Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information to

Rare Earth Recovery from End-of-Life Motors employing Green Chemistry Design Principles

*H.M. Dhammika Bandara, Kathleen D. Field, Marion H. Emmert**

Center for Resource Recovery and Recycling
Department of Chemistry and Biochemistry
100 Institute Road
Worcester Polytechnic Institute
Worcester, MA 01609

Table of Contents

1. General Procedures

Chevrolet Volt Spark Drive Units were obtained from GM; small motors containing NdFeB magnets were purchased from Great Planes through amazon.com. NdFeB magnets (non-bonded and bonded) were purchased from McMaster-Carr; copper wire was purchased from VWR; black oxide case-hardened steel washers and corrosion-resistant washers (iron alloy steel) were purchased from McMaster-Carr. Unless noted otherwise, all used acids (purity: ACS grade) were purchased through VWR.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed using a Perkin Elmer (Optima 8000) instrument and were calibrated using atomic spectroscopy standards purchased from Perkin Elmer. All solutions for ICP-AES measurement were prepared using ultrapure (Milli-Q) water generated by a Millipore (Synergy UV) instrument.

2. Leaching of Non-bonded NdFeB Magnets using Different Acids

In analogy to the general procedure, acid solution (20 mL) and one NdFeB magnet (0.77 g) were stirred in a vial equipped with a Teflon-coated stirbar and a pressure-relief cap at RT for 24 h. Recovery of the magnetic material (Table 1) was performed as described in the general procedure.

Table 1. Dissolution Behaviour of NdFeB Magnets in Different Strong and Weak Acids.

Acid	**Original Weight [g]**	**Remaining Weight [g]**	**Dissolved Mass [%]**
4 M HCl	0.77	0	100%
2 M H_2SO_4	0.77	0	100%
5 M AcOH	0.771	0.484	37%
5 M HCO_2H	0.773	0.464	40%
5 M $(CO_2H)_2$	0.774	0.75	3%
5 M $H_3CCH(OH)CO_2H$	0.771	0.756	2%

3. Leaching of NdFeB Magnets with Different Concentrations of HCl and H_2SO_4

In analogy to the general procedure, acid solution (20 mL) and one NdFeB magnet (0.77 g) were stirred in a vial equipped with a Teflon-coated stirbar and a pressure-relief cap at RT for 24 h. Recovery of the magnetic material (Table 2) was performed as described in the general procedure.

Table 2. Dissolution Behaviour of NdFeB Magnets in HCl and H_2SO_4.

	HCl		**H_2SO_4**	
$[H^+]$ Concentration	**Dissolved Mass**	**StDev[a]**	**Dissolved Mass**	**StDev[a]**
1 M	16.5%	0.7%	45.9%	1.1%
2 M	87.8%	0.8%	65.3%	1.1%
4 M	100.0%	0.0%	100.0%	0.0%
6 M	100.0%	0.0%	100.0%	0.0%
8 M	100.0%	0.0%	88.4%	0.2%
12 M	100.0%	0.0%	13.6%	1.1%

[a]The provided errors are standard deviations of at least 2 replicate trials.

4. Leaching Selectivity Experiments with Case-Hardened Steel Washers

In analogy to the general procedure, acid solution (10 mL) and one case-hardened steel washer (0.58 g) were stirred in a vial equipped with a Teflon-coated stirbar and a pressure-relief cap at RT for 24 h. Recovery and weight determination of the undissolved material (Table 3) was performed as described in the general procedure.

Table 3. Dissolution Behaviour of Case-Hardened Steel Washers in HCl and H_2SO_4.

	HCl		**H_2SO_4**	
Acid Concentration	**Dissolved Mass**	**StDev[a]**	**Dissolved Mass**	**StDev[a]**
1 M	3.1%	1.1%	14.3%	1.1%
2 M	4.8%	0.9%	30.2%	1.1%
4 M	9.4%	2.9%	36.2%	1.1%
6 M	22.7%	1.4%	40.9%	2.5%

[a]The provided errors are standard deviations of at least 2 replicate trials.

5. Leaching of Non-bonded NdFeB Magnets and Steel Washers with HCl and H_2SO_4 at 50 and 80 °C

In analogy to the general procedure, acid solution (20 mL) and one NdFeB magnet or steel washer were stirred in a vial equipped with a Teflon-coated stirbar and a pressure-relief cap. Recovery of the material was performed as described in the general procedure.

Table 4. Dissolution Behaviour of Case-Hardened Steel Washers and Non-Bonded NdFeB Magnets in HCl and H_2SO_4 and 50 and 80 °C.

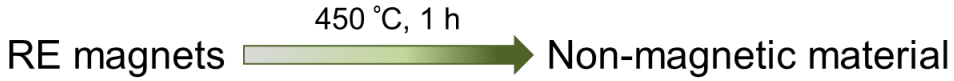
Acid (4 M)	Temperature (°C)	Material	Time (h)	% Dissolved
H_2SO_4	50	NdFeB magnet	2	67.8
			24	100
		Steel Washer	2	33.3
			24	100
H_2SO_4	80	NdFeB magnet	2	92
			24	100
		Steel Washer	2	85.2
			24	100
HCl	50	NdFeB magnet	2	100
			24	100
		Steel Washer	2	13.9
			24	59.86
HCl	80	NdFeB magnet	2	100
			24	100
		Steel Washer	2	40.2
			24	100

6. Demagnetization and Shredding

Demagnetization of RE magnets was performed by heating the magnets in a ThermoScientific model FD15454M bench top ultra-high temperature furnace to 450 ºC for 1 h in air. The complete heating cycle, including heating (rate of 5 ºC/min), holding at 450 °C for 60 min, and cooling (rate of 5 ºC/min), lasted 235 min.

After demagnetization, the magnets were shredded in a Schutte Buffalo Hammer Mill (Laboratory Scale, Model 6-H). The hammer mill contained a screen with 6 mm holes (diameter) and was run at 2000 rpm. After shredding, the recovered weight was determined by weighing (Table 5).

Table 5. Recovered weight of demagnetized vs. non-demagnetized RE magnets after shredding.



Material shredded	Weight shredded (g)	Weight recovered (g)	Recovered weight -%
RE magnets	18.6	4.8	26%
Demagnetized RE magnets	18.6	16.4	88%

7. Recovery of REs as Oxalates from Small Motors

Information on used motors

The motors for these experiments were obtained through amazon.com from the seller Great Planes. The obtained model was labeled as Great Planes ElectriFly RimFire .10 35-30-1250 Outrunner Brushless Motor.

Specifications:
Diameter: 1.38" (35mm)
Length: 1.18" (30mm)
Shaft Diameter: 0.16" (4mm)
Shaft Length: 0 .65" (16.5mm)
Lead Length: 3" (76mm)
Connectors: 3.5mm Gold-Plated Bullet
Max Constant Current: 30A
Max Surge Current: 35A
Max Constant Watts: 333W
Max Burst Watts: 390W
No Load Current: 1.2A
Input Voltage: 7.4 ~ 11.1V (2 ~ 3S Li-Po)
RPM/V (kV Rating): 1250
Weight: 2.5oz (71g)
Suggested Propeller Size: 10 x 4.5 ~ 10 x 7 Electric

Process for RE recovery from motors

A motor (76.6 g overall, determined independently by weighing), consisting of NdFeB magnets (14 × 0.57 g magnets corresponding to 8.0 g; 17 mmol of a 15:1:4 mixture of Nd, Dy, and Pr, as determined by ICP-AES), copper coils (7 g), and steel casing (56 g) was demagnetized in a furnace (temperature program: heat to 450 C for 105 min, keep at 450 ºC for 60 min, cool to room temperature for 105 min). After cooling, the motor was shredded with a hammer mill (Schutte Buffalo Hammermill, Model W-6-H, 19 or 6 mm screen openings; see **Error! Reference source not found.**). The resulting scrap was treated with 4 M hydrochloric acid (200 mL, 800 mmol, 47 equiv.) for 6 to 24 h; hydrogen evolution was observed during the leaching process. The resulting leach solution showed the presence of 88% of rare earths (15 mmol; Nd:Dy:P = 15:1:4) from the original magnet materials (as determined by ICP-AES). The solution was filtered through a paper filter (pore size 11 μm) to separate the remaining steel and copper solids. The pH of the filtrate was adjusted to pH 0.60 with 15 mL of concentrated hydrochloric acid. Oxalic acid (4.0 g, 45 mmol, 3 equiv. compared to previously determined 15 mmol of rare earths) was added as a solid to the solution. After stirring the resulting suspension for 120 min at

room temperature, the precipitate (mixed rare earth oxalates) was isolated by filtration and washed with 20 mL of water. TXRF analysis of the remaining filtrate showed the presence of Zn, Fe, Co, Ni, Mn, Nd, Dy, and Pr in the filtrate. For ICP-AES analysis, the precipitate was redissolved by addition of 20 mL of 4 M hydrochloric acid; the analysis showed the presence of 14 mmol of rare earths (Nd:Dy:Pr= 15:1:3) in a purity of 99.8% with an impurity of 0.02% Fe. The overall recovery can thus be calculated to be 82%, based on the amount of rare earths present in the original motor material.

8. Recovery of REs as Oxalates from 2014 Chevrolet Spark FWD Drive Unit

A 2014 Chevrolet EV Spark FWD drive unit rotor assembly (14.6 kg; containing 400 coated rare earth magnets with a total mass of 2.2 kg of rare earth magnet alloy) is disassembled into large pieces using a power press. The resulting pieces were cut into smaller pieces using an abrasive cutting wheel (9 inch diameter, reinforced aluminum oxide). One piece weighing 168.41 g, consisting of NdFeB magnets (4 large at 8.5 g each and 4 small at 2.4 g each, corresponding to 8 magnets, 43.6 g total, 87 mmol of a 1:3:2 mixture of Pr, Nd, and Dy as determined by ICP-AES) and steel casing was demagnetized in a furnace (temperature program: ramp to 450 °C for 105 minutes, keep at 450 °C for 60 minutes, cool to room temperature for 105 minutes). After cooling, the material was shredded with a hammer mill (Schutte Buffalo Hammermill, Model W-6-H, 19 mm screen openings), which provided 99% recovery of starting material. The resulting scrap was treated with 4 M Hydrochloric acid (1.1 L, 4.4 mol, 51 equiv.) for 24 hours; hydrogen evolution is observed during the leaching process. The mixture was filtered twice through filter paper (pore size 20-25 um in first filtration, followed by pore size 11 um in second filtration) to separate the remaining steel (mass of recovered material = 122 g). The pH of the filtered material was adjusted to pH 0.57 with concentrated hydrochloric acid. Oxalic acid (23.5 g, 0.261 mol, 3.0 equiv.) was added as a solid to the leach solution. After stirring the suspension for 2 hours at room temperature, the precipitate (mixed rare earth oxalates) was isolated by filtration, washed with Millipore water and dried in air with an overall 80% yield of 39.19 g. The composition of the precipitate was analyzed by dissolving 1.5 g precipitate in 20 mL 4 M HCl, which was then diluted to 200 ml with Millipore water and analyzed by ICP-AES. The precipitate was determined to be 99.7 % rare earths and 0.3 % iron impurity (as determined by ICP-AES).

Table 6. Metal Composition (mg/L) of Solutions from Recycling Process as Determined by ICP-AES.

Metal	Leach solution obtained from leaching materials mixture (mg/L)	Rare earth oxalate precipitate after dissolving 1.5 g precipitate in 20 mL 4 M HCl (mg/L)	Filtrate solution obtained from isolating rare earth oxalates (mg/L)
Fe	563 ± 2	0.027 ± 0.08	268.6 ±2.4
Co	87.9 ± 0.6	n/a	105.1 ± 0.9
Pr	16.3 ± 0.4	1.7 ± 0.2	25.1 ± 0.2
Nd	73.7 ± 0.1	4.4 ±- 1.9	61.9 ± 0.5
Dy	35.8 ± 0.4	3.6 ± 1.4	40.1 ± 0.3
B	34.6 ± 0.4	n/a	36.7 ± 0.3