



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

DELIVERABLE D3.2: REPORT ON THE PERSPECTIVES OF SEPARATION OF REE FROM OTHER METALS BY IONIC LIQUIDS

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1 EXECUTIVE SUMMARY

The purpose of this deliverable is to present all the results, until this date, about the possibility of effectively using ILs for the separation of REEs from other metals in the systems studied under the ENVIREE project.

The results of this deliverable are strongly connected with WP1 and WP2 results, since they condition the starting situation for the work described here, and with WP4, since the results here obtained can be useful for the prosecution of that WP.

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2 INTRODUCTION

A specific issue in the field of hydro extraction of metals is the use of ionic liquids to perform or enhance that extraction. Ionic liquids are environmentally friendly solvents with favourable properties such as extremely low vapour pressure, low combustibility, excellent thermal stability, and a wide temperature range in its liquid state. The low volatility and combustibility of ionic liquids (ILs) together with the high extractability presented in many cases make this extraction method a promising separation technology [1].

The use of ILs tends to improve the procedures used and make them more environment friendly and in a short/medium term they will become an inevitable method to recover REEs. Since 2003, an effort has been done in order to separate REEs using ILs [2]. Many studies have been performed [3, and references therein]. In more recent years the amount of publications devoted to the use of ILs to separate REEs has increased exponentially [4-47].

From those some are specifically devoted to the recovery of REEs from printed boards [4, 7, 9, 20, 21, 31, 38, 42-45, 47] but the great majority describe general processes that can be applied to any kind of secondary source for REEs. Many of them take not in consideration the importance of using really green ILs, that is ILs that have in their composition only CHON elements in order to be disposable easily and in an environmentally sustainable way.

3 SYNTHESIS OF THE USED IONIC LIQUIDS (ILS)

The synthesis and purification of three “CHNO” ionic liquids used until now in the ENVIREE project (tetraoctilammonium oleate-IL1 [48], 1-butyl-3-methylimidazolium-methyl-oxalate-IL2 [2], and 1-butyl-3-methylimidazolium-di(2-ethylhexyl)-oxamate-IL3 [49]) (Figures 1-3) were undertaken in the IST-ID team lab.

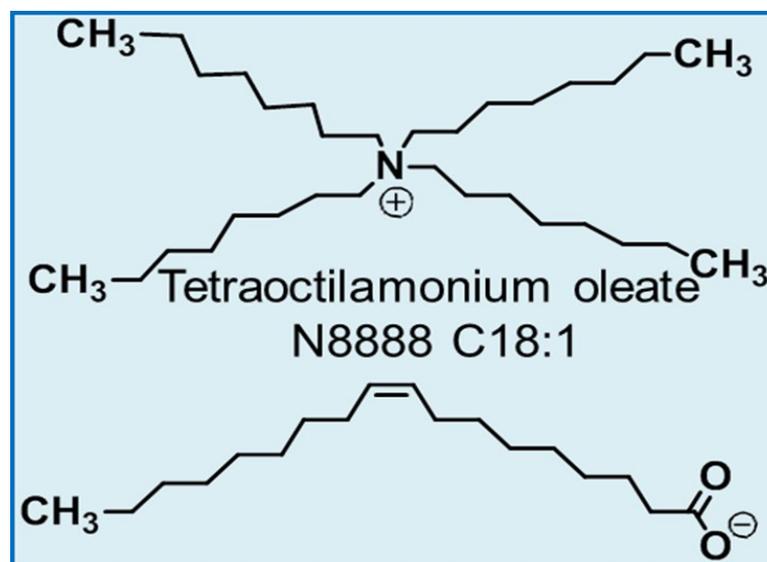


Figure 1: Tetraoctilammonium oleate - IL1



Figure 2: 1-butyl-3-methylimidazolium-methyl-oxalate – IL2

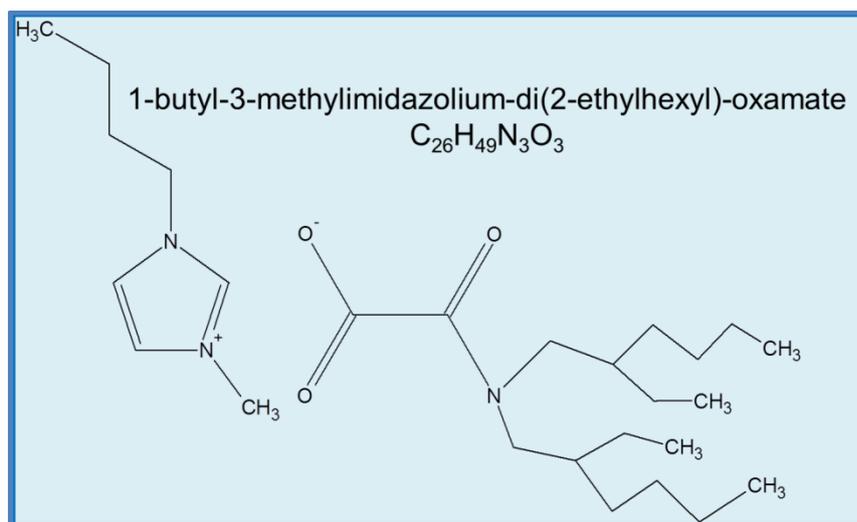


Figure 3: 1-butyl-3-methylimidazolium-di(2-ethylhexyl)-oxamate – IL3

Briefly, the syntheses were as follows:

IL1 – Sodium oleate was prepared by reacting equimolar amounts of NaOH and oleic acid in ethanol overnight at room temperature.

The obtained sodium oleate was then reacted with tetraoctylammonium chloride for 3 h at room temperature, in toluene/water. The IL1 was isolated from the organic phase as a viscous yellowish liquid.

IL2 - The syntheses were performed under a nitrogen atmosphere.

First, oxalyl chloride, dissolved in diethyl ether, was slowly added to 2 eq of methanol, also dissolved in diethyl ether, at 0 °C, and the solution stirred for 2 hours. The crude product was purified by distillation and the desired stable product, dimethyloxalate, was obtained as a white solid.

Next, 1 eq of 1-butylimidazole was mixed with 3 eq of dimethyloxalate for 4 days at 90 ° C. The reaction mixture was washed with n-hexane and the excess volatile reagents removed in vacuo. IL2 was obtained as a yellowish oil.

IL3 - The syntheses were performed under a nitrogen atmosphere.

First, methanol, dissolved in diethyl ether, was slowly added to 1 eq of oxalyl chloride, also dissolved in diethyl ether, at 0 °C, and the solution stirred for 2 hours. The crude product was purified by distillation and the desired moisture-sensitive product, methoxalyl chloride, was obtained as a white liquid.

Next, 1 eq of di-2-ethylhexyl amine and 2 eq of triethylamine were dissolved at -10 °C in diethyl ether; 1 eq of methoxalyl chloride, also in diethyl ether, were slowly added dropwise. The resulting triethylammonium was observed as a colorless solid. The reaction mixture was stirred for another hour at room temperature and the resulting solution was filtered, washed with water and the solvent removed in vacuo. The yellow crude was doubly distilled giving di(2-ethylhexyl)methyl-oxamate as a pale yellow oil.

Next, 1.5 eq of 1-butylimidazole and 1 eq of di(2-ethylhexyl)methyl-oxamate were mixed and heated for 4 days at 100 °C. Excess reactant was removed by vacuum. IL3 was obtained as a yellowish oil.

The intermediate products and ILs were characterized by 1H and ^{13}C NMR and by ESI-MS.

4 LANTHANIDE EXTRACTION BY IONIC LIQUIDS

4.1 First mockup solutions

Since in the beginning of the project there was not a real solution to work with, a first mockup solution with concentrations of 10^{-2} M in La, Sm, Ho and Fe (considered as an archetypal metal to be separated from Ln) was prepared to test the extraction ability of the ionic liquids. Both sulfuric and nitric media were used to test the influence of the acid used in a previous stage and allowing versatility in the choice of the process to be used.

Stock solutions of the metals (10^{-2} M) were prepared by dissolving the appropriate hydrated Ln(III) and Fe(II) nitrate or sulphate salts in ultrapure water (18.2 M Ω cm; obtained with a MilliQ[®] water purification system); anhydrous sulphate was used in the case of La; in the case of iron, hydrated Fe(II) chloride was used as an alternative to nitrate due to unavailability. The pH of the mockup solutions containing the 4 metals were ~ 3 and ~ 5.5 for the nitric and sulphuric media, respectively.

4.2 Extraction of the first mockup solutions

For studying the IL's ability to extract lanthanides from the prepared solutions, 1 mL of each metal stock solution was combined with 1 mL of solution of IL1 and IL3 in toluene and IL2 in dichloromethane (due to its insolubility in toluene). The molar ratio IL:metal was 4:1 in all cases. Ultrapure water was used as reference (blank). 1 replicate of each sample was made for all extractions. The samples were stirred for 1 h on a vortex mixer and afterwards placed for 10 min in a centrifuge at 4000 rpm.

Lanthanide concentrations in the aqueous phases, before and after extraction, were assessed with a quadrupole ICP-MS system, ELAN DRC-e from Perkin Elmer Sciex, equipped with a Peltier impact bead spray chamber, a concentric Meinhard nebuliser, sampler and skimmer nickel cones and a discrete dynode electron multiplier with a simultaneous pulse and analogue detector. In each session operating conditions were optimized to reach the performance criteria recommended by the manufacturer: low levels of oxides CeO^+/Ce^+ and double charged ions $\text{Ba}^{2+}/\text{Ba}^+$ (≤ 0.03); sensitivity for Mg ($\geq 50,000$ count s^{-1}); U ($\geq 200,000$ count s^{-1}) and In ($\geq 250,000$ count s^{-1}). Quantitative analysis was conducted using a $10 \mu\text{g mL}^{-1}$ multi-element calibration standard solution (STD 2, Perkin Elmer[®], 5% nitric acid), and calibration method used was with external standardisation. Calibration solutions were prepared by adequate dilution of the STD2 standard solution. The isotopes ^{139}La , ^{152}Sm and ^{165}Ho were used to assess elemental concentrations and internal standardisation with ^{103}Rh to correct for instrumental drifts and non-spectral interferences. Samples and standard solutions were prepared with HNO_3 65%, purified by sub-boiling distillation (bi-distilled) and ultrapure water (18.2 M Ω cm) obtained with a MilliQ[®] water purification system (Millipore). At every six samples, a quality control solution was measured in order to ensure the accuracy of the determinations. Matrix-induced background interferences were corrected using reagent blank subtraction.

The obtained results (expressed as the extracted percentage from the aqueous solution into the organic phase) are presented in Table 1 (sulfuric media) and Table 2 (nitric media) and in Figure 4 as distribution ratio (D_M) defined according equation 1.



(1)

Iron could not be determined by ICP-MS at this point, due to instrumental problems, but a semi-quantitative determination was achieved using ESI-MS (see below), which indicated that Fe extraction was similar to the Ln extraction.

Table 1: Percentage of extraction achieved in sulfuric media.

% extraction	La	Sm	Ho
IL1	5.7 ± 1.4	38.1 ± 1.1	39.6 ± 1.6
IL2	93.1 ± 1.4	96.3 ± 1.0	94.6 ± 1.4
IL3	99.6 ± 1.3	99.3 ± 1.0	99.2 ± 1.4

As can be seen, IL2 and IL3 extracted between 93 and 100% of the lanthanides from aqueous phase being IL2 slightly more efficient in nitric media and IL3 equally efficient in sulfuric and nitric media. Unfortunately, both ionic liquids also extract iron thus being not adequate to selectively extract lanthanides. IL1 extracted far less than the other two ILs but showed some discrimination between lanthanides (%; La, 5.7; Sm, 38.1; Ho, 39.6 in sulfuric media and La, 17.6; Sm, 76.2; Ho, 81.5 in nitric media) which can be advantageous in subsequent steps if separation of lanthanides among them is required.

Table 2: Percentage of extraction achieved in nitric media.

% extraction	La	Sm	Ho
IL1	17.6 ± 0.7	76.2 ± 0.5	81.5 ± 0.9
IL2	99.6 ± 0.7	100.0 ± 0.5	100.0 ± 0.9
IL3	99.3 ± 0.7	99.1 ± 0.5	99.1 ± 1.0

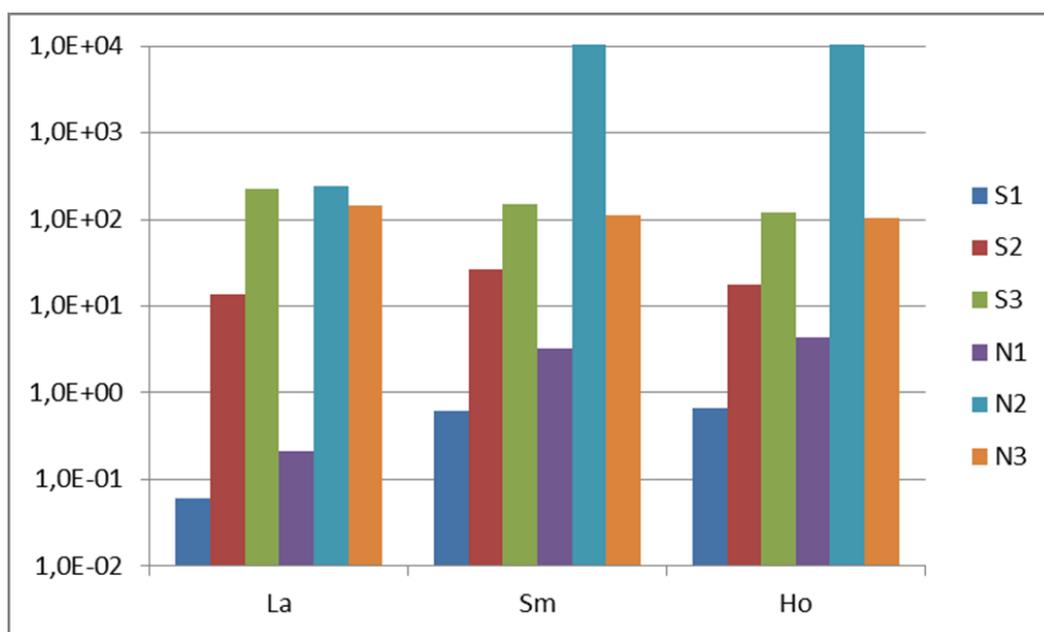


Figure 4: Distribution ratio of La, Sm and Ho in the aqueous and organic phases. Values in the y axis are distribution rates defined according to eq. 1.

A semi-quantitative analysis of the metals in some of the aqueous phases was performed by ESI-MS, using a Bruker HCT quadrupole ion trap mass spectrometer. Sample solutions approx. 10^{-4} M in water/methanol were introduced into the ESI source via a syringe pump at a flow rate of 150 mL min^{-1} . The heated capillary temperature was set to 250°C and the dry gas (N_2) to a flow rate of 4 L min^{-1} . The same acidified solutions used for ICP-MS analyses were spiked with a known amount of Lu nitrate solution (10^{-5} M) for internal reference and the metals (La, Sm, Ho and Fe) were determined as the tetranitrate anions.

Analyses of the non-aqueous fractions, diluted with methanol, were also made by ESI-MS, looking for an understanding of the underlying mechanism through the formed species. For IL1 and IL2 it was not possible to identify unequivocally the species present in solution but for IL3 the species involved were identified indicating that the metal ions (Ln and Fe) were extracted into the organic phase complexed by the IL3 anions, as the detected species corresponded to M(IL3-anion)_4^- .

Subsequent work will focus on IL1 and IL3 (as IL2 forced us to use a non-“CHNO” organic solvent (dichloromethane), mainly to examine the effect of pH on the extraction efficiency and selectivity.

4.3 Second mockup solutions

The participants in the WP3 of the ENVIREE project established a forum to discuss how to tackle the problem of not having a real solution coming from lixiviation. After a very participated discussion it was decided to define a solution that all the partners can use. These synthetic media were based on data from beneficiated samples (BRGM) and having in account the REEs available data (WP1) for the tailings of the New Kankberg and Covas mines. The defined composition for each one of these mines is presented in Tables 3 and 4. In these tables the pretended composition is the one that was agreed by the WP3 partners and the real composition is the determined one in the prepared solutions. In addition to the 4 REEs and some impurities decided by all the partners, the IST-ID team chose to include 3 additional

REEs (Gd³⁺, Er³⁺ and Yb³⁺) in order to have a full series coverage (Figure 5). Those additional REEs were added with the same concentration of the dysprosium metal ion.

Table 3: The Mockup solution for the New Kankberg tailings.

New Kankberg	Element	Pretended Composition	Real composition
REE ppm	Ce ³⁺	1000	999
	La ³⁺	500	509
	Nd ³⁺	500	509
	Dy ³⁺	100	109
Impurities g/L	PO ₄ ³⁻	10	
Additional REE ppm	Gd ³⁺	100	93
	Er ³⁺	100	98
	Yb ³⁺	100	101

Table 4: The Mockup solution for the Covas tailings.

Covas	Element	Pretended Composition	Real Composition
REE ppm	Ce ³⁺	50	51.0
	La ³⁺	25	24.8
	Nd ³⁺	25	25.0
	Dy ³⁺	5	4.4
Impurities g/L	Fe ³⁺	10	1.0
	Cu ²⁺	1	1.0
	W (WO ₄ ²⁻ ?)	0.5	0.5
Additional REE ppm	Gd ³⁺	5	6.1
	Er ³⁺	5	4.9
	Yb ³⁺	5	4.9



Figure 5: The lanthanide series with the proposed elements (black circles) and the additional ones (red circles).

4.4 Extraction of the second mockup solutions

The solutions defined in the previous point (4.3) had their pH value set to 1 (or a bit below that) and then an extraction was made using IL1 and IL3 (as previously described). In short, 1 mL of each stock solutions was combined with 1 mL of solution of IL1 and IL3 in toluene with a molar ratio IL:metal of 4:1 in all cases. Ultrapure water was used as reference (blank). One replicate of each sample was made for all extractions. The samples were stirred for 1 h on a vortex mixer and afterwards placed for 10 min in a centrifuge at 4000 rpm.

Lanthanide concentrations in the aqueous phases, before and after extraction, were assessed with the quadrupole ICP-MS system, ELAN DRC-e from Perkin Elmer Sciex, used previously (see 4.2). Quantitative analysis was conducted using a 10 µg mL⁻¹ multi-element calibration standard solution (STD 2 for the lanthanides and STD 3 for Fe and Cu, Perkin Elmer®, 5% nitric acid and a standard solution made from WO₃ for the W), and calibration method used was with external standardisation. Calibration solutions were prepared by adequate dilution of the standards solution. The isotopes ⁵⁷Fe, ⁶³Cu, ¹³⁹La, ¹⁴⁰Ce, ¹⁴⁶Nd, ¹⁵⁷Gd, ¹⁶³Dy, ¹⁶⁶Er, ¹⁷²Yb and ¹⁸⁴W were used to assess elemental concentrations and internal standardisation with ¹⁰³Rh to correct for instrumental drifts and non-spectral interferences.

The obtained results (expressed as the extracted percentage from the aqueous solution into the organic phase) are presented for New Kankberg in Tables 5 and 6 (sulfuric media and nitric media, respectively) and in Figure 6, and for Covas in Tables 7 and 8 (sulfuric media and nitric media, respectively) and Figure 7. The distribution ratio used in Figures 6 and 7 is defined according equation 1.

Table 5: New Kankberg mockup solution extraction in sulfuric media (pH=1).

% extraction	La	Ce	Nd	Gd	Dy	Er	Yb
IL-1	1.9 ± 1.7	2.2 ± 2.0	2.8 ± 2.2	2.2 ± 2.4	2.5 ± 2.3	3.4 ± 2.3	2.4 ± 2.1
IL-3	2.6 ± 1.1	2.8 ± 1.2	3.1 ± 1.4	2.5 ± 1.7	2.5 ± 1.2	3.1 ± 0.7	2.3 ± 0.9

Table 6: New Kankberg mockup solution extraction in nitric media (pH=1).

% extraction	La	Ce	Nd	Gd	Dy	Er	Yb
IL-1	0.3 ± 0.1	0.6 ± 0.1	0.6 ± 0.4	0.8 ± 0.7	0.7 ± 0.2	0.3 ± 0.1	0.6 ± 0.3
IL-3	0.0 ± 0.3	0.0 ± 0.2	0.0 ± 0.2	0.4 ± 0.1	0.2 ± 0.1	0.0 ± 0.3	0.2 ± 0.2

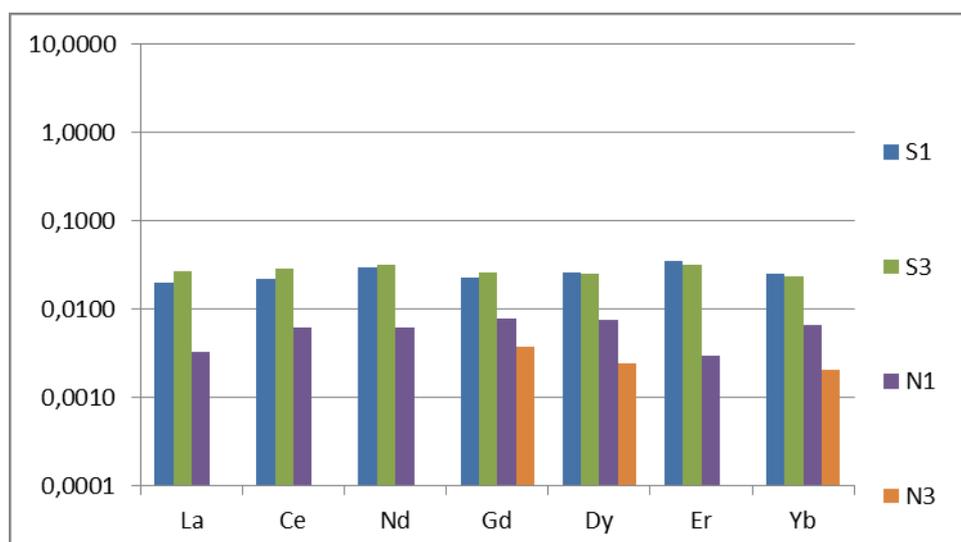


Figure 6: New Kankberg mockup solution distribution ratio of REE in the aqueous and organic phases. Values in the y axys are distribution rates defined according to eq. 1.

Table 7: Covas mockup solution extraction in sulfuric media (pH=1).

% extraction	La	Ce	Nd	Gd	Dy	Er	Yb	Cu	Fe	W
IL-1	0.2 ± 0.5	1.1 ± 0.4	0.8 ± 0.8	1.2 ± 0.2	1.1 ± 0.9	1.2 ± 0.6	1.1 ± 0.6	1.0 ± 0.3	0.4 ± 0.5	36.3 ± 3.2
IL-3	2.4 ± 2.1	3.4 ± 1.8	2.6 ± 2.0	2.9 ± 2.0	3.1 ± 2.3	2.9 ± 1.9	3.2 ± 2.4	3.4 ± 2.4	41.8 ± 0.3	30.2 ± 0.9

Table 8: Covas mockup solution extraction in nitric media (pH=1).

% extraction	La	Ce	Nd	Gd	Dy	Er	Yb	Cu	Fe	W
IL-1	0.0 ± 0.9	0.0 ± 1.6	0.0 ± 0.5	0.0 ± 0.4	0.0 ± 0.1	0.0 ± 0.4	0.1 ± 0.1	0.0 ± 0.3	0.0 ± 1.2	32.6 ± 4.5
IL-3	2.4 ± 0.5	3.9 ± 3.1	2.5 ± 0.9	2.2 ± 0.5	2.6 ± 0.3	2.5 ± 0.5	2.3 ± 0.5	3.8 ± 2.2	74.3 ± 0.8	32.8 ± 1.0

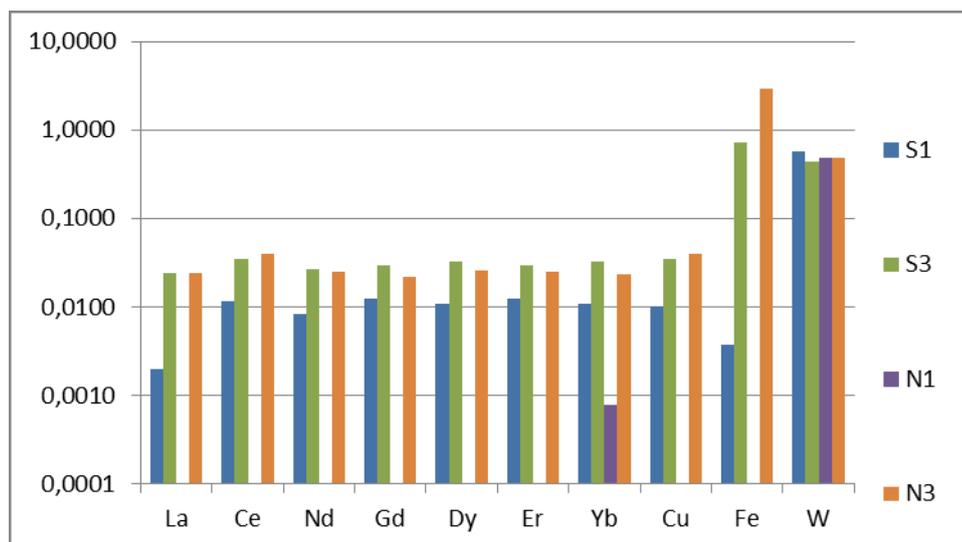


Figure 7: Covas mockup solution distribution ratio of REE, Cu, Fe and W in the aqueous and organic phases Values in the y axys are distribution rates defined accordind to eq. 1.

For studying the effect of the pH in the extraction of the REEs from those solutions, it was intention of the team to perform similar extractions at higher pH values. However, when the previous solutions were prepared at pH =3 (higher values were not attempted), it resulted always in the precipitation of lanthanide phosphates (for the Kankberg mockup solution) or lanthanide tungstates (for the Covas mockup solution). All efforts to change the order of addition, the initial or final set of the pH or any other parameter were unfruitfull and the final result was always solutions with a precipitate. Thus, it is not possible to extend this study to higher pH values.

5 CONCLUSIONS

The main conclusions that can be taken are:

1- In the first mock-up solution, at $\text{pH} \geq 3$, IL2 and IL3 extracted between 93 and 100% of the lanthanides from aqueous phase being IL2 slightly more efficient in nitric media and IL3 equally efficient in sulfuric and nitric media. However, both ionic liquids also extract iron at this pH range. IL1 extracted far less than the other two ILs but showed some discrimination between lanthanides.

2- REE percentage of extraction data at $\text{pH} \leq 1$ in sulfuric media does not seem to show remarkable differences between New Kankberg and Covas samples and with both IL-1 and IL-3 showing a similar behaviour. Higher percentage of extraction is shown for W and Fe, with IL1 in nitric media showing a great capability to select among Fe and W (it extracts no Fe but still extracts a lot of W).

3- REE percentage of extraction data at $\text{pH} \leq 1$ has shown to be slightly higher in nitric media than in sulfuric media for the same elements (La-Yb) for New Kankberg and Covas samples. IL-1 and IL-3 show similar behavior in terms of W extraction percentage but IL-3 is a better extraction agent for Fe in nitric media than in sulfuric media.

As said before mock-up solutions simulating both mines composition are impossible to prepare at pH values 3 or higher without rapid precipitation of lanthanide salts (tungstate or phosphate).

Other “CHNO” ILs are under scrutiny, to be tested for a selective extraction of the lanthanides in the presence of iron and other metals.

The observed discrimination among the lanthanides detected in the initial tests with IL1 will continue to be examined.

6 REFERENCES

- [1] Xiaoqi Sun, Huimin Luo and Sheng Dai, “Mechanistic investigation of solvent extraction based on anion-functionalized ionic liquids for selective separation of rare-earth ions”, *Dalton Trans.*, (2013), 42, 8270; DOI: 10.1039/c3dt50148e
- [2] Kazunori Nakasmina, Fukiko Kubota, Tatsuo Maruyama, Masahira Goto, “Ionic liquids as novel solvent for lantahanide extractation”; *Analytical Sciences*, (2003), 19, 1097
- [3] Yuko Baba, Fukiko Kubota, Noriko Kamiya, Masahira Goto, “Recent advances in extraction and separation of rare earth metals using liquid ionics”; *Journal of Chemical Engineering of Japan*, (2011), Vol. 44, n°10, 679
- [4] Hualing Yang, WeiWang, Hongmin Cui, Dongli Zhang, Yu Liu and Ji Chen, “Recovery of rare earth elements from simulated fluorescent powder using bifunctional ionic liquid extractants (Bif-ILEs)”; *J Chem Technol Biotechnol*, (2012), 87, 198, DOI 10.1002/jctb.2696
- [5] Xiaoqi Sun, Huimin Luo, Sheng Dai, “Solvent extraction of rare-earth ions based on functionalized ionic liquids”; *Talanta* (2012), 90, 132, DOI:10.1016/j.talanta.2011.12.069
- [6] LiLi Zhu, Lin Guo, Zhen Jiang Zhang, Ji Chen, Shao Min Zhang, “The preparation of supported ionic liquids (SILs) and their application in rare metals separation” *Sci China Chem*, (2012), Vol.55 No.8, 1479
- [7] Tom Vander Hoogerstraete, Sil Wellens, Katrien Verachtert and Koen Binnemans,” Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid separations relevant to rare-earth magnet recycling”, *Green Chem.*, (2013), 15, 919; DOI: 10.1039/c3gc40198g
- [8] Xiaoqi Sun, Kristian E. Waters, “Development of Industrial Extractants into Functional Ionic Liquids for Environmentally Friendly Rare Earth Separation”, *ACS Sustainable Chem. Eng.* (2014), 2, 1910; dx.doi.org/10.1021/sc500255n
- [9] Huabo Duan, Kun Hou, Jinhui Li, Xiaodong Zhu, “ Examining the technology acceptance for dismantling of waste printed circuit boards in light of recycling and environmental concerns”, *Journal of Environmental Management* (2011), 92, 392; doi:10.1016/j.jenvman.2010.10.057
- [10] Fan Yang, Yuko Baba, Fukiko Kubota, Noriko Kamiya, Masahira Goto, “Extraction and separation of rare earth metals ions with DODGAA in ionic liquids”, *Solvent extraction research and development, Japan*, (2012), 19, 69
- [11] Fukiko Kubota, Yuko Baba, Masahira Goto, “Application of ionic liquids for the separation of rare earths metals”, *Solvent extraction research and development, Japan*, (2012), 19, 17
- [12] Stefania Massari, Marcello Ruberti,” Rare earth elements as critical raw materials: Focus on international markets and future strategies”, *Resources Policy* (2013), 38, 36, <http://dx.doi.org/10.1016/j.resourpol.2012.07.001>

[13] Koen Binnemans, Peter Tom Jones, Bart Blanpain, Tom Van Gerven, Yongxiang Yang, Allan Walton, Matthias Buchert “Recycling of rare earths: a critical review”, *Journal of Cleaner Production*, (2013), 51, 1; <http://dx.doi.org/10.1016/j.jclepro.2012.12.037>

[14] Jesik Park, Yeojin Jung, Priyandi Kusumah, Jinyoung Lee, Kyungjung Kwon, Churl Kyoung Lee, “Application of Ionic Liquids in Hydrometallurgy”, *Int. J. Mol. Sci.* (2014), 15, 15320; DOI:10.3390/ijms150915320

[15] Ilya A. Shkrob, Timothy W. Marin, Mark P. Jensen, “Ionic Liquid Based Separations of Trivalent Lanthanide and Actinide Ions” *Ind. Eng. Chem. Res.* (2014), 53, 3641; dx.doi.org/10.1021/ie4036719 |

[16] Alok Rout, Koen Binnemans, “Liquid–liquid extraction of europium(III) and other trivalent rare-earth ions using a non-fluorinated functionalized ionic liquid” *Dalton Trans.*, 2014, 43, 1862; DOI: 10.1039/c3dt52285g

[17] Alok Rout, Sil Wellens, Koen Binnemans, “Separation of rare earths and nickel by solvent extraction with two mutually immiscible ionic liquids” *RSC Adv.*, (2014), 4, 5753; DOI: 10.1039/c3ra46261g

[18] Yamin Dong, Xiaoqi Sun, Yanliang Wang, Yujun Chai, “The development of an extraction strategy based on EHEHP-type functional ionic liquid for heavy rare earth element separation” *Hydrometallurgy*(2015)157,256;<http://dx.doi.org/10.1016/j.hydromet.2015.09.04>

[19] Menghao Zhu, Junmei Zhao, Yingbo Li, Nada Mehio, Yuruo Qi, Huizhou Liu, Sheng Dai “An ionic liquid-based synergistic extraction strategy for rare earths” *Green Chem.*, (2015), 17, 2981; DOI: 10.1039/c5gc00360a

[20] Sofía Riaño, Koen Binnemans; “Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets” *Green Chem.*, (2015), 17, 2931; DOI: 10.1039/c5gc00230c

[21] Quanyin Tan, Jinhui Li, Xianlai Zeng, “Rare Earth Elements Recovery from Waste Fluorescent Lamps: A Review” *Critical Reviews in Environmental Science and Technology*, (2015), 45, 749; DOI: 10.1080/10643389.2014.900240

[22] Kristian Larsson, Koen Binnemans; “Separation of rare earths by split-anion extraction”, *Hydrometallurgy* (2015), 156, 206; <http://dx.doi.org/10.1016/j.hydromet.2015.04.020>

[23] Daphne Depuydt, Wim Dehaen, Koen Binnemans, “Solvent Extraction of Scandium (III) by an Aqueous Biphasic System with a Nonfluorinated Functionalized Ionic Liquid”, *Ind. Eng. Chem. Res.* (2015), 54, 8988; DOI: 10.1021/acs.iecr.5b01910

[24] Nicolas Schaeffer, Sue Grimes, Chris Cheeseman, “Interactions between trivalent rare earth oxides and mixed [Hbet][Tf2N]: H2O systems in the development of a one-step process for the separation of light from heavy rare earth elements” *Inorganica Chimica Acta* (2016), 439, 55; <http://dx.doi.org/10.1016/j.ica.2015.09.015>

[25] R. Turgis, G. Arrachart, V. Dubois, S. Dourdain, D. Virieux, S. Michel, S. Legeai, M. Lejeune, M. Drayed, S. Pellet- Rostaing, “Performances and mechanistic investigations of a triphosphine trioxide/ionic liquid system for rare earth extraction” *Dalton Trans.*, (2016), 45, 1259; DOI: 10.1039/c5dt03072b

[26] Kazunori Nakashima, Fukiko Kubota, Tatsuo Maruyama, and Masahiro Goto, “Feasibility of Ionic Liquids as Alternative Separation Media for Industrial Solvent Extraction Processes” *Ind. Eng. Chem. Res.* (2005), 44, 4368

[27] Taro Toda, Takehiro Maruyama, Kimikazu Moritani, Hirotake Moriyama; Hirokazu Hayashi, “Thermodynamic Properties of Lanthanides and Actinides for Reductive Extraction of Minor Actinides” *Journal of Nuclear Science and Technology*, (2009), Vol. 46, No. 1, 18

[28] Xiaoqi Sun, Yang Ji, Lin Guo, Ji Chen, Deqian Li, “A novel ammonium ionic liquid based extraction strategy for separating scandium from yttrium and lanthanides”, *Separation and Purification Technology* (2011), 81, 25; DOI:10.1016/j.seppur.2011.06.034

[29] Xiaoqi Sun, Jason R. Bell, Huimin Luo, Sheng Dai, “Extraction separation of rare-earth ions via competitive ligand complexations between aqueous and ionic-liquid phases” *Dalton Trans.*, (2011), 40, 8019; DOI: 10.1039/c1dt10873e

[30] Alok Rout, Justyna Kotlarska, Wim Dehaen and Koen Binnemans, “Liquid–liquid extraction of neodymium (III) by dialkylphosphate ionic liquids from acidic medium: the importance of the ionic liquid cation “ *Phys.Chem. Chem. Phys.*, (2013), 15, 16533; DOI: 10.1039/c3cp52218k

[31] Fan Yang, Fukiko Kubota, Yuzo Baba, Noriho Kamiya, Masahiro Goto, “Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid system” *Journal of Hazardous Materials* (2013), 254, 79; <http://dx.doi.org/10.1016/j.jhazmat.2013.03.026>

[32] Fengyun Zhang, Wenyuan Wu, Xue Bian, Wensai Zeng, “Synergistic extraction and separation of lanthanum (III) and cerium (III) using a mixture of 2-ethylhexylphosphonicmono-2-ethylhexyl ester and di-2-ethylhexyl phosphoric acid in the presence of two complexing agents containing lactic acid and citric acid” *Hydrometallurgy* (2014), 149, 238; <http://dx.doi.org/10.1016/j.hydromet.2014.09.002>

[33] Xiaoqi Sun, Kristian E. Waters, “The Adjustable Synergistic Effects Between Acid–Base Coupling Bifunctional Ionic Liquid Extractants for Rare Earth Separation” *AIChE Journal* (2014), Vol. 60, No. 11, 3859; DOI 10.1002/aic.14563

[34] Mariusz Grabda, Mrutyunjay Panigrahi, Sylwia Oleszek, Dmytro Kozak, Franck Eckert, Etsuro Shibata, Takashi Nakamura, “COSMO-RS screening for efficient ionic liquid extraction solvents for NdCl₃ and DyCl₃” *Fluid Phase Equilibria* 383 (2014), 383, 134; <http://dx.doi.org/10.1016/j.fluid.2014.10.018>

[35] Bieke Onghena, Jeroen Jacobs, Luc Van Meervelt and Koen Binnemans, “Homogeneous liquid–liquid extraction of neodymium (III) by choline hexafluoroacetylacetonate in the ionic liquid choline bis(trifluoromethylsulfonyl) imide” *Dalton Trans.*, (2014), 43, 11566; DOI: 10.1039/c4dt01340a

[36] Alok Rout, Koen Binnemans, “Solvent Extraction of Neodymium(III) by Functionalized Ionic Liquid Trioctylmethylammonium Dioctyl Diglycolamate in Fluorine-free Ionic Liquid Diluent” *Ind. Eng. Chem. Res.* (2014), 53, 6500; dx.doi.org/10.1021/ie404340p

[37] Xiaoqi Sun, Chi-Linh Do-Thanh, Huimin Luo, Sheng Dai, ” The optimization of an ionic liquid-based TALSPEAK-like process for rare earth ions separation “ Chemical Engineering Journal (2014), 239, 392; <http://dx.doi.org/10.1016/j.cej.2013.11.041>

[38] Tom Vander Hoogerstraete, Koen Binnemans, “Highly efficient separation of rare earths from nickel and cobalt by solvent extraction with the ionic liquid trihexyl (tetradecyl) phosphonium nitrate: a process relevant to the recycling of rare earths from permanent magnets and nickel metal hydride batteries” Green Chem., (2014), 16, 1594; DOI: 10.1039/c3gc41577e

[39] Alok Rout, Koen Binnemans, “Liquid–liquid extraction of europium (III) and other trivalent rare-earth ions using a non-fluorinated functionalized ionic liquid”, Dalton Trans., (2014), 43, 1862; DOI: 10.1039/c3dt52285g

[40] Dmitry V. Filosofov, Nikolai A. Lebedev, Valery Radchenko¹, Alimardon V. Rakhimov, Steffen Happel, Frank Roesch, “Behaviour of Actinium, Alkaline, and rare earth elements in SR-resin/mineral acid systems” Solvent Extraction and Ion Exchange,(2015), 33, 496 ; DOI: 10.1080/07366299.2015.1046293

[41] Alok Rout, Koen Binnemans, “Influence of the ionic liquid cation on the solvent extraction of trivalent rare-earth ions by mixtures of Cyanex 923 and ionic liquids” Dalton Trans., (2015), 44, 1379; DOI: 10.1039/c4dt02766c

[42] David Dupon, Koen Binnemans, “Rare-earth recycling using a functionalized ionic liquid for the selective dissolution and revalorization of $Y_2O_3 \cdot Eu^{3+}$ from lamp phosphor waste” Green Chem., (2015), 17, 856; DOI: 10.1039/c4gc02107j

[43] David Dupon, Koen Binnemans , “Recycling of rare earths from NdFeB magnets using a combined leaching/extraction system based on the acidity and thermomorphism of the ionic liquid [Hbet][Tf₂N]” Green Chem., (2015), 17, 2150; DOI: 10.1039/c5gc00155b

[44] Tom Vander Hoogerstraete, Sil Wellens, Katrien Verachtert, Koen Binnemans, “Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: separations relevant to rare-earth magnet recycling” Green Chem., (2013), 15, 919; DOI: 10.1039/c3gc40198g

[45] Tom Vander Hoogerstraete, Koen Binnemans, “Highly efficient separation of rare earths from nickel and cobalt by solvent extraction with the ionic liquid trihexyl(tetradecyl)phosphonium nitrate: a process relevant to the recycling of rare earths from permanent magnets and nickel metal hydride batteries” Green Chem., (2014), 16, 1594; DOI: 10.1039/c3gc41577e

[46] Alok Rout, Koen Binnemans “Separation of rare earths from transition metals by liquid–liquid extraction from a molten salt hydrate to an ionic liquid phase” Dalton Trans., (2014), 43, 3186; DOI: 10.1039/c3dt52541d

[47] P. Zhu, Y. Chen, L.Y. Wang, M. Zhou, “Treatment of waste printed circuit board by green solvent using ionic liquid” Waste Management (2012), 32, 1914; <http://dx.doi.org/10.1016/j.wasman.2012.05.025>

[48] D. Parmentier, S. J. Metz, M. C. Kroon, “Tetraalkylammonium oleate and linoleate based ionic liquids: promising extractants for metal salts”, Green Chem. 2013, 15, 205-209.; DOI: 10.1039/c2gc36458a



[49] A. Braam, “Synthesis of alkyl oxalate and oxamate based ionic liquids as extractors for the separation of rare earths”, PhD thesis, Philipps-Universität Marburg, 2015.



7 ANNEXES