations and temperatures according to specific experiments described in [1] and [2]. The driving force of the precipitation process is given by the supersaturation ratio which is expressed using the mean activity coefficient $\gamma_{\pm}$ and the total concentrations of species as follows:

$$S = \sqrt[5]{\frac{a_{Nd}^{2} \times a_{C_2O_4}^{3}}{P_S}} = \gamma_{\pm} \sqrt[5]{\frac{[Nd]^2 \times [C_2O_4]^3}{P_S}} \quad (2)$$

where S is the supersaturation ratio, [Nd] and [C_2O_4] the total concentrations of neodymium and oxalate in solution. The mean activity coefficient $\gamma_{\pm}$ is calculated using the Bromley method [3]. Ps is the solubility product.

2.1.1. Primary nucleation

Experimental runs are performed in a specific apparatus patented by the French Atomic Energy Commission and AREVA [4], with different supersaturation ratios and temperatures. The principle of this apparatus is based on the stopped flow method of Nielsen [1]. The homogeneous nucleation rate R_N of the neodymium oxalate is expressed as the classical theory proposed by Volmer and Weber [5] to fit equation (3):

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

R is the ideal gas constant and T is the temperature (K).

2.1.2. Crystal growth

The crystal growth rate *G* is linked to the driving force as follows:

$$G = 2.9 \times 10^{-6} \exp\left(-\frac{14000}{RT}\right) (P_S)^{\frac{1}{5}} (S-1) \quad (4)$$

The crystal growth process is controlled by the surface integration into the crystal lattice, thanks to a screw dislocation mechanism [1].