Electrochimica Acta

Electrodialytic Recovery of Rare Earth Elements from Coal Ashes
--Manuscript Draft--

Manuscript Number:	EREM19-11R2
Article Type:	VSI: EREM 2019 Guanajuato
Keywords:	Coal ash; electrodialytic separation; critical raw materials; LREE; HREE
Corresponding Author:	Nazaré P.F.S Couto, PhD CENSE, Departamento de Ciências e Engenharia do Ambiente, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal. Caparica, Portugal
First Author:	Nazaré P.F.S Couto, PhD
Order of Authors:	Nazaré P.F.S Couto, PhD
	Ana Rita Ferreira, PhD
	Vanda Lopes, MSc
	Stephen Peters, Professor
	Eduardo P. Mateus, PhD
	Alexandra B Ribeiro, Professor
	Sibel Pamukcu, Professor
Manuscript Region of Origin:	PORTUGAL
Abstract:	Rare earth elements (REE) are critical raw materials crucial for modern technologies and used in a variety of industries. There is a need of investment in REE recovery from secondary sources. The present work was designed to assess the potential of the electrodialytic process to recover REE from coal ash. The content of REE was evaluated in bituminous and anthracite ash. Anthracite presented higher REE concentration (447 ppm vs. 138 ppm) and a triple concentration of critical REE compared with bituminous ash. Anthracite ash was treated aiming to test the REE recover potential, including differences between light REE (LREE) and heavy REE (HREE) fractions as well as the specific recovery of REE with high criticality. A two-compartment electrodialytic cell was tested with the matrix placed in the anode compartment and a cation-exchange membrane separating the compartments. Experiments lasted a maximum of 7 days applying different current intensities and pH adjustment in the catholyte (» 2). Three main steps are observed in the removal process 1) REE solubilization - from the solid to the liquid phase (anolyte); 2) REE mobilization - movement from the anolyte towards the cathode end; 3) REE removal - presence in the catholyte. The extent of each step observed for the REE depends on their individual position in the periodic table with HREE removal being more regulated by step 1 and LREE by step 2. At the best tested conditions (50 mA, 3 days, pH adjustment), more than 70% of REE were extracted from the ash with the catholyte enclosing up to » 50% of LREE and HREE. Combining the high criticality of neodymium with its high concentration in anthracite coal ash (65 ppm), the electrodialytic treatment is highly recommended to concentrate this REE in the catholyte. The results demonstrated the proof-of-concept for electro-assisted extraction of REE from anthracite coal ash, opening perspectives to a selective recovery of these elements from secondary sources.

Date: 07-08-2020

Ms. Ref. No.: ELECTACTA-S-20-00995

Title: Electrodialytic Recovery of Rare Earth Elements from Coal Ashes

Journal: Electrochimica Acta (EREM SI)

Letter to Editor

Dear Dr. Sergio Trasatti,

The authors would like to thank the Editor for the given opportunity to clarify the points risen to the manuscript "Electrodialytic Recovery of Rare Earth Elements from Coal Ashes". We analyzed all the reviewer's comments and the manuscript was revised accordingly (please see the reply to reviewer's comments below). Corrections and changes are highlighted with a yellow background. We trust these changes will clarify all the points risen by the referees. Authors would like to acknowledge the dedication, time and effort that reviewers put throughout the revision process. Additionally, authors included a Graphical Abstract & Highlights section and changed the word "Extraction" by "Recovery" in the Article title.

Yours sincerely,

Nazaré Couto

Reviewer 3

The authors have revised the manuscript according the reviewers' comments, and it can be considered for publication.

Previous Comment	Recent Comment	Author response	Changed text in the revised manuscript
pH adjustment with HNO3 1:1, it means 50% or 30% or other	I still suggest to include the concentration of the nitric solution in the text of the manuscript "(32.5% of HNO_3 in water).	Authors acknowledge all the reviewing process. The info was added to the manuscript	*Section 2.2.3.* (…) for 3 days, without (EDR3) or with (EDR4) pH adjustment in the catholyte (pH $\approx$ 2) using a HNO_3 ==solution in water (32.5%)"==

_____

Reviewer 4

The revised version of this manuscript shows improvement in clarity. But some questions were responded only partly and still need to be clarified. I am summarizing the concerned point below:

Previous Comment	Recent Comment	Author response	Changed text in the revised manuscript

1. The information on ashes used and leacheates obtained does contain just information on the REEs content. No information on other elements present in the solution and potentially transported through the membrane (or accumulated in the membrane) is provided. What is composition of the cathode compartment solution and metals deposited on the cathode? What are the other major elements present and their concentration? What is the value of Faradayic efficiency reached for the REEs transport?	ad 1) I understand from the response provided, that analysis of the leachate provided covers only REE. It is to the certain degree unfortunate, because important content of various ions may be expected. And this would have implications for the process studied. What I am not sure about about are the changes in manuscript provided. It, in majority, does not correspond to the question raised. Information on	Authors acknowledge the comment and inserted the information in two ways : • "Materials and methods" section - explaining that only REE were analyzed • "Technology feasibility and further investigations " section - explaining that the process efficiency did not consider the extraction and movement of other elements than REE	*Section 2.2.3* "Coal ash extract and the liquid samples <mark>were analysed for REE content by ICP-MS."</mark> *Section 3.4* <mark>Another point is the understanding about the potential presence of other extract constituents – elements present in the solution and potentially transported through the membrane (or accumulated in it) – as the process efficiency may increase if electrons or ions are not participating in (unwanted) side reactions and/or (electro)migration.</mark>

	the absence of information on other potential extract constituents would be sufficient.		
2. I did not find any information in the manuscript on the energy consumption related to the REEs removal/transport to the cathode compartment. This should provide sound conclusions, together with identification of the most promising conditions/directio n of research and development leading to the economically feasible technology.	ad 2) Thanks for added information on energy consumption. However, it shall be related to the kg (or gram) of the product, i.e. sum of recovered REEs. Relation to the kg of treated ash is not relevant. It can be set arbitrary and it does not provide information about energy costs per unit of product.	Author thanks for the valuable comment and output. Taking into consideration that "criticality" is different among rare earth elements, authors related energy consumption with Nd and Dy recovery. The relation with *kg of ash* is still present to have an idea of the overall process consumption / scale up.	*Section 3.4* Average energy consumption in EDR4, the optimized conditions, is of 2.84 kWh *per* kg of ash, ==representing a recovery [cathode end, *average (stdev)*] of 36.5 (9.2) mg of Nd and 4.0 (0.3) mg of Dy; to scale-up the process by increasing CEM area (same current density) the recovery would be of 2.4 (0.6) g Nd / m^2 / day.==
3. Description of design of the	ad 3) Thanks for the	Authors revised the text for sake of clarity	Still directed to the process up-

electrodialysis cell used for the reported experiments is not clear. Cell is claimed to be cylindrical. Figure 1 at the same time shows cell, which does not look like cylindrical, unless only cut through half of the cell is shown. At such case, however, stirrer will not work very well. In chapter 2.2.3, length of cathode compartment is given as 5 cm and that of the anode compartment as 10 cm. What does mean this length? Is it the radius, or height? If this is the distance between the electrode and membrane, it is extremely high and I do not see the reason for such	improvement of Figure 1. Now it is much clearer. I have some doubts about this design. This concerns energy efficiency, local potential and current density distribution homogeneity, mass transfer intensity, impact of ash particles on mechanical stability of the membrane during long time exposure etc., but if I consider this study just as a trial of transport of the REEs ions across the membrane, it may provide		scale, <mark>the impact of ash particles on mechanical stability of the membrane during long term exposure, test of other market available CEM (e.g. Fuji CEMT1 or Fumasep FKS),</mark> shorter treatment times and development of economically feasible solutions, e.g., by using pulse current or by changing energy sources such as solar or photovoltaic panels, should also be studied.

arrangement. Especially, if we consider, that ash is suspended in distilled water, i.e. in medium of very low conductivity. Moreover, we are dealing with highly diluted systems and mass transport pathway becomes extremely long.	some information.		
4. Cation selective membrane from IONICS has been chosen for the experiment. Why this particular membrane? Does it possess any specific properties needed for this application? Any information on membrane activation etc. prior the experiment? Is there any potential impact of the membrane	ad 4) My question did not concern polarity of the membrane. It is rather obvious, that cation selective membrane has to be used in this particular case. The question is more in direction, why this particular membrane (CR67) was used and not	The use of CR67 had the purpose to follow the working line previously developed by the group with different classes of contaminants and matrices (please see examples below). 1. A.R. Ferreira, N. Couto, P. Guedes, E.P. Mateus, A.B. Ribeiro (2018) "Electrodialytic 2-compartment cells for emerging organic contaminants removal from effluent", Journal of Hazardous Materials, 358, 467-474 DOI: 10.1016/j.jhazmat.2018.04.066 2. A.R. Ferreira, P. Guedes, E.P. Mateus, N. Couto, A.B. Ribeiro (2017) "Influence of the cell design in the electroremoval of PPCPs from soil slurry",	*Section 3.4* Still directed to the process up-scale, <mark>the impact of ash particles on mechanical stability of the membrane during long term exposure, test of other market available CEM (e.g. Fuji CEMT1 or Fumasep FKS)</mark>, shorter treatment times and development of economically

selection on the results obtained?	e.g. Fuji CEMT1 or fumasep FKS, which are also available on the market? Membrane may have significant impact on the separation process and this aspect is not treated here at all. So, I would welcome comment on this aspect.	Chemical Engineering Journal, 326, 162–168 DOI: 10.1016/j.cej.2017.05.148 3. P. Guedes, N. Couto, L.M. Ottosen, G.M. Kirkelund, E.P. Mateus, A.B. Ribeiro (2016) "Valorization of ferric sewage sludge ashes: potential as a phosphorus source", Waste Management, 52, 193-201, DOI: 10.1016/j.wasman.2016.03.040 4. P. Guedes, N. Couto, L.M. Ottosen, A.B. Ribeiro (2014) "Phosphorus recovery from sewage sludge ash through an electrodialytic process", Waste Management, 34(5), pp. 886-892, DOI: 10.1016/j.wasman.2014.02.021 In the manuscript, the possibility of testing other commercial membranes (giving Fuji CEMT1 and Fumasep FKS as exemples) was highlighted in the "Technology Feasibility and future investigations" section.	feasible solutions, e.g., by using pulse current or by changing energy sources such as solar or photovoltaic panels, should also be studied.
e) Terms like "ash pH" and "ash conductivity" (page 4 and Table 3) are misleading.	ad 5) Confusing terms corrected. Thanks.	-	

If I understand description provided well, it concerns conductivity of suspension of the ash in distilled water. In Table 3, moreover, units used are missing at the conductivity values reported.			
5. Definitions of the terms "removal efficiency" and "extracted fraction" provided at page 8 is not very clear. "Removal efficiency" - is the CEM counted as a cell compartment? Numerator contains REEs content in all cell compartments. It shall include also CEM. "Extracted fraction" - Denominator contains REEs in both ED cell	ad 6/5) Removal efficiency and extracted fraction are now clear. Thanks.	-	

compartments. Numerator contains again REEs content sum in all cell compartments. So, it means, it is by definition equal to 1.			
6. Figure 3 shows clear minimum at pH around 1.8. I did not find any comment on it. Is this observation reproducible?	ad 7/6) Yes, it concerns figure 2. Sorry for typo. Now the scale of axis X is changed and region between pH 1 and approx 2.8 is marked to indicate optimal pH of selected metals extraction. But my question on the REE recovery minimum occurring at pH approx 1.8 was not responded at all. Is this systematic local extreme?	In this revised version the lines connecting the dots were removed as the behavior of pH leaching could change between the tested pHs. Also, the legend of YY axis changed from "recovery" to "extraction". Authors studied Fig.2 and assume the reviewer was referring to pH 4 as the extraction efficiency is decreasing in the order 1.8 - 2.5 - 4. For this reason, authors will discuss this pH. Due to the absence of replicates the behavior for different pHs cannot be considered reproducible. Nevertheless, the decrease of REEs desorption with increased pH (1.8 > 2.5 > 4) is	*Section 2.2* Ash suspensions were shaken for 7 days in a vertical rotating mixer at 21 rpm, room temperature <mark>(n=1).</mark> *Section 3.2* REE were extracted (desorbed from ash to the liquid phase) at acidic pH, particularly at a pH ≤ 2.5 where between 70 and 100% of LREE, and 17 and 88% of HREE were

| | How many times it was reproduced? If it was reproduced, what is the reason for this behavior? If it was not reproduced, what is the accuracy of the data provided? | in line with the extraction observed at alkaline pHs (up to 13%).

The text was revised for sake of clarity. | extracted (Fig. 2). <mark>The extraction efficiency continued to decrease with increasing pH. At pH 4, up to 27% REE were desorbed from the ash to the liquid phase whereas in alkaline conditions the maximum value was of 13% (data not shown).</mark> There is a different tendency for REE desorption according to its position in the periodic table. Extraction efficiency is, generally, higher for LREE than for HREE. It is clear that, for pH desorption, Eu follows the behavior of LREE, in this |

			case, following the IUPAC classification.
7. On page 8 is mentioned possible complexation of the REE in the anolyte compartment. What shall be the complexing agent?	ad 8/7) Complexation - OK. Good it is removed. It will thus not confuse reader.	-	
8. On the page 8 again following sentence appears: "LREE stayed in the membrane whereas HREE reached catholyte - HREE presence in anolyte suggests migration would continue, but for LREE more time would be needed to allow extraction from the ash". This is not consistent. LREEs stay in membrane, or in the ash?	ad 9/8) OK, thanks for modification.	-	

9. Once more page 8. Different electromigration velocity of selected elements is mentioned at page 8. It concerns higher migration of atoms with higher atomic number. I am missing any discussion here. Are mobilities of concerned ions in the solutions known? If not, is there a chance for their estimation? At least discussion of the ions size, charge and from this following extend of their solvation shall can be used to discuss the phenomena observed.	ad 10/9) I assume, the original sentence is now changed to "... more efficient dissolution and electromigration towards ..." on page 9. But since the authors do not comment specifically in their response on corresponding change provided, it is just my guess. This formulation is slightly inaccurate. Dissolution and migration are interconnected. As the migration term in Nernst-Planck equation contains	Thank you for the comment. The expression was adjusted and authors inserted the explanation about Nernst-Planck equation in the manuscript.	*Section 3.3* The HREE with an odd atomic number (Eu, Tb, Ho, Tm, Lu) present a more efficient dissolution and thus more intensive electromigration towards the electrode of opposite charge, with a final value between 17 - 28% in the catholyte. In fact, a more efficient dissolution is connected with more intensive mass transfer, as the migration term in Nernst-Planck equation contains concentration.

	concentration, it is clear, that more efficient dissolution is connected with more intensive mass transfer via migration. May be something like " ... and thus more intensive electromigration ..." is more appropriate.		
10. Statement on page 10 on more efficient migration through CEM due to the presence of H+ in the cathode compartment is interesting and deserves discussion. Does it mean penetration of H+ to the bulk of the membrane and change of its transport properties due to the more extensive swelling? Or is it	ad 11/10) OK, question of the H+ ions impact is clearer now.	-	

related just to the blockage of the membrane surface by precipitates? Or something completely different, e.g. change of the membrane cycle?			
1l. Manuscript is rather descriptive in general. Discussion of the observed phenomena is close to zero and just results obtained are listed.	ad 12/11) This part is improved now. Thanks.	-	
	a) Experimental section - current load used, i.e. 10 mA and 50 mA, is reported in absolute values? So, average current density on the membrane is 0.2 and 1 mA cm-2? This provokes one	The information was added to the "Technology feasibility and further investigation" section taking into consideration the REE selected on ad 2.	*Section 3.4* Average energy consumption in EDR4, the optimized conditions, is of 2.84 kWh *per* kg of ash, ==representing a recovery [cathode end, *average (stdev)*] of 36.5 (9.2) mg of Nd and 4.0 (0.3) mg==

	question - how many grams of REE are transported to the cathode compartment per day and per meter square of the membrane? This information is missing in the manuscript. Just percents are given ... It is closely related to point (2) above. So, absolute values should be added as well.		==of Dy; to scale-up the process by increasing CEM area (same current density) the recovery would be of 2.4 (0.6) g Nd / m^2 / day.==
	b) line 248 - REE in an anolyte in form of uncharged species. What form it is? Metallic??? If we consider acidic pH of the anolyte, it will not be form of	Authors removed the part of "uncharged species" for sake of clarity.	*Section 3.3* REE in the anolyte may be ~~==as uncharged species or==~~ as ionic forms, mainly present with an ionic charge of +3. The recovery (REE in the cathode end)

	hydroxide precipitates.		was between 0.9 and 13.6%.

Graphical Abstract
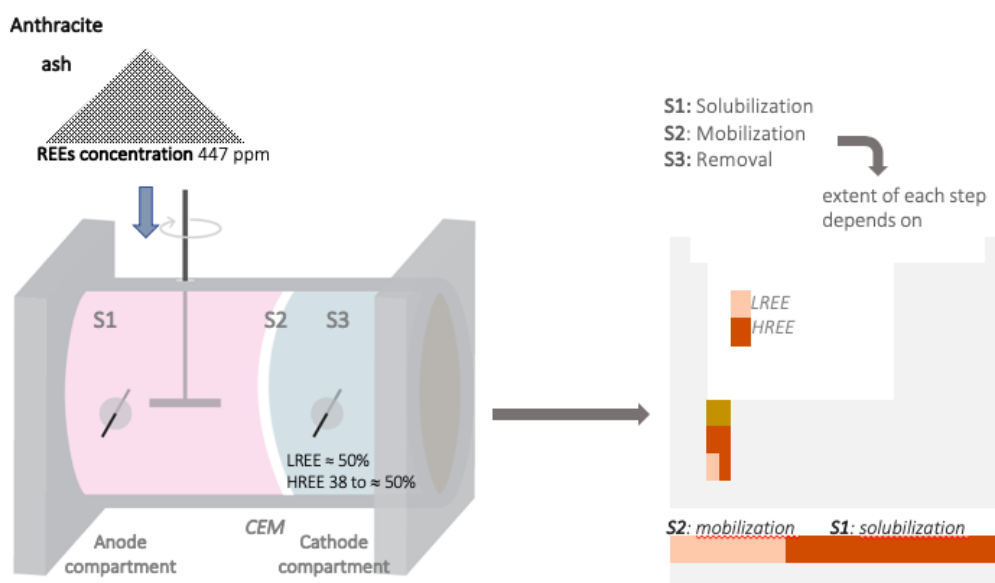
- Removal process regulated by 3 main steps dependent on REE position in the periodic table

- HREE removal more regulated by solubilization and LREE by mobilization.

- EDR under the tested conditions allow >70% REE extracted from ash and up to ≈ 50% in the catholyte

- Criticality, concentration and EDR-removal puts the process in the path of Nd recovery

1 **Electrodialytic Recovery of Rare Earth Elements from Coal Ashes**

2 **Nazaré Couto[1,2*], Ana Rita Ferreira[1,2], Vanda Lopes[1,2], Stephen Peters[3], Eduardo P.**

3 **Mateus[1], Alexandra B. Ribeiro[1], Sibel Pamukcu[2]**

4 [1] Center for Environmental and Sustainability Research (CENSE), NOVA School of
5 Science and Technology, NOVA University Lisbon 2929-516 Caparica, Portugal

6 [2] Department of Civil and Environmental Engineering, Lehigh University, Bethlehem,
7 PA 18015, USA

8 [3] Department of Earth and Environmental Sciences, Lehigh University, 1 West Packer
9 Avenue Bethlehem, PA 18015, USA

10 *Corresponding author: E-mail address: md.couto@fct.unl.pt

11

12 **Abstract**

13 Rare earth elements (REE) are critical raw materials crucial for modern technologies and

14 used in a variety of industries. There is a need of investment in REE recovery from

15 secondary sources. The present work was designed to assess the potential of the

16 electrodialytic process to recover REE from coal ash. The content of REE was evaluated

17 in bituminous and anthracite ash. Anthracite presented higher REE concentration (447

18 ppm *vs.* 138 ppm) and a triple concentration of critical REE compared with bituminous

19 ash. Anthracite ash was treated aiming to test the REE recover potential, including

20 differences between light REE (LREE) and heavy REE (HREE) fractions as well as the

21 specific recovery of REE with high criticality. A two-compartment electrodialytic cell

22 was tested with the matrix placed in the anode compartment and a cation-exchange

23 membrane separating the compartments. Experiments lasted a maximum of 7 days

24 applying different current intensities and pH adjustment in the catholyte (≈ 2). Three main

25 steps are observed in the removal process 1) REE solubilization - from the solid to the

26 liquid phase (anolyte); 2) REE mobilization - movement from the anolyte towards the

27 cathode end; 3) REE removal - presence in the catholyte. The extent of each step observed

28 for the REE depends on their individual position in the periodic table with HREE removal

29 being more regulated by step 1 and LREE by step 2. At the best tested conditions (50 mA,

30 3 days, pH adjustment), more than 70% of REE were extracted from the ash with the

31 catholyte enclosing up to $\approx$ 50% of LREE and HREE. Combining the high criticality of

32 neodymium with its high concentration in anthracite coal ash (65 ppm), the electrodialytic

33 treatment is highly recommended to concentrate this REE in the catholyte. The results

34 demonstrated the proof-of-concept for electro-assisted extraction of REE from anthracite

35 coal ash, opening perspectives to a selective recovery of these elements from secondary

36 sources.

37

38

39

40 **Keywords:** Coal ash, electrodialytic separation, critical raw materials, LREE, HREE

41

42

43

44 **Acronyms**:

45 CEM: Cation Exchange Membrane

46 ED: Electrodialytic Process

47 EDR: Electrodialytic Recovery

48 HREE: Heavy Rare Earth Elements

49 ICP-MS: Inductively Coupled Plasma-Mass Spectrometer

50 LREE: Light Rare Earth Elements

51 MMO: Mixed Metal Oxide

52 PCA: Principal Component Analysis

53 REE: Rare Earth Elements

54

55

56

57

58

59

60

61

1. Introduction

Rare earth elements (REE) are a group of metallic elements, similar to each other, composed of scandium, yttrium, and the 15 lanthanides. REE are divided in light (LREE) and heavy rare earth elements (HREE) according to their atomic number. Reserves of REE are unequally distributed in the world and for instance the European Union is entirely dependent on imports [1]. REE are listed as critical raw materials which are extremely important for economic growth, development of modern technology and environmental protection [2–4]. According to European Commission, LREE and HREE substitution indexes are low (between 0.89 and 0.93 in a scale from 0 to 1, where 1 is non substitutable) and the recycling rate between 3% and 8% for LREE and HREE, respectively [4]. The substitutes available for some applications may induce technical problems, loss of performance and/or high cost [5–7].

The medium-term criticality matrix (2015-2025) defined the five most critical REE as neodymium (Nd), dysprosium (Dy), europium (Eu), yttrium (Y) and terbium (Tb) [8]. However, due to market changes, recent studies show Nd and Dy as the elements presenting the highest criticality while Tb and Eu criticality is decreasing [9].

REE are not found in an isolated form but in a variety of minerals where, in most cases, they exist in concentrations too small for economical extraction [10]. Primary mining of REE focus on bastnaesite, monazite and loparite and the lateritic ion-adsorption clays, whereas secondary sources/ores are urban mines or industrial process residues [11]. Acid mine drainage, mine tailings, metallurgical slags, wastewater streams, coal and by-coal products [6,12–14] are examples of secondary sources with potential for REE recovery with socio-economical and environmental benefits.

Power plant coal ash may have a substantial enrichment of REE compared to feed coal [15,16]. USA is in a privileged position for REE recovery from coal ash attending to (i) the three USA geostrategic coal basins (Appalachian, Illinois and Powder River basins) and (ii) up to ≈ 90% of the consumed coal is burned for power generation [17]. In Europe, although the much-needed energetic transition is in place closing coal power plants, there are million tonnes of coal fly ash landfilled that can eventually be processed with innovative cost-efficient technology to satisfy the market needs.

The concentration of REE in coal fly ash depends on the coal origin and is in the order of hundreds of ppm [18–22]. Specifically, fly ash from Illinois Basin coals presented an

3

94 average total REE content of 403 mg/kg, Powder River Basin of 337 mg/kg and

95 Appalachian coals of 591 mg/kg, depending on the power plant location [22]. High

96 demand REEs according to the medium-term criticality matrix (2015-2025) (Nd, Y, Dy,

97 Er, Tb, and Eu) may represent 34 – 38% of total REEs in fly ash [22].

98 REE recovery may be achieved by a broad range of techniques and procedures such as:

99 leaching, digestion, electrolysis, ion exchange, sintering, calcination, chlorination,

100 precipitation, sublimation, magnetic separation, flotation and solvent extraction, e.g.

101 [12,18,23-25]. Almost all the technologies may have selectivity and purification limits.

102 In the case of acid leaching, recovery efficiency is dependent on the source and

103 characteristics of the coal ashes [19]. A preparation step may be carried out to increase

104 the extraction efficiency as, e.g., hindered solubilization happens when aluminosilicate

105 glass is the predominant phase in fly ash ([19], [26]).

106 The electrodialytic (ED) process (PCT/DK95/00209) has been investigated over the years

107 as a technique to separate a broad range of contaminants from different matrices under

108 the influence of an electric field generated between electrodes and using ion exchange

109 membranes to separate (physically and chemically) the contaminated matrix from the

110 electrolytes. ED process proved to be efficient in removing metals and/or phosphorus (a

111 critical raw material [4]) from, e.g., sewage sludge ash, in a cell divided into two or three

112 compartments [27-31].

113 This work aims to evaluate the possibility to recover REE from coal ash using the ED

114 recovery (EDR) process. Bituminous and anthracite coal ash was assessed in terms of

115 REE concentration for treatability studies. Anthracite ash was electrodialytically treated

116 as stirred suspensions in a two-compartment cell at different current intensities, treatment

117 period and with pH adjustment, aiming to study the selectivity of REE recovery, focus on

118 Nd, Dy and Tb.

119

2. Materials and Methods

2.1. Coal ash

122 Samples were collected from a strip mine in the Eastern Middle field, Columbia County,

123 Pennsylvania, USA (Lat. 40.8° N, Long. 76.36° W). For anthracite samples, the coal seam

124 sampled was the Mammoth Vein, a single bed up to 12-15 m (40-50 ft) thick. Coal was

4

125 cut, crushed and ground to *approx*. <1 mm using an electrical wet saw, jaw crusher and a
126 ball mill, respectively.

127 Anthracite and bituminous coal were processed in laboratory according to ASTM
128 (D3174-12). Briefly, the sample was gradually heated till 500 °C, for 1 h, then heated to
129 750 °C for another hour staying at this temperature for 2 h, followed by overnight cooling.

130

131 ### 2.2. Analytical

132 #### 2.2.1. Coal ash characterization

133 Bituminous and anthracite ashes were extracted by mixing 0.2 g of dry ash and 0.9 g of
134 lithium metaborate, heated till 1000 ºC for 8 min, dissolved in 50 mL of 5% nitric acid
135 and filtered (0.45 μm). REE were measured by Inductively Coupled Plasma-Mass
136 Spectrometry (ICP-MS, Thermoelemental X-Series 2, Winsford, UK). One sample of
137 bituminous and one of anthracite ash were analysed for initial REE characterization.
138 Three replicates were made for the initial and EDR treated ash. Conductivity and pH of
139 the ash suspension (1:15 in deionized water, mass:volume (m:v), after 1 h of agitation)
140 was measured using a Radiometer pH and conductivity electrodes.

141

142 #### 2.2.2. Leaching tests

143 Leaching tests of the anthracite coal ash were carried out with a liquid:solid ratio (L/S) of
144 15. Concentration ranged between 1.0, 0.5, 0.1, 0.05, 0.01 M using NaOH and HNO_3.
145 Ash suspensions were shaken for 7 days in a vertical rotating mixer at 21 rpm, room
146 temperature (n=1). The samples were filtered through a 0.45 μm filter and REE
147 determined by ICP-MS.

148

149 #### 2.2.3. Electrodialytic experiments

150 The EDR experiments tested with anthracite coal ash (Fig. 1) were carried out in a
151 Plexiglas cylindrical cell, with an internal diameter of 8 cm, divided in two compartments
152 and separated by a homogeneous cation exchange membrane (CEM) containing sulfonic
153 acid functional groups (CR67, MKIII, blank, GE Water & Process Technologies). The
154 cathode compartment had a length of 5 cm and 210 mL of 0.01 M $NaNO_3$ solution as
155 electrolyte. The anode compartment had a length of 10 cm, equipped with a stirrer and

5

156 the coal ash suspended in deionized water in a ratio of 1:15 (m:v). Mixed metal oxide

157 (MMO) electrodes with a length of 6 cm and a diameter of 3 mm (Force®) were used. A

158 power supply (Fisher Scientific FB1000) was used to maintain a constant DC current.

159

160 **Please insert Fig. 1**

161

162 At the beginning and at the end of experiments current intensity, voltage, pH and

163 conductivity were measured. At the end of the experiment CEM and electrodes were

164 soaked in HNO_3 (1 M and 5 M, respectively) for 24 h and the suspended ash was drained

165 through filter paper to separate the solid from the liquid phase. The solid phase was dried

166 (105 °C) and extracted as referred in section 2.2.1. The liquid phase (anolyte, catholyte,

167 CEM and electrodes soaking solution) was filtrated through a 0.45-μm filter. Coal ash

168 extract and the liquid samples were analysed for REE content by ICP-MS.

169 A total of four EDR experiments (Table 1, two replicates) were carried out. Experiments

170 were performed applying a current intensity of 10 mA for 3 days (EDR1) or 7 days

171 (EDR2), and applying a higher current intensity, 50 mA, for 3 days, without (EDR3) or

172 with (EDR4) pH adjustment in the catholyte (pH ≈ 2) using a HNO_3 solution in water

173 (32.5%).

174

175 **Please insert Table 1**

176

3. Results and discussion

177

3.1. REE content in Coal ash

178

179 The overall REE concentration in bituminous and anthracite coal ash is presented in Table

180 2. As reviewed in [9], IUPAC classifies La to Eu elements as LREE and Gd to Lu plus Y

181 as HREE, while in Europe La to Sm elements are classified as LREE and Eu to Lu

182 elements plus Y as HREE; Scandium is normally treated separately. This work assumes

183 the european classification. Total REE concentration is 3.2 times higher in anthracite than

184 in bituminous coal ash (447 *vs*. 138 ppm). REE concentrations in coal ash are in

185 accordance with values already reported in literature e.g. [20,21]. Promethium was not

6

186 detected in any of the ashes possibly due to the short half-life of its isotopes [9].
187 Comparing with bituminous ash, anthracite ash presented *approx.* quadruple
188 concentration (3.8x) of LREE (351 *vs*. 92 ppm) and triple of HREE (80 *vs*. 27 ppm). In
189 both cases, (i) LREE are more abundant than HREE and (ii) REE with even atomic
190 number are also more abundant than those of odd atomic number due to the Oddo-Harkins
191 rule, as reported in literature e.g., [9]. Anthracite ash presented 8.5 ppm of Dy and 65.3
192 ppm of Nd, *approx.* the triple concentration [Dy (2.9x higher) and Nd (3.2x higher)] when
193 compared to the bituminous ash. The Tb, still critical but with an expecting decreasing in
194 criticality, also has a triple concentration in anthracite ash (1.2 *vs*. 0.4 ppm). These results
195 suggested that Mammoth Vein ash was the best matrix for the recovery of the extremely
196 critical Nd (as well as Dy and Tb, despite being in a lower concentration).

197

198 **Please insert Table 2**

199

3.2. Leaching experiments

201 REE were extracted (desorbed from ash to the liquid phase) at acidic pH, particularly at
202 a pH ≤ 2.5 where between 70 and 100% of LREE, and 17 and 88% of HREE were
203 extracted (Fig. 2). The extraction efficiency continued to decrease with increasing pH. At
204 pH 4, up to 27% REE were desorbed from the ash to the liquid phase whereas in alkaline
205 conditions the maximum value was of 13% (data not shown). There is a different tendency
206 for REE desorption according to its position in the periodic table. Extraction efficiency
207 is, generally, higher for LREE than for HREE. It is clear that, for pH desorption, Eu
208 follows the behavior of LREE, in this case, following the IUPAC classification. They are
209 mostly desorbed at pH 1.2, whereas the remaining HREE had a better response for pH
210 0.9 followed by 1.2. Sc has a behavior different from the other elements with a desorption
211 decrease between pH 0.9 and 2.5 from 65 to only 6%, corroborating the literature that
212 treat this element separately. For the critical REE, the approximate maximum desorption
213 rate at acidic conditions (0.9 < pH < 2.5) is ordered in the way: Dy (44 – 31%) << Tb (65
214 – 48%) << Nd (95 – 79%).

215

216 **Please insert Fig. 2**

3.3. EDR experiments

Changes in voltage, pH, and conductivity throughout the EDR experiments are shown in Table 3. Voltage decreased at the end of all treatments reflecting the conductivity increase after the EDR treatments through an increased concentration of ions in solution: in anode compartment through H^+ formation and particle dissolution, and in cathode compartment through OH^- formation and cations migration.

The initial pH in the anolyte varied between 4 - 5 and catholyte around 5 - 6. At the end of EDR treatment pH increased till *approx*. 12 - 13 in catholyte (except for EDR4 where it was manually adjusted to acidic) and decreased till *approx*. 2-3 in the anolyte. Placing the coal ash in the anode compartment allowed to take advantage of the generated acidic pH that enhances REE solubility, thus converting them into mobile ionic species that may migrate towards the cathode compartment, where they are removed.

Please insert Table 3

Please insert Fig. 3

Desorption and distribution of each REE in different cell compartments after the EDR treatments is shown in Fig. 3. The REE recovery efficiency is considered the quotient between the element removed from the ash and transported to the cathode end (catholyte + electrode + CEM) and the sum of REE in all cell compartments after the EDR treatment (equation 1). The REE extracted fraction is considered the quotient between the element in the anode end except in the ash (i.e. anolyte + electrode + stirrer) plus the element in the cathode end and the sum of REE in all cell compartments after the EDR treatment (equation 2).

$$Recover\ Efficiency\ (\%) = \frac{REE\ content\ in\ cathode\ end}{REE\ content\ in\ [cathode\ end + anode\ end\ (including\ ash)]} \times 100 \quad \textbf{(1)}$$

$$Extraction\ Efficiency\ (\%) = \frac{REE\ content\ in\ [cathode\ end + anode\ end\ (excluding\ ash)]}{REE\ content\ in\ [cathode\ end + anode\ end\ (including\ ash)]} \times 100 \quad \textbf{(2)}$$

8

246 The application of 10 mA for 3 days, EDR1, resulted in REE extraction between 1.1 and

247 23.4%, showing that the majority of REE were still bound to coal ash particles (not

248 desorbed). REE in the anolyte may be ~~as uncharged species or~~ as ionic forms, mainly

249 present with an ionic charge of +3. The recovery (REE in the cathode end) was between

250 0.9 and 13.6%. The critical REE were extracted in the order Dy (5.4%) < Nd (12.0%) <

251 Tb (14.4%) with 5 – 11% being mobilized to the cathode end [recovery Dy (4.8%) < Tb

252 (9.5%) ≈ Nd (10.6%)].

253 Extending the treatment for 7 days (EDR2; 10 mA, 7 d) enhanced REE extraction

254 (between 19.9 and 78.1%) and recovery (between 14.8 and 40.9%) suggesting that an

255 increase in the variable time improves the release of REE from the ash to the liquid phase

256 and promotes their movement towards the electrode of opposite charge. At the end of the

257 treatment, a total of *approx*. 60% of LREE were in the ash fraction, 27 - 38% in the CEM,

258 up to 6% in the anolyte, and ≈ 0.5 - 4% in the catholyte. Concerning the HREE between

259 23 – 79% were in the ash, 7 – 25% in the CEM, 21 - 34% in the anolyte [except for Gd,

260 Dy (and Sc) where the value was 5%] and 9 – 27% in the catholyte (except for Gd, Dy

261 and Y where the value was 2-3%). The HREE with an odd atomic number (Eu, Tb, Ho,

262 Tm, Lu) present a more efficient dissolution and thus more intensive electromigration

263 towards the electrode of opposite charge, with a final value between 17 - 28% in the

264 catholyte. In fact, a more efficient dissolution is connected with more intensive mass

265 transfer, as the migration term in Nernst-Planck equation contains concentration. The

266 HREE with even atomic number, are mainly present in the ash. Critical REE had a

267 maximum extraction and recovery for Tb [extraction: Dy (26.0%) < Nd (34.6%) < Tb

268 (64.3%); recovery: Dy (20.2%) < Nd (32.0%) < Tb (34.6%)].

269 Applying a higher current for a short time-period (EDR3, 50 mA, 3 d) resulted in an

270 extraction between 27 and 86% and a recovery between 22 and 50%. This treatment

271 slightly enhanced the recovery efficiency comparing with EDR2 (10 mA, 7 d) suggesting

272 that the increased current may substitute the need for a longer treatment time. On the other

273 hand, comparing the same treatment period for 10 and 50 mA, EDR1 and EDR3, the

274 application of higher current increased the desorption and electromigration of critical

275 REE. As already reported for other elements, after solubilization, mobilization towards

276 the opposite electrode compartment appears to be fast [27]. In EDR3 treatment, LREE

277 were mainly found in the ash fraction (51 - 61%), CEM (29 - 41%) and catholyte (up to

278 5%), as observed in Fig. 3. Europium, Tb, Ho, Lu - HREE with odd atomic number – are

279 mainly in the liquid phase of the EDR cell: 22 - 31% in the catholyte, 27-38% in the

280 anolyte, whereas those with an even atomic number in the ash (44 - 69%) and CEM (Gd

281 28%, Dy 16%). Regarding critical REE, extraction ranged between 33 and 74% with 24

282 - 38% already in the cathode end [extraction Dy (33.1%) < Nd (39.9%) < Tb (74.3%);

283 recovery Dy (24.0%) < Nd (36.0%) < Tb (38.4%)].

284 By applying 50 mA for a short time-period with catholyte pH adjustment (EDR4, 50 mA,

285 3 d, pH ≈ 2) the REE extraction increased compared with the previous applied treatments,

286 ranging from 70 to 100%. The percentage that was extracted and present in the cathode

287 end was between 49 and 78%. The catholyte presented ≈ 50% of LREE and between 38

288 and ≈ 50% of HREE. Looking to the critical REE, recoveries were in the range 55 - 74%

289 [recovery Tb (54.9%) < Dy (62.0%) < Nd (74.1%); extraction Dy (73.7%) < Nd (80.1%)

290 < Tb (89.8%)]. More specifically, the presence in catholyte follows the order: Tb (41.8%)

291 < Dy (45.9%) < Nd (50.1%) and shows that EDR4 conditions are very promising to

292 achieve high recovery efficiency in high criticality REE. The data supports that the

293 increased efficiency in the arrival of the REE to the catholyte is related to pH adjustment.

294 Table 3 shows that pH difference between anolyte and catholyte in EDR1-EDR3 is

295 between 9 and 10 whereas in EDR4 is 0.2, which attending to the experimental error, puts

296 EDR4 with a uniform acid pH value throughout the EDR cell. Considering that, without

297 pH adjustment, CEM is the interface between an acidic (anode compartment) and an

298 alkaline environment (cathode compartment), one hypothesis is that REE (or other

299 elements) may precipitate at the membrane due to the pH transition between sides,

300 promoting the clogging/blockage of the CEM surface hindering species migration

301 towards catholyte (EDR1-EDR3).

302

303 **Please insert Fig. 4**

304

305 To summing up, a principal component analysis (PCA) biplot was created to allow a

306 comprehensive analysis and the establishment of some patterns from the experimental

307 datasets (Fig. 4). Overall the biplot mainly divides, through the second component (F2),

308 the REE whose removal is controlled by the presence of CEM (and pH adjustment) from

309 those in which it is not a determining factor. By the first component (F1) the REE are

310 separated according to their presence in the solid phase (ash) *vs.* their presence in liquid

10

phase (anolyte and catholyte). LREE behave more homogeneously across all EDR experiments and present a lower scattering, on the plot quadrants, than HREE. Focusing on LREE: LREE in EDR1 are in ash, in EDR2 and EDR3 they are moving to the CEM, and in EDR4 they are found in the catholyte. Gd (an HREE with even atomic number) follows the LREE behavior in all EDR experiments. La is the REE with higher percentage in CEM.

From EDR1 to EDR4 the observed pattern for LREE suggests that: (i) LREE are desorbed from ash; (ii) move towards the cathode end till CEM influenced by time and/or current and (iii) then arrive to the catholyte following pH adjustment.

Focusing on HREE: HREE with odd atomic number are clustered in the ash in EDR1, starting to scatter but grouped in pairs (e.g. Tm and Lu; Tb and Ho) in EDR2 - EDR4. From EDR2 to EDR4 they form a cluster in the anolyte quadrant being closer or in catholyte quadrant in the EDR4. The HREE with even atomic number follow the same pattern of pairing, namely Er and Yb. From EDR1-EDR3, they are mainly "moving" across the ash and anolyte quadrants. In EDR4 Er is in the border of catholyte quadrant and Yb close in the anolyte quadrant, suggesting that pH adjustment may also slightly improve their removal, independently of the CEM interface. Dy (even) and Y (odd), that can also be seen as a "behavioral" pair, follow a different pattern: in EDR1 to EDR3 they are in the ash and in EDR4 they are observed in the catholyte suggesting a positive effect of pH adjustment in reaching the catholyte. Eu is observed in EDR2 to EDR4 in the catholyte, suggesting that all tested experimental variables (time, current and pH) improved their removal.

Regarding the observed distribution in EDR4 of critical elements. Nd, a LREE, is expected to be mainly distributed in the catholyte, 50%, and CEM, 24%; Dy, a HREE with even atomic number, mainly present in catholyte, 46%, and CEM, 16%; Tb, a HREE with odd atomic number, expected to be mainly divided between catholyte, 42%, and anolyte, 30%.

Overall, when applying EDR treatment aiming to remove REE from anthracite coal ash, 3 main steps mediate the process:

Initial State (Step 0): REEs are in the solid matrix (ash).

341 *Step 1:* REEs solubilization; passing from the solid to the liquid phase (anolyte). This step

342 is based on an equilibrium and depends on the concentration of REEs in the anolyte as

343 well as their individual solubility.

344 *Step 2:* REEs mobilization from the liquid phase towards the cathode through the CEM

345 (for example, observed through the presence of REE in CEM). This step promotes a

346 gradient formation towards the cathode and depends on step 1.

347 *Step 3:* REEs removal; when they already reached the catholyte (after passing CEM).

348 This step depends on the previous steps 2 and 3.

349 On the other end, the mobilization (step 2) and catholyte arrival (step 3) will contribute

350 to balance REE saturation on anolyte and thus promoting "continuously" their ash

351 desorption (step 1).

352 Two main pathways are suggested to explain the REE removal from the ash to the

353 catholyte, based on the PCA analysis. From the ash (step 0: 3rd quadrant) to the catholyte

354 (step 3: 1st quadrant), HREE are more influenced by solubilization (step 1: 4th quadrant)

355 and LREE are more influenced by mobilization through the CEM, as observed on the

356 experimental data by REE "trapping" on the membrane (step 2: 2nd quadrant). The

357 division between LREE and HREE is now associated to their EDR distribution on the

358 PCA biplot supporting differences in elements according to their position in the periodic

359 table (e.g. lanthanide contraction and/or in formation of nona-hydrates or octa-hydrates

360 when LREE and HREE are in aqueous solution, respectively [32,33]). Exceptions in the

361 "expected" distribution as happened with, e.g., Gd, also confirms the mixed behavior of

362 some REE.

363

3.4. Technology feasibility and further investigation

365 These results are the proof-of-concept for the potential of the ED process to recover REE,

366 taking advantage of the low pH produced in the anode compartment, thus preventing the

367 use of acids to promote REE desorption. REE individual separation is challenging due to

368 the similar physico-chemical properties of elements and further work is needed to

369 promote a selective recovery instead of having REE in a mixed solution. One possibility

370 is selective precipitation that may be coupled to the EDR process to achieve this purpose.

371   Average energy consumption in EDR4, the optimized conditions, is of 2.84 kWh *per* kg

372   of ash, representing a recovery [cathode end, *average (stdev)*] of 36.5 (9.2) mg of Nd and

373   4.0 (0.3) mg of Dy; to scale-up the process by increasing CEM area (same current density)

374   the recovery would be of 2.4 (0.6) g Nd / m^2 / day.

375   Still directed to the process up-scale, the impact of ash particles on mechanical stability

376   of the membrane during long term exposure, test of other market available CEM (e.g. Fuji

377   CEMT1 or Fumasep FKS), shorter treatment times and development of economically

378   feasible solutions, e.g., by using pulse current or by changing energy sources such as solar

379   or photovoltaic panels, should also be studied. Another point is the understanding about

380   the potential presence of other extract constituents – elements present in the solution and

381   potentially transported through the membrane (or accumulated in it) – as the process

382   efficiency may increase if electrons or ions are not participating in (unwanted) side

383   reactions and/or (electro)migration.

384

4. Conclusions

386   This work shows the potential of the electrodialytic process to promote REE recovery

387   from coal ashes. In a first stage the concentration of REE was studied in anthracite and

388   bituminous ash. Anthracite presented higher REE concentration (447 ppm *vs*. 138 ppm),

389   and a triple concentration of critical elements comparing with bituminous ash. Anthracite

390   ash was then treated in a two compartment EDR cell aiming to assess the potential for

391   REE recovery, including differences between LREE and HREE fractions, as well as the

392   selective separation of the critical elements (Dy, Tb and Nd). In EDR treatment three

393   main steps were identified: 1) REE solubilization, 2) REE mobilization, 3) REE removal.

394   It is suggested that HREE removal are controlled mainly by step 1 (anolyte solubilization)

395   and LREE by step 2 (movement towards the cathode end through the CEM),

396   corroborating the division of REE in light or heavy according to the position in the

397   periodic table. Nevertheless, some exceptions, such as Gd, also support the mixed

398   behavior of some REE. At the best tested conditions (EDR4, 50 mA, 3 d, pH 2 adjusted

399   at cathode) more than 70% of REE were extracted from coal ash and catholyte presented

400     $\approx$ 50% of LREE and 38 to $\approx$ 50% of HREE. From most critical REE, recovery was in the

401   range between 55 - 62% for Tb and Dy, and $\approx$ 74% for Nd. Attending to the high criticality

402   of Nd and its high concentration in anthracite ash (65 ppm *vs*. 8.5 ppm to Dy and 1.2 ppm

403   to Tb), the EDR treatment is highly recommended for this element extraction by, e.g.

404 further EDR process operational optimization with an additional step that promotes a
405 selective recovery.

406

407

408

409

410 **Acknowledgments**

14

References

[1]   S. Massari, M. Ruberti, Rare earth elements as critical raw materials: Focus on international markets and future strategies, Resour. Policy. 38 (2013) 36–43.

[2]   S. Cao, C. Zhou, J. Pan, C. Liu, M. Tang, W. Ji, T. Hu, N. Zhang, Study on influence factors of leaching of rare earth elements from coal fly ash, Energy Fuels. 32 (2018) 8000–8005. https://doi.org/10.1021/acs.energyfuels.8b01316.

[3]   K. Binnemans, P.T. Jones, B. Blanpain, T.V. Gerven, Y. Pontikes, Towards zero-waste valorisation of rare-earth-containing industrial process residues: a critical review, J. Clean. Prod. 99 (2015) 17–38. https://doi.org/10.1016/j.jclepro.2015.02.089.

[4]   European Comission, 2017 list of Critical Raw Materials for the EU, Brussels, 2017, COM(2017) 490 final. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52017DC0490&from=EN.

[5]   R.M. Izatt, S.R. Izatt, R.L. Bruening, N.E. Izatt, B.A. Moyer, Challenges to achievement of metal sustainability in our high-tech society, Chem Soc Rev. 43 (2014) 2451–2475. https://doi.org/10.1039/C3CS60440C.

[6]   S.M. Jowitt, T.T. Werner, Z. Weng, G.M. Mudd, Recycling of the rare earth elements, Curr. Opin. Green Sustain. Chem. 13 (2018) 1–7.

[7]   M.V.R. Garcia, A. Krzemien, M.Á. Manzanedo del Campo, M. Menéndez Álvarez, M.R. Gent, Rare earth elements mining investment: It is not all about China, Resour. Policy. 53 (2017) 66–76.

[8]   D. Bauer, D. Diamond, J. Li, D. Sandalow, P. Telleen, B. Wanner, U.S. Department of Energy Critical Materials Strategy, Report, 2010.

[9]   K. Binnemans, P.T. Jones, T. Müller, L. Yurramendi, Rare Earths and the balance problem: How to deal with changing markets?, J. Sustain. Metall. 4 (2018) 126–146. https://doi.org/10.1007/s40831-018-0162-8.

[10]   USDOE, Report on Rare Earth Elements from Coal and Coal Byproducts, United States Department of Energy, 2017.

[11]   V. Balaram, Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact, Geosci. Front. 10 (2019) 1285–1303. https://doi.org/10.1016/j.gsf.2018.12.005.

[12]   R. Lin, B.H. Howard, E.A. Roth, T.L. Bank, E.J. Granite, Y. Soonga, Enrichment of rare earth elements from coal and coal by-products by physical separations, Fuel. 200 (2017) 506–520.

[13]   J. López, M. Reig, O. Gilbert, J.L. Cortina, Integration of nanofiltration membranes in recovery options of rare earth elements from acidic mine waters, J. Clean. Prod. 210 (2019) 1249–1260.

[14]   K. Binnemans, P.T. Jones, B. Blanpain, T. van Gerven, Y. Yang, A. Walton, M. Buchert, Recycling of rare earths: a critical review, J Clean Prod. 51 (2013) 1–22.

[15]   D. Smolka-danielowska, Rare earth elements in fl y ashes created during the coal burning process in certain coal- fi red power plants operating in Poland e Upper Silesian Industrial Region, J. Environ. Radioact. 101 (2010) 965–968. https://doi.org/10.1016/j.jenvrad.2010.07.001.

[16]   M. Stuckman, C. Lopano, E. Granite, Distribution and speciation of rare earth elements in coal combustion by-products via synchrotron microscopy and spectroscopy Mengling, Int. J. Coal Geol. 195 (2018) 125-138 https://doi.org/10.1016/j.coal.2018.06.001.

[17]   U.S. Energy Information Administration, Quarterly Coal Report, (2019).

[18]   C. Lanzerstorfer, Pre-processing of coal combustion fly ash by classification for enrichment of rare earth elements, Energy Rep. 4 (2018) 660–663.

467 [19] J.F. King, R.K. Taggart, R.C. Smith, J.C. Hower, H. Hsu-Kim, Aqueous acid
468 and alkaline extraction of rare earth elements from coal combustion ash, Int. J. Coal
469 Geol. 195 (2018) 75–83.
470 [20] R.S. Blissett, N. Smalley, N.A. Rowson, An investigation into six coal fly ashes
471 from the United Kingdom and Poland to evaluate rare earth element content, Fuel. 119
472 (2014) 236–239. https://doi.org/10.1016/j.fuel.2013.11.053.
473 [21] W. Franus, M.M. Wiatros-Motyk, M. Wdowin, Coal fly ash as a resource for
474 rare earth elements, Environ. Sci. Pollut. Res. 22 (2015) 9964–9474.
475 [22] R.K. Taggart, J.C. Hower, G.S. Dwyer, H. Hsu-Kim, Trends in the Rare Earth
476 Element Content of U.S.-Based Coal Combustion Fly Ashes, Environ. Sci. Technol. 50
477 (2016) 5919–5926. https://doi.org/10.1021/acs.est.6b00085.
478 [23] X. Yang, J. Werner, R.Q. Honaker, Leaching of rare Earth elements from an
479 Illinois basin coal source, J. Rare Earths. (2018).
480 [24] A.R.K. Gollakota, V. Volli, C.M. Sun, Progressive utilisation prospects of coal
481 fly ash: A review, Sci. Total Environ. 672 (2019) 951–89.
482 [25] B.K. Mutlu, B. Cantoni, A. Turolla, M. Antonelli, H. Hsu-Kim, M.R. Wiesner,
483 Application of nanofiltration for Rare Earth Elements recovery from coal fly ash
484 leachate: Performance and cost evaluation, Chem. Eng. J. 349 (2018) 309–317.
485 [26] R.K. Taggart, J.C. Hower, H. Hsu-Kim, Effects of roasting additives and
486 leaching parameters on the extraction of rare earth elements from coal fly ash, Int. J.
487 Coal Geol. 196 (2018) 106–114.
488 [27] P. Guedes, N. Couto, L.M. Ottosen, A.B. Ribeiro, Phosphorus recovery from
489 sewage sludge ash through an electrodialytic process, Waste Manag. 34 (2014) 886–92.
490 https://doi.org/10.1016/j.wasman.2014.02.021.
491 [28] L.M. Ottosen, P.E. Jensen, G.M. Kirkelund, Phosphorous recovery from sewage
492 sludge ash suspended in water in a two-compartment electrodialytic cell, Waste Manag.
493 51 (2016) 142–148. https://doi.org/10.1016/j.wasman.2016.02.015.
494 [29] B. Ebbers, L.M. Ottosen, P.E. Jensen, Comparison of two different
495 electrodialytic cells for separation of phosphorus and heavy metals from sewage sludge
496 ash, Chemosphere. 125 (2015) 122–129.
497 https://doi.org/10.1016/j.chemosphere.2014.12.013.
498 [30] R.P. Viader, P.E. Jensen, L.M. Ottosen, J. Ahrenfeldt, H. Hauggaard-Nielsen,
499 Sequential electrodialytic recovery of phosphorus from low-temperature gasification
500 ashes of chemically precipitated sewage sludge, Waste Manag. 60 (2017) 211–218.
501 https://doi.org/10.1016/j.wasman.2016.11.030.
502 [31] R.P. Viader, P.E. Jensen, L.M. Ottosen, J. Ahrenfeldt, H. Hauggaard-Nielsen,
503 Electrodialytic extraction of phosphorus from ash of low-temperature gasification of
504 sewage sludge, Electrochim. Acta 181 (2015) 100–108.
505 https://doi.org/10.1016/j.electacta.2015.05.025.
506 [32] W.W. Rudolph, G. Irmer, On the Hydration of the Rare Earth Ions in Aqueous
507 Solution, J. Solut. Chem. 49 (2020) 316–331. https://doi.org/10.1007/s10953-020-
508 00960-w.
509 [33] E.N. Rizkalla, G.R. Choppin, Hydration of lanthanides and actinides in solution,
510 J. Alloys Compd. 180 (1992) 325–336. https://doi.org/10.1016/0925-8388(92)90398-S.

511

512

513

514

515 **Captions for Figures**

516   **Fig. 1.** Schematic representation of the two-compartment electrodialytic cell used in

517   experiments: ash suspension in the anode compartment. The separation between anode

518   compartment and cathode compartment was carried out through a cation exchange

519   membrane (CEM).

520   **Fig. 2.** REE coal ash leaching at acidic pH.

521   **Fig. 3.** Percentage of REE in the electrodialytic cell sections at the end of the experiments.

522   Error bars represent standard deviation (n=2).

523   **Fig. 4.** PCA biplot of REE distribution according to the applied experimental conditions

524   (EDR1-EDR4, the number accompanying each REE reports to the respective EDR

525   experiment). Legend: **HREE (E)** heavy REE with even atomic number; **HREE (O)**

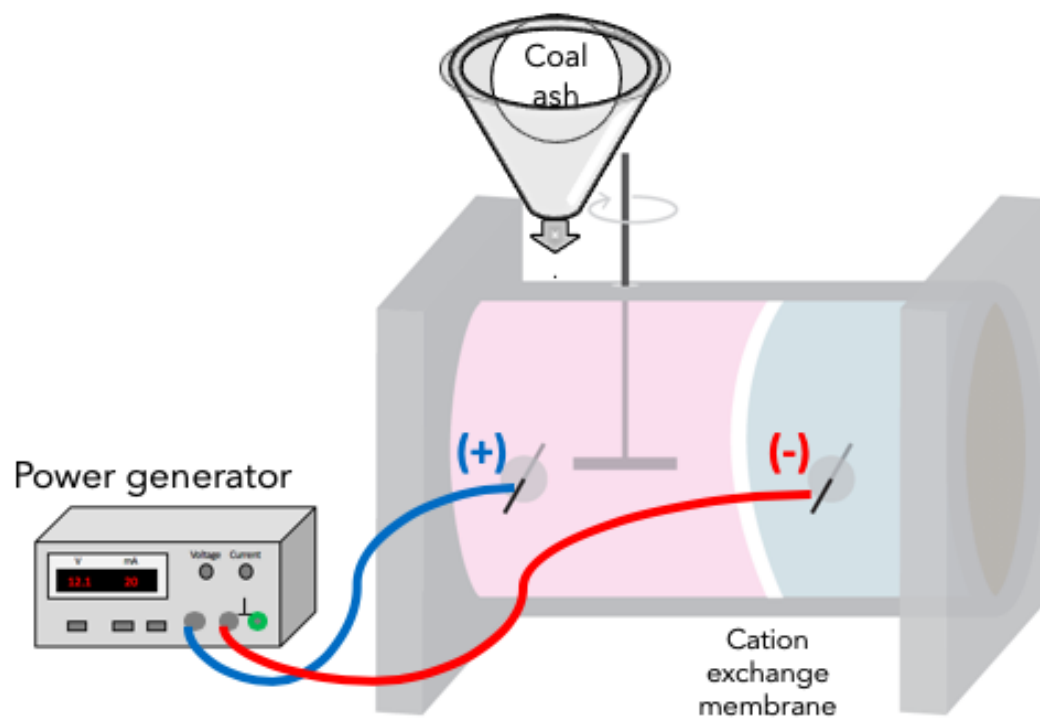526   heavy REE with odd atomic number; **LREE** light REE

527

528

529

530

531

532

Fig. 1

Fig. 1. Schematic representation of the two-compartment electrodialytic cell used in experiments: ash suspension in the anode compartment. The separation between anode compartment and cathode compartment was carried out through a cation exchange membrane (CEM).
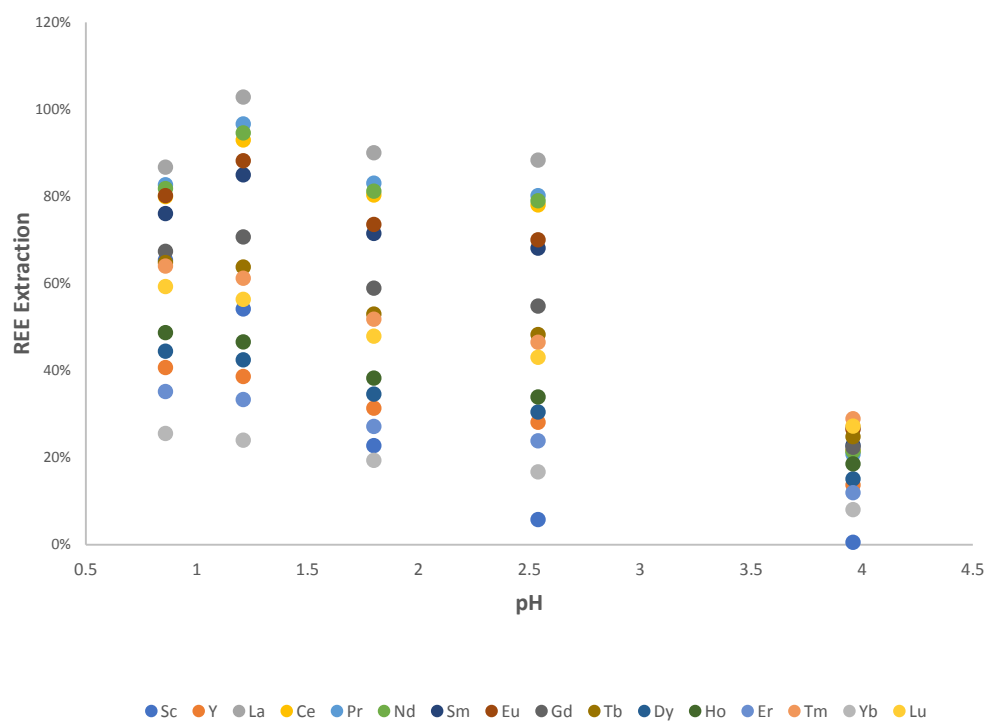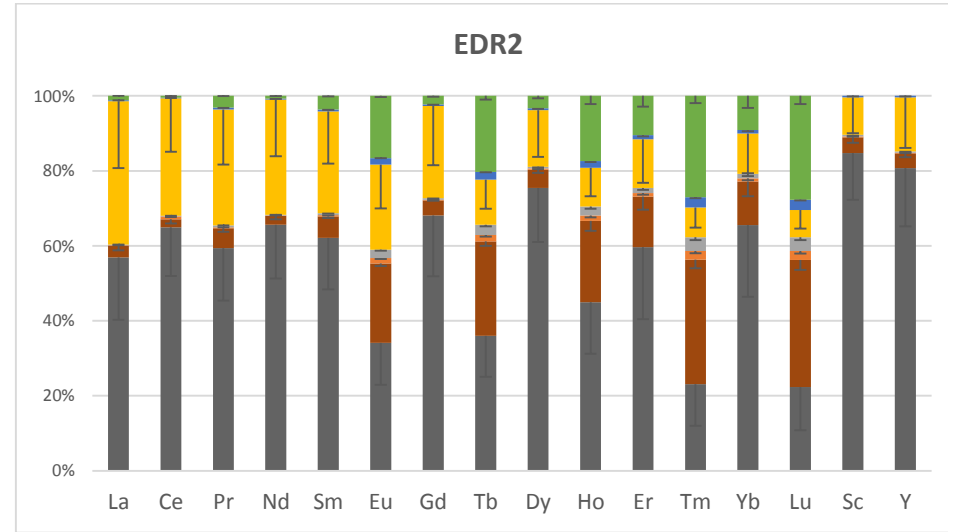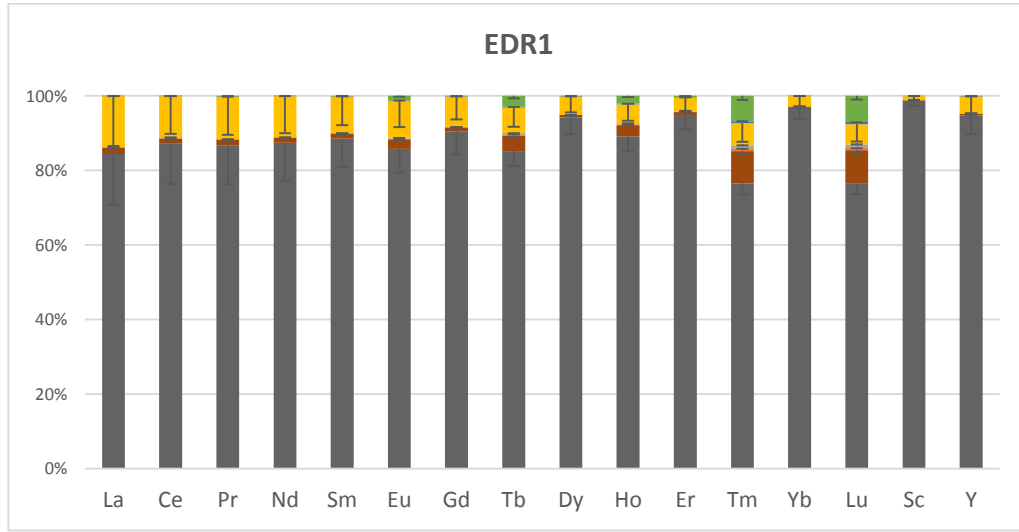
Fig. 2

Fig. 2. REE coal ash leaching at acidic pH.

Fig. 3
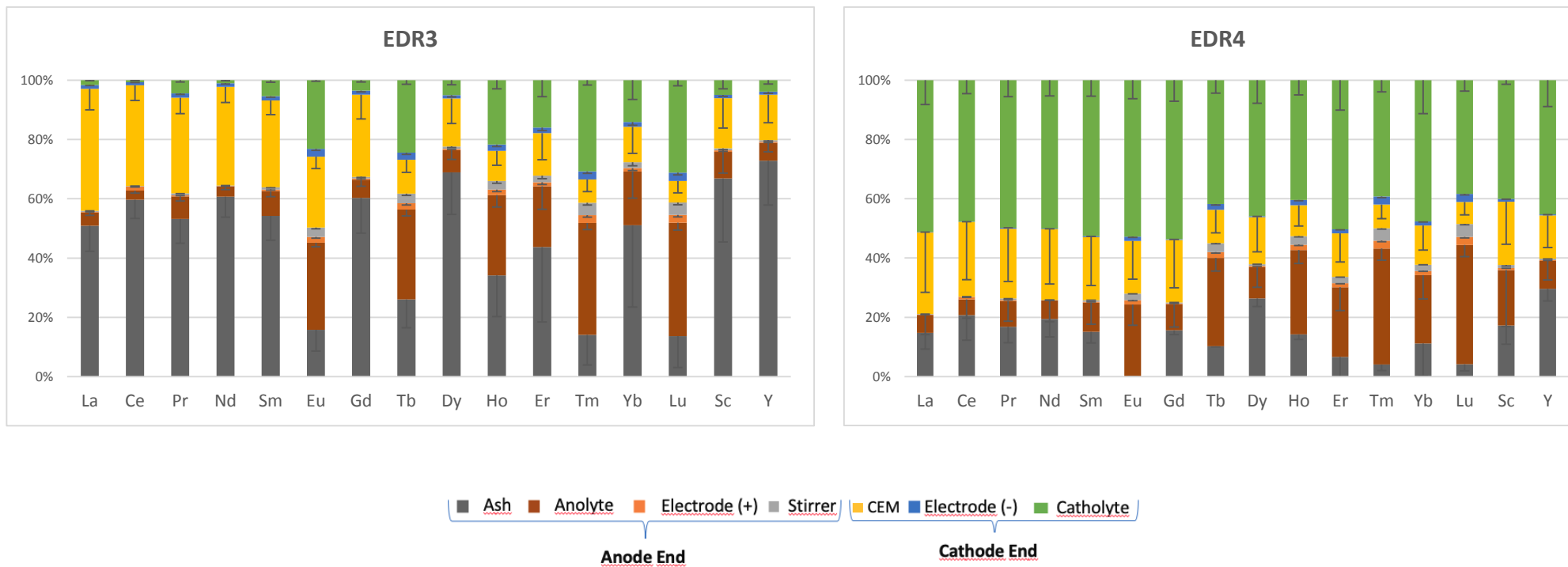
Fig. 3. Percentage of REE in the electrodialytic cell sections at the end of the experiments. Error bars represent standard deviation (n=2).

Fig. 4
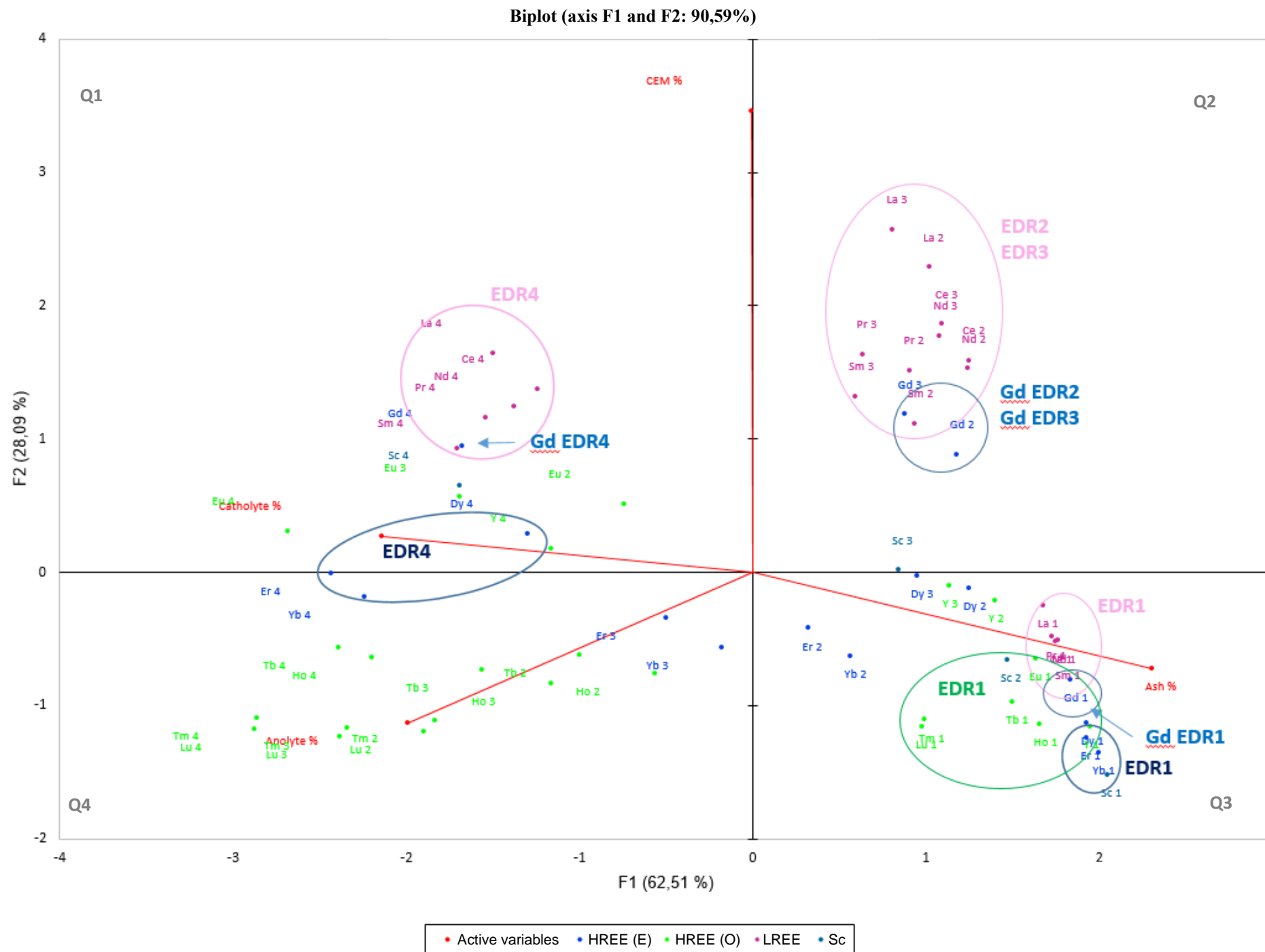
Fig. 4 PCA biplot of REE distribution according to the applied experimental conditions (EDR1-EDR4, the number accompanying each REE reports to the respective EDR experiment). Legend: **HREE (E)** heavy REE with even atomic number; **HREE (O)** heavy REE with odd atomic number; **LREE** light REE

Table 1

Table 1. Experimental conditions for the different electrodialytic experiments.

Experiment	Time (days)	Current intensity (mA)	pH adjustment
EDR1	3	10	No
EDR2	7	10	No
EDR3	3	50	No
EDR4	3	50	Yes*

* cathode compartment with pH adjusted to 2 with HNO_3

Table 2

Table 2. REE atomic number, concentration in bituminous and anthracite coal ash samples. (n.d: below detection limit).

	Element	Symbol	Atomic number	REE (ppm)	
				Bituminous	*Anthracite*
LREE	Lanthanum	La	57	19.6	86.5
	Cerium	Ce	58	42.7	170.2
	Praseodymium	Pr	59	5.1	18.0
	Neodymium	**Nd**	**60**	**20.3**	**65.3**
	Promethium	Pm	61	n.d.	n.d.
	Samarium	Sm	62	4.1	10.7
HREE	Europium	Eu	63	1.4	1.9
	Gadolinium	Gd	64	3.9	9.4
	Terbium	**Tb**	**65**	**0.4**	**1.2**
	Dysprosium	**Dy**	**66**	**2.9**	**8.5**
	Holmium	Ho	67	0.3	1.5
	Erbium	Er	68	1.3	5.4
	Thulium	Tm	69	n.d.	0.5
	Ytterbium	Yb	70	1.4	5.7
	Lutetium	Lu	71	n.d.	0.4
	Yttrium	Y	39	15.4	45.1
	Scandium	Sc	21	19.5	16.6
			Total	138.3	446.9
			LREE	91.8	350.7
			HREE	27.0	79.6
			Critical	**23.6**	**75.0**

Table 3

Table 3. Parameters measured at the beginning and at the end of the electrodialytic experiments.

			EDR1			EDR2			EDR3			EDR4		
Voltage (V)		initial	21.0	±	11.0	10.0	±	2.7	48.0	±	0.9	26.6	±	23.3
		final	8.0	±	0.8	5.0	±	0.3	16.0	±	0.9	5.0	±	0.9
pH	anolyte	initial	4.9	±	0.4	4.5	±	0.4	4.2	±	0.4	4.0	±	0.1
		final	2.7	±	0.1	3.2	±	0.4	2.8	±	0.1	2.3	±	0.2
	catholyte	initial	5.6	±	1.3	6.2	±	0.6	6.4	±	0.8	3.1	±	1.5
		final	11.8	±	0.4	12.7	±	0.2	12.7	±	0.2	2.1	±	0.1
Conductivity (µS/cm)	anolyte	initial	70	±	28	712	±	244	534	±	146	200	±	2
		final	207	±	46	2240	±	877	3310	±	14	3300	±	37
	catholyte	initial	614	±	23	1441	±	151	1187	±	561	1140	±	56
		final	892	±	298	1650	±	71	2540	±	28	2700	±	13

CRediT author statement

Nazaré Couto: Conceptualization, Investigation, Writing- Original draft preparation.

Ana Rita Ferreira: Methodology, Investigation, Writing- Reviewing and Editing.

Vanda Lopes: Methodology, Investigation, Writing- Reviewing and Editing.

Stephen Peters: Resources, Methodology, Writing- Reviewing and Editing.

Eduardo P. Mateus: Writing- Reviewing and Editing.

Alexandra B. Ribeiro: Supervision, Funding acquisition, Writing- Reviewing and Editing.

Sibel Pamukcu: Supervision, Resources, Writing- Reviewing and Editing.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: