Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2015

Electronic Supplementary Information (ESI)

Recycling of rare earths from NdFeB magnets using a combined leaching/extraction system based on the acidity and thermomorphism of the ionic liquid [Hbet][Tf$_2$N]

David Dupont and Koen Binnemans*†

1. Scanning Electron Microscope (SEM) images

SEM images were taken with a Philips XL 30 FEG scanning electron microscope (SEM) and ImageJ software was used to determine the average particle size of the roasted NdFeB particles based on different images and at least 100 particle diameter measurements per sample. After crushing with a pestle and mortar a particle size of (310 ± 140) µm was obtained and after ball milling a particle size of (73 ± 40) µm and (6 ± 3) µm, was found (Figure S1).

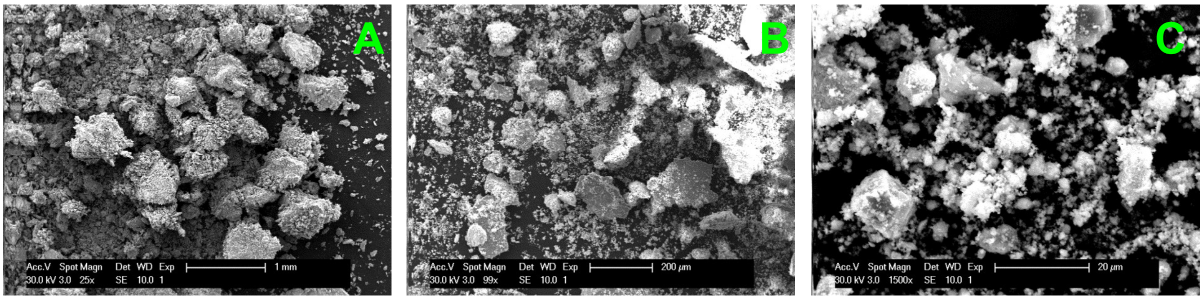

Figure S1. SEM images of the roasted NdFeB particles after grinding (A) and milling (B, C). Image A is magnified 25×, image B is magnified 99× and image C is magnified 1500×. Particles A, B and C had an average particle diameter of (310 ± 140) µm, (73 ± 40) µm and (6 ± 3) µm respectively.

2. Powder X-ray Diffraction (XRD)

The roasted NdFeB magnet was ground in a pestle and mortar and placed into a 0.3 mm diameter glass capillary. The samples were then placed into the center of an Agilent SuperNova X-ray diffractometer using Mo Kα radiation (λ = 0.71073 Å) and a CCD detector. One 240 s exposure was recorded whilst rotating the sample about the φ axis giving the powder diffraction up to 1.0 Å (2θ = 40° for Mo Kα radiation). The recorded powder pattern clearly showed the presence of Fe_2O_3 and Nd_2O_3 (Figure S2), confirming the successful roasting of the magnet. Dy_2O_3 and CoO were not detectable due to their low concentration.

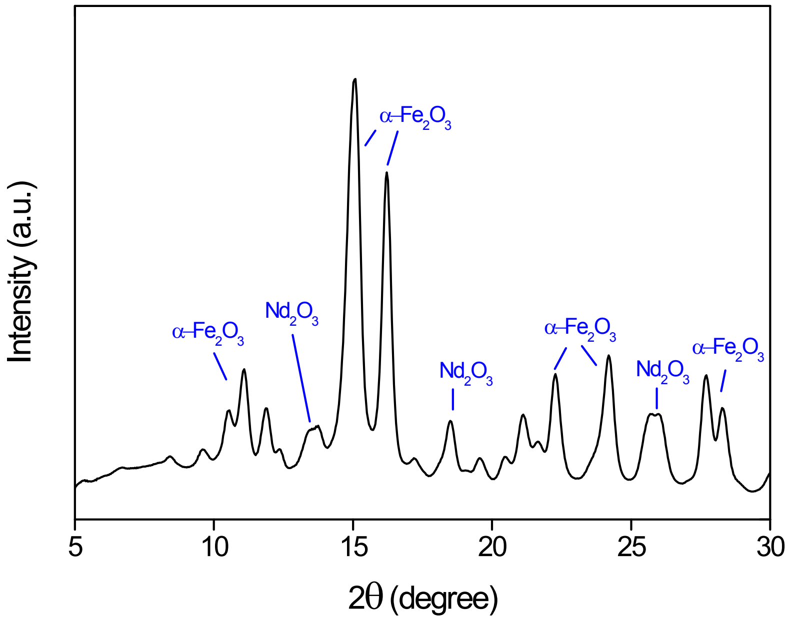

Figure S2. Powder XRD patterns of the roasted NdFeB magnet, collected with Mo Kα radiation (λ = 0.71073 Å).

3. Determination of the magnet composition by ICP-MS analysis

The composition of the magnets (before roasting) was determined by ICP-MS analysis (Table S1). Two types of magnets were compared. The main difference between both magnets is the cobalt and dysprosium content, but there are also differences in the amount of trace elements present in the magnet.

Table S1. Composition (wt%) of two different NdFeB magnets as determined by ICP-MS. Magnet 1 is a high-performance cobalt- and dysprosium-rich magnet, while magnet 2 contains much smaller amounts of cobalt and dysprosium.

	Magnet 1	**Magnet 2**
Element	Composition (wt%)	Composition (wt%)
Fe	58.16	66.01
Nd	25.95	29.17
Co	4.22	0.36
Dy	4.21	1.98
B	1.00	1.02
Nb	0.83	0.40
O	0.41	0.43
Al	0.34	0.29
Pr	0.34	0.10
C	0.07	0.06
Si	0.06	0.04
Mn	0.05	0.05
Cu	0.04	0.05
Ni	0.02	/
N	0.02	0.01
Total	**95.72**	**99.97**

4. TXRF analysis of metals in a high-matrix ionic liquid sample

Total reflection X-ray (TXRF) analysis is a very useful technique since it allows the direct determination of all elements with a higher atomic number than sodium. Contrary to ICP-MS, it does not require the digestion of the sample in strong acids prior to the analysis. In aqueous solutions with low ionic strengths, the matrix effect is negligible for TXRF and one standard suffices to quantify the concentration of all the elements present in the sample. However, in a high-matrix sample such as this ionic liquid, it is important to consider the secondary absorption of x-rays which is energy dependent. By using a standard that emits x-rays with a similar energy than those of the probed element, the error (caused by secondary adsorption) can be reduced significantly (Figure S3). The lower the energy of the emitted x-rays, the stronger the secondary absorption is by the organic matrix.[1] A standard with higher energy X-rays than the probed element therefore causes an underestimation of the element's concentration as fewer of its x-rays are reaching the detector. The opposite is true for a standard with lower energy X-rays than the probed element. Therefore, a multiple-standard method was developed to successfully analyze the various metals (Nd, Fe, Dy, Co) directly in the high-matrix ionic liquid sample.

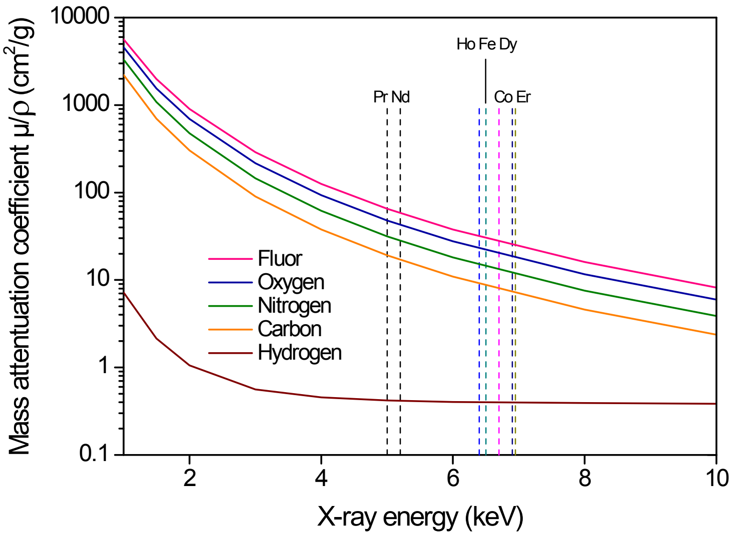

Figure S3. The adsorption of X-rays by the ionic liquid matrix (H, C, N, O, F) is shown as function the X-ray energy.[1] The (average) energy of the X-rays emitted by the various relevant elements (Nd, Fe, Dy, Co) and standards (Pr, Ho, Er) are shown as vertical lines.[2]

Tests showed that the use of three standard elements was required in this specific case due to the large matrix effect in the ionic liquid sample. By choosing a mixed Pr, Ho, Er standard, it was shown that accurate measurements were possible for Nd, Fe/Dy and

Co respectively (Table S 2). Praseodymium standard (5.0 keV) allows the accurate detection of neodymium (5.2 keV), while the holmium standard (6.7 keV) allows the accurate detection of iron (6.4 keV) and dysprosium (6.5 keV). An erbium standard (7.0 keV) can be used for the detection of cobalt (6.9 keV).[2] When the quantification of one of these elements was based on a standard with non-matching X-ray energies, a large error resulted (Table S2) due to the difference in secondary absorption of their X-rays by the matrix (Figure S3).[1] In aqueous solutions one standard is of course sufficient.

Table S2. Analysis of a synthetic Nd, Fe, Co, Dy sample (100 ppm each) with 50 mg of [Hbet][Tf2N] to mimic the matrix of the real TXRF samples. A mixed Pr, Ho, Er standard was added to analyse the different elements. The results were averaged over 6 samples. An optimal standard should closely match the X-ray energy of the analyzed metal (bold, blue).

Measured metal content	Pr standard	Ho standard	Er standard
Nd (ppm)	**100.2 ± 1.3**	66 ± 5	45 ± 4
Fe (ppm)	151 ± 9	**100.03 ± 2.1**	69 ± 2
Dy (ppm)	208 ± 17	**102.2 ± 1.7**	66 ± 5
Co (ppm)	202 ± 18	115 ± 4	**100.1 ± 1.7**

5. Salting-out effect of anions

The effect of salt anions on the miscibility of [Hbet][Tf2N] in the water phase is shown (Figure S4). The [Hbet][Tf_2N] content in the water phase was measured using ^1H NMR and 1,4-dioxane as an internal standard.

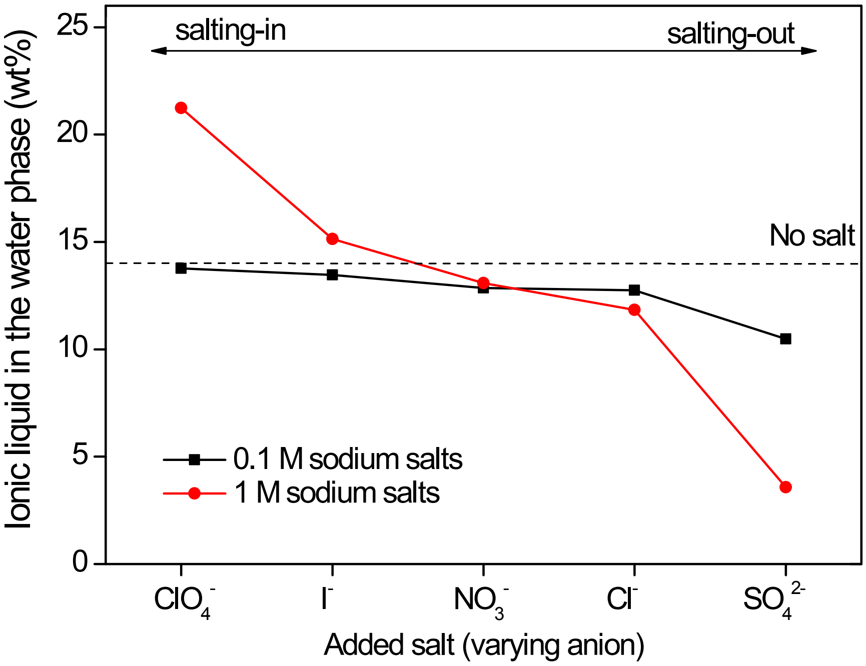

Figure S4. [Hbet][Tf_2N] content (wt%) in the water phase when adding sodium salts with varying anions. When no salt is added, the water phase contains 14 wt% of [Hbet][Tf_2N].

6. Water treatment

As mentioned in the paper, the treatment of the water phase is important in order to recover all of the ionic liquid dissolved in the water phase (≈ 14 wt%). This can be done with different methods such as adsorbents, special membranes, electrodialysis or nanofiltration, but here a recovery process is proposed based on the salting-out of the ionic liquid using inorganic salts. First the water is cleaned using $Ca(OH)_2$ to precipitate the iron(III) as $Fe(OH)_{3(s)}$ and the oxalate as $CaC_2O_{4(s)}$ together with other possible impurities. After filtering off the precipitates, the water is treated with Na_2SO_4 (3 M) to completely remove the ionic liquid from the water (< 0.15 wt% IL in the water phase after one step). This process is shown schematically in Figure S5. In order to avoid consumption of Na_2SO_4, this salting-out step can also be performed in an evaporation pond in which the rate of incoming water is equal to the evaporation rate, effectively keeping the Na_2SO_4 concentration constant while continuously salting-out the ionic liquid from the water phase.

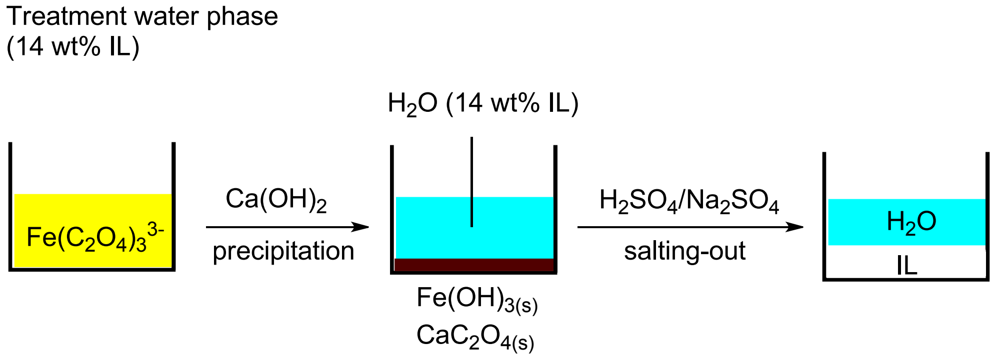

Figure S5. Possible water treatment process to recover the ionic liquid from the water phase.

References

1. J. H. Hubbell and S. M. Seltzer, National Institute of Standards and Technology (NIST), NIST X-ray Attenuation Databases, http://physics.nist.gov/PhysRefData/XrayMassCoef/tab3.html, 2014.
2. J. B. Kortright and A. C. Thompson, Lawrence Berkeley National Laboratory, X-RAY DATA BOOKLET, http://xdb.lbl.gov/Section1/Sec_1-2.html, 2009.