Chemical Engineering Journal 293 (2016) 273–280

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Milli-channel mixer and phase separator for solvent extraction of rare earth elements

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HIGHLIGHTS

- An intensification study was performed on a rare earth elements recycling process.
- A membrane phase separator was adapted for liquid–liquid metal solvent extraction.
- Milli-mixer–separator decreased the required residence time down by 120 times.
- A design of experiments tool was utilized to optimize the process parameters.
- It was shown that lower phase ratio and higher pH enhance separation performance.

ARTICLE INFO

Article history:
Received 19 November 2015
Received in revised form 26 January 2016
Accepted 19 February 2016
Available online 27 February 2016

Keywords:
Solvent extraction
Rare earths
Millireactor
Process intensification
Phase contacting
Separation design

ABSTRACT

A process intensification study was performed on the standard mixer–settler unit used in recycling of rare earth elements (REE) in lamp phosphors. A phase separation design was constructed to operate coupled to a milli-channel mixer. For this particular design, the phase separation is not driven by differences in density but by differences in wetting and pressure drop across a hydrophobic membrane. The phase separation device was selected since it is easier to scale than other devices seen in literature. The device was shown to decrease the passage time required to separate the phases. The whole mixing and phase separation process was completed in 10–20 s in contrast to ~25 min observed in mixer–settlers used in industry. A full factorial parametric study was also performed to observe how the distribution coefficients and separation coefficient (S) of the REE species as well as the time needed for phase separation (τ) is affected by the REE concentration, organic to aqueous phase ratio and initial pH of the REE solution. Results of parametric studies show that the S values vary between 50 and 3 while τ values vary between 17 s and 5 s. The results also show that increasing phase ratio has a desired decreasing effect on τ but also decreases S, which is undesired. An optimization calculation was also performed to illustrate the tradeoff between S and τ.

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1. Introduction

1.1. Background

Rare earth elements (REE) are among the natural resources for which the market demand is increasing rapidly [1]. This demand is particularly due to green energy applications (e.g. magnets in wind turbines) and high-tech (e.g. batteries) uses of these metals. Currently, more than 90% of the REE is supplied from China [2]. In addition to the effort to ease this monopoly scenario, for decreasing the environmental effects of REE mining, recycling of these materials is a vital step [2]. As of 2015, the biggest markets for REE are the permanent magnet and lamp phosphors (LP) [3] and it is estimated that less than 1% of the LP is being recycled [4].

The recycling scheme of LP involves mechanical separation of the phosphor powder from lamps, followed by acid leaching and solvent extraction of the REE in the leachate [5]. The solvent extraction step is particularly important for the final product purity and it is a low-yield process consisting of multiple steps of mixing and settling [6].

This works considers the case of *Y* and *Eu* mixtures since these two elements are found in high concentrations in LP wastes, particularly in *Eu* doped Y_2O_3 (YOX) red lamp phosphors [4]. It is known that acidic complexing agents, particularly the bis-2-ethylhexyl phosphoric acid (DEHPA) yields relatively high selectivity between the REE [7]. The solvent extraction equilibrium with acidic complexing agents can be given as [8,9]

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http://dx.doi.org/10.1016/j.cej.2016.02.083
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$$M^{3+} + 3\overline{(RH)}_2 \rightleftarrows \overline{MR_3(RH)_3} + 3H^+ \qquad (1)$$

where M is the trivalent metal ion, R is the acidic complexing agent which exists in $\overline{(RH)}_2$ dimers dissolved in organic phase, for which kerosene or dodecane is commonly used as the solvent. It can be seen from Eq. (1) that the process is, in essence, a cation exchange equilibrium by a weak carboxylic acid. Another important aspect of working with DEHPA is that it is a surfactant [10]. Since DEHPA decreases the surface tension between organic and aqueous phases, it makes the emulsions created in the mixing units more stable which requires longer residence time in the settling chambers to separate. This also decreases the efficiency of the mixing–settling unit. Since the time spent in settling has no role in the mass transfer, it is better to shorten it or, ideally, to avoid it. Therefore the process intensification task for the industrial mixer–settler can be summarized with the following two aims:

1. Reducing settling time or eliminating the need for gravity settling.
2. Maintaining and/or intensifying the surface generation and high mass transfer rate.

The following section sets the industry standard mixer–settler as a benchmark and investigates how the previous process intensification efforts attacked the aims stated above, comparing the resulting designs to the industrial throughput and yield.

1.2. State of the art

In a mixer–settler patent filed in 2007, Zhang defines the passage time of a single mixer–settler unit to vary between 13 and 80 min [11]. The same patent claim states that the mixer passage time varies between 3 and 20 min while the settling passage time is three times that of the mixing passage. For this work, the daily throughput of an industrial mixer–settler is assumed to be 30 $m^3\,d^{-1}$. The total volume was considered to be 400 L (100 L mixer and 300 L settler) and total passage time was assumed 19 min which falls within the limits claimed by the patent. The space–time yield (STY) of a standard mixer–settler unit is therefore 75 L of total throughput per every litre of mixer–settler volume per day ($L\,L^{-1}\,d^{-1}$). The STY values which will be reported in this section are calculated via the following relation:

$$\mathrm{STY} = \frac{V_R}{\tau} = \frac{1\ \mathrm{L}}{\tau} \qquad (2)$$

where, V_R is the unit volume the reactor is normalized to and τ is the passage time in days. The V_R was selected as 1 L for this work so the STY relation yields the ($L\,L^{-1}\,d^{-1}$) units. As shown in Fig. 1, two main strategies have been followed for the process intensification of metal solvent extraction.

The first strategy aims at addressing the settling problem by complete elimination of the settling step using laminating flow regime. Nishihama et al. [8] were the first to perform the metal solvent extraction in a microfluidic chip. The chip worked by contacting the two phases cocurrently by a *Y* joint without causing any chaotic advection or vorticity. The two laminating phases were separated by a symmetrical *Y* separator. The characteristic thickness of the used chip was 200 μm (100 μm for each phase). The chip (actually) succeeded in elimination of settling and the overall residence time was 30 s to reach equilibrium. This resulted in a STY of 2880 ($L\,L^{-1}\,d^{-1}$), which indicates that a bundle of more than 400,000 chips that make up a total volume of 10 L can have a throughput close to the industrial mixer–settler unit. A more recent example of this design was introduced by Yin et al. [12] which had a characteristic length of 160 μm (80 μm for each phase) and a volume of 0.6 μL (Fig. 1a). The residence time used in this chip (by the authors) was 0.37 s resulting in a STY of 416,000 ($L\,L^{-1}\,d^{-1}$). The STY indicates that if these chips were to be numbered up 220,000 times, they would make up a total volume of 0.14 L and the total mass flow would be enough for the throughput of an industrial unit.

In addition to the disadvantage of requiring a bundle of 10^5 chips, the flow obtained in these chips is very sensitive to phase ratio variations and, in case of slight distribution errors and/or fouling in only a few inlets, the phase ratio of the entire bundle can be affected. These disadvantages limit the flexibility and make the use of these designs very difficult for high throughput applications such as REE separations.

The second strategy pursued for mixer–settler intensification is to use chaotic advection for better mass transfer. Kumar et al. have used slug flow through a microchannel of 100 μm coupled to a 2 mL gravity settler (Fig. 1b) [13]. Slug flow, due to the induced vortices in each slug, is known to renew mass transfer surfaces and enhance mass transfer compared to the laminating mixers such as the first two designs. Kumar et al.'s setup decreased the required residence time down to 180 s which corresponds to a STY of 480 ($L\,L^{-1}\,d^{-1}$). The required volume for this system to achieve industrial throughput is 62.5 L which is significantly higher than other microchannel units in comparison. The reason is the gravity settler coupled to the mixer. This unit adds additional residence time, however does not contribute to the mass transport. Necessity of this settling unit is due to the slug flow regime in the mixing part of the design. This flow regime is not diffusion limited like the laminating flow obtained in the previous design, however requires more cumbersome phase separation. The volume of this system is 2.4 mL therefore, 26,000 of these mixer–settler units are required to be bundled for REE separation on the industrial scale.

A bundle of thousands of microchannels is, in fact, not unrealistic. Based on Kumar et al.'s design, a monolith of 200 × 200 channels can form a mixing unit of almost twice the required throughput. However, scaling out the micro settler with the interface control system is the main problem. Therefore, the design can be a good solution for actinide separation (the actual proposed use by the authors) which (supposedly) has a lower throughput requirement, however for the REE separation, the scale-up of micro-settler part of the system seems unrealistic.

Since both strategies for eliminating or intensifying the phase separator, are difficult to scale-up to industrial throughput, a different, easy to scale up, concept which can adapt to the varying process parameters such as phase ratio, pH and feed concentration has to be developed.

This work focuses on a membrane phase separation device which was first designed by Kralj et al. [14] in micro scale (25 μL min^{-1} throughput). The device was coupled to a microfluidic chip and proven effective for Suzuki–Miyaura cross coupling reactions [15]. This design can be fitted with an automatic back pressure control system which enables failsafe operation [16]. There are also commercial versions of the unit with various operation flow rate capacities sold under the name of Zaiput© Flow Technologies [17].

The aim of this work is to scale the unit from micro-scale to milli-scale working at mL min^{-1} throughput, to prove that this new design can operate for REE solvent extraction under varying operating conditions and to calculate the operating window for these variations.

2. Experimental

2.1. Materials and methods

The organic phase is prepared by dissolving DEHPA (98%) (VWR) in dodecane. The DEHPA concentration was varied

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