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# Intensified extraction of uranium(VI) in impinging-jets contactors

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# HIGHLIGHTS

- High-throughput impinging-jets contactors used for solvent extraction of U(VI).
- Results highlight high extraction efficiencies at short residence times.
- $\bullet$   $k_L \alpha$  was up to 3 orders of magnitude higher than in conventional contactors.
- A model is proposed to predict  $k_L \alpha$  in impinging-jets contactors.

### ARTICLE INFO

Keywords: Extraction Uranium Confined impinging-jets Mass transfer coefficients Drop size

## ABSTRACT

The mass transfer performance of confined impinging-jets (CIJs) contactors was investigated for metal separations. In particular, the extraction of uranium(VI) from aqueous nitric acid solutions (3 M) into 30% v/v TBP/ Exxsol D80, relevant to spent nuclear fuel reprocessing, was studied for different cell geometries, i.e. main chamber size (D = 2 and 3.2 mm) and jet diameter ( $d_j = 0.25$  and 0.5 mm), and different operating conditions, i.e. residence time ( $\tau = 1-9$  s), total jet velocity ( $u_{tot} = 2.6-8.6$  m/s), and reactor length (L = 7-85 cm). For all conditions investigated, the aqueous phase was the dispersed one. Drop sizes were also measured with highspeed imaging. It was found that the extraction efficiency increased by increasing residence time for a constant total jet velocity regardless of the chamber size. At a constant residence time, higher extraction efficiency was achieved at high total jet velocities, which are associated with larger interfacial areas (smaller drops). The extraction efficiency reached 70% in most of the cases investigated in less than 2 s. In addition, high overall volumetric mass transfer coefficients (up to 1 s<sup>-1</sup>) were obtained at short residence times. Using regression analysis, a correlation for the overall volumetric mass transfer coefficient was developed from the experimental data with an average deviation of 9%.

#### 1. Introduction

Impinging-jets contactors, where two liquid streams collide at high velocities, have attracted significant research interest in recent years and have been found to benefit heat and mass transfer applications [1–5]. The impinging-jets concept was first proposed by Elperin [6] and further investigated by Tamir [7]. Miscible, but also immiscible liquids have been used in either open or confined environments, where the resulting jet is enclosed in a channel. In confined environments, the liquid jets collide in small cells generating high energy dissipation rates within small volumes, which can significantly increase heat and mass transfer rates, and in the case of immiscible liquids, the interfacial areas. Reduction of the size of the impinging jets in sub-mm scale cells intensifies the process further and also offers better control of the flow dynamics. In confined jets, the presence of the channel walls can change substantially the flow dynamics during collision and results for

constrained and unconstrained streams cannot be directly related to each other. Confined impinging-jets approaches have found applications in crystallization [8,9], nanoparticle synthesis using liquid precipitation [10,11] and micromixing [12,13].

A main challenge in developing confined impinging-jets (CIJs) systems is the identification of the important parameters and quantification of their effects on the resulting flow; these factors include geometrical configuration of the system, kinetic energy of the jets, flow rates, and fluid properties. A subsequent difficulty is the scaling-up of the impinging-jets contactors to achieve the high throughputs necessary for industrial applications, while maintaining mixing intensity. So far, most of the studies have focused on the collision of miscible liquid streams in T-shape mixers where the flow regimes were characterised either experimentally using high-speed imaging, laser induced fluorescence and particle image velocimetry approaches or numerically [13–19]. The transition between the different flow regimes, for example

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$ \begin{array}{llllllllllllllllllllllllllllllllllll$
$ \begin{array}{c} C_{aq,fin} & \mbox{final concentration of dioxouranium(VI) in aqueous phase} & \alpha \\ & \mbox{[mol } L^{-1}] & & \gamma \\ C_{aq,eq} & \mbox{concentration of dioxouranium(VI) in aqueous phase at} & \mu \\ & \mbox{equilibrium [mol } L^{-1}] & & \rho \\ C_{aq} & \mbox{concentration of dioxouranium(VI) in aqueous phase [mol } \tau \\ & \mbox{L}^{-1}] & & \phi \\ D & \mbox{chamber diameter [mm]} & & \mbox{Sub} \\ d_j & \mbox{jet diameter [mm]} & & \mbox{Sub} \\ E_{eff} & \mbox{extraction efficiency [\%]} \\ h & \mbox{channel height [µm]} & \mbox{aq} \\ \end{array} $
$\begin{array}{c} C_{aq,eq} & \mbox{concentration of dioxouranium(VI) in aqueous phase at} & \mbox{$\mu$} \\ equilibrium [mol L^{-1}] & \mbox{$\rho$} \\ C_{aq} & \mbox{concentration of dioxouranium(VI) in aqueous phase [mol $\tau$} \\ L^{-1}] & \mbox{$\phi$} \\ D & \mbox{chamber diameter [mm]} \\ d_j & \mbox{jet diameter [mm]} \\ E_{eff} & \mbox{extraction efficiency [\%]} \\ h & \mbox{channel height [$\mu$m]} \\ \end{array}$
$ \begin{array}{c} C_{aq} & \mbox{concentration of dioxouranium(VI) in aqueous phase [mol} & \tau \\ & L^{-1}] & \phi \\ D & \mbox{chamber diameter [mm]} & \\ d_j & \mbox{jet diameter [mm]} & Sub \\ E_{eff} & \mbox{extraction efficiency [\%]} \\ h & \mbox{channel height [}\mu m] & aq \\ \end{array} $
$\begin{array}{llllllllllllllllllllllllllllllllllll$
E <sub>eff</sub> extraction efficiency [%]       h     channel height [μm]
h channel height [µm] aq
Id impinging distance [mm] C
k <sub>L</sub> overall mass-transfer coefficient [m/s] ch
$k_{I}\alpha$ overall volumetric mass transfer coefficient $[s^{-1}]$ d
L length of the contactor [m] j
Q volumetric flow rate of fluid $[m^3/s]$ org
u velocity [m/s]
V volume [m <sup>3</sup> ] tot

from segregated steady flow to irregular oscillations that cause a chaotic flow regime, is highly affected by the kinetic energy introduced in the impingement zone by each liquid stream and the transition boundaries are usually reported in terms of Reynolds and Weber numbers [20,21]. It has also been found that the position of the impingement location between the two jets plays a crucial role on the mass transfer efficiency of the process, since slight changes can lead to large recirculation areas of incomplete mixing and affect the flow dynamics in the plane of the collision point [22,23].

Impinging-jets contactors of immiscible liquids have been used in applications such as liquid–liquid extractions [24–26], transesterification of waste cooking oil [27], and oil/water emulsification [28–30]. Despite their importance, however, they have been studied to a lesser extend compared to impinging jets of miscible liquids. When immiscible liquid streams collide the high energy dissipation rates produce a dispersion of one phase into the other. The formation of dispersion is affected by the kinetic energy change in the collision region of the liquid streams, while the uniformity of the dispersions depends on the operating conditions and cell configuration [31].

Among the many applications, liquid-liquid extraction has been one of the main processes in spent nuclear fuel reprocessing for the separation of uranium(VI), plutonium(IV), and thorium(IV) [32-35]. In addition, in advanced nuclear fuel cycles, various technologies based on solvent extraction have been proposed over the last two decades for the recovery and recycling of fissile elements [36]. The separations are largely carried out in mixer-settlers or pulsed columns that have large inventories and residence times and thus suffer from criticality restrictions and solvent radiolytic damage. In addition, the flow fields within these units are not uniform and not well characterised, leading to variations in conditions and low predictive capabilities. The inability to determine interfacial areas precisely can lead to uncertainties in design and performance of the processes [37]. Intensification of the spent nuclear fuel reprocessing using innovative technologies, such as confined impinging-jets, can enhance mass transfer rates leading to increased efficiency, and can offer real-time monitoring and control. In addition, operating in small systems, thus reducing the required volumes, makes criticality control easier and can potentially minimise safety risks [38].

On this basis, the present work investigates the applicability of confined impinging-jets contactors on the separation of uranium(VI) from nuclear waste. This is the first study on separations in the spent nuclear fuel reprocessing cycle using impinging jets and follows from

channel width [µm] ek Letters specific interfacial area [m<sup>2</sup>/m3] interfacial tension [N/m] dynamic viscosity [kg m<sup>-1</sup> s<sup>-1</sup>] density [kg m<sup>-3</sup>] residence time [s],  $\tau = V_{ch}/Q_{mix}$ organic-to-aqueous phase ratio oscripts aqueous continuous channel dispersed phase jet organic reactor total

recent work on the hydrodynamic characterisation of these systems in confined cells [31]. The effects of operating conditions and geometrical configuration on the extraction efficiency are investigated. The results are compared with contactors of different types and a simple model is proposed that relates the mass transfer coefficient to the operating conditions.

#### 2. Experimental setup and procedure

The continuous extraction of uranium(VI) from aqueous nitric acid solutions (3 M) into an organic phase was carried out in the confined impinging-jets (CIJs) contactor shown in Fig. 1. The organic phase was Exxsol D80, which contained 30% v/v Tributylphosphate [TBP; O = P  $(OC_4H_9)_3$ ] as the extractant of the metal ions. The confined impinging-jets contactor was manufactured in a PTFE block using a CNC machine. It consists of two circular side channels, the inlets of the jets, in-line with each other, and connected perpendicularly to the main circular chamber that has diameter D. To vary the diameter of the jet channels, stainless steel (SS) nozzles with different internal diameters (d<sub>j</sub>) were inserted in them. At the end of the main chamber, an FEP channel was connected with internal diameter (D) the same as that of the main chamber (i.e. 2 or 3.2 mm). The fluids were fed into the side channels using high-precision continuous syringe pumps (Harvard PHD Ultra), one for each phase.

The operating conditions were chosen based on our previous studies [31] and are shown in Table 1. For the two-phase system used in this work (see Table 2), the aqueous phase (HNO<sub>3(aq)</sub>/U(VI)) formed the dispersion within the organic phase (TBP/Exxsol D80; 30% v/v). The surface and interfacial tension, shown in Table 2, were measured using a Kruss 100 tensionmeter. The density and viscosity values of the fluids reported were given by the supplier. The concentration of the uranium (VI) at the outlet was measured using a UV–Vis spectrometer (USB2000+, Ocean Optics). For each set of conditions, the concentration at the outlet was measured a number of times to ensure that the standard deviation of 4 consecutive measurements was below 3%. This resulted to an average error of 2.2% and 3.5% for the estimation of the extraction efficiency ( $E_{eff}$ ) and the overall volumetric mass transfer coefficient ( $k_L\alpha$ ), respectively. The uncertainty of each value is given in the form of error bars within the graphs.

Drop size measurements in the formed dispersion were carried out in the main FEP channel, which was enclosed in a flat visualization box to minimise reflections from the wall curvature and improve the quality



Fig. 1. Schematic representation and photograph of the confined impinging-jets cell.

#### Table 1

Range of geometric and operating parameters in the current study.

Temperature, T	22 ± 1 °C
Organic (aqueous) phase flow rate, Qorg (Qaq)	7.5–35 cm <sup>3</sup> /mir
Organic (aqueous) jet velocity, $u_{j,org}(u_{j,aq})$	1.3-4.3 m/s
Nozzle diameter, d <sub>i</sub>	0.25, 0.5 mm
Main chamber diameter, D	2, 3.2 mm
Reactor volume, Vr	$0.5-7 \text{ cm}^3$
Impinging distance, Id	1.6-3.2 mm
Organic jet Re, Re <sub>org</sub>	244-570
Aqueous jet Re, Re <sub>aq</sub>	650-1630
Organic jet We, We <sub>org</sub>	28-154
Aqueous jet We, We <sub>aq</sub>	13-72
Initial $UO_2^{2+}$ concentration in the aqueous phase, $C_{aq,init}$	0.05 M
-	

of the images. In the cases where very dense dispersions were formed, it was difficult to distinguish the interfaces in the main FEP channel. In these cases, the exit of the FEP channel was immersed in a rectangular acrylic box which contained the organic phase (TBP/Exxsol D80; 30% v/v), where the drops spread out and the measurement of their size was easier than in the main channel, as shown in Fig. 2.

### Table 2

Physical properties of the test fluids (T =  $22 \pm 0.5$  °C).

Property	Chemicals		
	TBP/Exxsol D80 (30% v/v)	HNO <sub>3</sub> (3M)	
<sup>a</sup> Density (kg m <sup>-3</sup> ) <sup>a</sup> Viscosity (kg m <sup>-1</sup> s <sup>-1</sup> ) <sup>b</sup> Surface tension (N/m) <sup>b</sup> Interfacial tension (N/m)	$852 2.22 \cdot 10^{-3} 23.5 \cdot 10^{-3} 11.35 \cdot 10^{-3}$	1079 0.981·10 <sup>-3</sup> 66.3·10 <sup>-3</sup>	

<sup>a</sup> Values as given by the manufacturer.

<sup>b</sup> Values as measured in the UCL laboratory.

Drop sizes were measured with a CMOS high-speed camera (Phantom V1212), which has a maximum resolution of  $1280 \times 800$  at 12,600 fps and is equipped with a magnification lens (×12, LEICA Monozoom 7 optical system). The acquired images were analysed using a post processing routine developed within an image analysis software (MIPAR) (for details see Tsaoulidis and Angeli [31]). From the drop size measurements the Sauter mean drop diameter, D[3,2], was calculated as follows:



Fig. 2. Schematic representation of the drop size measurement method and photograph of the aqueous dispersion.

$$D[3,2] = \frac{\sum_{i=1}^{n} d_{i}^{3}}{\sum_{i=1}^{n} d_{i}^{2}}$$
(1)

where n is the number of drops, and  $d_i$  is the diameter of drop i in the distribution.

#### 3. Results and discussion

For the characterisation of the mass transfer performance of the confined impinging-jets contactor two parameters were used, i.e. the extraction efficiency (% $E_{eff}$ ) and the overall volumetric mass transfer coefficient ( $k_L\alpha$ ). The rate of mass transfer of uranium species from the aqueous to the organic phase is given by

$$\frac{dC_{aq}}{dt} = -k_L \alpha (C_{aq,eq} - C_{aq})$$
(2)

where  $C_{aq}$  is the concentration of the uranium species in the bulk aqueous phase (at time t), and  $C_{aq,eq}$  is the concentration of the uranium species in the aqueous phase at equilibrium with the organic phase (t =  $\infty$ ).  $C_{aq,eq}$  was pre-determined experimentally for the different flow rate ratios used in this work, by stirring in vials the initial organic and aqueous solutions, until they reach their equilibrium values. The equilibrium concentrations of uranium in the two phases are described by the distribution coefficient,  $D_U$ .

$$D_{\rm U} = \frac{C_{\rm org,eq}}{C_{\rm aq,eq}} \tag{3}$$

By applying a mass balance over the entire extraction unit, Eq. (2) can be integrated from the initial contact time of the two phases in the impingement zone (t = 0) to t =  $\tau$ , the residence time in the cell, which is estimated from the flow rates of the two phases and the volume of the reactor, and from the initial concentration  $C_{aq,init}$  to the final concentration  $C_{aq,init}$  as

$$\int_{C_{aq,init}}^{C_{aq,init}} \frac{1}{(C_{aq,eq} - C_{aq})} dC_{aq} = -k_L \alpha \int_0^\tau t dt$$
(4)

The overall volumetric mass transfer coefficient is then found as follows

$$k_{L}\alpha = \frac{1}{\tau} ln \left( \frac{C_{aq,eq} - C_{aq,init}}{C_{aq,eq} - C_{aq,fin}} \right)$$
(5)

The extraction efficiency, which is defined as the ratio of the amount of species transferred from one phase to the other, to the maximum amount transferrable can be written as:

$$\%E_{\rm eff} = \frac{C_{\rm aq,fin} - C_{\rm aq,init}}{C_{\rm aq,eq} - C_{\rm aq,init}}$$
(6)

The overall mass transfer coefficient and the extraction efficiency are related as follows:

$$k_{\rm L} a = -\frac{1}{\tau} \ln(1 - E_{\rm eff}) \tag{7}$$

The effects of different parameters such as total jet velocity,  $u_{tot}$ , (the sum of the velocities of the two jets), residence time ( $\tau$ ), flow rate ratio ( $\phi = Q_{org}/Q_{aq}$ ), main chamber size (D), jet channel diameter (d<sub>j</sub>), and distance between the nozzles (Id) on  $\% E_{eff}$  and  $k_L \alpha$  are discussed in the following sections. The confined impinging-jets contactor is a continuous system and can be compared to an ideal plug flow system. In the plug flow contactor it is assumed that there is uniform velocity and concentration perpendicular to the flow direction, while axial mixing is negligible.

# 3.1. Effect of operating conditions on the extraction performance in the confined impinging-jets contactors

The effect of total jet velocity (utot) and residence time on the extraction efficiency of the system is illustrated in Fig. 3. The flow rate ratio  $(Q_{org}/Q_{ag})$  between the two phases was kept constant at 1. The residence time,  $\tau$ , was varied by changing the channel length (L) of the contactor rather than by changing the flow rates (or velocities), which would also affect the flow patterns and the drop sizes formed in the impingement zone. The length of the channel varied from 7 to 85 cm. The distance between the jets (Id) was at 3.2 mm. The chamber size (D) was 3.2 mm and the internal diameter of each jet (d<sub>i</sub>) was 0.5 mm. The total jet velocity varied from 3.4 to 5.1 m/s, which corresponds to residence times approximately from 1 to 7 s. As expected, the extraction efficiency increases with increasing residence time. In all cases, 50% extraction efficiency is achieved within the first second, whilst the extraction efficiency reaches 70% within 2-3s depending on the total jet velocity. For the first 2 s, it can be seen that the extraction efficiency increases linearly independently of the total jet velocity, indicating that the concentration difference is the dominant parameter that controls



**Fig. 3.** Extraction efficiency as a function of residence time for different total jet velocities (D = 3.2 mm, d<sub>j</sub> = 0.5 mm). The dotted rectangle corresponds to extraction efficiency obtained in a reactor of 28 cm length at different total jet velocities.

mass transfer at short residence times. After 2 s, however, the total jet velocity, which changes the interfacial area, also affects the extraction efficiency. Moreover, the extraction efficiency increases rapidly at the first 3.4 s for all cases, while at longer residence times the rate of increase is small, as can be seen in Fig. 3. The length of the reactor (L) required for this change in the gradient of %E changes with total velocity. For example when uttot increases from 3.4 to 5.1 m/s the length of the reactor needed to reach this point increases from 28 to 42 cm. For a constant reactor length (L = 28 cm) the same extraction efficiency is achieved at decreasing residence time by increasing total jet velocity (see Fig. 3 for L = 28 cm). Higher extraction efficiency is obtained by increasing the total jet velocity for the same residence time (see  $\tau = 3.4$  s in Fig. 3). An extraction efficiency of ~85% was obtained at total jet velocity of 5.1 m/s in less than 7 s, whilst at uttot of 4.3 and 3.4 m/s for the same time, the extraction efficiencies were  $\sim$  78% and 73%, respectively. This is attributed to the increase in energy dissipation rate and specific interfacial area  $(m^2/m^3)$  with increasing  $u_{tot}$  [31]. When the two immiscible liquids collide at the impingement zone, drops form with diameters that are equal to the diameter of the dispersed phase jets down to 1 order of magnitude smaller. In general, the drop size distribution is dominated by drops whose diameters do not exceed 150 µm (more than 95% of the number population). As can be seen in Fig. 4, the number of small drops increases as the total jet velocity increases. The Sauter mean diameter decreases from 0.172 to 0.145 mm, when the total jet velocity increases from 3.4 to 5.1 m/s. This is associated with a 20% increase in interfacial area.

The Sauter mean diameters calculated in this work showed good agreement with drop sizes obtained in similar confined impinging-jets cells made from acrylic blocks for a two-phase system of water-Exxsol D80, as reported in Tsaoulidis and Angeli [31]. In Fig. 5 results from this work are plotted against the current data as a function of the Weber number of the continuous phase  $\left(We_c = \frac{\rho u_{j,org}^2 d_j}{\gamma}\right)$ . Both data sets follow the same trend, with the Sauter mean diameter decreasing with increasing We<sub>c</sub>; the decrease is steep at low We<sub>c</sub>, whilst it reaches a plateau for We<sub>c</sub> numbers higher than 100.

In Fig. 6, the extraction efficiency is plotted against the total jet velocity for different channel lengths. In the shorter channel (14 cm) the extraction efficiency decreases with increasing  $u_{tot}$ , indicating that residence time is the dominant parameter, rather than the mixing intensity. Residence times in the case of the 14 cm tube varied between 1.1 and 1.7 s. By increasing the channel length further, to 28 and 56 cm respectively, and thus the residence time, the effect of the total jet velocity on the extraction efficiency becomes more apparent. The strong collisions of the jets favour mixing and the generation of fresh interfaces between the two liquids that enhance mass transfer. For example, in the 56 cm channel when the total jet velocity increases from 3.4 to 5.1 m/s, the extraction efficiency also increases from 6.8 to 4.5 s.

In Fig. 7 the extraction efficiency is plotted against the total jet velocity for constant residence time. It can be seen that the extraction efficiency increases slightly (3.4%) with total jet velocity at residence time equal to 1.7 s, indicating that although the mixing intensity increased, the residence time required for the separation was not enough. At residence times 3.4 and 6.8 s, the increase on the extraction efficiency was similar and equal to 12.8% and 13.7%, respectively, by increasing the total jet velocity from 3.4 to  $5.1 \text{ m s}^{-1}$ , indicating that at residence times higher than 3.4 s the extraction efficiency did not increase significantly with mixture velocity. It can also be seen that at low total jet velocity (3.4 m/s) the increase in the extraction efficiency with residence time is lower than at high total jet velocity (5.1 m/s), illustrating the impact of high intensity collisions on the mass transfer performance of the contactor.

To study the effect of the distance between the two jets on the extraction efficiency, two different distances (Id), i.e. 3.2 and 1.6 mm, for different total jet velocities in the case of the D = 3.2 mm channel, have been tested. The length of the main channel was 28 cm. As can be seen in Fig. 8, the extraction efficiency is slightly lower for the short distance case between the two jets. This difference is related to the size of the droplets formed and the specific interfacial area available for mass transfer. The Sauter mean diameter varied from 0.10 to 0.17 mm when the jets were 3.2 mm apart, while it was larger and varied from 0.123 to 0.178 mm when the distance between the jets was 1.6 mm. In both cases, the extraction efficiency decreases with increasing total jet velocity indicating that residence time controls the mass transfer process. For the conditions plotted the residence time varied from 2 to 3.4 s.

The effect of scale was investigated in two different chamber sizes (D), 2 and 3.2 mm, respectively. In both cases, the jet diameters,  $d_j$ , were 0.25 mm, whilst the distance between the jets was equal to the diameter of the main channel, and the total jet velocity varied between 6 and 8.5 m/s. As can be seen in Fig. 9, slightly higher extraction efficiency was obtained in the small chamber, which is attributed to the shorter diffusional distances and the slightly smaller drop diameters obtained, compared to the large chamber. The Sauter mean diameter varied from 0.09 to 0.124 mm in the small chamber, and from 0.1 to 0.131 mm in the large one.

The extraction efficiency of two different cell configurations (D = 3.2 mm,  $d_j = 0.5$  mm, Id = 3.2 mm; D = 2 mm,  $d_j = 0.25$  mm, Id = 2 mm) was also investigated and the results are shown in Fig. 10. The total jet velocity in the small cell was 7.64 m/s, whilst in the big cell was 5.1 m/s. To vary the residence time at constant total jet velocity, different channel lengths were used. Better extraction efficiency was achieved in the small chamber at short residence times (below 3.5 s). In both cases, the extraction efficiency reaches ~90% at around 7 s. It can be observed that smaller cells are preferable for applications with short residence times (below 3.5 s), whilst at longer residence times the extraction efficiency is similar in both cases and the bigger chamber is preferred because it increases the volumetric throughput at reduced pressure drop.

The effect of flow rate ratio  $(Q_{org}/Q_{aq})$  for different total jet velocities on the extraction efficiency is shown in Fig. 11. It should be noted that, according to the stoichiometry of the reaction, TBP in the organic phase is in excess for the extraction of uranium(VI) from the nitric acid solution for all flow rate ratios studied. For each total jet velocity, by increasing the flow rate ratio, and thus the volume of the continuous organic phase, the extraction efficiency improves. A change in the flow rate ratio results to a change in the flow pattern between the phases in the impingement zone; by increasing the ratio, the flow rate of the continuous organic phase increases, while that of the dispersed aqueous phase decreases. As can be seen in Fig. 11, at the lowest flow rate ratio



Fig. 4. Number-based drop size distribution at different total jet velocities and equal phase ratio (D = 3.2 mm,  $d_i = 0.5 \text{ mm}$ ).





Fig. 6. Extraction efficiency as a function of total jet velocity for different channel lengths (D = 3.2 mm, d<sub>j</sub> = 0.5 mm).



Fig. 7. Extraction efficiency as a function of the total jet velocity at different residence times (D = 3.2 mm, d<sub>j</sub> = 0.5 mm, L = 14–84 cm).

(0.67) the flow pattern consists of aqueous plugs and drops flowing in the continuous organic phase, and also drops of the organic phase trapped in the aqueous plugs, which results to low interfacial area, and thus low extraction efficiency. The irregular flow pattern accounts for the large variation in  $\&embed{E}_{eff}$  at this ratio, depending on the total jet velocities and jet diameters. In some cases the  $\&embed{E}_{eff}$  is high, indicating large interfacial areas. By increasing the ratio, finer dispersions form, which also result in higher interfacial area available for mass transfer. For example, at total jet velocity equal to 4.3 m/s, the mean Sauter diameter at ratio equal to 1 is 0.157 mm and decreases slightly to 0.121 mm for ratio 1.5.



Fig. 8. Extraction efficiency as a function of total jet velocity for two different jet distances (D = 3.2 mm,  $d_i = 0.5 \text{ mm}$ , L = 28 cm).



Fig. 9. Extraction efficiency as a function of the residence time for two different main chamber sizes ( $d_j = 0.25$  mm).



Fig. 10. Extraction efficiency as a function of the residence time for two different cell configurations (D = 3.2 mm,  $d_j = 0.5 \text{ mm}$ ,  $u_{tot} = 5.1 \text{ m/s}$ ; D = 2 mm,  $d_j = 0.25 \text{ mm}$ ,  $u_{tot} = 7.64 \text{ m/s}$ ).

# 3.2. Overall volumetric mass transfer coefficients and predictive correlations

The overall volumetric mass transfer coefficient was also calculated to enable direct comparison of the extraction performance of the CIJ system with other two-phase contactors. The values of the overall volumetric mass transfer coefficients presented, were averaged for the whole region of the contactor from the point of impingement (t = 0) to the outlet (t =  $\tau$ ). Thus, they account for the mass transfer in the impingement zone and the downstream main section of the extraction channel. In general, it was found that  $k_L\alpha$  decreases with increasing



Fig. 11. Extraction efficiency as a function of flow rate ratio,  $Q_{org}/Q_{aq}$  (D = 3.2 mm).



**Fig. 12.** Overall volumetric mass transfer coefficient as a function of residence time for different total jet velocities (D = 3.2 mm,  $d_i = 0.5 \text{ mm}$ , Id = 3.2 mm).



Fig. 13. Overall volumetric mass transfer coefficient as a function of total jet velocity  $(u_{tot})$  for two different jet diameters (D = 3.2 mm, Id = 3.2 mm, L = 28 cm).

residence time, and thus reactor length, almost linearly (Fig. 12) at each total jet velocity. For low residence times (< 2 s) mass transfer coefficients are similar for a specific residence time at different  $u_{tot}$ . At higher residence time (> 3.4 s), however, slightly higher mass transfer coefficients are obtained when the total jet velocity is increased.

In Fig. 13 the mass transfer coefficient is plotted against the total jet velocity,  $u_{tot}$ . Overall, the mass transfer coefficient increases with increasing velocity, and thus flow rate, for both jet diameters, which is in agreement with similar works on intensified continuous contactors [26,39,40]. For a constant reactor length (L = 28 cm) and chamber diameter (D) equal to 3.2 mm, when the large jets were used ( $d_j = 0.5$  mm) the residence time varied between 1.9 and 4.5 s, whilst in



**Fig. 14.** Overall mass transfer coefficient as a function of the residence time for two different chamber sizes (D = 3.2 mm, d<sub>j</sub> = 0.25 mm, ID = 3.2 mm; D = 2 mm, dj = 0.25 mm, Id = 2 mm).



Fig. 15. Comparison of experimental and predicted  $k_L \alpha$  values.

the small jets ( $d_j = 0.25 \text{ mm}$ ) it varied from 5.4 to 9 s. As a result, for a given  $u_{tot}$  the mass transfer coefficient values are higher when the bigger jets are used.

The mass transfer coefficients for the two different chamber sizes at increasing residence times are shown in Fig. 14. Higher mass transfer coefficients are obtained in the small chamber at short residence times with values up to  $1 \text{ s}^{-1}$ , indicating the suitability of smaller chambers for applications of short duration. However, as the residence time increases, both cell configurations give similar values of  $k_L \alpha$ . The mass transfer coefficients decrease with increasing residence time and reach a minimum value of  $0.25 \text{ s}^{-1}$  for residence time around 6 s. The decrease is steeper in the small chamber compared to the large one; the associated total jet velocities were 7.6 and 6.8 m/s, for the small and the large chambers, respectively.

According to the findings, the mass transfer coefficient depends on the residence time, the total jet velocity and the ratio of the nozzle to main chamber diameters. From the results, the following simple predictive model was developed:

$$k_{L}\alpha = 0.234 - 0.062\tau + 0.045u_{tot} + 1.353\frac{d_{j}}{D}$$
(8)

As shown in Fig. 15, the above correlation can adequately describe the experimental data with an average deviation of 9%, for  $\tau$ ,  $u_{tot}$ , and  $d_j/D$  ranging from 1.1 to 9s, from 1.9 to 8.5 m/s, and from 0.078 to 0.125, respectively. As expected, the coefficient of the residence time is negative to account for its effect on  $k_L\alpha$ , as shown above.

#### Table 3

Overall mass transfer coefficients in intensified and conventional extractors.

Equipment	System	$k_L\alpha \not \ s^{-1}$	Reference
Confined impinging-jets contactors (Present work)	TBP/kerosene-U-HNO <sub>3</sub>	0.15-1.05	-
Microchannels ( $D = 0.5-2 \text{ mm}$ )	TBP/ionic liquid-U-HNO <sub>3</sub>	0.05-0.3	[53]
Annular pulsed column	TBP/kerosene-U-HNO3	0.009-0.012	[54]
Two-impinging-jets device	H <sub>2</sub> O-acetone-toluene	0.001-0.19	[26]
Impinging jet extractor	butanol-succinic acid-H2O	0.015-0.2	[24]
Mixer-settler	NPH-TBP-HNO <sub>3</sub>	0.5–13.3 (x10 <sup>-5</sup> )	[55]
Centrifugal extractor	aqueous NaOH-(butyl acetate, iso-amyl acetate, hexyl acetate)	0.2–2	[56]
Rotating disc contactor	toluene-H <sub>2</sub> O-acetone	4–9.5 (×10 <sup>-3</sup> )	[57]
Rotating disc contactor	toluene-H <sub>2</sub> O-acetone	4–9.5 (×10 <sup>-3</sup> )	[57]

#### 3.3. Comparisons with intensified and conventional contactors

The contractors that have mainly been used in spent nuclear fuel reprocessing are mixer-settlers and pulsed columns [41-43], whilst lately centrifugal contactors [44] have also been investigated. Operation in mixer-settlers and pulsed columns is associated with large inventories, high investment and operational costs, and long residence times. Centrifugal contactors are promising but they are difficult to scale-up, and require very high specific energy input [37]. Recent advances in process intensification have shown that operating in small scale (and microchannel) contactors [45-47] can dramatically increase the mass transfer coefficients up to three orders of magnitude compared to conventional ones (as shown in Table 3) and reduce the residence time of the process. There are a few studies on solvent extractions in microchannels relevant to spent nuclear fuel cycle [48-50], but generally their application is limited because of the small throughputs possible. For example, Hotokezaka et al. [51] investigated the extraction of uranium from nitric acid solutions using TBP (pure) and TBP/ dodecane in glass microchannels ( $w = 100.5 \,\mu m$ ,  $h = 43.5 \,\mu m$ , L = 120 mm), and found that equilibrium was achieved in 1 s; the flow rates though were very low, ranging between 2.2 and 4.3 µL/min. In a similar study, Darekar et al. [52] used capillary tubes (D = 300–800  $\mu$ m, V<sub>r</sub>=19–212  $\mu$ L) for the extraction of uranium from nitric acid solutions into an organic phase (30% v/v TBP in dodecane). They reported mass transfer coefficients ranging from 0.00082 to  $0.15 \text{ s}^{-1}$  for residence times from 2 to 60 s. Sen et al. [39] also reported high mass transfer coefficients  $(0.003-1 \text{ s}^{-1})$  in microchannels for residence times ranging between 1.5 and 100 s, for the extraction of nitric acid in an organic-aqueous system. The microchannels had diameters from 71 to  $319\,\mu m$  resulting in total reactor volumes from 0.2 to 0.33 cm<sup>3</sup>, respectively. Impinging-jets combine high mass transfer coefficients with large volumetric throughputs. Dehkordi et al. [40] carried out liquid-liquid extractions using a two-opposed-jets contacting device and obtained mass transfer coefficients up to  $0.23 \, \text{s}^{-1}$ , higher than that in conventional contactors (see Table 3). In addition, the system had a volume of 47 cm<sup>3</sup> and was able to operate at flow rates up to 300 cm<sup>3</sup>/min. In the present work, by using confined impingingjets contactors, mass transfer coefficients varied between 0.15 and  $1.05 \,\mathrm{s}^{-1}$  and extraction efficiencies up to 90% were achieved for residence times between 1 and 7 s and for total flow rates ranging from 15 to 70 cm<sup>3</sup>/min. At the conditions investigated, the Sauter mean diameters of the aqueous dispersed drops ranged from 0.093 to 0.174 mm giving specific interfacial areas of  $17,000-32,000 \text{ m}^2/\text{m}^3$ .

#### 4. Conclusions

The mass transfer performance of intensified confined impingingjets (CIJs) contactors was investigated for uranium(VI) separations relevant to spent nuclear fuel reprocessing. The impinging-jets cells were evaluated for different operating and geometric parameters, i.e. residence time, total jets velocity, reactor length, and main chamber size. The extraction efficiency was found to be affected by both the residence time and the total jets velocity. Higher extraction efficiency was achieved by increasing the residence time; this increase was almost linear for the first 2 s, whilst as the residence time increased further, the efficiency increased at a slower rate. High total jet velocities were associated with increased mixing intensity and interfacial areas (smaller drops were generated), and thus high extraction efficiency. The mass transfer coefficients obtained with the impinging-jets cells were up to 3 orders of magnitude higher than in conventional contactors. High mass transfer coefficients were obtained at short residence times; almost up to  $0.65 \text{ s}^{-1}$  for the large chamber investigated (D = 3.2 mm), and up to  $1 \text{ s}^{-1}$  for the small chamber (D = 2 mm). Results indicate that at short residence times, the small chambers have higher mass transfer coefficients than the large ones. However, at long residence times, the mass transfer coefficients between the two chamber sizes are similar; in this case the large chamber should be preferred because it has larger throughput and smaller pressure drop compared to the small one. A simple correlation was developed for the mass transfer coefficient using regression analysis, which was able to predict the experimental data with 9% deviation.

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