Co and Ni extraction and separation in segmented micro-flow using a coiled flow inverter

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Abstract

The segmented micro-flow extraction and separation of the adjacent elements of Co from Ni sulphate solution with Cyanex 272 was developed using a micro-scale coiled flow inverter (CFI). This was compared with the conventional batch extraction at comparable conditions. Continuous operation of a process involving liquid-liquid extraction and then two-phase separation was achieved. For the latter a micro-scale separator was used. Compared with batch extraction, the segmented micro-flow extraction process showed by order-of-magnitude faster extraction times, higher extraction ability for Co, lower extraction for Ni, and then a better selectivity between Co and Ni for industrial-matching sulfate solutions with high Co and Ni ions concentration. In addition, flow patterns were recorded in the CFI by a high speed camera. Regular columnar slug flow was formed at low flow rates, and the length of the inlet slug was found to be a Gaussian function of the flow rates. In- and outlet flows matched, i.e. there was no change in the flow pattern when passing the CFI. At higher flow rates, deviations from the ideal pattern were found and in- and outlet flow did not match. Finally, the mass transfer coefficient in the range of 0.014 to 0.24 $\text{mm}\cdot\text{s}^{-1}$ was obtained.

Key words: liquid-liquid extraction, slug, microflow, coiled flow inverter, phase separator

1. Introduction

Cobalt and Nickel are amongst the most important nonferrous metals applied in many fields[1]. Cobalt and its compounds are promisingly used in super-alloys,

lithium ion battery cathodes, catalysts, blue pigments, and radioisotopes, etc[2]. Due to the growing demand for lithium ion batteries, the use of Co is growing rapidly during the past decades[3]. Nickel is primarily used as an alloying metal in the iron and steel industry and other uses are in rechargeable batteries, electroplating, catalysts, etc[1]. Because of the very similar chemical and physical properties, the elements Co and Ni always occur together in nature. One significant source of Co is its recovery as a by-product of the hydrometallurgical treatment of nickel sulphide and nickel laterite ores in sulphate media wherein it is contained as a minor component. The separation and recovery of Co from Ni particularly at low ratio of cobalt to nickel have mainly been conducted through direct solvent extraction[4-6].

In the batch solvent extraction system, to obtain high extraction efficiency and selectivity of the desired solutes, two immiscible liquids are expected to mix turbulently in a reactor where numerous minute droplets of one liquid are dispersed in the other. Minute droplets increase the liquid-liquid interfacial area and decrease the molecular diffusion length, leading to an enhanced mass transfer between the two dispersed phases. However, the two-phases interface increase is very limited owing to the optimized droplet size equilibrium between turbulent mixing and next settling for phases separation by gravity. If instead the size of the droplets is too small, the separation of the two phases takes place very slowly. The contradictory effect between mixing and settling hydrodynamics results in some disadvantages, such as huge footprint of settler for long settling time, a third phase crud and emulsion droplets formation leading to difficulty in phases separation, mechanical entrainment between

two phases leading to expensive extractant losses, and requiring extra process to remove organic solvent from aqueous phase[7-9].

The drawbacks in conventional solvent extraction may be addressed by continuous flow through microreactors with characteristic internal dimensions typically in the range of 50 to 1000 μm [10,11]. A decrease in the channel dimension then can induce a high increase of specific surface area and reduction of molecular diffusion distances[10,12,13]. Process intensification can be realized through microstructured reactors[14-17]. In addition, orderly laminar multiphase flow can be formed due to the typically low Reynolds numbers (<2000) encountered in the microchannel[18]. Mixing in the microchannels occurs primarily by molecular diffusion and convection due to insetting recirculations. Liquid-liquid extraction, including mixing and phase separation, especially benefits from such microflow systems as mass transfer is rapidly completed by the short diffusion distances and effective convection, chemical reactions are significantly accelerated by large interfacial areas, and excellent phase separation performance is achieved by surface tension over inertial and gravitational force[19,20]. Many investigations of extraction metal ions and organic compounds using different kinds of microreactors have been conducted as an significant alternative to conventional macro processes[21-27]. It demonstrates several advantages of microflow extraction, such as improved extraction and separation efficiency, high selectivity of target solutes, shortened extraction time, reduced reagent consumption, “numbering-up” parallel processing, excellent separation of two phases without formation of particle-stabilised emulsions (crud),

and so on.

Stratified and segmented (also called as slug and plug) flow are the most commonly used flow patterns in microreactors concerning biphasic gas-liquid and liquid-liquid flows. The latter provides better mass transport due to the recirculation causing convection within the segment and faster surface concentration renewal, and thus enables a higher overall throughput[28-30]. It has been widely used for gas-liquid and liquid-liquid two-phases mixing and reactions, especially for the liquid-liquid extraction applications[31-35]. Two-phase separation of segmented flow can be successfully achieved through a porous membrane phase separator[20], a slit shaped separator[33], a plastic capillary inserted a metal needle[36], a flow splitter[37], etc. Therefore, the continuous operation of liquid-liquid extraction and two-phase separation can be achieved instantly in the segmented flow system.

Microfluidic chip[38,39] and capillary microreactors[40,41] are popular devices used for process intensification. In order to realize even more efficient heat and mass transfer efficiency, some novel equipments with unconventional structure are observed in laboratory and industrial application. Circular cross-section[42] and square microchannels[39] are introduced to investigate the performance of liquid-liquid slug microflow. Some helically coiled tubes have also been proposed to enhance the mass transfer. Nigam et al.[43] firstly reported this new technique, the bending of helical coil at 90° with equal arm lengths before and after the bend, to induce multiple flow inversions, which provides most effectively narrow residence time distribution (RTD). The further research[44] indicated that this microstructured

coiled flow inverter(CFI) bended of helical coil at 90° offers a 38.5% higher heat transfer coefficient compared to straight helically coiled tubes. Additionally, it provides 3.5- to 5.5-fold enhancement in Sherwood number compared to helical coil tube and straight tube due to the intensified radial mixing caused by complete flow inversion[45]. Kurt et al.[46] reported a CFI fabricated in different structures, including step-wise, zigzag, and frame-wise, to offer improved residence and thermal time distribution because of the formation of Dean vortices via centrifugal forces on the cross section of the tube. In our previous work[34], the microstructured CFI was firstly applied to liquid-liquid extraction of an organic compound. The results showed about 20% higher extraction performance in the CFI than that in straight tube. All in all, the CFI structure exhibited higher efficiency in heat exchange, inline mixing, even chemical reaction, and showed a promising potential for practical use. However, there is, to our best knowledge, no report concerning the process of metal ions separation on such micro-scale CFI with solvent extraction.

In this study, a segmented microflow extraction process in micro-scale CFI for the separation of Co from Ni sulfate solution was investigated using Cyanex 272 (Diisooctylphosphinic acid) as extractant. Continuous operation of a process involving liquid-liquid extraction and then two-phase separation was achieved. For the latter a micro-scale slit separator was used. This is compared with the conventional batch extraction at the comparable conditions. In addition, flow patterns at different flow rates were recorded in the CFI by a high speed camera, and the segment length was also evaluated. A high mass transfer coefficient was also

obtained.

2. Experimental

2.1. Materials and analysis

The commercial extractant Cyanex 272 (Diisooctylphosphinic acid, $C_{16}H_{35}O_2P$, 90%) was provided by Sigma-Aldrich and was used without any further purification. Prior to be used, the acidic Cyanex 272 needed to be pre-neutralized by certain quantity of 10 mol/l NaOH to control different equilibrium pH of the aqueous solution. Organic phase was prepared by dissolving certain pre-neutralized Cyanex 272 in kerosene. The aqueous phase was prepared by dissolving stoichiometric amounts of CP grade $NiSO_4 \cdot 6H_2O$ and $CoSO_4 \cdot 7H_2O$ (both supplied by Alfa Aesar) in deionized water (Millipore Elix UV-5 water purification system, 18.2 M Ω , Germany). The initial concentrations of Co and Ni were 2.578 and 66.34 g/l, respectively, and the initial pH was 4.43 for all experiments.

The pH values in the aqueous phase were measured by a pH meter (PHM210, MeterLab). The concentrations of Co in the aqueous solution before and after extraction were measured by a ICP-OES spectrometer (model: SPECTROBLUE-EOP, SPECTRO, Germany), after suitable dilution with high pure water and 5 wt% nitric acid. The high Ni concentrations in the aqueous phase were determined by complexometric titration using 0.02 mol/L Na_2EDTA standardised solution with murexide as indicator agent. Both of Co and Ni concentrations in the organic phase were calculated according to the mass balance between the aqueous and organic phase.

2.2. Apparatus and extraction procedure

[Fig. 1a](#) shows the setup of continuous segmented micro-flow extraction system used in this study (hereinafter termed “micro-flow”). All the experiments were performed at room temperature ($T=298 \pm 2$ K). A dual channel syringe pump (Fusion 200, Chemyx Inc. US) loaded with two 25 ml gastight syringes was used to pump the green aqueous and light yellow organic phase at given flow rates. In order to achieve the phase volume ratio of organic and aqueous phase (A/O) of 1.0, the volumetric flow rate of both phases was equal for all experiments. The total flow rates were set at 24, 60, 120, 240, 360, 480 ml/h for 300, 120, 60, 30, 20, 15 s of the residence time in the CFI, respectively. For generation of segment flows, the two-phase liquids were joined in an orthogonal T-type joint (1/16” ID), shown in [Fig. 1b](#). The stable segment flow and droplet size was controlled by the flow rates. A coiled flow inverter(CFI) made with a PFA (perfluoroalkoxy) capillary tube (1 mm ID and 2.5m length), which was coiled around a 5mm OD stainless steel cylindrical bar that was welded to make a square shape, was used as the extraction microreactor, shown in [Fig. 1c](#). With the square shape, 90° bends were introduced and it enabled the direction of the centrifugal forces to change 4 times resulting more efficient mixing.

At the end of the CFI outlet the two phases were separated immediately by a micro-scale slit separator as described previously[33], shown in [Fig. 2](#). The separator consisted of a slit between two glass bars and a slit between two Teflon bars, assembled in a stainless steel housing. Separation was achieved based on the different wetting properties of the liquids on bars material. A continuous two phase separation

was expected to be possible with this configuration at all flow rates, where a pure green aqueous phase was obtained from the glass outlet and the blue organic phase from the Teflon outlet.

Fig.1 (a)Schematic diagram of the micro-flow extraction system, (b)T-type joint for segment generation, (c)Design

parameters of CFI structure[44], d_i -inner tube diameter, 1mm, d_{ct} -coil tube diameter used as supporting structure,

5mm, d_c -coil diameter, about 7mm, L_c -length of a single coil, 66.5 mm.

To study the microflow patterns, high speed imaging system was used. The equal aqueous and organic phase were fed as the total flow rates were in the range of 24-480 ml/h. As stable flow regime was achieved, flow patterns were recorded by MotionPro X3 high speed camera. The camera was placed at a set distance from the CFI inlet and outlet to take unambiguous pictures. Two lamps were placed as light source. Image analysis was carried out with MotionPro software in a computer.

In comparison, batch solvent extraction experiments (hereinafter termed “batch”) were accordingly carried out at room temperature by equilibrating equal volumes of 20 ml of organic and aqueous phase for different residence time using a mechanical shaker (Lab-line instruments, Inc.). Then the loaded extract phase and the raffinate phase were separated gravimetrically in the separating funnel for 30 min to get perfectly clear lower aqueous phase and upper loaded organic phase, and each aqueous phase was removed for concentration analysis.

Fig. 2 (a) the micro-scale slit separator, and (b) inside view and size of the separator [33].

2.3. Calculation of extraction and separation efficiency

In order to compare the extraction and separation efficiency, extraction ratio (E), distribution ratio (D), and separation factor ($\beta_{Co/Ni}$) were introduced as follows.

The extraction ratio (E), defined as the metal ion concentration in the organic phase to that in the feed aqueous phase, was generally represented by the following equation (1):

$$E(\%) = \frac{[M]_{org}}{[M]_{aq_o}} \times 100 = \frac{[M]_{aq_o} - [M]_{aq}}{[M]_{aq_o}} \times 100 \quad (1)$$

Where [M] represented the metal ions concentrations, the subscript org, aq_o , and aq

denotes organic phase, aqueous phase before and after extraction, respectively.

The distribution coefficient (D), defined as the ratio of the metal ion concentration in the organic phase to that in the aqueous phase after extraction, was represented by the following equation (2):

$$D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} = \frac{[M]_{\text{aq}_o} - [M]_{\text{aq}}}{[M]_{\text{aq}}} \quad (2)$$

The separation efficiency of Co from Ni in aqueous phase is described by the separation factor ($\beta_{\text{Co/Ni}}$), defined as one distribution coefficient divided by another:

$$\beta_{\text{Co/Ni}} = \frac{D_{\text{Co}}}{D_{\text{Ni}}} = \frac{[Co]_{\text{aq}_o} - [Co]_{\text{aq}}}{[Co]_{\text{aq}}} \times \frac{[Ni]_{\text{aq}}}{[Ni]_{\text{aq}_o} - [Ni]_{\text{aq}}} \quad (3)$$

3. Results and discussion

3.1. Effect of equilibrium pH

The effect of equilibrium pH (pH_{eq}) on the extraction and separation of Co from Ni sulfate solutions was investigated. The total flow rate was 240 ml/min corresponding to 30 s residence time in micro-flow. 10 min was required to achieve batch extraction equilibrium. Thus, three cases, including micro-flow of 30s, batch of 10 min and batch of 30s were compared here. Complex formation and extraction of Co and Ni were carried out by 20 % v/v Cyanex 272 varying the pH_{eq} , i.e. adjusting the pre-neutralization rates of Cyanex 272 from 0~60% stepped by 10%. The extraction mechanism for Co and Ni can be described by the following extraction equilibrium equations.

The pre-neutralization reaction was given in equation (4):

Where H_2A_2 represented the Cyanex 272 extractant dimer.

The sodium ions in the extractant were replaced by cobalt and nickel ion according to the following reactions:

Once the sodium ions have been replaced, extraction of Co and Ni took place by the following reactions[47,48]:

Co(II) extraction (Equation (5) and (7)) was implemented in preference to Ni(II) (Equation (6) and (8)) by the given extractant Cyanex 272, due to the geometric differences between the Co(II) and Ni(II) extracted complexes, which forms complexes of tetrahedral symmetry with cobalt and of octahedral symmetry with nickel.

The relationship between the different neutralization level and pH_{eq} after extraction is shown in Fig. 3. pH_{eq} significantly increases with higher pre-neutralization level. In the case of the un-neutralized organic phase, the pH_{eq} sharply reduces from initial 4.43 into about 3.2 after extraction due to lots of H^{+} release via proton-exchange reactions in Equation (7) and (8). As the pre-neutralization level is increased from 10 to 40%, the order of pH_{eq} in three cases was batch of 10 min > micro-flow of 30 s > batch of 30s. With further increasing of

pre-neutralization level from 50 to 60%, the pH_{eq} became closer in batch of 10 min and micro-flow of 30 s indicated easier achievement of extraction saturation of metal ions, but bigger gap between micro-flow of 30 s and batch of 30 s. Thereby, the extraction efficiency was ultimately affected by the pH_{eq} .

Fig.3 Effect of the pre-neutralization level on the equilibrium pH after extraction, using 20% v/v

Cyanex272 with different pre-neutralization level as the organic phases.

Fig. 4a represents the effect of pH_{eq} on the extraction ratio (E) of Co and Ni. As the extraction of the metal ions with a mixture of sodium salt and un-neutralized acid proceeds by a proton-exchange reaction, the extraction is pH dependent both in micro-flow and batch. The preferred selectivity and extractability was exhibited towards Co over Ni at different pH_{eq} , and the extraction of metal ions was favorable at high pH_{eq} . This means that Co can be easily separated from Ni. As observed in the case of micro-flow, the extracted amount of Co greatly increases from 2.13 to 97.54% when the pH_{eq} is increased from 3.23 to 5.82 and then the extraction ratio becomes constant. The co-extraction of Ni also increases from 2.31 to 13.19% as pH_{eq} is increased from 3.23 to 6.45. The similar results were also observed in other two cases

of batch.

Fig. 4b shows how the separation factor $\beta_{\text{Co/Ni}}$ either increases to a peak and then declines in all the cases. Part of this effect can be explained by the fact that as the pH_{eq} increased, the cobalt loading increases obviously over the nickel loading. The drop in separation factor at higher pH is probably due to cobalt depletion of the aqueous while continuously increasing nickel loading. The pH must, therefore, be optimized for a certain set of solution conditions to give the maximum cobalt and nickel separation. Therefore the appropriate pH_{eq} is set as 5.8-5.9, i.e. 40 wt% Cyanex 272 is pre-neutralized in the following experiments.

Fig. 4 Effect of the equilibrium pH on the extraction efficiency of Co and Ni, (a) extraction ratio, and (b) separation factor between Co and Ni, using 20% v/v Cyanex272 with different pre-neutralization level as organic phases.

As compared the three cases, at the same 30 s residence time, the extraction and separation efficiency of micro-flow is much better than that of batch, which the maximum extraction ratio of Co and separation factor are 97.75% and 401 for micro-flow, and 83.53% and 48 for batch, respectively. With increasing the residence time of batch up to 10 min, the extraction efficiency is only slightly superior than that

of micro-flow at low pH_{eq} conditions, but the opposite results can be obtained at high pH_{eq} (>5.8). The extraction equilibrium is much more quickly reached in micro-flow than that in batch. This is because the larger interfacial area and shorter diffusion distance result in enhanced mass transfer in liquid-liquid segmented microflow processes.

3.2. Effect of residence time

As commonly and conveniently done, residence time was controlled by setting different flow rates of liquid-liquid phases in CFI. The effect of residence time on the extraction efficiency is shown in [Fig. 5 a](#) and [b](#). It can be seen from [Fig. 5a](#) that in the case of micro-flow, the residence time had little effect on the extraction efficiency. The extraction equilibrium of Co and Ni is rapidly attained. 96.7% of Co and 6.3% of Ni at 15s and 97.6% of Co and 6.7% of Ni at 60s respectively are extracted into organic phase in micro-flow. However, in the case of the corresponding batch, the extraction ratio of Co is obviously influenced by the residence time before it reached the plateau at 300s, whereas the co-extraction of Ni is also continuously increased with the increasing of residence time. This indicates that the extraction kinetics of the batch are much slower than that in the micro-flow system.

Fig. 5 Effect of residence time on the extraction efficiency of Co and Ni, (a) extraction ratio, and (b) separation

factor between Co and Ni, using 20 v/v % Cyanex272 with 40% pre-neutralization

Additionally, in view of the high concentration of Co and Ni sulfate system, it is remarkable that the metal ions could be quantitatively extracted into organic phase by a certain amount of extractant. The higher extraction of one metal would eventually lead to the lower extraction of other metals. Therefore, a higher Co extraction and lower Ni co-extraction can be achieved in micro-flow. It leads to a much better separation factor in micro-flow than that in batch, as shown in Fig. 5b. The $\beta_{\text{Co/Ni}}$ was achieved to 748 at 60 s in micro-flow, while 426 at 600s in batch.

According to the results of extraction ratio and separation factor, a residence time of 60s was determined as the best contacting time for separation of Co from Ni in micro-flow. However, more than 450 s is required to reach the extraction equilibrium in batch.

3.3. Effect of the extractant concentration in the organic phase

The amount of the valuable extractant would be desirable to be reduced for costs saving. Therefore, the effects of the different Cyanex272 concentration varying in

5~25 % v/v were investigated. The results are shown in Fig. 6 a and b. As shown in Fig. 6a, a better extraction ratio of Co in micro-flow than in batch is obtained at any extractant concentration. In contrast, the co-extraction of Ni is slightly less severe in micro-flow than that in batch. When increasing Cyanex 272 concentration from 5 to 15% v/v, the extraction ratio of Co raises from 62.6 to 96.9% in micro-flow. But with further enhancing of Cyanex 272 above 15% v/v, the increase of Co extraction ratio becomes a plateau, wherein Ni extraction ratio increases linearly with increasing extractant concentration. The same trend is also observed in batch.

Similarly, both in micro-flow and batch, the separation factor obviously increases until the extractant concentration reached up to 15 % v/v with the notable increase of Co extraction. This factor slows down as the co-extraction of Ni became more and more severe, shown in Fig. 6b. Preston[49] demonstrated that the composition of the nickel complex varies among the different extractant concentrations but the stoichiometry of the cobalt complexes formed all refer to the stable $\text{Co}(\text{HA}_2)_2$ tetrahedral symmetry. With further increasing extractant concentration, the following reaction is likely to occur:

Where $x=0, 1$ or 2 , correspond to low, moderate and high concentrations, respectively. The incorporation of additional H_2A_2 molecules into the nickel complex results in a higher-order dependence of metal distribution upon extractant concentration than is the case for cobalt. In consequence, for decreasing Co-Ni separations were observed

as the extractant concentration was further increased. The maximum separation factor of 775 in micro-flow and 383 in batch is then reached.

Fig. 6 Effect of extractant concentration on the extraction efficiency of Co and Ni, (a) extraction ratio, and (b)

separation factor between Co and Ni, 40% pre-neutralization of Cyanex272 and 60s residence time.

3.4. Liquid-liquid flow patterns

As described in the foregoing experimental section, a series of segment of two immiscible liquid-liquid phases occurs through a T-type joint and then transmits into the CFI of 1 mm diameter. Fig. 7a shows the flow patterns of the two phases through the inlet and outlet of CFI at different flow rates. As the CFI tube is made of PFA, a hydrophobic material, the inner walls of the tube are wetted by organic thin films, and the aqueous droplets dispersed in intervals. An alternating sequence of uniform columnar slugs are formed at lower flow rates (≤ 360 ml/h), and in- and outlet flows match, i.e. there is no change in the flow pattern when passing the CFI. Good mixing between the interface of the two immiscible phases is obtained due to internal circulation within the slugs. However, as the flow rates are set at and above 420 ml/h, disordered and uneven distribution of slugs dominates in the CFI tube. Deviations

from the ideal pattern are found and in- and outlet flow do not match due to the disorder of the slugs.

(a)

(b)

Fig. 7 (a) Flow Patterns and (b) Aqueous slug length of inlet CFI of 1 mm diameter at different flow velocity, using 20% v/v CYANEX 272 with 40% pre-neutralization.

Fig. 7b shows the average aqueous slug length at different flow rates. For the regular slug flow (≤ 360 ml/h), the inlet lengths of the slug is found to be a Gaussian function of the flow rates. At low flow rates between 12 and 180 ml/h, the inlet slug

length slowly increases with the increasing flow rates gradually from 1.85 to 2.10 mm. The longest slug is up to 3.87 mm as the flow rate increases to 240 ml/h. Then, the slug length decreases conversely with further increasing of flow rates from 240 to 360 ml/h. The shorter slug length indicates a larger ratio of the interface area to the volume of the aqueous and organic phases, which improves the extraction equilibrium.

3.5. Mass transfer characteristic in segmented flow

For the evaluation of the performance of liquid-liquid mass transfer in segmented microflow, the mass transfer coefficient is conveniently taken as parameter. The transfer rate of metal ions between the slugs can be written as follows:

$$\frac{dC}{dt} = k \cdot A \cdot \Delta C \quad (10)$$

Where ΔC is the concentration differential between the organic and aqueous slugs, mol/l. A is the specific surface area, m^{-1} . k is the mass transfer coefficient, $mm \cdot s^{-1}$. C and t are chemical concentration, mol/l, and transfer time, s, respectively. The concentration differential between the slugs can be written as:

$$\Delta C = C_{org} - C_{aq} \approx C_{org} \quad (11)$$

Combining the equation (10) and (11) leads to the following equation:

$$\frac{dC_{org}}{dt} = -K \cdot A \cdot C_{org} \quad (12)$$

According to the slug flow patterns in [Fig. 7a](#), only the ends of the slugs participated in the mass transfer. The slugs were considered as regular cylinder. Therefore, the specific surface area could be assumed as:

$$A = \frac{2S}{V} = \frac{2\pi(\frac{D}{2})^2}{\pi(\frac{D}{2})^2 \cdot L} = \frac{2}{L} \quad (13)$$

Where S is the interfacial area of one end of the slug, m². V is the slug volume, m³. D is the channel width, m. L is the slug length, m.

Combining the equation (12) and (13), the mass transfer coefficient k can be proposed as:

$$k = -\frac{L}{2t} \ln(1 - \alpha) \quad (14)$$

where α is proportion of metal ion extracted, dimensionless.

Based on equation (14), the mass transfer coefficient for the segmented flow can be calculated, and the results are shown in Fig. 8. The mass transfer coefficient in the range of 0.014 to 0.24 mm·s⁻¹ is obtained at total flow rates from 24 to 240 ml/h, with higher value corresponding to the faster flow rates. Then, it reduces to 0.19 mm/s at 360ml/h.

Fig. 8 Mass transfer coefficient at different flow rates

4. Conclusions

The segmented micro-flow extraction and separation of Co from Ni sulfate

solution with Cyanex 272 has been successfully developed in a micro-scale coiled flow inverter. Continuous operation of a process involving liquid-liquid extraction and then two-phase separation is achieved in this study. For the latter a micro-scale split separator was used. The effects of equilibrium pH of aqueous phase, residence time and extractant concentration on the extraction efficiency were investigated. A very short residence time of 60 s, 15% v/v Cyanex 272 with 40% pre-neutralization is utilized in micro-flow extraction system. 96.9% of Co can be extracted into the organic phase and the separation factor is up to 775. Compared to batch extraction, a more effective extracting process with better extraction ratio for Co over Ni and higher separation factor have been demonstrated in this micro-flow system.

Additionally, flow patterns were recorded in the CFI by a high speed camera. An alternating sequence of uniform columnar slugs were formed at lower flow rates (≤ 360 ml/h), and the length of the inlet slug was found to be a Gaussian function of the flow rates. In- and outlet flows match, i.e. there is no change in the flow pattern when passing the CFI. At higher flow rates, deviations from the ideal pattern are found and in- and outlet flow do not match.

It is discussed how the flow rates of two immiscible phases affect the flow patterns and slug length, and ultimately influence the mass transfer coefficient. The mass transfer coefficient is in the range of 0.014 to $0.24 \text{ mm}\cdot\text{s}^{-1}$.

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