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# Design of an intensified coprecipitation reactor for the treatment of liquid radioactive wastes

J. Flouret [a],*, Y. Barré [a], H. Muhr [b], E. Plasari [b]

[a] CEA-Marcoule, DEN, DTCD/SPDE/Laboratoire des Procédés Avancés de Décontamination, BP 17171, 30207 Bagnols-sur-Cèze Cedex, France
[b] Ecole Nationale Supérieure des Industries Chimiques-INPL, Laboratoire Réactions et Génie des Procédés-CNRS, 1 rue Grandville, BP 20451, 54001 Nancy Cedex, France

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ABSTRACT

In the nuclear industry, important volumes of liquid wastes have to be treated to reduce their contents in radioactive contaminants. The coprecipitation is the method mostly applied to perform decontamination of liquid wastes which cannot be concentrated by evaporation. Two operating modes are typically used for an industrial scale treatment by coprecipitation: the continuous and the semi-batch process. It was proved experimentally and theoretically that the semi-batch reactor ensures decontamination efficiency much higher than the continuous stirred tank reactor. An innovative reactor with an infinite recycling ratio is therefore designed to optimize the continuous treatment: the reactor/classifier reaches the same efficiency decontamination as the semi-batch process and represents an efficient device for the coprecipitation process intensification. Hereafter is presented this new coprecipitation reactor and its experimental application to a concrete case of nuclear decontamination. Modelling of this process is totally new: it validates experimental results and also presents theoretical equations to predict decontamination efficiency.

## 1. Introduction

A wide variety of radioactive liquids is produced by the nuclear industry. Most of these effluents require treatment to reduce their content of radioactive contaminants to levels authorised for disposal. To treat these contaminated streams, different processes can be used (Carley-Macauly et al., 1981) with degree of efficiency depending to the characteristics of waste streams. The processes using solid precipitates for the removal of radioactive elements are the most versatile (IAEA, 1994) and can be divided into two groups. When the solid precipitate is directly introduced in the effluent, that is an adsorption process, and when it is formed in situ, that is a coprecipitation process.

The coprecipitation treatment has been chosen for many years to perform decontamination of liquid wastes which cannot be concentrated by evaporation. It is especially used in the reprocessing plant of La Hague and in nuclear research centres of CEA (Commissariat à l'Energie Atomique). Currently, it remains the most widely used technique for two main reasons. First, the waste solutions present a very complex composition and a high ionic strength making the use of other methods (ion-exchange, membrane processes, electrodialysis…) very uncertain. In these cases, only the coprecipitation process allows to separate and recover with efficiency the radioactive compounds from wastes before discharging. Second, the main interest of coprecipitation is to perform a transfer of radioactive contaminants from a liquid phase to a solid phase easily separable and storable. This step is crucial in the management of nuclear wastes. The coprecipitation is therefore a robust and inexpensive process for the treatment of important volumes of low and intermediate radioactive level liquid wastes. Industrially, this process is easily implemented but usually needs a very large reactor volume.

In the industrial plants, significant quantities (2–20 g/L) of barium sulfate are precipitated to decontaminate liquid nuclear effluents containing radioactive strontium traces (isotope $^{90}$Sr). Based on this industrial application, the experimental model chosen for this study is the coprecipitation of strontium with barium sulfate. This adsorbent is chosen because not only it is used to perform strontium decontamination in the nuclear industry, but it is also a compound deeply studied, often used as a model substance for precipitation studies.

Two kinds of process are typically used for an industrial scale treatment by coprecipitation:

- the continuous process where the effluent passes through a series of stirred tank reactors in which reagents are successively added,
- the semi-batch process where reagents are successively added to a given volume of effluent.

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* Corresponding author. Tel.: +33 466397407.
*E-mail address:* julie.flouret@cea.fr (J. Flouret).

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Pacary et al. (2008) developed a model to compare these reactors under the same operating conditions and proved that the best configuration to carry out the decontamination process is the semi-batch stirred tank reactor. This coprecipitation model was also validated with experiments (Pacary et al., 2010) and can be used to predict the strontium decontamination factor of nuclear waste solutions in a continuous stirred tank reactor (CSTR). Furthermore, using a CSTR with recycling of sludge, it was experimentally and theoretically proved that the decontamination rate increases significantly when increasing the solid concentration in the reactor (Pacary, 2008a). Based on this result, an innovative reactor with an infinite recycling ratio is designed to optimize the continuous process: it is a reactor/classifier or MSCPR (Mixed Suspension Classified Product Removal) reactor which is patent pending (Pacary et al., 2008b). This kind of reactor was used by Pastor et al. (2008) in the case of the struvite precipitation process to remove phosphorus from waste water. In our study, the purpose of the reactor/classifier is to optimize the coprecipitation continuous process by achieving the following objectives: maximize the decontamination efficiency, minimize the volume of sludge generated by the process, and reduce the treatment cost by decreasing the installation size.

## 2. Experimental

### 2.1. Experimental set up

The pilot-scale reactor/classifier is presented in Fig. 1. The apparatus of a total volume of 20 L is a multifunctional reactor composed of two different zones:

- a perfectly mixed precipitation zone: the bottom part is a stirred and baffled reactor where the effluent and the barium nitrate solution are introduced,
- a classifier: the settling zone in the top of the reactor has a larger diameter to perform the liquid–solid separation.

This innovative process is used for the first time to remove radioactive strontium from liquid nuclear wastes. The effluent containing sulfate ions and the barium nitrate solution are injected in the reaction zone where strontium and barium coprecipitate as sulfates. Indeed, the concentration of strontium is extremely low, so it cannot independently precipitate as strontium sulfate. On the contrary, during the precipitation of barium sulfate, strontium coprecipitates due to an adsorption phenomenon on the surface of barium sulfate which is continuously renewed by crystal growth (Pacary, 2008a).

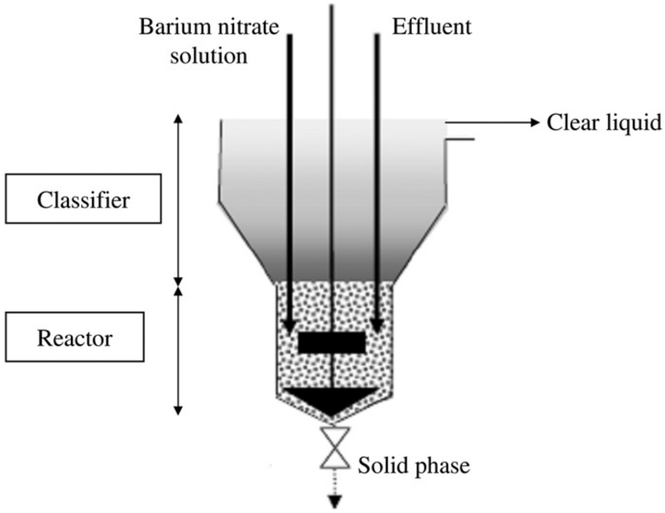

**Fig. 1.** Schematic presentation of the reactor/classifier.

The produced solid phase is returned into the reaction zone by the classifier and goes out slowly from the reactor bottom with a residence time much higher than the liquid phase. This creates both a high concentration of solid phase in the reaction zone and a high efficiency of decontamination.

### 2.2. Material and methods

Liquid nuclear effluents often contain a high concentration of soluble salts (10–100 g/L), particularly sodium nitrate. Taking this consideration into account, the experimental conditions can be fixed and are similar to those used by Pacary et al. (2010) since the nuclear application is exactly the same. The decontamination experiments are carried out by mixing two different solutions: a simulated effluent containing 0.5 mol/L of sodium nitrate, 0.1 mol/L of sodium sulfate and $1.14 \times 10^{-4}$ mol/L of strontium nitrate (corresponding to 10 mg/L of $Sr^{2+}$ ions), and a reactive solution containing 0.29 mol/L of barium nitrate. Barium nitrate, strontium nitrate, sodium sulfate and sodium nitrate, all analytical grade (Prolabo, France), and demineralised water are used to prepare the aqueous solutions.

The laboratory conditions simulate the industrial conditions of the reprocessing plant of La Hague, regarding the residence time and feed conditions. The same residence time is considered: $\tau = V/Q = 10$ min, where $V$ is only the precipitation zone volume (not the settling zone one) and $Q$ is the total treatment flow rate. The total treatment flow rate is $Q$=17 L/h, with an effluent flow rate of 16 L/h and a reactive flow rate of 1 L/h. The solutions are continuously added in the reactor at these flow rates such as the non-stoichiometric ratio $[SO_4^{2-}]/[Ba^{2+}]$ after mixing corresponds to 4.9. Coprecipitation experiments are performed at room temperature in the reactor/classifier stirred by a device composed of two blade stages. The stirring speed is fixed to 75 rpm, corresponding to a compromise between a good mix and a satisfactory liquid–solid separation. Experiments are conducted during a complete day (around twenty four hours) in order to reach the continuous steady state. During the experiments, samples of suspension are regularly taken from the reactor to be analysed. A particle size analysis with a Malvern Mastersizer 2000 is realised to determine the particle size distribution of aggregates and elementary crystals after 10 min of ultrasounds in the analysis tank. The specific power input of the ultrasound treatment is 35 W. For this particle size analysis, the samples are neither filtered nor dried, but only diluted in a solution saturated in barium sulfate with the same ionic strength as in the reactor/classifier. A scanning electron microscopy (SEM, Leo 435Vpi) is also realised to determine morphology of crystals and aggregates. For the SEM analysis, the samples are filtered with a 0.2 μm pore filter, washed and dried. Moreover, other samples of suspension are directly filtered with a 0.2 μm pore filter and the residual strontium concentration is measured in the filtrate by ICP-MS. An analysis ICP-MS is also realised on samples without filtration step.

### 2.3. Results and discussion

#### 2.3.1. Particle size distribution and morphology

Fig. 2 represents the particle size distribution measured with and without ultrasounds. This graph indicates that the elementary particles are agglomerated in the reactor/classifier, since the particle size analysis give different results with the ultrasound treatment. The mean diameter $L_{43}$ of the agglomerates is 13 μm whereas the elementary crystals present a mean diameter $L_{43}$=3 μm. The agglomeration in the reactor/classifier is strongly favoured by the high ionic strength due to sodium nitrate and the