Oxalate precipitation in emulsion: from the drop scale to the industrial process

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Abstract

An original process of actinides coprecipitation, based on either pulsed or Taylor-Couette flows column, is studied. The novelty of this process lies in the confinement of the aqueous reagents in droplets, dispersed in an inert organic phase (W/O emulsion). Besides the implementation of well-known technologies of the nuclear industry, the emulsion process is particularly convenient for the control of supersaturation, and ensures the sticky precipitates confinement within drops, thereby limiting the fouling risk and its adverse consequences on productivity and safety.

A thorough understanding of the precipitation mechanisms and their interactions with the hydrodynamic conditions prevailing around and inside the drops is essential for the process optimization. In this context, numerical simulations were conducted, accompanying experiments, to study the process sensitivity. Different levels were considered in the modeling task, going from the emulsion behavior inside the column, to the reagents mixing and precipitation within the drops. Regarding the drops scale, on which we focus in this paper, population balance equations (PBE) were coupled to fluid dynamics simulation. Different methods of resolution of the PBE were tested. The behavior of the precipitate was also assessed using a Lagrangian approach. Thanks to these drop scale simulations, process experiments were discussed and analyzed.

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1. Introduction and context

An alternative to the current method of reprocessing spent nuclear fuel would be to co-extract the actinides and to co-precipitate them in a single step. Such a co-converted powder production requires however the development of specific equipments to meet the industrial production rates, the latter being significantly enhanced by the joint precipitation of uranium and minor actinides as compared to the precipitation of plutonium oxalate alone.

To this end, we are studying a continuous oxalic precipitation process based on the use of either pulsed or Taylor-Couette flow columns [1]. The novelty of this process lies in the containment of the reagents in drops of aqueous phase dispersed in an inert organic phase (Fig. 1). It has therefore the double advantage of: i) implementing a well-known technology of the nuclear industry, and ii) ensuring the confinement of the sticky precipitates by the inert organic diluent (Tetrapropylene Hydrogen TPH), thereby limiting the risk of contamination of the device and its adverse consequences in terms of productivity, safety, etc.

![Fig. 1. Cerium oxalate precipitation in pulsed column. The aqueous drops, enclosing the solid phase, are confined in an inert organic phase (TPH), thus avoiding contacts between the sticky particles and the column walls and packing](image)

To reduce the inventory of the radioactive materials involved, the feasibility studies were generally dedicated to the precipitation of cerium oxalate by the following reaction:

\[
2\text{Ce(NO}_3\text{)}_3 + 3 \text{H}_2\text{C}_2\text{O}_4 + 10 \text{H}_2\text{O} \rightarrow \text{Ce}_2(\text{C}_2\text{O}_4)_3\cdot10\text{H}_2\text{O} + 6 \text{HNO}_3
\]

Mixed oxalates production (regarding cerium, CeIII, and uranium, UIV) was also investigated.

2. Work in progress: experimental and numerical aspects

A first campaign of tests was conducted using a small-scale pulsed column (15 mm inner diameter) packed with PTFE truncated disks. The process feasibility demonstrated the feasibility in a wide range of flow-rates and chemical conditions, for either the production of CeII precipitates or the production of UIV+CeIII mixed precipitates [2]. The morphology and sizes of the obtained particles (Fig. 2) are comparable to the quality of the product obtained in the classical "vortex flow reactor", today used to run the precipitation of plutonium oxalate.
A thorough understanding of the precipitation mechanisms and their interactions with the particular hydrodynamic conditions prevailing around the drops in the apparatus is essential for the process optimization. In this context, modeling and numerical simulation are powerful tools complementary to the experiments in order to study both the drops behavior within the column (and there from their residence times and collision frequency) and the reagents mixing within the drops (and there from the nucleation, growth and agglomeration of the solid product). Different levels of modeling have been considered.

First, a chemical engineering approach, assuming plug flow with axial dispersion, was preferred in order to study the evolution of the chemical species along the column.

CFD has been used in a second time to study the flow surrounding droplets in the column. This purely hydrodynamic approach allowed us to determine the nature of the velocity boundary conditions prevailing around the drops, which is required for the “in drop” precipitation model.

The “in drop” precipitation mechanisms were considered in a third step. The droplets dispersed in the inert organic phase flowing in the column are indeed the micro-reactors where the chemical reactions take place, and consequently the central part of the chemical model.

Prior to the modeling approach, the major mechanisms involved in the drops were investigated experimentally. Specific devices were specially designed and developed in order to study the relevant phenomena occurring within a drop, possibly subjected to hydrodynamic solicitations similar to those prevailing in the pulsed column [3]. All tests were performed with a simulated load of cerium nitrate in nitric acid medium, and oxalic acid as the complexing agent. The drops were in each case immersed in TPH. The major simplifying assumptions of the “in drop” models were derived from these “drop scale” observations.

According to the intensive mixing inside the flowing drop, highlighted by the “dynamic” experiments, a first model was developed, assuming the drop was perfectly stirred (Continuously Stirred Tank Reactor, CSTR). The reagents were assumed to be either entirely enclosed in the drop volume at the beginning of the simulation, or fed with a finite rate simulating a diffusion mass transfer process. The model is based on the resolution of the transient population balance equation (PBE), coupled with the mass balances of the liquid-phase chemical species. The PBE is solved by finite differences, using an upwind scheme, which avoids the occurrence of negative values for the variable during the iterative process [4].

A second model was developed using ANSYS-FLUENT software (v12.0). The relative motion of the drop compared to the continuous phase was accounted for by imposing a fixed velocity (translational and / or rotational) at the wall. The objective here is to understand the influence of the inner flow-field on the progress of the precipitation process. By analogy with a recent study on the precipitation of barium carbonate in a fluidized bed reactor [5], we first chose to test the discrete model available in the code to solve the PBE. The Quadrature Method of Moment (Q MOM) model, less CPU consuming, was used in a second time for comparison. The simulated flow field was in good agreement with the experimental observations. The evolutions of the mean...
cerium nitrate concentration predicted by each model (Fluent, CSTR and CSTR with finite feed rate) are compared in Fig. 3, illustrating the role of the recirculation vortices in the apparent reaction rate.

Finally, the combination of these models allows for a “first level” of simulation of the overall process. The initial drop concentrations and wall-velocity conditions are estimated respectively by the plug-flow with axial dispersion column model and the CFD column model. In each possible configuration (regarding initial concentrations and wall velocity), the “in drop” model developed with Fluent provides the reaction progress, thanks to the coupled resolution of the liquid flow-field and the solid PBE.

At last, a second campaign of tests has been initiated using a Taylor-Couette flow column, in order to study the sensitivity of the solid properties to the operating conditions and to validate the modeling strategy. Given the quite-well characterized flow fields in this apparatus, the Taylor-Couette column is particularly convenient to study the interactions between the hydrodynamics features (i.e. mixing) and the fast kinetics of the mechanisms involved in this precipitation.

![Fig. 3.](image_url) **Fig. 3.** Evolution of the cerium liquid phase concentration predicted under various hydrodynamic conditions: full flow-field resolution, CSTR and CSTR with finite feed-rate.

**References**


