



ENVIREE

ENVironmentally friendly and efficient methods for extraction of Rare Earth Elements from secondary sources

DELIVERABLE D3.4: REPORT ON THE PERSPECTIVES OF SEPARATION OF REE BY MEMBRANE PROCESSES

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1 EXECUTIVE SUMMARY

The deliverable *Report on the perspectives of separation of REE by membrane processes* reflects the author's view on the applicability of membrane based solvent extraction for the recovery of rare earth elements (REE) from secondary sources.

The literature claims several advantages for performing solvent extraction using membrane devices rather than conventional solvent extraction equipment. Not all of them stand up to closer inspection. While numerous papers report laboratory studies on membrane based solvent extraction for the recovery and purification of metals, this technique seems not to be applied on an industry scale. However, only an industry application can help judging its perspectives.

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2 INTRODUCTION

ENVIREE's main goal is the development of *environmentally friendly* and *efficient* methods for the recovery of rare earth elements from secondary sources such as mine tailings. This covers aspects of prospection, minerals beneficiation, leaching of metal ions from beneficiated minerals and finally their purification. A suitable means of purification is solvent extraction.

Solvent extraction is a widely-used technique for separating and purifying ionic species. It is applied on an industrial level e.g. for the reprocessing of spent nuclear fuels by the PUREX process¹ and for the large-scale copper production by the SX/EW (solvent extraction, electrowinning) technique.²

Principle: In a first step (“extraction”), an ionic solute in an aqueous phase forms a complex with a complexing agent present in an immiscible organic phase. This complex is preferentially soluble in the organic phase; the solute is being extracted. This way, the solute is separated from other solutes not forming complexes with the complexing agent. In a second step (“back-extraction” or “stripping”), the solute is transferred from the organic phase back into a different aqueous phase; the organic phase can be recycled to a new extraction step.

Technological application: To achieve reasonably fast mass transfer, a large specific interfacial area between the organic and the aqueous phase is required. This is usually achieved by mechanical energy input, forming an emulsion of small droplets of one phase in the other phase. Furthermore, a technological application of solvent extraction requires continuous operation. Finally, since the chemistry involved usually does not exhibit sufficient selectivity to achieve a desired purity and recovery in a single step, multi-stage equipment has to be utilised.

Solvent extraction equipment: Further to some exotic equipment, three types of devices are used for continuous counter-current solvent extraction: mixer-settlers, centrifugal contactors and column contactors.

A *mixer-settler* consists of a stirred tank to create the emulsion by means of an impeller. Mass transfer takes place during the emulsion's residence time in the stirred tank. The emulsion then flows into the settler, where the phases disengage by coalescence and gravity settling.

Centrifugal contactors create an emulsion by shear forces and separate the phases by centrifugal force. One example is the annular centrifugal contactor: the emulsion is formed in the annular gap between a stator bowl and a hollow rotor placed inside the stator. The emulsion flows through a bore in the bottom of the rotor into its inside, where phases quickly separate by centrifugal force.

By interconnecting a number of mixer-settlers or centrifugal contactors, a multi-stage counter-current rig is established.

A *column contactor* in its most simple form is a vertical tube with one phase (the “continuous phase”) flowing in one direction and the other phase (the “dispersed phase”) flowing counter-currently in the form of droplets. Depending on whether the dispersed phase has a lower or higher density than the continuous phase, the droplets rise or fall while the continuous phase flows downstream or upstream. To increase mass transfer, the tube usually contains packing, plates or sieve trays.

Further details on solvent extraction principle, applications, processes and equipment are found in textbooks.³⁻⁵

3 MEMBRANES IN SOLVENT EXTRACTION

The aqueous effluents from any solvent extraction equipment inherently contain a small fraction of the organic phase. This contamination is due to (a) fine organic phase droplets not being separated in the gravity field (so-called entrainment) and (b) the partial solubility of the organic phase's components in the aqueous effluent phases. While the former is mainly governed by the design and operation of the equipment, the latter is intrinsic to the aqueous and organic phase compositions.

Such contamination evidently conflicts ENVIREE's "environmentally friendly" approach — membrane based solvent extraction offers a solution.

3.1 Principle and claimed advantages

The basic principle of a membrane based solvent extraction process is (a) placing a porous membrane between the organic and aqueous phases, immobilising the organic-aqueous interface in the membrane pores or (b) immobilising the organic phase in the pores and contacting the membrane on one side with the aqueous feed phase and on the other side with an aqueous receiving phase (so-called supported liquid membrane, SLM).

With operating mode (a), a membrane contactor operates more or less like a conventional column-type solvent extraction contactor (see above), requiring individual contactors for extraction and back-extraction. Operating mode (b) combines extraction and back-extraction in one device.

Usually, to achieve a substantially large specific interfacial area, a bundle of thin hollow fibre membranes (a so-called hollow fibre module, HFM) is used rather than flat sheet membranes. Nevertheless, stacks of flat sheet membranes may also be used.

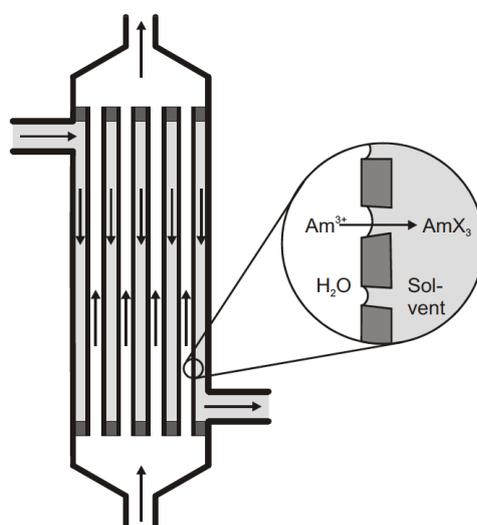


Figure 1. A HFM used as a counter-current solvent extraction contactor. In this example, the aqueous phase flows in the lumen of the fibres, the organic phase flows counter-currently on the shell-side. The hydrophobic membrane material is wetted by the organic phase; the interface is stabilised inside the pores by applying a small over-pressure to the aqueous phase.

Contrary to common equipment, flow rates in membrane based solvent extraction contactors are essentially not confined by hydrodynamic restrictions. This offers several advantages:

- No entrainment is generated
- Flow rates can be adjusted independently of one another, permitting volume reduction
- No density difference is required for phase separation
- Systems having low interfacial tension or high viscosities can be processed

An additional advantage claimed for the SLM mode is the very low volume of organic phase, being as low as the pore volume of the membranes used. However, the organic phase will be

washed out during long term operation, turning the claimed advantage into a drawback. This can be overcome by a continuous re-impregnation of the membrane.⁶ A further drawback of the SLM configuration is the fact that the organic phase flow rate cannot be adjusted, meaning that one degree of freedom for process optimisation is lost.

3.2 Do the claimed advantages hold up?

3.2.1 No entrainment is generated

Since organic and aqueous phases are macroscopically separated by the membrane material, no entrainment is generated with membrane-based solvent extraction. Organic contamination of aqueous effluents is thus limited to the solubility of organic phase components in the respective aqueous phases.

Depending on the amount of entrainment tolerable for a certain application, further treatment of aqueous effluents may be required when using conventional solvent extraction equipment.

3.2.2 Flow rates can be adjusted independently of one another, permitting volume reduction

Extreme phase ratios (i.e. aqueous-to-organic flow rate ratios) are feasible with membrane based solvent extraction. This is advantageous if the concentration of the solute to be recovered is low: e.g. an increase in Zn(II) concentration of approximately three orders of magnitude was demonstrated.⁷⁻⁸ Theoretically, the flow rate of one of the phases could approach zero, resulting in a phase ratio approaching infinity. However, the phase ratio is also limited by the capacity of the receiving phase.

Extreme phase ratios are also viable in conventional contactors. E.g. Asymmetric Rotating Disc (ARD) columns can handle phase ratios in the range of 0.01–100,⁹ meaning that a volume reduction of up to 10^4 would be feasible when performing extraction and stripping in ARD columns.

A way of attaining phase ratios which otherwise are not viable in a given contactor is internal recycling. This means that a certain fraction of the phase moving at the lower flow rate is recycled back to the entrance section.

3.2.3 No density difference is required for phase separation

Again, this is true for membrane-based solvent extraction. Any kind of classical equipment requires a density difference to separate the phases. But does this advantage have any practical relevance? In most cases, no: aqueous phase densities are in the range of 1000–1200 kg/m³ while organic phase densities are in the range of 750–950 kg/m³ (or 1100–1400 kg/m³ if “heavy” organic diluents are used). An exemption would be very high loading of an organic phase which already has a small density difference towards the aqueous phase.

3.2.4 Systems having low interfacial tension or high viscosities can be processed

If a two-phase liquid-liquid system has very low interfacial tension and/or if one (or both) of the phases has unusually high viscosity phase separation by gravity or centrifugal settling may become very slow. This in turn will reduce the feasible throughput, requiring larger equipment for a given flow rate.

Basically, membrane based solvent extraction is less sensitive to low interfacial tension or high viscosity due to the phase being separated by the membrane.

3.2.5 Verdict

Of the claimed advantages—absence of entrainment, volume reduction, no density difference required, ability of handling systems with low interfacial tension or high viscosities—only the

first and (to some extent) the last one support the application of membrane based solvent extraction.

3.3 A glance at the literature

3.3.1 Laboratory studies

The major part of literature on membrane based solvent extraction reports SLM studies and/or studies where phases were recycled and the concentration evolution in the reservoirs was determined. Considering this, its relevance to this deliverable report is limited. Furthermore, a large share of this work is of rather low quality. For these reasons, no comprehensive literature review is given.

An excellent piece of work from as early as 1984¹⁰ reports the use of two HFM for a continuous coupled extraction/back-extraction setup. The feed and the strip phases were operated in a once-through mode, the organic phase was recycled, mimicking a practical application.

Using a one-through setup with only one module, the extraction of Zn(II) was studied, performing separate extraction and back-extraction experiments.⁷⁻⁸ Larger HFM were used, realising feed flow rates of up to 200 L/h. With phase ratios of > 100 (feed/organic) and 10 (organic/strip phases), a volume reduction (and hence, increase in Zn(II) concentration) of ≈ 1000 was achieved. Experiments were accompanied by predictive mass transfer calculations. This setup was later expanded, using two coupled HFM for extraction and back-extraction.¹¹ Also, the co-extraction/separation of various metal ions in a single HFM was studied.¹²⁻¹³

To process small volumes and to use non-commercial extracting agents, miniature HFM were fabricated, consisting of 50–100 hollow fibres.¹⁴ By coupling several miniature HFM to perform extraction, scrubbing and back-extraction, various versions of a HFM micro-plant were built. Such HFM micro-plants were used for lanthanides separation¹⁵ and for separating trivalent actinide and lanthanides from PUREX raffinate by the DIAMEX process.¹⁶

Using a HFM micro-plant, a feed solution containing each 100 mg/L Pr(III) and Nd(III) was treated to separate the two Ln(III) from one another using the HDEHP extracting agent. Flow rates were in the range of 2 mL/h. The raffinate (which should contain mainly Pr(III) as it is less extracted by HDEHP than is Eu(III)) contained $\approx 96\%$ Pr(III) and $\approx 2\%$ Eu(III) while the product contained $\approx 3\%$ Pr(III) and $\approx 84\%$ Eu(III). The spent solvent contained $\approx 0.3\%$ Pr(III) and $\approx 15\%$ Eu(III). Calculations predicted that reducing the scrub and solvent flow rates to ≈ 0.5 mL/h and adjusting the acidity of the scrub solution would yield recoveries of $> 99.9\%$.¹⁵

3.3.2 Real-world applications

While membrane modules are used for applications such as water gasification, degasification and purification and for food and biopharmaceutical applications, the scientific literature does not reveal evidence for an application of membrane based solvent extraction of metal ions in an *industry* environment. There *may* be applications in an industrial environment which go unnoticed because unpublished. However, talking to people from industry involved in solvent extraction, no one expressed a positive attitude towards applying membrane based solvent extraction.

Prior to an industrial application, long-term performance must be assessed. Even such studies are scarce. One example, the stability of a continuously re-impregnated SLM containing a HDEHP solvent was demonstrated over almost 5000 h of operation.⁶

3.4 Own experience

Having performed many dozens solvent extraction runs using HFM, it is noteworthy that, despite using laboratory conditions and clean, filtered solutions, not all tests were successful. In

some cases, aqueous phase broke through the membrane pores despite using low trans-membrane pressure differences. This sometimes happened during start-up (which could be fixed by replacing the respective module) but occasionally was encountered during the run. A further problem encountered several times was a slow but steady decrease of mass transfer efficiency over the course of an experiment. A possible explanation is the formation of a precipitate or crud layer at the interface, i.e. in the membrane pores. The clogging of pores by solids contained in the feed solutions would be an explanation in a real-world application but can be excluded for the laboratory environment in which the experiments were performed.

4 CONCLUSIONS

Many advantages of membrane based solvent extraction are being claimed in the scientific literature. Nevertheless, this technique does not seem to have ever replaced conventional solvent extraction equipment.

Carrying out more studies in a laboratory environment will not lead to breakthrough development in the field. Only real industry applications could give an — albeit predictable — answer. The predictability of this answer is what seems to keep industry from even trying.

All told, the *perspectives of separation of REE by membrane processes* are not very promising.

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