Contents lists available at SciVerse ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Actinides oxalate precipitation in emulsion modeling: From the drop scale to the industrial process

Sophie Charton[a,*], Amine Kacem[a], Abdenour Amokrane[a,b], Gilles Borda[a], François Puel[b], Jean-Paul Klein[b]

[a] CEA, DEN, DTEC, SGCS, F-30207 Bagnols-sur-Cèze, France

[b] Université de Lyon, Université Lyon 1, CNRS, CPE Lyon, UMR 5007, Laboratoire d'Automatique et de Génie des Procédés (LAGEP), 43 Bd du 11 Novembre 1918, F-69622 Villeurbanne, France

ABSTRACT

An original process of actinides coprecipitation based on pulsed flow column is studied. The novelty of this process lies in the confinement of the aqueous reagents in separated droplets, dispersed in an inert organic phase (W/O emulsion). Precipitation occurs inside drops when they coalesce. Besides the implementation of well-known technologies of the nuclear industry, this precipitation in 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 drop scale, on which we focus in this paper, preliminary static and dynamic observations revealed a stage of mixing of the reagents, followed by a progressive concentration of particles at the drop center leading to their agglomeration. In the modeling three configurations of the reagents' mixing were therefore considered relatively to the Hill vortices experimentally noticed. CFD simulations allowed calculating possible mean supersaturation profiles in the drop. Two simplified models were proposed to simulate the precipitation inside the drops. Based on the population balance modeling framework, they consider primary nucleation and growth mechanisms and take into consideration either instantaneous or progressive mixing of the reagents. These simplified models were validated with CFD + PBM simulations. Based on the drop scale simulations, process modeling has been discussed.

Keywords: Precipitation in emulsion processes; Population balance modeling; Multiscale modeling; Nuclear fuel reprocessing

1. Introduction

Oxalic acid precipitation is used in the nuclear fuel treatment industry to recover selected actinides dissolved in nitric acid media. This operation is currently processed in a vortex flow apparatus (Auchapt and Ferlay, 1983), which size and capacity are limited, to mitigate the risk of criticality. In order to manufacture new compositions of nuclear fuel and/or transmutation targets, an alternative to the current method of reprocessing spent nuclear fuel, would be to co-extract chosen actinides and then to co-precipitate them in a single step.

The production of such a co-precipitate solid would require the development of a specific apparatus, either in order to increase the production rates, the latter being significantly enhanced by the joint precipitation of uranium and minor actinides for new nuclear fuel production, or to process high

* *Corresponding author*. Tel.: +33 466796229.
E-mail address: sophie.charton@cea.fr (S. Charton).
Received 27 July 2012; Received in revised form 24 January 2013; Accepted 1 February 2013
0263-8762/$ – see front matter
http://dx.doi.org/10.1016/j.cherd.2013.02.001

activity elements for transmutation purpose. To this end, we are studying a new concept of oxalic precipitation process, based on the use of either a pulsed or a Taylor–Couette flow column (Borda et al., 2008).

In this process, an inert organic phase (Tetra Propylene Hydrogen TPH) is pumped from bottom to top in a closed circuit. Both reagents: the complexing agent (oxalic acid) and the cations to be precipitated (dissolved in nitric acid) are fed individually in the contactor, where they are immediately dispersed as droplets: (i) thanks to the complex flow around the column's internals, generated by the pulsation (pulsed column Nemri et al. (2012)), (ii) or due to the Taylor vortices (Taylor–Couette column). The droplets are moving countercurrently to the inert organic phase, down to the settler, where the organic, aqueous and solid phases separate, thus enabling the solid recovery by filtration. The principle of the process is depicted in Fig. 1 for the pulsed column. The novelty of this process lies in the confinement of the reagents in drops of aqueous phase dispersed in the inert organic phase as shown in Fig. 1.

This "in emulsion" process exhibits the double advantage of (i) implementing well-known technologies of the nuclear industry, and (ii) ensuring the confinement of the sticky precipitate in the organic diluent, thereby limiting the risk of contamination of the apparatus and its adverse consequences in terms of productivity, safety, etc. Moreover, contrary to conventional contactors where the precipitation process is strongly dependent on the position of the two feed lines, here the initial mixing of the reagents and reaction induction time are not directly influenced by the apparatus feed conditions.

Regarding pulsed column, the process feasibility was demonstrated in a wide range of flow-rates and chemical conditions. The apparatus, operating conditions and main results are described in (Borda et al., 2011). Feasibility was also demonstrated recently in Taylor–Couette configuration, for which a parametric study is under progress. For these production tests of Ce^{III}, Nd^{III} and mixed $U^{IV} + Ce^{III}$ precipitates, neodymium (Nd^{III}) and cerium (Ce^{III}) cations are used to simulate actinides, in order to reduce the inventory of radioactive materials involved in feasibility studies. The precipitation reaction of cerium in nitric media follows:

$$2Ce(NO_3)_3 + 3H_2C_2O_4 + 10H_2O \rightarrow Ce_2(C_2O_4)_3{\cdot}10H_2O + 6HNO_3 \quad (1)$$

Whatever the column technology, besides the classical chemical parameters known to influence supersaturation (pH, reagents ratio, etc.), purely hydrodynamic conditions were observed to have an effect on the produced solid properties, such as particle size distribution and particle habit, presumably due to the evolution of the emulsion properties. Indeed, the droplets' size, their residence time, collision frequencies, etc. are strongly related to the pulsation amplitude and frequency in the pulsed column (respectively the gap size and the rotor speed regarding the Taylor–Couette contactor).

Therefore, as for the vortex flow reactor today used in the fuel processing plant (Bertrand et al., 2012), a comprehensive modeling study of the interactions between the precipitation mechanisms and the hydrodynamic conditions prevailing around the droplets in the pulsed column has been undertaken. The methodology is transposable to the Taylor–Couette configuration. In this aim, CFD is used both at the column and at the drop scales independently. Indeed, contrary to usual emulsion crystallization processes, where the particles derive from solidification of the dispersed droplets (Davey et al., 1997; Khalil et al., 2012), where reagents are transferred from the continuous phase (Bandyopadhyaya et al., 1997), or where the crystallization occurs by a quasi-crystallization mechanism (Espitalier et al., 1997), in the studied process the continuous phase is totally inert. Its only role is to allow collisions between droplets, i.e. the actual reactors, whose coalescence initiates the reaction. Actually, despite the increased complexity of the modeling task, the decoupling of these two scales eliminates the influence of the column's feeding conditions on the nucleation process and the properties of the solid.

At the column level, the drop population behavior is considered in order to correlate their size distribution, residence times and collision frequency to the reactor operating conditions, such as column and packing geometry, amplitude and frequency of the pulsed flow, feed rates, etc. (Amokrane et al., 2012). Whereas at the drop scale, which is the object of this article, the reagents mixing within the drops, depending on their outer and initial conditions, and the resulting solid particles nucleation, growth and agglomeration processes are considered.

After examining the available precipitation data in Section 2, the methodology developed to model the processes occurring in the droplets is presented. The detailed description of the mixing process during the coalescence is not taken into account for the moment, however, preliminary experimental observations, supplemented by flow simulations, allowed us to simplify the problem in the framework of a chemical engineering approach, described in Section 3. To conclude, the extrapolation to the simulation of the precipitation in emulsion process, and its performances, is discussed in Section 4.

2. Precipitation data

The obvious required parameters, for precipitation modeling purpose, are the equilibrium data (product solubility) and kinetic data. Both types are empirically determined, and are therefore closely related to the thermodynamic description of the ionic media, and in particular the model used for calculating activity coefficients. Moreover, kinetic data are generally dependent on operating conditions (reactor type, injection point position, stirrer speed, etc.) as discussed Section 3.3.2. While it is already difficult to obtain reliable kinetic data, little data are available regarding either actinides oxalate precipitation and their nonradioactive stand-in:

- The uranium oxalate and the neodymium oxalate systems had been studied by Andrieu (1999) and more recently by Lalleman et al. (2012). Regarding the calculation of activity coefficients, and from there the calculation of solubility products, supersaturation values, and kinetic parameters, both works relied on the Bromley model (1973), which is valid for ionic strength up to $I = 6\,mol\,l^{-1}$.
- Cerium oxalate precipitation has, to our knowledge, not been investigated since the experimental work of Chang (1987) in SRNL. The study was purely empirical and the given correlation results from non-linear regression of experimental data.