A new oxalate co-conversion technology
based on liquid/liquid extraction columns

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Abstract: *The current objective of fabricating nonproliferating nuclear fuel by "direct" coprecipitation of uranium, plutonium and minor actinides requires a new process to replace the (co)precipitation step. The technological impact of an increased capacity on the work zone could require the development of a different concept for a continuous device capable of ensuring the proposed goal. A new type of device designed and patented by the CEA was tested in 2007. The patent is for organic confinement in a pulsed column (PC). First, precipitation of cerium or neodymium alone has been carried out in this device, with satisfactory results. Moreover, a recent test campaign demonstrated that a uranium-cerium coprecipitate easily forms when the two nitrates are mixed in a pulsed column of the same size operating under very similar process conditions. Qualitatively, the coprecipitate meets the process requirements.*

INTRODUCTION

The current objective of fabricating new nonproliferating nuclear fuel by "direct" coprecipitation of uranium, plutonium and minor actinides requires a reexamination of the (co)precipitation step. In addition to defining a new continuous coprecipitation process to address these issues [1], it was necessary to examine its adaptability to a plant flowsheet implementing devices capable of ensuring this function at suitable continuous flow rates.

Coprecipitation of a fraction of the cycle uranium flow together with the plutonium appreciably increases the flow rates at each process step.

The technological impact of the increased capacity on the facility must therefore be examined, and could require the development of a different concept for a continuous device capable of ensuring the proposed throughput, as the flow rate of the vortex effect reactors [2,3] currently used for plutonium precipitation at La Hague appears too limited. A new type of device designed and patented by the CEA [4] was tested in 2007.

DEVICE DESCRIPTION

Concept

The concept can be applied to a device shown schematically in Fig 1.

The patent is for organic confinement in a pulsed column (PC). The precipitation reaction between the oxalic complexing agent (supplied at 2) and the surrogate nitrate (supplied at 1)—Ce(III) or Nd(III) alone, or a mixture of U(IV) and Ce(III) for coprecipitation—occurs within an emulsion created in the device by a countercurrent flow between these two phases and a chemically inert organic phase (supplied at 3) (for example TPH) produced by the stirring action of pulsating flow (PC: 8b).
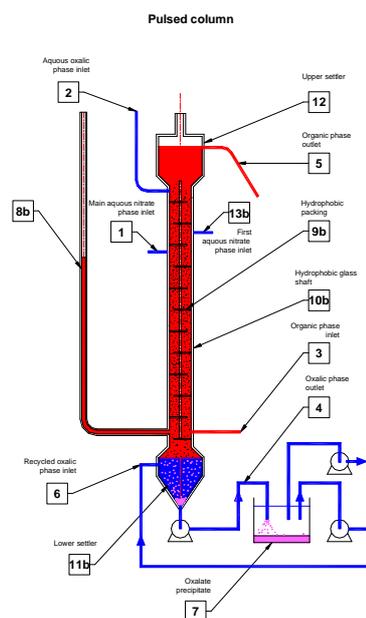

Fig.1. Device developed for oxalate co-conversion (pulsed column)

The inert organic phase from the column (5) is entirely recycled. The nitrate load can be supplied at several additional points to spike the flow (13b). The precipitate is confined and thus, although it is very gummy, it does not form deposits on the vessel walls (9a & 10a), which are also water-repellent [5]; it flows downward

by gravity and exits the column continuously (11b) into a settling flask (7). In an industrial facility this flask could be replaced by a filtration device for continuous recovery of the precipitate. Removal of the precipitate from the column can be favored by recycling a fraction of the oxalic mother liquors (4) at the bottom of the device (6).

Adjusting the upward flow rate of the organic phase in the column directly affects the rate at which the precipitate descends in the column, and thereby controls the residence time and hence the quality of the precipitate output from the device. The organic phase is inert with respect to the aqueous phases in the device. The organic flow therefore has no effect on the precipitation chemistry but only on the residence time.

Advantages of this concept

This device concept has several features:
The precipitate or coprecipitate exhibits little or no adherence because the reactive (oxalate + nitrate) aqueous phases are confined in an emulsion in a solvent that is inert with respect to precipitation (for example TPH diluent). The column and internal packing also receive a patented hydrophobic silanization surface treatment [5].
The device operates continuously and produces a good quality precipitate controlled by the residence time determined by the stirring intensity creating the emulsion (pulsating flow in a pulsed column) and by the countercurrent TPH flow rate.
The concept is directly suitable for scaling up, as the criticality risk is controlled by annular geometry (as in the liquid-liquid extraction pulsed columns in UP3 and UP2-800).
It is currently subject to the following limitations:
This is a new concept and although R&D has been carried out mainly under inactive conditions, validation with U is now in progress. The phenomena occurring in the device are not sufficiently known to be correctly described and modeled. The main difference with a vortex reactor is the reagent concentration profile in a PC, resulting in precipitation under different chemical conditions along the column.
This type of device appears to be suitable for scaling up to high capabilities. A specific R&D project will investigate this concept.

SIMPLE PRECIPITATION TESTS (NEODYMIUM OR CERIUM)

Several types of tests were carried out in 2007 on continuous precipitation with organic confinement in a pulsed column (PC).
The tests carried out in a small (15 mm) diameter silanized pulsed column are described; this device was immediately available and its precipitation capacity proved to be extremely promising.

Test procedure

The precipitation of cerium nitrate and neodymium nitrate, trivalent elements with precipitation behavior similar to that of Pu(III), was tested during the first half of 2007.
The 15 mm silanized pulsed column was packed with truncated PTFE (TEFLON®) disks. The test flowsheet with excess oxalic acid with respect to the surrogate was adapted from the reference flowsheet. The precipitate was allowed to settle in a separate settling flask supplied by the lower settler. A fraction of the supernatant was recycled at a high flow rate to the bottom of the column to enhance the transfer from the lower settler.
The test setup corresponded to the principles claimed in the CEA patent [4].
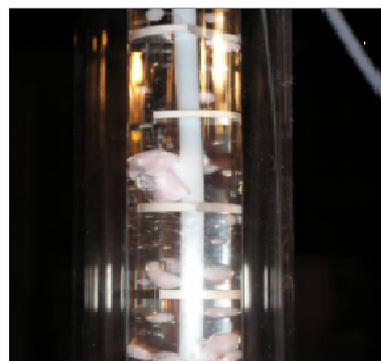
Summary of test results

Fig.2. PC precipitation tests

The hydraulic performance was excellent, with little or no adhesion on the column wall or on the internals (plates). At low flow rates the precipitate was carried in the aqueous emulsion and passed through the column at the same rate as the aqueous phase.
At high flow rates, the emulsion tended to agglomerate due to the presence of the precipitate, and progressed in the form of large

cells that were deformed on impact with the packing. The "cells" were broken up, however, at the interphase boundary in the lower settler and never plugged the column (Fig 2).

The particle size of the precipitate collected in the lower settler corresponded to the values obtained with vortex precipitators, i.e. about 30 µm for cerium and 20 µm for neodymium.

The particle size fraction versus the load injection rate differed according to the element precipitated. The particle size increased for cerium when the flow rate diminished, but appeared relatively unrelated to the residence time in the case of neodymium.

The precipitation reaction was complete for both elements tested. The concentration at the bottom of the column corresponded to the respective solubilities of the two elements under the test chemical conditions.

The morphology of the precipitates revealed increasing agglomeration at higher flow rates. In the case of cerium the agglomerates consisted of small, highly elongated rodlets (Fig 3)
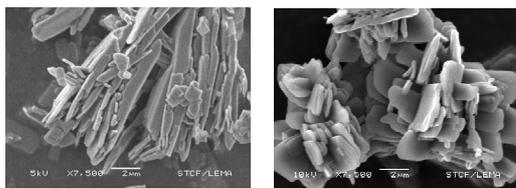

Fig.3. SEM images (X 7500) of Ce precipitate

Simple precipitation test conclusions

The tests under inactive conditions showed that continuous coprecipitation in a column precipitator resulted in stable operation without clogging, and suggest that the process can be scaled up to high flow rates. During these tests a precipitate flow rate per unit area of about 700 kg·h^{-1}·m^{-2} was obtained in a pulsed column 15 mm in diameter. This result implies very reasonable dimensions for the flow rate specified for the future plants.

The quality of the resulting precipitate (particle size and visual appearance) is comparable to the product obtained with a vortex precipitator.

The next step was to precipitate a mixture of uranium and cerium nitrate to test coprecipitation in this device.

URANIUM-CERIUM TESTS

Test procedure

A pulsed column was used with the process based on the reference flowsheet

Summary of test results

As for the inactive tests, the 15 mm silanized pulsed column was packed with truncated PTFE (TEFLON®) disks. The test flowsheet with excess oxalic acid with respect to the surrogate was adapted from the reference flowsheet. The precipitate was allowed to settle in two settling flasks supplied in series from the lower settler. A fraction of the supernatant was recycled from the oxalic mother liquor receiving vessel at a high flow rate to the bottom of the column to enhance the transfer from the lower settler.

The resulting precipitate did not adhere to the vessel wall. Its very cloudy appearance suggests a very fine particle size resulting in increasing turbidity in the settling flasks during the 1-hour test.

The "droplets" in which the precipitate formed were small, and descended in the column at a constant rate. When it reached the lower settler the precipitate easily crossed the interphase and was transferred into the settling flasks.

The precipitation reaction was complete. U and Ce losses from the bottom of the column or the oxalic mother liquor flask correspond roughly to the solubility in the oxalic mother liquor flask.

The particle size distribution indicates a fine precipitate. The particle size increased with the residence time, but did not exceed 10 µm for the lowest load injection rate tested. This result was less satisfactory than the behavior observed for precipitation of cerium alone.

The morphology of the precipitates revealed increasing agglomeration at higher load injection rates (Fig 4). The individual crystallites appeared to be much smaller than for the cerium oxalate precipitate.
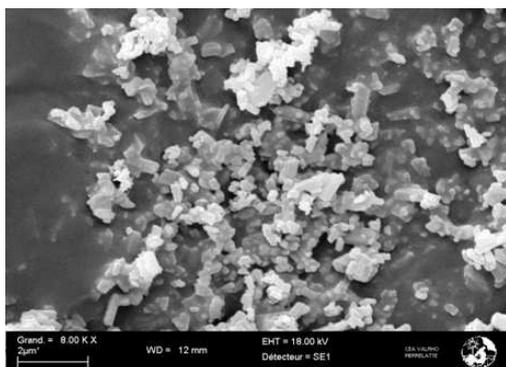
Fig.4. SEM images (X 8000) of UCe precipitate

X-ray diffraction (XRD) analysis confirmed the formation of a mixed uranium-cerium coprecipitate after each test.
At low test load injection rates, however, traces of uranium precipitate and cerium precipitate were nevertheless observed. These traces diminished at a rate of 100 mL·h^{-1} and completely disappeared at 500 mL·h^{-1}, with the appearance of the characteristic signature of a mixed compound with hexagonal structural. (Fig 5)
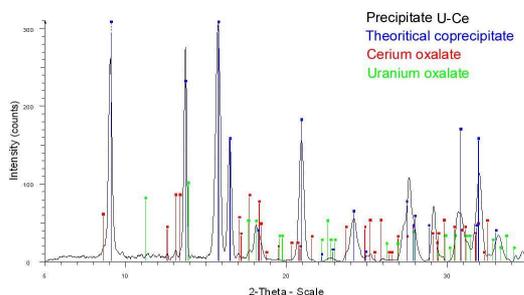

Fig.5. X-ray diffraction diagram of the precipitate formed compared with the theoretical mixed oxalate

At higher rates a mixed precipitate formed in each case, gradually forming an orthorhombic structure due to deformation.

PRELIMINARY CONCLUSIONS AFTER UCE COPRECIPITATION TESTS

A UCe coprecipitate was always obtained regardless of the column flow rate and the corresponding range of chemical conditions in which coprecipitation occurred (an extended range of $H_2C_2O_4$ and HNO_3 concentrations).
A precipitate of optimum "purity" (hexagonal close to the theoretical model) appears to have been obtained at about 500 mL·h^{-1}.

The precipitation reaction appears to have been complete over the full height of the test column.
The particle size of the resulting precipitate was less satisfactory than under inactive conditions (Ce alone). The UCe coprecipitate formed small aggregates, as confirmed by the results obtained with a vortex precipitator.
The coprecipitation tests again demonstrated stable device operation without clogging. A precipitate flow rate per unit area of about 875 kg·h^{-1}·m^{-2} was reached during these tests. This exceeded the performance obtained with cerium alone, and suggests that the dimensions of an industrial-scale column will allow suitable capacity.

Future development of the new co-conversion technology

It will focus on two areas of investigation:
Consistently obtain a precipitate of optimum quality over a wide range of flow rates, and successfully grow the precipitate to sizes compatible with an industrial-scale filtration step.
Determine a tradeoff between the column height and the column output losses to limit the column to the only necessary length.

REFERENCES

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