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An instrumented microfluidic tool for complex fluid phase diagram determination:  
Enabling in-line and real-time screening of solvent extraction processes.

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Keywords: Solvent extraction, rare earth, phase diagram, screening, process development, recycling

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## 1 Scientific and technological background: Solvent extraction of metal ions and circular economy

If Richard Feynman is often cited as a pioneer in Nanosciences, one should also cite Glenn Seaborg, 1951's Nobel prize in chemistry who stated in 1980 in a visionary conference that: « In the future, chemistry will be called upon to extend our natural resources of copper, lead, zinc, and other non-ferrous metals by making it possible to recover these metals more economically from low-grade ores or to recycle materials now discarded as waste » [1].

And indeed, rare earth elements as trivalent cations are absolutely irreplaceable for strong magnets, “energy-saving” light bulbs and high capacity batteries, amongst other applications. They are in fact not rare, just highly diluted in the earth crust. They are also chemically very similar. For these two reasons, their extraction and separation is a lengthy and very polluting process. Consequently, cost and environmental constraints led to the closure of most mining facilities in western countries over the past few decades, leading to today's quasi-monopoly of China which controls approximately 97% of the world's rare earth element market as per 2012 figures [2]. The same year, the first industrial recycling of rare earth elements by solvent extraction was started in Saint-Fons and La Rochelle, France, showing that supply autonomy, economical and ecological considerations are of importance in today's society. Following 2011 figures [3], Japan detains 300 kT of WEEE, corresponding to nearly three times the annual global production of rare earths. In order to recycle these resources, solvent extraction processes need to be rendered ecologically friendly, and be rapidly adapted to each kind of urban mining material.

Solvent extraction, i.e. control of the reversible transfer of cations between feed and extraction phases, is a core chemical process for metal purification and recycling in hydrometallurgy. These processes are very complex chemical two-phase systems, where slight changes in parameters may imply huge effects on the phase behavior of the involved complex fluids. This may lead to so-called “third-phase accidents”, representing huge financial losses for a production plant. The overall behavior of these complex fluids is analyzed in multi-dimensional phase diagrams, requiring several years of thorough analysis by techniques ranging from simple pH measurements to scattering techniques implying consequent instrumental and time efforts. Thus, solvent extraction process tweaking is frequently based on empirical data.

The objective of the “REE-CYCLE” project (Rare Earth Element reCYCling with Low harmful Emissions) [4] is to develop the fundamental understanding involved in the process' complex fluids (both experimental and theoretical) in order to enable a quantum leap in process analysis and thereby rapidly innovating environmentally friendly and economically competitive processes.

## 2 Instrumented microfluidic device for complex fluid phase diagram exploration

If extraction microfluidic devices have already been reported [5], the presented work takes this approach beyond the state of the art. Indeed, we will describe the instrumented and computer-controlled microfluidic device enabling the first steps towards simultaneous fast measurement of the free energy of mass transfer per ion pair between complex fluids. In the longer run, high-throughput screening in this lab-on-a-chip tool, and complete automation and robotization of the experimental setup, will enable:

- 1) Rapid evaluation for innovative “green” processes issued of synthetic chemistry,
- 2) Benchmarking for numerical approaches and predictive theories, e.g. ienais [6],
- 3) Process intensification and ecologilization regarding principles of green chemistry and circular economy.

Screening of a manifold parameter set, including e.g. multi-component phase composition, pH, temperature, etc., will be enabled by integrating inline and real-time measurements into a fully robotized system. Ultimately, the

device will be designed to deliver continuous, in-line and real-time exploration of phase diagrams by combining several miniaturized spectroscopy and sensing methods for characterization of kinetic & thermodynamic time scales, partition coefficients of extraction, chemical potential differences and constituent activities, without user intervention.

Here, we show first results of the microfluidic device (cf. Figure 1) and compare these with batch mode assays concerning temperature and pH variation. Examples will be shown on TODGA reverse micelles diluted in dodecane as model system, and extraction of five rare earth elements: La, Nd, Eu, Dy and Yb; in the presence of iron. Partition coefficients and kinetics data for different parameters will be addressed as well as pathways explored to enhance separation and selectivity. First data on solvent activity coefficient measurements will also be presented, giving insight on molecule aggregation, solvent chemical potentials and constituents' vapor pressures.

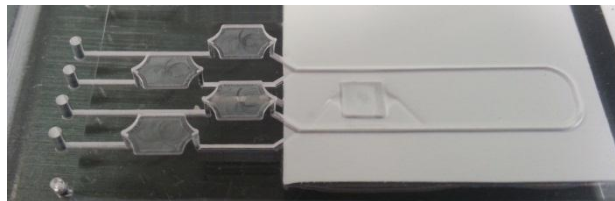


Fig. 1. Microfluidic chip for solvent extraction with in-line measurement sites.

### Conclusions

The microfluidic device stands as a first pillar of the REE-CYCLE project, enabling benchmarking for meso-scale modelling and numerical analysis, testing of newly synthesized extraction agents, and paving the way to assisted pertraction devices. On the longer time range, a semi-industrial prototype device for solvent extraction will be conceived gathering the results of all working groups. Furthermore, the microchemistry and -analysis activity is meant to be developed and extended beyond solvent extraction, involving research as well as industrial partners.

### Acknowledgements

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP/2007-2013) / ERC Grant Agreement n. [320915] "REE-CYCLE": Rare Earth Element reCYCling with Low harmful Emissions [4].

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