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Dimitrios A. Tsaoulidis

# Studies of Intensified Small-scale Processes for Liquid–Liquid Separations in Spent Nuclear Fuel Reprocessing

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*This Thesis is dedicated to my family.*

*My parents*

*Alexandros Tsaoulidis and Panagiota  
Papadopoulou*

*and my sister*

*Alexia Tsaoulidou*

*For their endless & unconditional love,  
sacrifices, and encouragement throughout  
my life.*

# Supervisor's Foreword

The current thesis presents studies on the development of small-scale processes for ionic liquid-based extractions for the intensification of the liquid–liquid separations in the spent nuclear fuel reprocessing cycle. This is a novel case of liquid–liquid small-scale flow with great potential for intensifying reprocessing operations.

Liquid–liquid systems find applications in many areas of engineering, physics and chemistry, such as liquid–liquid extractions, phase transfer catalysis, nano-particle synthesis, coating flows and interfacial measurements. The efficiency and stability of the separation depends on the fluid flow field, the thermodynamic equilibria and the mass transfer between phases. Although experimental studies on liquid–liquid flows exist in the literature, both the use of ionic liquids and the nuclear application make this research particularly novel and timely.

The thesis is divided into eight chapters. After a short introduction to the subject of the research, an extensive literature review follows covering many aspects of multiphase flows in small channels such as flow regimes, pressure drop and mass transfer characteristics as well as the important features of ionic liquids and their applications in the spent nuclear fuel reprocessing. The review offers general information on the state of the art in these flows and highlights the need for experimental studies on liquid–liquid systems involving ionic liquids because of their appealing properties for extraction. The experimental setup, methods and procedures, as well as the parameters defining the problem considered in each chapter, are described in detail. Bright-field imaging is used to map the flow regimes that can exist in ionic liquid–aqueous systems as a function of channel material and dimensions, as well as flow rates.  $\mu$ -PIV (micro-Particle Image Velocimetry) is applied to characterise the flow patterns inside the two phases. The findings in hydrodynamics are complemented by pressure drop, mass transfer, and extraction measurements involving dioxouranium(VI). Errors associated with the measurements have been carefully considered and quantified. The advanced optical techniques on two-phase flows developed in this work also contributed in hydrodynamic studies in polymer electrolyte membrane water electrolysers and fuel cells.

In the following chapters the work on the hydrodynamics, pressure drop and mass transfer in the two-phase liquid–liquid system is described. Firstly, the various flow regimes and pressure drop of the ionic liquid–aqueous two phase flows in small channels of various sizes are reported followed by a study of the plug flow characteristics, which is the main flow regime considered in the study. Plug flows are further characterised using  $\mu$ -PIV and the circulation patterns and mixing efficiencies within the two phases for different conditions are measured. Mass transfer experiments involving extraction of dioxouranium(VI) from nitric acid solutions into ionic liquid/TBP (30 % v/v) mixtures are performed and the results are discussed in conjunction with the flow characteristics. The scaling aspects of the small-scale intensified extractors for industrial applications are also discussed, and the findings are compared with extraction units already in operation in spent nuclear reprocessing plants. In the final part of the study, a 2D numerical model is developed which takes into account the hydrodynamic properties of the flow and predicts reasonably well extraction performance, while most empirical models available in the literature failed to do so. In the last chapter the conclusion on the overall work is summarised and suggestions for future work are proposed.

Finally, the hydrodynamic and the extraction results, as well as the numerical studies in this work will be used as a basis for the development of intensified processes using liquid impinging jets for high efficiency extractions in a multi-discipline programme that supports a future nuclear fuel cycle.

London, UK  
February 2015

Prof. Panagiota Angeli



# Abstract

The main contribution of the thesis is to study and develop small-scale processes for ionic liquid-based extractions that can intensify the liquid-liquid separations in the spent nuclear fuel reprocessing cycle. The industrial application of small-scale processes requires that their hydrodynamics and mass transfer behaviour are well characterised and predicted. In addition, modelling methodologies are proposed to evaluate the applicability of the small-scale extractors in reprocessing the large volumes of nuclear waste used in industrial scale.

The first part of the work involves the study of the hydrodynamic behaviour of two-phase (ionic liquid-aqueous) flows. Flow pattern formations within channels have been identified for a wide range of operating conditions and were found to be strongly affected by channel size and material, fluid properties and flow rates. The main patterns observed were plug flow, annular flow and drop flow. Subsequently, the work focused on the investigation of the plug flow which has been found to enhance mass transfer because of circulation patterns that develop within the phases. Plug flow was thoroughly investigated in various channel sizes of different materials mainly for TBP/ionic liquid (30 % v/v) mixtures-nitric acid solutions, relevant to spent nuclear fuel reprocessing. Several hydrodynamic characteristics, such as plug length, plug velocity, film thickness and pressure drop have been investigated for different ionic liquids, channel sizes and phase flow rates. Results have been compared with the literature, and new (or modified) correlations have been proposed for estimating the plug length, film thickness and pressure drop. Furthermore, circulation patterns and mixing characteristics within aqueous plugs were investigated by means of  $\mu$ -PIV (micro-Particle Image Velocimetry). The mixing within a plug was locally quantified by the non-dimensional circulation time and the results were correlated with the mass transfer performance. Mixing within the plug was found to be affected by several parameters, but the most decisive one was the size of the channel; mixing was enhanced by decreasing the channel diameter. The last stage of the experimental part of this research involves studies of the extraction of dioxouranium(VI) ions from nitric acid solutions into TBP/IL mixtures (30 %, v/v), relevant to spent nuclear fuel reprocessing in channels with sizes ranging from 0.5 to 2 mm ID. The effects of ionic liquid type, initial

nitric acid concentration and residence time on the extraction performance of the contactor were studied. Experimental mass transfer coefficients were compared against predictive models derived from the literature and good agreement was found with those for liquid–liquid contactors. Experimental results were also compared with extraction units already in operation in spent nuclear reprocessing plants. It was found that comparable amount of spent nuclear fuel (1045 tonnes per year) can be reprocessed and extraction of dioxouranium(VI) >99 % can be achieved in 4 stages (cycles) with approximately 400 assemblies (one assembly consists of 6 channels of 2 mm internal diameter and 285 cm length). Finally, a numerical finite element model for the hydrodynamics and mass transfer was developed, and the results were compared with the experimental findings. The model used experimental data for the geometric characteristics of the plug flow and predicted reasonably well the experimentally measured extraction efficiencies (with a 11.3 % mean relative error).

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# Nomenclature

A	Cross sectional area ( $\text{m}^2$ )
Bo	Bond number = $\frac{ID^2 \Delta \rho g}{\gamma}$ (dimensionless)
$(C)_{\text{aq,init}}$	Initial concentration of dioxouranium(VI) in aqueous phase ( $\text{mol L}^{-1}$ )
$(C)_{\text{aq,fin}}$	Final concentration of dioxouranium(VI) in aqueous phase ( $\text{mol L}^{-1}$ )
$(C)_{\text{aq,eq}}$	Concentration of dioxouranium(VI) in aqueous phase at equilibrium ( $\text{mol L}^{-1}$ )
Ca	Capillary number = $\frac{\mu u}{\gamma}$ (dimensionless)
Dh	Hydraulic diameter (m)
D	Diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
E	Extraction (%)
$E_{\text{eff}}$	Extraction efficiency (%)
Fr	Froude number = $\frac{u}{(gL^*)^{0.5}}$
g	Gravity ( $9.81 \text{ m s}^{-2}$ )
$(\text{HNO}_3)_{\text{aq,init}}$	Initial concentration of nitric acid ( $\text{mol L}^{-1}$ )
ID	Internal diameter (m)
$K_U$	Distribution coefficient of dioxouranium(VI) (dimensionless)
$k_L$	Overall mass-transfer coefficient ( $\text{m s}^{-1}$ )
$k_L \alpha$	Overall volumetric mass transfer coefficient ( $\text{s}^{-1}$ )
$l^*$	Vortex length (dimensionless)
L	Length (m)
$L^*$	Characteristic length (m)
P	Pressure (Pa)
$\Delta P$	Pressure drop (kPa)

q	Flow rate ratio (dimensionless)
Q	Volumetric flow rate of fluid ( $\text{m}^3 \text{s}^{-1}$ )
r	Radius (m)
R	Radius of the channel (m)
Re	Reynolds number = $\frac{\rho u D}{\mu}$ (dimensionless)
u	Velocity ( $\text{m s}^{-1}$ )
V	Volume ( $\text{m}^3$ )
We	Weber number = $\frac{\rho u^2 D}{\gamma}$ (dimensionless)
w	Width (m)
CMPO	(octyl(phenyl)-NN-diisobutylcarbamoylmethylphosphine oxide)
HDEHP	(bis(2-ethylhexyl)phosphoric acid)
TBP	tributylphosphate
TTA	(2-thenolytrifluoroacetone)

## Greek Letters

$\alpha$	Specific interfacial area ( $\text{m}^2 \text{m}^{-3}$ )
$\gamma$	Interfacial tension ( $\text{n m}^{-1}$ )
$\delta$	Film thickness ( $\mu\text{m}$ )
$\varepsilon$	Volume fraction (dimensionless)
$\theta$	Angle ( $^\circ$ )
$\lambda$	Viscosity ratio ( $\mu_d/\mu_c$ )
$\mu$	Dynamic viscosity ( $\text{kg m}^{-1} \text{s}^{-1}$ )
$\rho$	Density ( $\text{kg m}^{-3}$ )
$\sigma$	Surface tension ( $\text{N m}^{-1}$ )
$\tau_{\text{re}}$	Residence time (s)
$\tau$	Non-dimensional circulation time in 2-D (dimensionless)
$\tau_{3\text{-D}}$	Non-dimensional circulation time in 3-D (dimensionless)
$\tau_f$	Non-dimensional formation time (dimensionless)

## Subscripts

c	Continuous phase
cap	Cap
ch	Channel
circ	Recirculation
d	Dispersed phase
Eff	Efficiency
film	Film
g	Gas phase
max	Maximum
min	Minimum
mix	Mixture

l	Liquid phase
IL	Ionic liquid
p	Plug
o	Oil
UC	Unit cell
w	Water