Mathematical modelling of intensified extraction for spent nuclear fuel reprocessing

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ABSTRACT

Small scale extractors seem to be a promising intensified alternative to the conventional solvent extraction technologies, because of the well described hydrodynamics, enhanced mass transfer, and good phase separation at the end. One of the most interesting applications of intensified extractions is the reprocessing of spent nuclear fuel. Operating in small channels can reduce the volumes of involved hazardous materials and the residence times, thus minimising the degradation of the solvent and its regeneration cost. Finally, nuclear criticality safety may be easily achieved.

In this paper, the application of small channels on spent nuclear fuel reprocessing has been investigated. A mathematical model of a multi-component liquid-liquid extraction has been developed. The multi-component system consists of U, Pu, HNO_3, HNO_2, Zr, Ru, Tc, Np(IV), Np(V) and Np(VI), the organic solvent is a mixture of 30% (v/v) Tri-Butyl Phosphate (TBP) and a paraffinic diluent. A segmented flow pattern, with the aqueous phase dispersed in a continuous organic phase, has been assumed. Calculations for the estimation of mass transfer, redox reactions, pressure drop, nuclear criticality and TBP hydrolysis have been included in the model. To increase the flow rates, the number of small channels was increased (scale out) and a comb-like manifold was considered to ensure good flow distribution in each channel. The problem is formulated as a mixed integer nonlinear programming problem and is implemented in the General Algebraic Modeling System (GAMS).
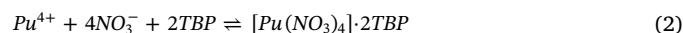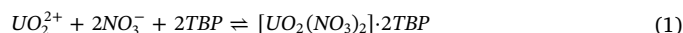
The results show that this alternative technology for liquid-liquid extraction offers advantages, especially in terms of solvent degradation and low holdup volume.

1. Introduction

Nuclear power is a low-carbon energy source which, due to the increasing concerns about global warming, continues to be an option for electricity generation. A major concern is the management of Spent Nuclear Fuel (SNF), which can remain toxic for hundreds of years. SNF consists of, approximately, 96% uranium and 1% plutonium, that can be reused (Todd, 2008). SNF reprocessing is beneficial to reduce volume and long-term radiotoxicity of high-level waste (IAEA, 2008).

Several studies on spent nuclear fuel have been done. Issues of concern include design of improved disposal concepts (Ahlstrm, 1997; Kim et al., 2014; Lee et al., 2012, transportation Jiang and Wang, 2016), alternative uses or technologies (Mohamed, 2014; Kim et al., 2013).

SNF, previously dissolved in a nitric acid solution, is extracted by TriButyl Phosphate (TBP) in the PUREX (Plutonium URanium EXtraction) process. Uranium and Plutonium are present, respectively, as U(VI) (in the form of UO_2^{2+}) and Pu(IV) (in the form of Pu^{4+}). These two components are extracted according to the following reactions:

$$UO_2^{2+} + 2NO_3^- + 2TBP \rightleftharpoons [UO_2(NO_3)_2] \cdot 2TBP \qquad (1)$$

$$Pu^{4+} + 4NO_3^- + 2TBP \rightleftharpoons [Pu(NO_3)_4] \cdot 2TBP \qquad (2)$$

The reactions may be carried out in pulsed columns, mixer-settlers or centrifugal extractors. These technologies, however, have drawbacks including the need for large amounts of head space for pulsed columns, large floor space and poor geometry for criticality control for mixer-settlers. Also, long solvent residence times are necessary, leading to solvent degradation. Centrifugal contactors are the most promising as a result of the short residence time and low holdup volume. However, their use is limited in industry since they are the least reliable of the three technologies, because of their poor tolerance to solids and need of periodic replacement of the motor and the rotor (Law and Todd, 2008).

Volume and solvent residence times may be significantly reduced if small scale extractors are used instead of columns and mixer settlers. The large surface area to volume ratio of small scale extractors can also address criticality issues. There are no moving parts and their diameter may be large enough to avoid occlusion; therefore, they can sufficiently

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Nomenclature

a	interfacial area ($m^2 m^{-3}$)
$ACapEx$	annual capital expenditure ($£y^{-1}$)
B^2	buckling (cm^{-2})
C	concentration ($mol\, m^{-3}$)
Ca	capillarity number ($\frac{\nu\mu}{\gamma}$)
$CapEx$	capital expenditure ($£$)
D	diameter/distribution coefficient m
DF	decontamination factor (m)
$\mathscr{D}$	diffusion coefficient ($m^2 s^{-1}$)
ΔP	pressure drop (kPa)
E	extraction
F	TBP volume fraction
F_d	flow maldistribution
g	Gravitational acceleration (9.81) ($m\, s^{-2}$)
L	length (m)
k	multiplication factor
K_L	mass transfer coefficient ($m\, s^{-1}$)
K	pseudo-equilibrium constant
M^2	migration area (cm^2)
N	number of stages
P	power (W)
Pe	Peclet number ($\frac{\nu L}{\mathscr{D}}$)
$OpEx$	Operating expenditure ($£\, y^{-1}$)
r	radius (m)
R	hydraulic resistance/reaction rate (kPa m^{-3}) ($mol\, L^{-1} s^{-1}$)
Re	Reynolds number ($\frac{\rho\nu D}{\mu}$)
ν	superficial velocity ($m\, s^{-1}$)
$\dot{V}$	volume flowrate ($m^3\, s^{-1}$)

Greek symbols

α	ratio between disperse plug length and unit cell
γ	Interfacial tension ($N\, m^{-1}$)
λ_{NC}	non-circular coefficient
μ	viscosity (Pa s)
ρ	mass density ($kg\, m^{-3}$)
θ	contact angle/correction factor for interfacial area ($^\circ$)
τ	temperature dependent function for distribution coefficient calculation
φ	phase holdup
ζ	resistant coefficient

Subscripts and superscripts

aq	aqueous phase
c	continuous phase
ch	channel
d	dispersed phase
eff	effective
eq	equilibrium
fr	frictional
H	hydraulic
i	generic index
in	inlet
int	interfacial
mix	mixture
or	organic phase
out	outlet
tot	total
UC	unit cell
∞	infinite

Acronyms

GAMS	general algebraic modeling system
PTFE	polytetrafluoroethylene
PUREX	plutonium uranium extraction
TBP	tributyl phosphate

tolerate solids unlike centrifugal contactors. Furthermore, mass transfer as well as mixing are significantly enhanced in small channels (Tsaoulidis and Angeli, 2015). The strategy of reducing the plant size without affecting the performance (which in this case may be even improved) is known as "process intensification" (Becht et al., 2009; Ramshaw, 1983; Cross and Ramshaw, 1986; Tsouris and Porcelli, 2003; Stankiewicz and Moulijn, 2000; Van Gerven and Stankiewicz, 2009).

Although many flow patterns can be achieved with biphasic flow in small scale contactors (Tsaoulidis et al., 2013), in this work segmented flow has been considered, which enhances two-phase mixing (Dore et al., 2012). In addition, in segmented flow, where one phase forms elongated drops (plugs) separated by continuous phase slugs, the hydrodynamics may be more easily controlled to improve mass transfer (Kashid and Agar, 2007; Tsaoulidis et al., 2013; Tsaoulidis et al., 2013; Tsaoulidis and Angeli, 2015). Hydrodynamics play a key role in these systems and, with an appropriate design, it is possible to:

- increase interfacial area;
- design phase separation at the end of the extractor; and,
- reduce pressure drop and, therefore, design more energetically efficient systems (Tsaoulidis et al., 2013).

Important plug flow characteristics, such as plug size and film thickness, have been investigated and several empirical correlations for predicting these parameters have been proposed (Leclerc et al., 2010; Xu et al., 2013). Models to predict pressure drop have been suggested as well (Kashid and Agar, 2007). Mass transfer in small channels has been

investigated by several authors and equations to predict mass transfer coefficients for two-phase flows have been suggested (Kashid et al., 2010; Vandu et al., 2005).

There are only a few works on nuclear applications of liquid-liquid extraction in small channels (Tsaoulidis et al., 2013; Tsaoulidis et al., 2013; Tsaoulidis et al., 2013; Tsaoulidis and Angeli, 2015). Specifically, Tsaoulidis et al. (2013) and Tsaoulidis and Angeli (2015) studied the extraction of U(VI) in small channels from nitric acid solutions into a 30% v/v TBP and ionic liquid mixture, which is a potential alternative to the current organic diluent. They also developed a CFD model for the extraction of dioxouranium(IV) in segmented flow: in the 2-D axisymmetric model, the behaviour of a unit cell, i.e. one dispersed plug and one continuous slug, was investigated (Tsaoulidis and Angeli, 2015). Results predicted by the model were in good agreement with the experimental data.

In this paper, a model for the design of SNF reprocessing flowsheet using small channel extractors is presented. Extraction of uranium(VI), plutonium(IV), zirconium, technicium, ruthenium, neptunium, nitric and nitrous acid from a nitric acid solution into a 30% v/v TBP/paraffinic diluent mixture is predicted. Distribution coefficients, mass transfer coefficients and pressure drop are estimated as suggested by the literature (Richardson and Swanson, 1975; Groenier, 1972; Asakura et al., 2005; Hongyan et al., 2017; Kumar and Koganti, 2001; Natarajan et al., 2012; Kashid and Agar, 2007; Kashid et al., 2010). Redox reactions between the three oxidation states of Np in nitric acid solutions have been included in agreement with the literature (Birkett et al., 2007; Hongyan et al., 2017; Tachimori, 1994). The design of the phase