Design, Development and Testing of Miniature Liquid-liquid Extraction Contactors for R&D Studies in Nuclear Environment

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Design, development and testing of miniature Liquid-Liquid Extraction contactors for R&D studies in nuclear environment

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Abstract

Testing liquid-liquid extraction flowsheets on radioactive solutions at laboratory scale requires specific contactors, that must be as small as possible (to minimize the quantities of reagents) and suitable for use in glove boxes or hot cells. As such contactors are not commercially available, CEA designs dedicated apparatus for its experiments. Two examples of such contactors are highlighted: a stage-wise one (a miniature mixer-settler) and a differential one (the Taylor-Couette column). Both combine similarities with larger contactors that make possible flowsheet extrapolation to industrial scale, and specific features, mainly because of the major role of materials wettability when volumes are reduced.

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Keywords: liquid-liquid extraction, laboratory-scale contactors, miniature mixer-settler, Taylor-Couette extraction column

1. Introduction

Spent nuclear fuel contains re-usable products (uranium and plutonium) and numerous other elements including radionuclides with short to very long half-lives. Nuclear fuel reprocessing aims at separating these components, in order to reuse or store them adequately. In the classical industrial PUREX process, implemented for instance in the Areva La Hague plant, these separations are carried out by liquid-liquid extraction (LLE). Several other processes under development at CEA Marcoule, intended to complement the PUREX process or to propose an alternative to it, are also based on liquid-liquid extraction.

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At industrial scale, LLE of nuclear elements is operated with flowrates typically ranging from 100 to 1000 L/h (and even much more in other fields such as metals refining). LLE operations are implemented in different kinds of apparatus sorted into stage-wise contactors (e.g. mixer-settlers, centrifugal contactors) or differential ones (e.g. pulsed or agitated columns). The development of such solvent extraction processes starts with the selection of the adequate extracting molecule and the measurement of relevant data regarding thermodynamics (distribution ratios) and kinetics (mass transfer rate). Then, a key step consists in testing the whole extraction flowsheet at laboratory scale on radioactive solutions (first on laboratory-made representative solutions, then on solutions produced from actual used fuel). Because handling these radioactive solutions implies several issues (effluent storage and reprocessing, operators protection against radiations), these tests should be conducted at a very small scale, involving as few reagents as possible. Therefore, the laboratory liquid-liquid contactors used for these pilot trials must fulfil the following requirements:

- to be as small as possible,
- to be similar to the industrial contactors, in order to make easier a later scaling-up of the process,
- to be operable in nuclear environment (glove boxes or hot cells).

According to our knowledge, at present the smallest commercially available laboratory contactors are:

- regarding differential contactors, agitated columns with 30 mm inner diameter (SULZER Kühni-type column),
- regarding stage-wise contactors, mixer-settlers whose mixer's volume is 25 mL (MEAB MSU 0,1).

Both are appropriate for flowrates of several liters per hour, and thus are too large for experiments in high activity conditions. Furthermore, they were not especially designed in order to be used in hot cells. Thus, CEA has been developing for several decades more appropriate liquid-liquid contactors.

For many reasons, it is not possible to design a small contactor by simple scale reduction of a larger model. Obviously some mechanical parts (motors, walls) cannot be reduced proportionally to the mixer and settler inner volumes. More important, dominating phenomena in hydrodynamics are changing while reducing the size: at lower size, capillary effects grow in importance and, for instance, getting smooth low flows through small openings becomes challenging. The development and optimization of miniature contactors usually begins with the design of a first prototype and ends up with the testing in pilot plant. This challenging task will be introduced hereafter by two examples: a stage-wise contactor and a differential one.

2. Example of a stage-wise contactor: the « Next Generation » mixer-settler

Mixer-settlers (MS) are well-known and widely used liquid-liquid contactors. In MS, each stage consists of an agitated compartment (the mixer, where mass transfer occurs) and a non-agitated one (the settler, where both phases separate). To reach the required overall efficiency of each operation of a liquid-liquid separation process (extraction, stripping…) several stages are interconnected together to form batteries where both phases circulate in opposite directions (countercurrent flow). Classical features among the numerous models of MS are:

- the head to tail positioning of adjacent stages (the mixer of a stage is on the same side as the settlers of the adjacent stages), thus eliminating connection pipes between stages,
- the agitating mobiles (called "pump-mixer") that ensure both pumping of the liquids from adjacent stages into the mixer and mixing by shearing the fluids inside of the mixer.

The following paragraphs deal with the transposition of these features to tiny MS and highlight the performances achieved so far regarding hydrodynamics and extraction.

2.1. Design

A very compact and quite simple mixer-settler model had been designed by CEA three decades ago. The mixer and settler volumes (respectively 6 mL and 20 mL) are adequate for total flowrates (aqueous + organic) in the range 200 - 500 mL/h. Although it was gradually optimized, the alternative separation processes currently under study triggered the need for a new MS model, more convenient to extracting systems with low transfer kinetics (e.g. enabling appropriate control of the interfacial area and of the residence time), and that could handle larger variations of the liquids properties (e.g. higher viscosity) or of the operating conditions (e.g. when aqueous and organic flowrates are very different). The newly developed apparatus, named mixer-settler "Next Generation", is shown on

Fig. 1. It combines classical MS features, and peculiarities by reason of the small size and of the utilization in nuclear environment.

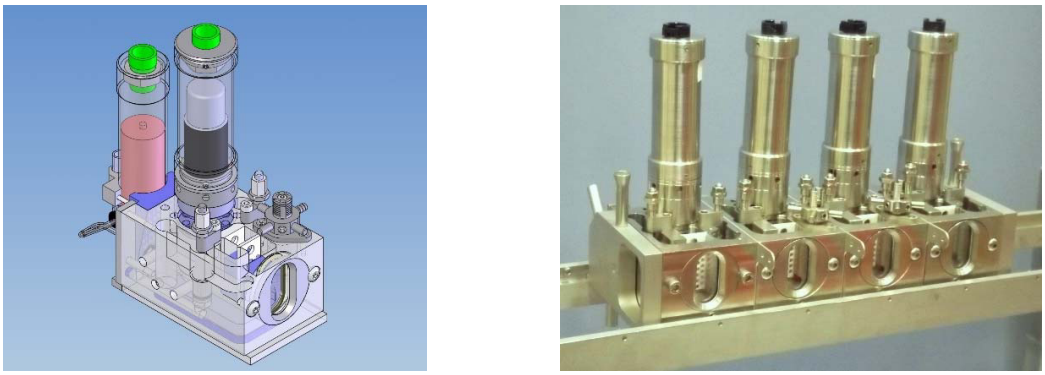

Fig. 1. (a) 3-D view of one stage; (b) 4-stage battery.

A first example of this combination of classical and specific characteristics is the mixing chamber (Fig. 2). It has a nearly cubical shape with baffles, in order to avoid vortex formation, which is widely inspired from larger devices. However, because walls wettability plays a major role when the size decreases (the surface/volume ratio increases), the mixing chamber is exchangeable and can be made of stainless steel (hydrophilic, favoring oil-in-water emulsion) or of PTFE (hydrophobic, favoring water-in-oil emulsion).

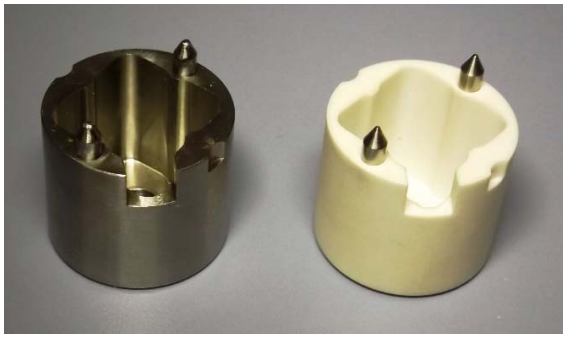

Fig. 2. Mixing chamber (stainless steel and PTFE).

As these MS are devoted to testing new flowsheets, adjustable size modular batteries are formed by arranging together individual stages on CEA-patented rails[1]. On these rails, all MS stages are oriented in the same direction (whereas usual orientation is head to tail), so that all settlers may be viewed by the operators when used in hot cells. This enables a more convenient control of the interface level and the aqueous weir height can be adjusted as necessary.

The internal recirculation is another feature where general rules meet miniaturization specificity. MS perform better when both phase flowrates in the mixer do not differ too much. If the process flowsheet does not fulfil this condition, the low flowrate phase must be recirculated inside each stage through a pipe connecting the settler outlet to the mixer inlet. Usually, the recirculating flowrate is adjusted via a valve. The MS “Next generation” is also fitted with such a feature. However, in order to get an even recirculating flow in spite of the relatively high capillary forces in a narrow pipe (diameter about 5 mm), the recirculation is carried out by a miniature pump bound to each stage. This pump, fixed at the back of a stage, can be seen on Fig. 3.

Fig. 3. Stage with recirculation pump.

2.2. Characterization

The characterization of the MS "Next Generation" went through the usual steps: the hydrodynamic functioning was first checked, and then mass transfer trials were performed.

2.2.1. Hydrodynamics

The main functions (pumping, dispersing, settling) were straightaway satisfactory, while some auxiliary parts like the adjustable aqueous weir needed further improvement. The aqueous phase outflow over this weir was noticed to be quite uneven, particularly at flowrates below 50 mL/h, causing undesirable residence time variations in the following stages. The first design of the weir was a wide horizontal opening (Fig. 4a) and, although stainless steel is rather hydrophilic, the aqueous phase accumulated periodically behind the weir, instead of flowing continuously. A first improvement consisted in a V-shaped opening (Fig. 4b), which worked satisfactorily at very low flowrate, but that hindered larger flowrates. Finally, a double V-shaped opening was designed that ensures a smooth flow for the whole range of flowrates (Fig. 4c). Hence, even in such an unspectacular function, the extreme size reduction calls for an innovative design.

Fig. 4. Aqueous weir, from left to right: original (a), first improvement (b), final shape (c).

2.2.2. Mass transfer efficiency

In a second step, the mass transfer efficiency of the new MS was investigated. In order to quantify this efficiency, extraction tests were performed using nitric acid as extractible solute and a monoamide extracting molecule. These tests were led at various flowrates (corresponding to various residence times in the mixer) and agitation speeds. The

organic to aqueous ratio was kept constant (O/A = 4). This value leads to an extracting factor about 1 (since the distribution ratio is about 0.25), providing better accuracy in efficiency determination.

The results are shown in Table 1.

Table 1. Nitric acid extraction tests.

agitation speed (rpm)	residence time (min.)	Murphree efficiency
1100	5.1	100 %
1100	2.9	92 %
1100	2.0	91 %
1100	1.3	84 %
1500	5.0	98 %
1500	2.0	98 %
1500	1.2	84 %

The achieved transfer efficiency is above 90% in all cases, except at very low residence time (< 1.5 min.), which is similar to results get with larger mixer-settlers. This high efficiency suggests good overall performances for forthcoming tests of solvent extraction processes and will facilitate the extrapolation of process flowsheets to industrial scale.

The design of the mixer-settler "Next Generation" is currently under optimization (mainly width reduction, in order to get more stages in limited workspace). These innovative MS will soon be used for process testing involving uranium solutions.

3. A differential contactor: the Taylor-Couette-flow column.

In the field of differential contactors, size reduction is more challenging. First, the lower energy input in a pulsed column compared to a mixer-settler enhances the influence of materials wettability ("wall effects"). Former experiments at CEA had shown that the lowest achievable diameter for a pulsed column is 15 mm. Thus, the minimum acceptable total flowrate (aqueous + organic) is about 2 L/h (contrary to MS, efficiency in a differential contactor decreases when flowrates are too low). Next, as the height equivalent to a theoretical stage (HETS) is quite diameter-independent, a "small-scale" laboratory pulsed column has to be as high as the industrial one that it represents (typically 8 meters in a nuclear reprocessing plant). For all these reasons, pilot tests involving pulsed columns are very difficult to implement in nuclear environment.

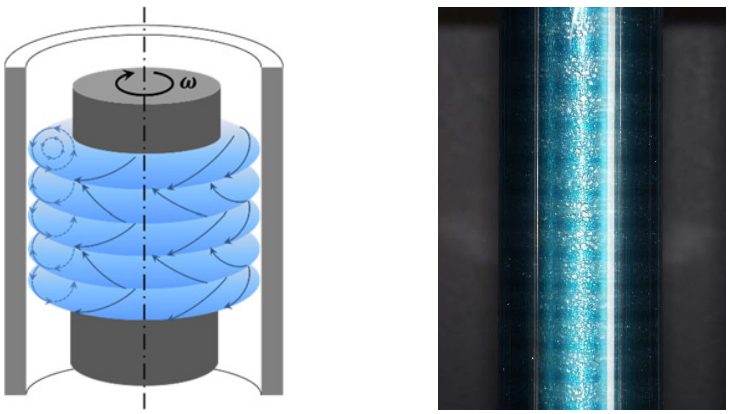

Fig. 5. Taylor vortices (a) schematic drawing; (b) photograph.

Therefore, in order to allow significant size reduction, a new differential liquid-liquid contactor has been designed, which has similarities with pulsed columns but which is based on a Taylor-Couette flow[2]. The column consists of two concentric cylinders with the inner one rotating and the outer one fixed. The counter-current flow takes place in the annular gap between the two cylinders. Beyond a critical speed of the rotating cylinder, pure azimuthal Couette flow results in the formation of toroidal vortices, called Taylor vortex flow (TVF). Thanks to this particular flow structure, Taylor-Couette column exhibits:

- low axial mixing (no back and forth moving of the fluids as in pulsed flow);
- high residence time (entrapping of the droplets in the Taylor vortices);
- low flowrates (about 100 mL/h) in the small annular gap (of typical width 1.5mm).

3.1. Design

The current Taylor-Couette column (Fig. 6) is the result of a several years development process, leading from the first functional prototype to a reliable model suited to using in hot cells. The active part is 75 cm long. The inner and outer diameters of the annular gap are respectively 8.5 and 10 mm. The column is also fitted with various features facilitating the realization of experiments. For instance:

- The shaft and the upper and lower settlers have integral thermal jackets, for efficient temperature control,
- The shaft consists of six glass cylinders linked by metal flanges. Each flange has an opening that can be used as an intermediary flow inlet or as sampling port.

Additionally, materials wettability can be controlled in order to stabilize the expected emulsion type. Raw glass and stainless steel are hydrophilic, thus stabilizing oil-in-water emulsion. By proper treatment these materials can be made hydrophobic (silanes grafting for glass and Teflon coating for steel), stabilizing water-in-oil emulsion.

Fig. 6. Taylor-Couette column designed for use in hot cells.

3.2. Characterization

As usually done for other columns, transfer efficiency of a Taylor-Couette column is measured by the height equivalent to a theoretical stage. In order to determine this height, extraction experiments have been performed in a 75 cm high hydrophobic column, at varying rotation speed. The aqueous feed was a nitric acid solution ($[HNO_3]$ = 5 mol/L). The solvent was the classical tri-butyl-phosphate (TBP) diluted at 30 % (v/v) into branched dodecane. The flowrates were: A=30 mL/h ; O=160 mL/h.

The HETS were determined from the nitric acid concentration in the raffinate flow by means of the graphical McCabe-Thiele method. Fig. 7 depicts the evolution of the HETS against the rotation speed.

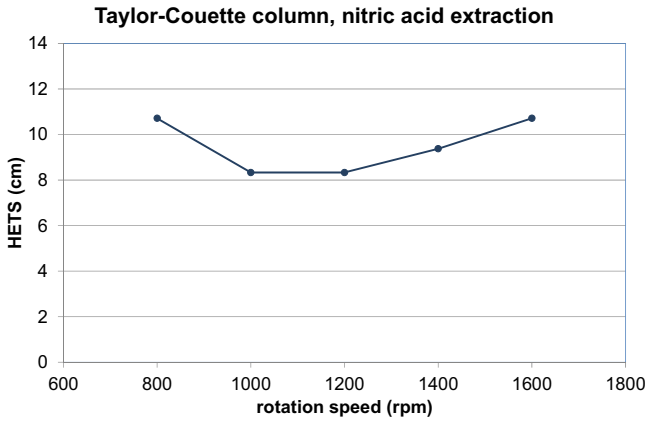

Fig. 7. Taylor-Couette column, HETS vs rotation speed.

The HETS are remarkably low: about 10 cm, which is one tenth the usual value in pulsed columns. That means that a 75 cm Taylor Couette columns achieves the same separation performance than a 8 m pulsed column.

The shape of the HETS curve shows that the column efficiency is optimal for a rotation speed ranging from 1000 to 1200 rpm. At lower speed, large aqueous drops are not split into smaller ones, thus reducing both their residence time and the interfacial area. At higher speed, the Taylor-Couette vortices become oscillating, that increases the unfavorable axial mixing.

Thanks to their small size and the low operating flowrates, Taylor-Couette-flow columns are particularly convenient for R&D studies nuclear environment. However, as this peculiar flow can only be observed in a narrow gap between two cylinders, they will never replace pulsed columns as industrial apparatus. The extrapolation of results from pilot (Taylor-Couette) columns to industrial (pulsed) columns will be based on simulation, which requires an accurate modelling of the flow in both apparatus and of the chemical phenomena. In this goal, an exhaustive study of the behaviour of the Taylor-Couette column is in progress.

4. Conclusion

As an answer to the need of miniature liquid-liquid contactors, specific apparatus has been developed at CEA Marcoule. They combine, as far as achievable, a small size and a good similarity with industrial contactors. In comparison to larger contactors, the behaviour of small-scale contactors is strongly affected by the surface properties their constitutive materials, which have to be properly controlled.

These small devices, initially devoted to tests in nuclear environment, may also find their use in other fields, where feed solutions or extractant are available only in limited quantities, such as processes for rare earth recycling.

Acknowledgements

The above described contactors have been initially designed by J.-Y. Lanoë and F. Gandi. Theses designs are currently under improvement by the authors and F. Dutilh (CEA, DEN, DTEC, SGCS).

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