

A modelling approach for the comparison between intensified extraction in small channels and conventional solvent extraction technologies

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Abstract

In this paper, the application of small channels to the extraction separations in spent nuclear fuel reprocessing has been investigated via a modelling approach. The results are compared with conventional liquid-liquid extraction technologies such as mixer-settlers and pulsed columns, using models from the literature.

In the model mass transfer, redox reactions, pressure drop and nuclear criticality are taken into account, as well as manifold and two-phase separator designs for the small-scale technology. The resulting model, posed as an optimisation problem, is a mixed integer nonlinear problem, implemented in the General Algebraic Modeling System (GAMS).

An alternative flowsheet for the codecontamination section of the PUREX process, as a case study, has been investigated. The results show that the small-scale technology could be beneficial, in particular in terms of volumetric mass transfer coefficients, nuclear criticality safety and short residence time, which improves neptunium separation and reduces solvent degradation.

Keywords: Liquid-liquid extraction; small channels; spent nuclear fuel reprocessing; optimisation; process design.

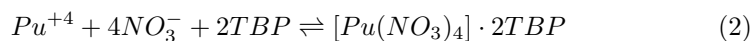
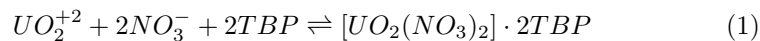
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1. Introduction

Nuclear power generation could continue to be a viable option for the future, providing lower CO₂ emissions than fossil fuels. However, hazardous materials are generated, motivating the need for adequate treatment and disposal. The spent nuclear fuel (SNF) consists of, typically, 96% uranium and 1% plutonium [1], although the composition varies with type of fuel, reactor, enrichment, etc. The uranium and plutonium are reusable materials since they may be used as a mixed oxide fuel in a suitable nuclear reactor. The reprocessing of SNF would allow:

- a reduction in the volume of high level waste (HLW);
- a further 25% of energy from the original uranium [2];
- a reduction in the long-term radiotoxicity of HLW [2].

All the commercial plants use the PUREX process for SNF reprocessing to recover uranium and plutonium by several liquid-liquid extraction operations [3, 4]. The PUREX process is generally based on two liquid-liquid extraction cycles: the first one includes codecontamination and U/Pu partitioning sections, whilst the second one includes U and Pu purification sections. The SNF is first dissolved in a nitric acid solution and then U and Pu are recovered by a selective solvent, tri-n-butyl-phosphate (TBP), diluted to 20-30% (v/v %) with paraffinic diluent because of its high density and viscosity. The TBP selectivity depends on the oxidation state of the actinide: it is high for the +6 state (U(VI) as UO₂⁺²) and the +4 state (e.g. Pu(IV) as Pu⁺⁴), lower for the 5+ state (Np(V) as NpO⁺²) and practically zero for +3 and lower states [5]. The chemical equilibria for U(VI) and Pu(IV), in the nitrate media, are:



Besides reactions 1 and 2, extraction of nitric acid in the organic phase inevitably

occurs [6]:



In the first section of the modern PUREX processes of La Hague (France) and Rokkasho-mura (Japan) plants, U and Pu are typically separated from the other components in the SNF through four main extraction steps [5]:

1. main extraction, where U, Pu and low concentrations of other components are extracted from the aqueous feed;
2. Zr and Ru scrub, where Zr and Ru are separated from the organic stream loaded with U and Pu in the previous step, using diluted nitric acid solution, and the aqueous outlet is recycled to the previous step to increase U and Pu recovery;
3. Tc scrub, as the above scrub but removing Tc, through concentrated nitric acid solution;
4. complementary extraction, where U and Pu are back extracted from the aqueous phase outoing the previous step and recycled to the main extraction step, to increase U and Pu recovery.

This first section of the process, which is the highly active one, is called the “codecontamination” section. It is one of the most challenging sections because of the presence of minor actinides and fission products. Therefore, particular attention to nuclear criticality safety is needed. Typically, safety is achieved through extraction equipment and with neutron absorbers. An example is pulsed columns, currently used in all commercial plants for this section. Mixer-settlers, widely employed for SNF reprocessing, are not safe by geometry and hence they may be used only for diluted concentrations or low liquid holdup. Difficulties arise from the high extraction and decontamination requirements for U and Pu. These targets require several recycle streams and different scrubbing operations to remove components that show different thermodynamic behaviour, such as Zr and Tc, as already mentioned. Finally, in the codecontamination area, significant solvent degradation occurs, due to radiolysis, therefore

40 reduction of unit operations or volumes, to decrease the contact time and solvent exposure, would be beneficial.

In addition, there are several drawbacks due to the conventional solvent extraction equipment. Pulsed columns and mixer settlers require respectively large amounts of headroom and floor space. Centrifugal extractors are the 45 least reliable equipment from amongst the traditional ones [7]. They have low tolerance to solids and require periodic maintenance for the replacement of the rotor and/or the motor. For these reasons their use has been limited[8].

Some of these disadvantages may be overcome if intensified extraction in small-scale contactors is used. The concept of intensification is to decrease size 50 and cost while improving the performance of a process unit. This can be the case of liquid-liquid extractions in small scale contactors where mass transfer is enhanced [9, 10]. Other benefits are improved control of hydrodynamics and the reduction in the amounts of hazardous materials involved, which may be particularly advantageous in the nuclear industry.

55 The use of small channels for liquid-liquid extraction of U(IV) in nitric acid solution, has been investigated in the literature [11, 12, 13], with diameter between 0.5 and 2 mm. Capillaries with Bond numbers lower than 3.37 may be defined as small channels [14, 15]. It is fundamental to properly design a flow distribution network to increase the number of channels (“number up”) and 60 therefore increase the throughput. In this work, a 4-level comb-like network will be investigated, as it seems the most suitable manifold type to arrange a large number of channels in a compact stack. Alternative manifolds may be the monolithic reactor type or the tree-like network. Nowadays, the field of flow distribution networks is extensively investigated [16, 17, 18, 19, 20, 21]. 65 Several types of two-phase separators (coalescers, sidestream needles, *etc.*) are currently being studied, as well. In this work, the design of manifolds, separators and small channels will be optimised. The resulting size of these elements provide indications on possible future investigations.

An alternative process flow diagram for the codecontamination section of 70 the PUREX process is presented below and optimised on the basis of economic

criteria. The short-cut models used, described in the following section, allow for a preliminary process design and optimisation. These type of models, widely used in Process Engineering, are not as computational expensive as CFD models, although with the latter a more detailed analysis of a single unit operation is possible. Applications of small-scale contactors, pulsed columns and mixer-settlers are investigated, using mathematical models developed in the literature. The performance and the main chemical engineering attributes of the liquid-liquid extraction technologies are investigated and compared.

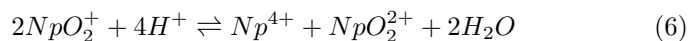
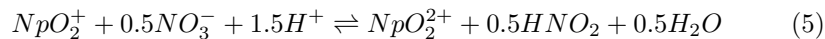
2. Summary of mathematical models

Mathematical models developed in the literature have been used to design, optimise and compare the liquid-liquid extraction processes. In particular, technologies investigated are the novel small-scale process units, pulsed columns and mixer-settlers. In this section, the main aspects of the models used are summarised. Assumptions considered to develop the mass balance model, as well as correlations used to predict thermodynamics, mass transfer, hydrodynamics, pressure drops, flow network design, redox reactions and criticality, are stated.

2.1. Chemistry

The system, suitable for SNF reprocessing, involves the following components: U(VI), Pu(IV), Zr, Ru, Tc, Np(IV), Np(V) and Np(VI), HNO₃. Nitrous acid HNO₂ has also been included, to simulate the radiolytic degradation of HNO₃. The distribution coefficients of all components have been estimated according to the sources listed in Table 1.

A difficult task in the PUREX process is the control of Np since Np exists in nitric acid solution with three different, easily inter-convertible, oxidation states, Np(IV), Np(V) and Np(VI):



Reaction rates are taken from the literature [22, 23, 24, 25]. Details of the equations implemented to calculate all distribution coefficients and reaction rates are given by Bascone *et al.* [26].

Table 1: Sources for the calculation of distribution coefficients used in this work.

Component	Source
U(VI), Pu(IV), HNO ₃	Richardson and Swanson[6]
Zr, Ru	Natarajan <i>et al.</i> [27]
Tc	Asakura <i>et al.</i> [28]
Np(IV), Np(VI)	Benedict <i>et al.</i> [29], coefficients re-calculated by Kumar <i>et al.</i> [30]:
Np(V)	Nominal value of 0.01 [23]:
HNO ₂	Uchiyama <i>et al.</i> [31]

2.2. Nuclear criticality safety

SNF contains fissile materials. Hence, nuclear criticality safety must be guaranteed in the reprocessing. The nuclear criticality safety should be rigorously analysed by codes that solve the time-dependent transport equation of the neutron flux. However, these types of codes are too computational expensive and not suitable for flowsheet optimisation. Here, the *migration-area* approximation has been used to estimate the effective multiplication factor k_{eff} , *i.e.* the ratio between the number of neutrons produced by fission in one neutron generation and the number of neutrons lost in the previous neutron generation, due to absorption and leakage [32]. Hence, by definition, to guarantee subcriticality, the k_{eff} must be lower than 0.95, a value lower than 1, which indicates criticality, for safety reasons. This method is not sufficient to determine nuclear criticality safety, but it can provide a first measure and valuable insight to compare liquid-liquid extraction technologies.

110 *2.3. Modelling of intensified extraction*

The mathematical model for liquid-liquid extraction in small channels was presented previously [26]. The mass balance is based on the assumption of ideal plug flow. Hence, gradients of concentration and velocity along the radial direction are neglected, as well as axial mixing. Steady state is assumed. The

115 resulting mass balance is given by

$$-v_k \frac{dC_{i,k}}{dL} - k_L a (C_{i,k} - C_{i,k}^{eq}) + \sum R_{i,k} \varphi = 0 \quad (7)$$

where $\sum R_{i,k} \varphi$ is the sum of all chemical reactions involving the component i in the phase k . Eq. 7 is converted to a set of algebraic equations through the application of a fourth order Runge-Kutta method. Eq. 7 does not take into account the effect of the flow rate ratio, therefore an empirical equation has

120 been used to consider the latter [26].

The volumetric mass transfer coefficient $k_L a$ has been calculated as suggested by Kashid *et al.* [33]:

$$k_L a = 0.88 \frac{v_{mix}}{L} Ca^{-0.09} Re_{mix}^{-0.09} \left(\frac{D}{L} \right)^{-0.1} \quad (8)$$

where v_{mix} is the superficial velocity of the two-phase flow, D and L are respectively the diameter and length of the channels. The equation above showed good

125 agreement with experimental data of uranium extraction in small channels up

to 2 mm using a mixture of ionic liquid with TBP, although with recalculated parameters [13]. In this work, as the physical system is similar to the one used by Kashid *et al.*, the original parameters have been used.

Eq. 8 is valid for slug flow. According to Kashid and Agar [34], for the

130 system water-cyclohexane with both main capillary and Y-junction channels

with diameter varying from 0.5 mm to 1 mm, the slug flow is stable in polytetrafluoroethylene (PTFE) capillaries for aqueous to organic flow rate ratios from 0.17–0.33 to 2.5–5. The maximum reported superficial velocity of the mixture, for slug flow, is approximately 4 cm s⁻¹. The flow behaviour of the system

135 TBP-kerosene/nitric acid solution, in small channels up to 2 mm, has not been fully characterised. Hence, the most conservative limits for aqueous to organic

flow ratios (0.33–2.5) and velocities reported by Kashid and Agar [34] have been used as bounds for these variables in the model.

Channels are assumed to be hydrophobic to disperse the aqueous phase, as
140 in the extraction channels used for the main extraction to protect the solvent
from contaminants (all the solids are directed with the dispersed phase)[5]. The
cost of channels and manifolds, assumed as first estimation equal to the sum of
channels and mixing tees, is estimated using prices provided by CM Scientific
Laboratory Supplies [35] for transparent polymers. These costs are multiplied by
145 a material factor (0.1, based on the current market for nontransparent polymers
such as PTFE), to reasonably compare costs between liquid-liquid extraction
technologies. A linear scaling factor is assumed [36]. Operating cost consists of
pumping cost. See Bascone *et al.* [26] for the full set of equations..

2.3.1. Unit description

150 The flow network design is essential to distribute the organic and aqueous
phases in the parallel small channels ensuring a good flow uniformity. Here,
the methodology developed by Commenge *et al.* [21] has been used to design
the manifolds. This methodology, based on the electrical resistances network
model and assuming isothermal and laminar flow, allows to design a comb-like
155 manifold, which seems the most appropriate manifold to arrange a large number
of small channels in a compact stack [21]. Due to the throughput investigated
in this work, a four-level structure has been considered (see Figure 1). The
4th level is the single largest distributor/collector, which connects the different
modules. The 3rd level distributes/collects the single phase flow through the
160 stack of plates, the 2nd one distributes/collects the single phase flow through
the channels of the plates. The 1st level consists of the small channel extractors
and it is shared by the two manifolds (one for each phase) through a mixing
junction. At the end of level 1, a sidestream channel is used to separate the
dispersed plug from the continuous slug, as described by Scheiff *et al.* [37]. Each
165 channel or distributor in each level is defined as “element”.

A multi-stage counter-current configuration has been considered, to achieve

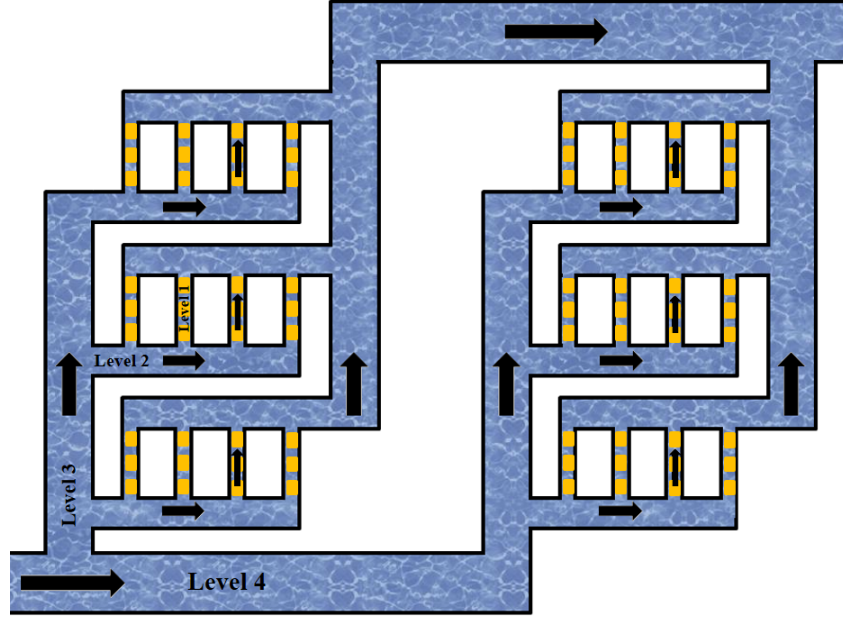


Figure 1: Schematic of the four-level network. In this sketch, one element in the level 4, two in the level 3, three in the level 2 and four in the level 1 are shown. The level 1 consists of the small extractors (yellow dispersed plugs are shown).

a high extraction efficiency. Two manifolds are required for each stage, one for each phase. For more details, see [26].

170 2.4. Modelling of mixer-settler units

Mixer-settlers have been widely investigated in the last 60 years. Assuming homogeneous concentrations and steady state, the mass balance model for the component i in the phase k is given by:

$$\text{mixer} \quad \dot{V}_k(C_{i,k}^{in} - C_{i,k}) + k_L a V (C_{i,k} - C_{i,k}^{eq}) + \sum R_{i,k} \varphi_k V_{mix} = 0 \quad (9)$$

$$\text{settler} \quad \dot{V}_k(C_{i,k}^{in} - C_{i,k}) + \sum R_{i,k} \varphi_k V_{set} = 0 \quad (10)$$

Mixer-settlers are modelled considering a counter-current configuration, according to the mixer-settler bank used in nuclear industry: the aqueous phase leaving the settler is the inlet of the mixer in the previous stage, whilst the organic outlet is the inlet of the mixer in the next stage. See [8] for further details.

The overall mass transfer coefficient can be calculated as a combination of film mass transfer coefficients of the dispersed and the continuous phase. According to Gonda et al. [38], the rate determining step in agitated vessels is the mass transfer in the dispersed phase. Therefore, the mass transfer coefficient in the continuous aqueous phase can be neglected [38]. The expression suggested by Treybal is used to estimate the mass transfer coefficient k_L in the dispersed phase, and hence the overall mass transfer coefficient [39, 40]:

$$Sh_d = \frac{k_L d_{32}}{\mathcal{D}_d} = \frac{2\pi^2}{3} \quad (11)$$

The Sauter mean diameter has been calculated by the Calderbank equation for a stirred vessel with a four bladed-impeller [41].

The operating cost is the agitation cost. The maximum settling velocity of dispersed drops, required to design the settlers, is assumed equal to 1.5 mm s^{-1} [42]. The capital costs of mixer-settler units are estimated considering the costs of vessels and agitators, as suggested by Seider *et al.* [43]

2.5. Modelling of pulsed column units

A stagewise mass balance model is used for pulsed columns, as suggested by Steiner [44], because the distribution coefficients are not constant. Steady state conditions have been assumed. Hence, the mass balance for component i in the aqueous phase is given by

at the bottom, stage 1

$$(1 + \alpha_{aq}) (C_{2,aq}^i - C_{1,aq}^i) - \frac{N_{oc}}{N} (C_{1,aq}^i - C_{1,aq}^{i,eq}) + \sum R_{aq}^i \varphi_{aq} V = 0 \quad (12)$$

typical stage n

$$(1 + \alpha_{aq})(C_{n+1,aq}^i - C_{n,aq}^i) + \alpha_{aq}(C_{n-1,aq}^i - C_{n,aq}^i) - \frac{N_{oc}}{N}(C_{n,aq}^i - C_{n,aq}^{i,eq}) + \sum R_{aq}^i \varphi_{aq} V = 0 \quad (13)$$

at the top, stage N

$$C_{in,aq}^i + \alpha_{aq} C_{N-1,aq}^i - (1 + \alpha_{aq}) C_{N,aq}^i - \frac{N_{oc}}{N}(C_{N,aq}^i - C_{N,aq}^{i,eq}) + \sum R_{aq}^i \varphi_{aq} V = 0 \quad (14)$$

N_{oc} is the number of transfer units (which is affected by the column height, as $N_{oc} = k_L a H / v$), α is equal to $N / Pe - 0.5$, where Pe is the Peclet number calculated as $v \Delta H / E$, ΔH is the plate spacing, assumed equal to 5 cm (typical value [45, 46]), E is the axial dispersion coefficient. Hence, α represents the deviation from plug flow due to back-mixing. In each stage, perfect mixing is assumed. The mass balance for component i in the organic phase is calculated similarly [44].

Expressions for the calculation of mass transfer coefficients of U(VI), Pu(IV) and HNO₃, as well as hydrodynamics correlations, are taken from [45, 47]. The mass transfer coefficient for U(VI) during extraction (from dispersed aqueous phase to continuous organic phase) is calculated by the following correlation:

$$k_L = 2.8 \times 10^7 (1/Pe)^{1.8} + \frac{3.55 \times 1014}{m} (1/Pe)^{2.95} \quad (15)$$

In Eq. 15 the Peclet number is calculated as $v_t d_p / \mathcal{D}$ [47]. Similar expressions have been used for mass transfer of Pu(III), U(IV), Pu(IV) and HNO₃.

Conditions of insufficient pulsation and flooding are calculated as suggested by Berger and Walter [48]. Ranges for pulse frequency and amplitude are taken from Kumar and Hartland [46]. To estimate the operation cost, pumping cost and power requirement for pulse generations are considered [49]. Capital costs are calculated as suggested by Seider et al. for columns (considering vessels, plates and platforms) [43]. Costs of the top and bottom settlers are also included. The cost of other equipment and instrumentation needed, such as the

neutron absorber and the pulsator, has not been included due to the lack of information for confidentiality reasons.

3. Case study

220 A case study is now presented. The goal is to investigate the potential benefits and drawbacks that the small-scale contactor could bring to SNF reprocessing when compared against traditional liquid-liquid extraction equipment. The process investigated is an alternative flowsheet for the modern codecontamination section (described in Section 1) where the two scrubbing steps, typically
225 with the first step using a 1.5 M HNO_3 solution and the second step a 10 M HNO_3 solution, are merged in a single scrubbing step. The possibility of reducing the number of unit operations while achieving the minimum separation required, using a nitric acid solution of intermediate concentration in the single scrubbing step and varying equipment design and operating conditions, is investigated. The process flow diagram is shown in Figure 2. The aqueous stream
230 leaving the scrubbing step could be either recycled to the main extraction (step 1 in Figure 2), fed to the complementary extraction (step 3) or split between these two steps. The design variable χ , which can vary between 0 and 1, describes the fraction of aqueous stream recycled to step 1 and can be: $\chi\dot{V}_{aq}$ is fed
235 to step 1, $(1 - \chi)\dot{V}_{aq}$ to step 3. The organic stream from step 3 is entirely recycled to step 1, which is the standard approach in the modern PUREX processes [5]. In the commercial plants there are also unit operations to recover the small amount of TBP ended up in the aqueous phase. However, as the mass transfer of TBP is neglected in this work (very small solubility in nitric acid solution),
240 these unit operations are not included in this case study.

The aqueous stream leaving step 1 is categorised as HLW. These radioactive effluents typically undergo vitrification or solidification for final storage and, then, disposal. In the aqueous stream leaving step 3 the concentration of fissile materials is significantly lower compared to the aqueous stream leaving step 1.
245 Hence, the handling of the aqueous stream leaving step 3 is not more complex

than the typical handling and disposal of the one leaving step 1.

3.1. Optimisation framework

The goal is to optimise the process shown in Figure 2 minimising the total annualised cost (TAC), which includes operating expenditure ($OpEx$) and
250 annualised capital expenditure ($ACapEx$):

$$TAC = OpEx + ACapEx \quad (16)$$

A payout time of 5 years has been assumed (typical values between 5 and 10 years [50]) with a 5% interest rate. Free variables are all the design variables related to the geometry of the equipment. For the small-scale contactor, these variables are the length and width or diameter (for small extractors and distribution channels) of each level of the flow network and the number of stages
255 and elements within each level (integer variables). For mixer-settlers, the design variables are width, depth and length of mixers and settlers and the diameter of the impeller and number of stages. For pulsed columns, the design variables are column diameter and the number of perforated plates (integer variable),
260 which will determine the column height. Further free variables are the operating conditions: the flow rate of all inlet streams except the feed, both aqueous and organic, as well as nitric acid concentration of the aqueous stream entering step 2. Also, the impeller speed is a free variable in the mixer-settler model and the pulse frequency and amplitude are free variables in the pulsed column.
265 Constraints such as minimal requirements for recovery (Rec) of U and Pu, or decontamination factor (DF) of hazardous components such as Zr and Ru, are included in the optimisation problem. The recovery is defined as the amount of metal in the product stream divided by the amount of metal in the feed, whilst the decontamination factor is the ratio between the amount of a certain contaminant in the feed and in the product stream. All the inequality constraints
270 included in the optimisation problem are shown in Table 2.

The optimisation problem has been solved three times, one for each technology, to identify their potential advantages and disadvantages. Inputs of the

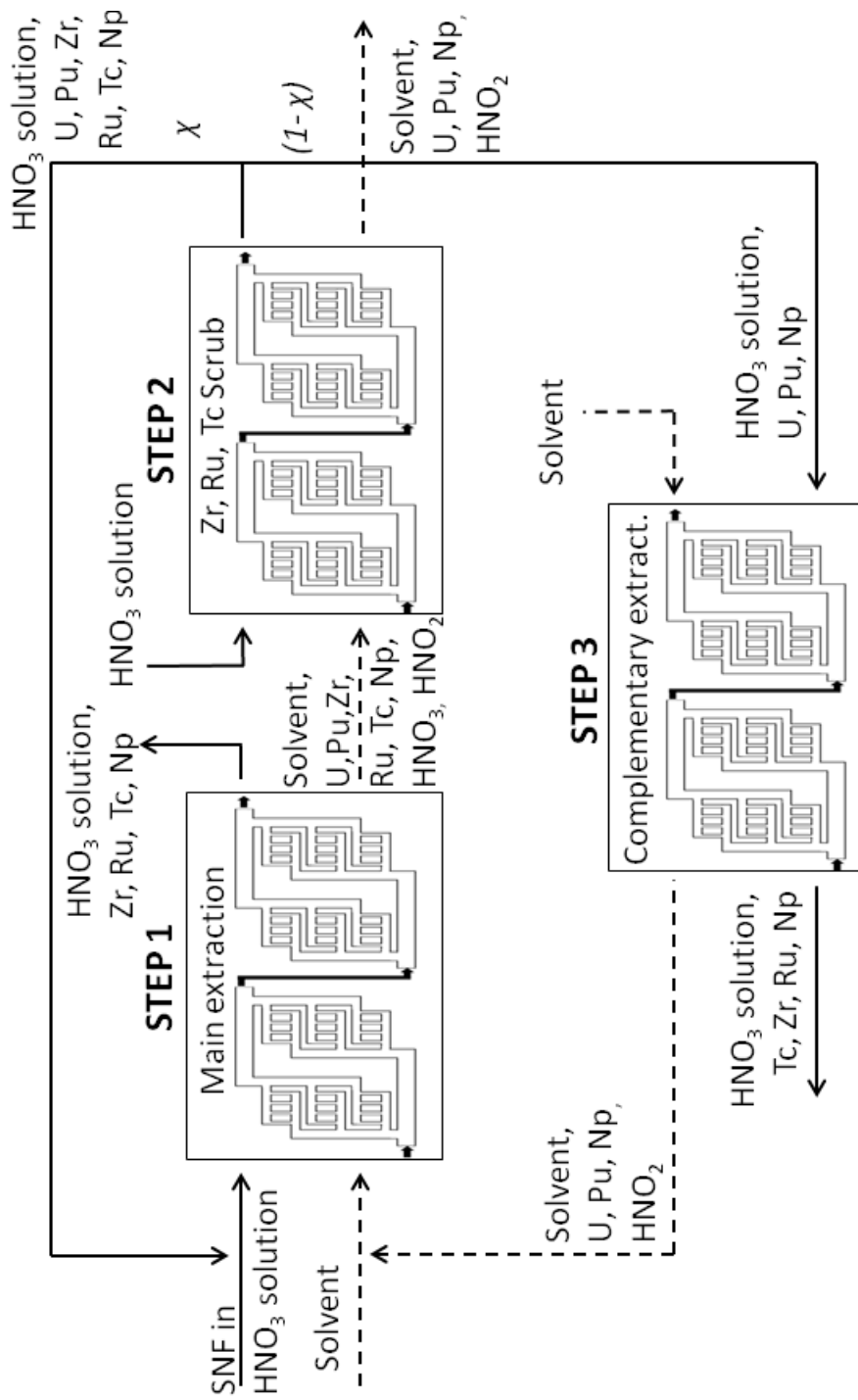


Figure 2: Schematic of the flowsheet investigated in this work. A sketch of the equipment needed for two generic stages and the manifold of one of the phases only is shown for simplicity. Continuous line refers to aqueous stream. Dotted line refers to organic stream. No aqueous recycle from step 2 to step 1 if $\chi = 0$, no step 3 and organic recycle to step 1 if $\chi = 1$. χ is defined as the ratio between the aqueous flow rate recycled from step 2 to step 1 and the overall aqueous flow rate leaving step 2. Feed concentration: U(VI) 250 g L⁻¹, Pu(IV) 3 g L⁻¹, Zr 1.18 g L⁻¹, Ru 0.77 g L⁻¹, Tc 0.27 g L⁻¹, Np(V) g L⁻¹ 0.15, [HNO₂]=0.001 M. Throughput: 500 t of heavy metal y⁻¹. Solvent: 30% TBP/odourless kerosene (v/v). Temperature: 25° C.

Table 2: Inequality constraints used.

Inequality constraints	Comment
$Rec_U \geq 0.99$	Minimum uranium recovery
$Rec_{Pu} \geq 0.99$	Minimum plutonium recovery
$[U]_{aq,out}^{Step1} \leq 1.68 \text{ M}$	Maximum typical uranium concentration in the HLW from step 1
$DF_{Zr} \geq 10^4$	Typical requirement [5]
$DF_{Ru} \geq 10^4$	Typical requirement [5]
$DF_{Tc} \geq 10$	Typical requirement [5]
$k_{eff} \leq 0.95$	Nuclear criticality safety

problem are throughput, feed concentration, temperature and materials. The
275 same feed concentration and rate, 500 t of heavy metals per year (MTHM y^{-1}),
have been used for all cases. This throughput is an average one for SNF from
Light Water Reactors (600 MTHM y^{-1} at THORP in Sellafield, 400 MTHM y^{-1}
at Mayak in Russia [51]). The feed concentration of the dissolved SNF in nitric
acid solution is the typical one from a Light Water Reactor.

280 The combination of the nonlinear models and the integer variables leads
to the optimisation problem which is described as a mixed integer nonlinear
programme. This problem is implemented and solved in GAMS [52]. The integer
variables are the number of stages in the models for intensified extraction in
small channels and mixer-settlers, whilst in pulsed columns the integer variable
285 represents the number of perforated plates. The optimisation problems defined
for each of the three configurations have been solved using the SBB (Simple
Branch and Bound) solver. The relative gap criterion (OPTCR) is 1%.

The optimisation model for the small-scale contactor is the largest, with
approximately 270 000 equations, because of the 50 grid points used to convert
290 the differential mass balance equation 7 to a set of algebraic equations. For
the pulsed column alternative, there are approximately 20 000 equations due

to the 50 theoretical stages, which must not be confused with the number of actual compartments (which vary with the height of the column and the number of plates). For the mixer-settler configuration, there are approximately 6 000 equations.

4. Results

The main results of the optimisation problems are shown in Table 3. These results allow a first comparison between the extraction technologies, which is the aim of this work. A general comparison of the most important chemical engineering attributes of all liquid-liquid extractors, including the centrifugal extractor, are shown in Figure 3. In the latter, ratings for conventional technologies are taken from Law [7], except the last four rows where the ratings are based on the results obtained in this work. The ratings for small channels have been estimated assuming proportionality between the typical values of the attribute for the traditional technologies (provided by Arm *et al.* [8]), its rating (provided by Law), the value of the attribute of small channels achieved in this work and its rating. If values for conventional technologies are not provided by Arm *et al.*, the values obtained in this work are used. Where the attribute cannot be directly measured, such as ease of scale-up or process flexibility, a first estimation is provided by the authors, referring to the ratings given by Law for the other equipment.

According to the models, the pulsed column height in the main extraction is significantly shorter than the typical value (12 m [8]), due to the operating conditions achieved by the optimisation problem. As a result of this design, the pulsed column is the most cost effective technology.

The optimal process design using intensified extraction in small channels is shown in Tables 4–6, whereas the designs of conventional technologies are illustrated in Tables 7–9. The small contactor is the only one which makes use of the complementary extraction, step 3. The flow diagrams achieved by the optimisations are further discussed in section 4.1. Based on the process

designs, the most important criteria (*i.e.* economics, size, safety, mass transfer, Np control) and further considerations are discussed in sections 4.2–4.7.

4.1. Optimal flowsheet

Using the conventional technologies, the optimal flowsheet does not include
325 step 3, *i.e.* $\chi = 1$. This choice reduces the total annualised cost for the conven-
tional technologies. With the small scale technology, the optimal value of χ is
0.69, therefore 31% of the aqueous stream leaving step 2 undergoes treatment
in step 3. There is an approximately 3% difference between the case with $\chi = 1$
and the optimal solution, *i.e.* $\chi=0.69$. When χ is 1 and step 3 is not included,
330 the first step involves 5 stages and the second step 3 stages, whilst the optimal
solution ($\chi=0.69$) involves 4 stages in steps 1 and 2 but 1 stage in step 3, as
shown in Table 6. Therefore, there is the same total number of stages in both
cases for the first two steps, plus a small unit for step 3 (single stage) in the
optimal flowsheet, similar overall cost and operating conditions and similar de-
335 signs. The optimal solution ($\chi=0.69$) involves slightly lower overall capital cost,
mainly manifold cost, as a result of the 30% more cost effective manifold for
step 1 (one stage less than the case with $\chi=1$). These differences in the total
annualised cost and process design show the benefits of the modular nature and
hence the flexibility of the small-scale technology.

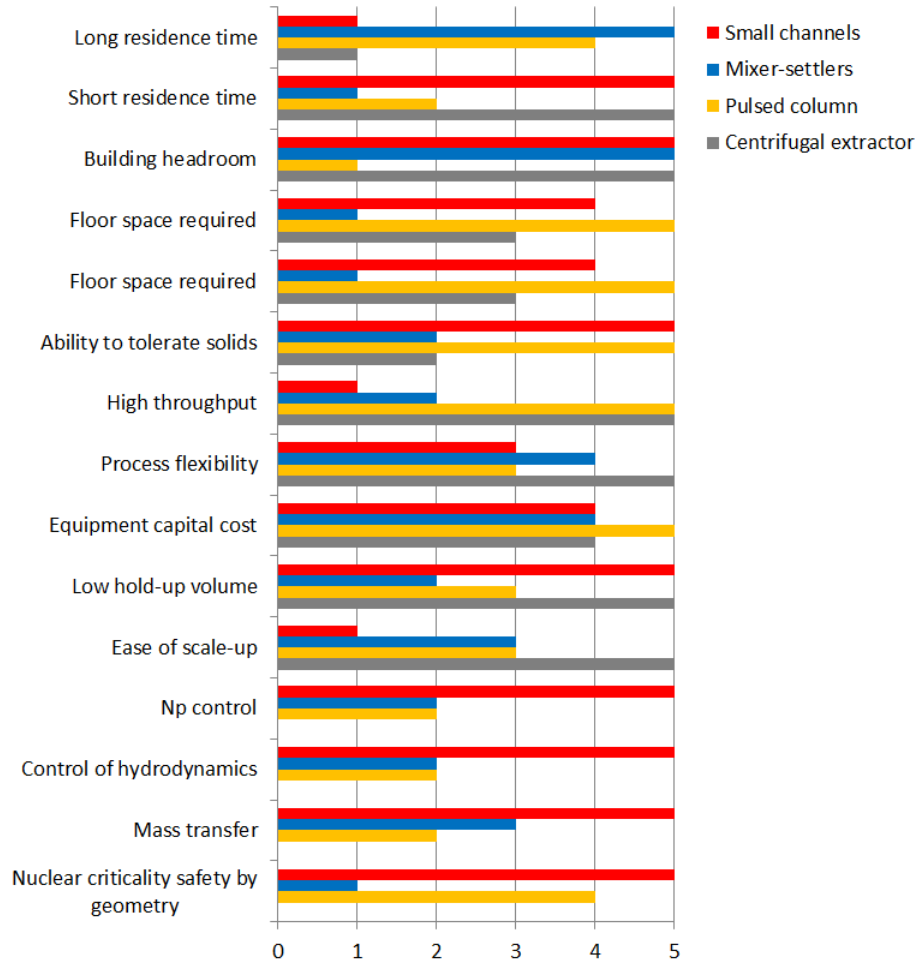


Figure 3: General comparison of small channels, mixer-settler, pulsed columns and centrifugal extractors. Ratings: 5 = superior, 4 = good, 3 = average, 2 = below average, 1 = poor. The ratings for the conventional technologies (except the last four rows) are taken from Law [7]. Process flexibility includes factors such as aqueous to organic flow ratio and turndown in flowrate. The long residence time is considered an advantage when it is required by the process kinetics, the short residence time is considered an advantage to limit the solvent degradation [7]. Ratings for Np control, control of hydrodynamics, mass transfer and nuclear criticality safety are not reported for centrifugal extractors, as they have not been investigated or provided by Law [7].

Table 3: Comparison of small channels, pulsed columns and mixer-settlers. The total residence time is referred to the two-phase flow in the whole process.

Criteria	Small channels	Mixer-settler	Pulsed column
Total annualised cost [$\text{£y}^{-1} \times 10^3$]	39	58	27
Recycle ratio χ	0.69	1.00	1.00
Total solvent flow rate [L h^{-1}]	645	617	940
Total liquid volume [L]	82	350	239
Total residence time [min]	0.8	18.4	6.3
Np decontamination factor	29.9	3.4	1.7
Zr decontamination factor	1.0×10^4	1.0×10^4	1.3×10^4
Ru decontamination factor	1.1×10^6	3.6×10^7	9.0×10^9
Tc decontamination factor	10.0	10.0	10.0
U recovery (%)	99.2	99.9	99.6
Pu recovery (%)	99.0	99.0	99.0
Average k_{La} [s^{-1}]	0.35	0.19	0.11
Criticality safety: k_{eff}	0.3	0.7	0.6

340 *4.2. Economics*

Pulsed columns were expected to be the least expensive conventional equipment [7]. The low cost of pulsed columns achieved in this work is due to the short height achieved, significantly shorter than the typical height reported in the literature for SNF reprocessing [8]. This is the result of the dilution of
345 the feed with the aqueous stream leaving step 2 and the increased solvent flow rate (see Table 3), which improves extraction at the expense of a high usage of solvent and the related costs. These operating conditions lead to height and volume lower than expected. As the costs of some equipment has not been included in the calculation, the overall cost of pulsed columns may be significantly
350 underestimated.

The operating cost of small channel contactors, the pumping cost, is negligible if compared to the annualised capital cost. The proper design of the manifolds reduces the pressure drop along distributors and collectors, minimising the pumping power required. In all steps, approximately 94% of the overall
355 pressure drop in the small scale technology occurs in the mixing junction at the entry of the small extractor (1st level of the manifold), where the two phases join. This result confirms the very small pressure drop achieved with laminar flow in the distributors and collectors. Compared to the operating costs required by conventional technologies, the resulting operating cost for small channels is
360 one order of magnitude lower.

4.3. Size

The size of equipment has a direct impact on safety as the amount of hazardous liquids present depends on the equipment volume. Furthermore, for equal flow rates, smaller sizes lead to shorter residence times. The residence
365 time affects the solvent degradation and hence the solvent regeneration and makeup costs. The optimal design achieved with small channels involves the lowest total liquid volume among all the alternatives considered, about one third of the one required by the pulsed column.

Compared with the volume of mixer-settlers typically used in the nuclear
370 industry [5], a lower volume was expected. Mixer-settlers are used mostly in
second cycles of liquid-liquid extractions where, together with small amount of
contaminants, only either uranium or plutonium are present. Hence, there is
no risk of nuclear criticality and large mixer-settler banks can be used. Also,
a large number of stages is used to achieve high purities. Furthermore, high
375 purities of U and Pu are not required in this flowsheet, hence a lower number
of stages is reasonable.

Generally, as shown in Figure 3, pulsed columns require a large amount of
head space and mixer-settlers require large floor space. These requirements
could be significantly reduced by using small channels.

380 The size of the extraction step using small-scale technology may be further
decreased if higher TBP concentrations in the organic solvent were used. A high
TBP concentration would improve extraction and reduce organic phase. The
opposite trend is expected for back extraction: the aqueous flow rates required
for scrubbing operations would increase, as a result of the higher affinity between
385 organic phase and solute. Therefore, a trade off for the TBP concentration must
be found. The current TBP volume fraction in the organic solvent, which is 30%,
is the typical one used in the nuclear industry to reduce density and viscosity
of the organic phase. In small channels, contrary to conventional technologies,
the separation does not rely on gravitational forces. Thus, the volume fraction
390 in the organic solvent of TBP, which is as dense as water, could be potentially
increased to 100% with no separation issues. Higher TBP fractions could be
investigated with small channels.

4.4. Safety

In terms of nuclear criticality safety, the results confirm that the small scale
395 technology is safer than mixer-settlers and pulsed columns by geometry. There-
fore, the use of small channels in the highly active section, in place of pulsed
columns, can be a viable option for future SNF reprocessing. The low effective
multiplication factor k_{eff} is due to the high surface area to volume ratio and

the small liquid holdup in each small channel. The value of k_{eff} in small chan-
nels, which is 0.3, refers to the highest value achieved in the largest distributor.
400 However, in pulsed columns, a neutron absorber can be used to reduce the risk
of criticality. Mixer-settlers may be employed for low liquid holdup or diluted
solutions, but more detailed investigations on nuclear criticality are required
since only approximated calculations have been done and the method used does
405 not take into account fission products and minor actinides.

4.5. Mass transfer and hydrodynamics

The volumetric mass transfer coefficient k_La achieved in small channels is
three times greater than the one in the pulsed column and almost two times the
one in mixer-settlers (see Table 3). This is not surprising, since the high mass
410 (similarly heat) transfer coefficients is one of the main advantages of the small-
scale processes. The k_La in the pulsed column, the only technology currently
used when highly active material is involved, is the smallest between the three
technologies, hence the application of small channels in that section would be
of particular interest from an industrial point of view. Values of k_La achieved
415 for the conventional technologies are of the same order of magnitude as those
reported in the literature.

The hydrodynamics in small channels are easier to control and predict. A
common flow pattern is plug or slug flow, which is relatively regular and the
sizes of the plugs and slugs can be predicted reasonably well in the laminar flow
420 conditions prevailing in the small channels [53]; predictions in good agreement
with the experimental data have been developed [54]. Conversely, the turbu-
lent two-phase flow in mixer-settlers and pulsed columns produces a dispersed
droplet size distribution which may be affected by changes in geometry or oper-
ating conditions and, also, challenging to accurately predict because of droplet
425 breakage and coalescence.

4.6. Np control

The control and separation of neptunium is improved using small channels
because the residence times are short; this is a result of the efficient mass trans-

fer. The short residence time is not sufficient to allow high conversion of Np(V),
430 unextractable, to Np(VI), easily extractable. Formation of Np(IV), with these
nitric acid concentrations, is negligible as expected [55]. The decontamination
factor of Np, *i.e.* the ratio between the amount of Np in the feed and the one
in the product stream (the organic stream outgoing step 2) is around 30, which
means that over 95% is removed with the high level wastes. Using conventional
435 technologies, the decontamination factor for Np is between 1.7 (pulsed columns)
and 3.4 (mixer-settlers), *i.e.* Np removal respectively of 40% and 70%. The pres-
ence of Np complicates the next cycles of the PUREX process (not investigated
in this case study), which could hence benefit from the employment of small
channels.

440 4.7. Other results

One of the most important advantages of the small-scale technology is the
low solvent degradation due to the short residence time of the two-phase flow
in the contactor, approximately 5 seconds for each stage of each step. Con-
sequently, the need of solvent makeup and the solvent regeneration costs are
445 reduced. Solvent regeneration requires expensive evaporation and rectification
operations [5].

Criticality, process volumes, costs, solvent exposure and the other aspects
discussed above are not the only factors to consider for the application of liquid-
liquid extraction equipment in the nuclear industry. Process flexibility could
450 benefit from using small channels: turndown in flow rate and change in the
aqueous to organic flow ratio could be achieved by decreasing the number of
parallel channels although the consequent possibility of flow maldistribution
along the channels (*i.e.* non-uniform flow distribution in the channels) would
need to be considered [56]. Small channels could be used in any section of the
455 process, being safe from nuclear criticality by geometry.

To increase throughput, scale up of the small scale contactors by increasing
the sizes of the channels can be considered. Above a certain size, however, the
mass transfer coefficient could decrease and the resulting extraction will be less

efficient. Scale-out, or numbering-up, is the use of more channels in parallel to
460 achieve higher throughput. In scale-out, channel sizes are not modified. How-
ever, scale-out is limited by the design of the manifold: a very large and not
practical number of channels may be required and high throughput could be dif-
ficult to achieve. Using small channels, scale-up and scale-out must be combined
to increase throughput and ensure high separation performance. The maximum
465 processing capacity depends on the type of manifold used. With the 4-level
comb-like network used here and throughput of 500 tons of heavy metals per
year, the largest step involves about 4650 parallel channels. Assuming a linear
relationship between feed and number of channels needed, which is reasonable
for this technology, with an increase of the feed by 100%, approximately 10 000
470 channels may be required. However, these numbers of channels regard only the
first section of the PUREX process, which is the one investigated here. The
following process sections may require unpractically large numbers of channels.
Hence, to properly identify the maximum throughput using small channels, the
entire process should be investigated.

475 Contrary to technologies with moving parts, such as mixer-settlers and cen-
trifugal extractors, small channels could tolerate solids. With diameters of the
channels in the order of millimetres, the risk of occlusion is minimised.

Table 4: Optimal design of flow network for intensified extraction in small channels. Steps: 1 = main extraction, 2 = scrubbing, 3 = complementary extraction.

Step	Phase	Scale	No. elements	Length [cm]	Diameter/ Width [cm]
1	aq.,org.	1	47	10.0	0.2
1	aq.	2	11	27.6	0.7
1	aq.	3	9	19.6	1.1
1	aq.	4	1	26.9	6.1
1	org.	2	11	27.6	0.8
1	org.	3	9	23.2	1.5
1	org.	4	1	35.1	4.1
2	aq.,org.	1	40	10.0	0.2
2	aq.	2	11	23.4	0.6
2	aq.	3	9	17.8	1.0
2	aq.	4	1	23.0	4.0
2	org.	2	11	23.4	0.7
2	org.	3	9	20.7	1.4
2	org.	4	1	33.9	4.1
3	aq.,org.	1	45	10.0	0.2
3	aq.	2	8	26.4	0.6
3	aq.	3	3	13.3	1.0
3	aq.	4	1	5.7	1.4
3	org.	2	8	26.4	0.7
3	org.	3	3	15.4	1.3
3	org.	4	1	7.9	1.9

Table 5: Optimal design of phase separator for intensified extraction in small channels. Steps: 1 = main extraction, 2 = scrubbing, 3 = complementary extraction.

Step	Stream	Length [cm]	Diameter [cm]	Material
1	Mainstream	2.9	0.2	PTFE
1	Sidestream	1.0	0.1	Stainless steel
2	Mainstream	2.6	0.2	PTFE
2	Sidestream	1.0	0.1	Stainless steel
3	Mainstream	2.8	0.2	PTFE
3	Sidestream	1.0	0.1	Stainless steel

Table 6: Optimal design of liquid-liquid extraction using small channels. Steps: 1 = main extraction, 2 = scrubbing, 3 = complementary extraction.

Variable	Step 1	Step 2	Step 3
No. stages	4	4	1
Aq. to org. flow ratio	0.63	0.42	0.51
[HNO₃] aqueous scrubbing stream [M]	N.A.	4.7	N.A.

Table 7: Optimal geometry of mixer-settlers. Steps: 1 = main extraction, 2 = scrubbing.

Step	Unit	Width [m]	Length [m]	Height [m]	Impeller diameter [m]
1	Mixer	0.23	0.23	0.23	0.15
1	Settler	0.23	0.90	0.23	N.A.
2	Mixer	0.20	0.20	0.20	0.13
2	Settler	0.20	0.80	0.20	N.A.

Table 8: Optimal design of liquid-liquid extraction using mixer-settlers. Steps: 1 = main extraction, 2 = scrubbing.

Variable	Step 1	Step 2
No. stages	4	3
Aq. to org. flow ratio	0.78	0.42
[HNO₃] aqueous scrubbing stream [M]	N.A.	5.2
Impeller speed [rpm]	200	200

Table 9: Optimal design of liquid-liquid extraction using perforated plate pulsed column. Steps: 1 = main extraction, 2 = scrubbing. Plate spacing = 0.05 m, plate free area = 23%, hole diameter 0.003 m. Minimum flooding: 70%.

Variable	Step 1	Step 2
Height [m]	0.47	3.17
Diameter [m]	0.23	0.20
No. plates	9	61
Aq. to org. flow ratio	0.41	0.22
[HNO₃] aqueous scrubbing stream [M]	N.A.	4.5
Pulse frequency [s⁻¹]	0.67	0.55
Pulse amplitude [m]	1.77×10^{-2}	0.89×10^{-2}

5. Conclusions

A case study in spent nuclear fuel reprocessing has been presented to compare intensified extraction in small channels to conventional technologies, *i.e.* mixer-settlers and pulsed columns. To investigate the behaviour of the small-scale technology, models developed in a previous work have been used [26]. Mathematical models developed in the literature for specific aspects of the process (mass balance, thermodynamics, hydrodynamics, mass transfer coefficients, pressure drops, economics, nuclear criticality) have been used for pulsed columns and mixer-settlers. These models have been combined into a single process model allowing for the design of alternative configurations. The validation of the models have not been carried out, hence the feasibility of the design must be further investigated. The aim of the study is to explore potential designs, in order to capture the theoretical benefits and drawbacks that each technology may provide. Experimental investigations, in particular to gain a better understanding of the small scale technology, will be the subject of future works.

A multi-component liquid-liquid extraction has been investigated with U, Pu, HNO₃, Zr, Ru, Tc, Np, and HNO₂ solutes. Redox reactions between the three different oxidation states of Np have been considered.

It was found that pulsed column may be the most cost effective technology, at the expense of large solvent flow rate, the largest among all technologies. This low cost is due to the large dilution of the feed with the aqueous stream recycled from step 2, which leads to reduced column height. However, the cost of some equipment, such as the pulsator, has not been included in the calculations, due to lack of information. The small channels can be less expensive than mixer-settler banks. However, the choices of materials and the design of manifolds are crucial. An important saving may be related to the significantly shorter residence time, which can decrease the solvent degradation and thus the solvent regeneration and cleanup costs. Another important consequence of the short residence time is Np separation: over 95% can be removed with small channels while only 40% is removed with pulsed columns.

Small channels are safe in terms of criticality due to their geometry, resulting in small volume and a high surface area to volume ratio. Hence, their employment in the highly active section of the process, as an alternative to pulsed columns, should be considered more extensively. Small channels can lead to smaller volume required, easier control of N_p and exhibit more efficient mass transfer.

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Nomenclature

<i>Symbols</i>	<i>Description</i>	<i>Units</i>
a	Interfacial area	$\text{m}^2 \text{m}^{-3}$
C	Concentration	mol m^{-3}
$ACapEx$	annualised capital expenditure	£ y^{-1}
d_{32}	Sauter diameter	m
d_p	Drop diameter	m
DF	Decontamination factor	m
\mathcal{D}	Diffusion coefficient	$\text{m}^2 \text{s}^{-1}$
ΔH	Plate spacing	m
E	Extraction (unless differently stated)	
L	Length	m
k_{eff}	Effective multiplication factor	
k_L	Mass transfer coefficient	m s^{-1}
m	Distribution coefficient	
N	number of stage	
N_{oc}	number of transfer units	
$OpEx$	Operating expenditure	£ y^{-1}

Pe	Peclet number	
	Reaction rate	$\text{mol L}^{-1} \text{s}^{-1}$
Sh	Sherwood number	
T	Temperature	K
t	time	s
TAC	Total annaulised cost	£y^{-1}
v	Superficial velocity	m s^{-1}
v_t	Drop velocity for rising drop or falling drop	m s^{-1}
V	Volume	m^3
\dot{V}	Volume flowrate	$\text{m}^3 \text{s}^{-1}$

Greek Symbols

φ	Phase holdup
χ	Recycle ratio of aqueous stream leaving step
	2

Subscripts and superscripts

aq	Aqueous phase
eq	Equilibrium
k	Generic phase
i	Generic component
in	Inlet
mix	Mixer
n	Generic n^{th} stages
N	Final N^{th} stage
set	Settler

Acronyms

HLW	High Level Waste
PUREX	Plutonium Uranium Extraction
SNF	Spent Nuclear Fuel
TBP	Tributyl Phosphate

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