

Recovery of technologically critical lanthanides from ion adsorption soils

DOI:

[10.1016/j.mineng.2021.106921](https://doi.org/10.1016/j.mineng.2021.106921)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Stockdale, A., & Banwart, S. A. (2021). Recovery of technologically critical lanthanides from ion adsorption soils. *Minerals Engineering*, 168, Article 106921. Advance online publication. <https://doi.org/10.1016/j.mineng.2021.106921>

Published in:

Minerals Engineering

Citing this paper

Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights

Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy

If you believe that this document breaches copyright please refer to the University of Manchester's Takedown Procedures [<http://man.ac.uk/04Y6Bo>] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.



1 Recovery of technologically critical lanthanides from ion adsorption soils

2

3 Anthony Stockdale^{a,b,1}, Steven A. Banwart^b

4

5 ^aDepartment of Earth and Environmental Sciences, The University of Manchester,
6 Manchester, M13 9PL, United Kingdom

7 ^bSchool of Earth and Environment, University of Leeds, Leeds, LS2 9JT, United Kingdom.

8 ¹Corresponding author E-mail: tony@biogeochemistry.org.uk

9

10 VERSION – This is the accepted version of the manuscript prior to final production. The
11 definitive version of the manuscript is available from the publisher at
12 <https://dx.doi.org/10.1016/j.mineng.2021.106921>

13

14 © 2021. Licensed under the Creative Commons. This manuscript version is made available
15 under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

16

17 Abstract

18 Rare earth elements (REEs) are in increasing demand due to rapidly rising use in consumer
19 technology, the automotive industry and in renewable energy generation systems, amongst
20 other technology sectors. Ion-adsorption type REE ore deposits are currently being exploited
21 in China's southern provinces and there is increasing interest in identifying potential reserves
22 globally. Here we investigated the extraction of REEs from an ion-adsorption clay sampled at
23 a surficial deposit in Madagascar. Using a 1 M NH₄Cl lixiviant salt solution, chosen based on
24 experimental evidence to maximise REE extraction, minimises undesirable dissolved Al in
25 eluate. Lower Al concentration in solution reduces its interference with NH₄⁺ in oxalate
26 precipitation of REEs in the extraction process. We show that NH₄Cl solutions can be used to
27 efficiently extract REE with relatively low lixiviant volumes in a through-flow column system.
28 We show that when extraction with a pulse of lixiviant is followed by a rinsing step, there are
29 several identifiable stages during the extraction process, including a marked increase in total
30 lanthanides extracted, which is correlated with the breakthrough of ammonium ions, and
31 where the eluted dissolved Al concentration decreases from its peak concentration.

32 Keywords: rare earth elements; lanthanides; technologically critical elements; lixiviant; ion-
33 adsorption deposits

34 1. Introduction

35 Rare earth elements (REEs; Y, Sc and lanthanide elements) are increasingly in demand due
36 to rapidly rising use in consumer technology, the automotive industry and in renewable energy
37 generation systems, amongst other technology sectors (Chakhmouradian and Wall, 2012). A
38 significant majority of the world's REE supply comes from China, with Bayan Obo (Inner
39 Mongolia) one of the largest deposits (Kynicky et al., 2012). In 2019 significant mine
40 production was also undertaken in Myanmar, USA and Australia (10-12% of total mine
41 production); with Brazil, Vietnam and Russia estimated to have significant reserves (10-18%
42 of the global total) but representing only 0.4-1.3% of total production (USGS, 2020).

43

44 The majority of REE metals are mined from open pits of bastnasite and/or monazite. A smaller
45 fraction is extracted from leaching of surficial deposits of ion-adsorption clays (Vahidi et al.,
46 2016). Grades within bastnasite and monazite deposits can be as high as 8%, whereas ion-
47 adsorption type rare earths ore are typically 0.02%–0.5% as weight percent of rare earth
48 oxides (Kanazawa and Kamitani, 2006; Moldoveanu and Papangelakis, 2013b). However, ion-
49 adsorption deposits can contain a much higher proportion of higher value heavy REEs. Life
50 Cycle Assessments have concluded that these deposits result in lower environmental impacts
51 due to lower energy requirements for mining and extraction compared to other sources when
52 an economic value-based allocation is used (Vahidi et al., 2016). Current exploitation of these
53 deposits is being conducted in China's southern provinces (Kanazawa and Kamitani, 2006).

54

55 In situ leaching of ion-adsorption deposits involves direct injection of an extraction lixiviant
56 solution (typically $(\text{NH}_4)_2\text{SO}_4$) into the orebody via a leaching hole. Typically at a depth of 1.5-
57 3 m, generally above the water table, diameter of 0.8 m in an array 2-3 m apart that can span
58 up to 100 m across. The lixiviant solution is injected at high pressure and flows through the
59 pores of the orebody and is either pumped above-ground through the recovery wells, or
60 collected in sumps at the water table surface. The loaded leach solution is pumped above-
61 ground for further processing, with the maximum possible REE extraction taking up to 400
62 days, primarily controlled by the residence time of injected fluids during largely vertical
63 downward flow to the collection wells (Moldoveanu and Papangelakis, 2016). A feature of
64 recovery from these deposits is fast extraction kinetics (minutes for terminal extraction),
65 instantaneous compared to transport time scales of extracted metals, and is independent of
66 lixiviant concentration (above a threshold value related to the ion exchange capacity of the
67 ore) and pH. Elevated temperatures do not increase extraction efficiency but have a positive

68 effect on extraction time (Xiao et al., 2015). However, establishing temperatures above
69 ambient within an ore body will be technically difficult and add to energy demands and
70 engineering costs with only small potential gains in metal extraction.

71

72 For downstream processing, loaded lixiviant solutions are generally put through a lanthanide
73 precipitation procedure as an initial concentration step before further processing of the
74 concentrated solids. Examples of uses of oxalate precipitation as part of lanthanide recovery
75 processes can be found in Fernandes et al., 2013; and Josso et al., 2018, presenting recovery
76 from environmental deposits and battery recycling, respectively.

77

78 The increase in demand for REEs has led to a greater focus on security of supply by many
79 national governments and this has fuelled interest in assessment of previously unexploited
80 international ion-adsorption deposits. Recent studies have assessed deposits in the
81 Philippines (Padrones et al., 2017), Madagascar (SRK Exploration Services Ltd, 2013),
82 Malawi (Le Couteur, 2011), Brazil (Rocha et al., 2013), Laos (Sanematsu et al., 2009) and
83 Vietnam (Mentani et al., 2010). Further studies have also investigated the efficacy of
84 compound leaching (using combinations of dissolved salts), which aims to either improve
85 extraction efficiency, reduce interference of REE concentration by Al, or reduce the
86 environmental impact of lixiviant solutions (e.g., Yang and Zhang, 2015; He et al., 2016; and
87 Xiao et al., 2017). Bioleaching has also been investigated with the aim of providing an
88 economically and environmentally viable alternative to current approaches (Barnett et al.,
89 2018).

90

91 Several prior studies have presented data on the optimum lixiviant composition and its
92 concentration as well as reaction conditions (e.g., pH and temperature). To date there are few
93 investigations that present high resolution data on REE extraction that are obtained under
94 reactions conditions that potentially replicate those within an ore body. In particular, covering
95 conditions that represent a more complete processing stream of the lixiviant injection,
96 extraction and washing phases. The primary aim of this work was to investigate, at high
97 temporal resolution at laboratory bench scale, processes occurring when lixiviants are
98 pumped through ion-adsorption soils, simulating in situ extraction (using packed columns). In
99 addition we sought to investigate some of the soil properties, the effects of lixiviant cations
100 and anions on extraction efficiencies and to perform a preliminary investigation on the potential

101 interference of lixiviant cations on the precipitation of lanthanide oxalate salts by formation of
102 lixiviant cation-oxalate precipitates.

103

104 **2. Methods**

105 Our experimental design was planned as an analogue to the process stream of extraction,
106 recovery and washing of REEs from ion adsorption clays. Batch desorption studies
107 investigated lixiviant extraction efficiency, column studies identified lixiviant volume
108 requirements and oxalate precipitation studies identified interference from lixiviant cations.
109 Results were used to select conditions for further high temporal resolution column
110 experiments. In addition, we characterised several soil properties relevant to in situ extraction
111 of REEs. Descriptions of the main methods are included below, detailed methods are included
112 in the Supporting Information (SI) Section S2.

113

114 **2.1 Source of soil samples**

115 Ion-adsorption soils were obtained from a deposit located in the Cenozoic Ambohimirahavavy
116 alkaline complex in northern Madagascar, conducted as part of the UK Natural Environment
117 Research Council project SoS RARE (NE/M011232/2). The mineralized lateritic regolith being
118 derived from the weathering of alkaline igneous rocks (Estrade et al., 2019; see also a
119 comprehensive characterisation of the same region in SRK, 2008; and Stoltz, 2017; these
120 include; lithology structures and regolith of the local geology; parent ion-adsorption mineral
121 characterisation using quantitative evaluation of minerals by scanning electron microscopy,
122 XRF and XRD; REE sequential extractions; as well as airborne geophysical surveys and
123 outcrop sampling). A subset of 6 bulk samples were chosen for analysis here, to represent the
124 range of pit locations, depths and soil properties. Sample 0547 was used for a significant
125 number of experiments due to it representing a large depth horizon and falling in the middle
126 of the range of total lanthanide concentrations of soils across the site (Estrade et al., 2019).

127

128 **2.2. Soil properties and preparation**

129 Analyses were performed to determine mineral composition, BET surface area, particle size
130 distribution and complexed-copper-method cation exchange capacity (full methods described
131 in SI Section 2.1). For batch and column experiments the soil samples were air-dried and
132 sieved through a 1.4 mm mesh to remove large mineral fragments. The remaining soil was

133 gently disaggregated in a pestle and mortar until all of the sample passed through a 250 μm
134 sieve. Any further processing for supplementary experiments is detailed in the SI.

135

136 **2.3. Experimental procedures**

137 **2.3.1. Batch experiments.** These tested the efficiency of various lixiviant solutions containing
138 different cations (H^+ , NH_4^+ , Ca^{2+} , Mg^{2+}) and anions (ClO_4^- , Cl^- , NO_3^- , SO_4^{2-}). SI Table S2.1.
139 details the range of reagents used for the experiments. Lixiviants of monovalent salts were 1
140 M, those of salts containing divalent cations or anions were 0.5 M (consistent with good
141 extraction rates in lixiviants of 0.5 M or greater as determined by Moldoveanu and
142 Papangelakis, 2013). To a 1 g sample of soil 0547 in a micro-centrifuge tube was added 1 mL
143 of solution, thorough mixing was achieved with a vortex mixer. Each solution experiment was
144 performed in triplicate. After 24 hours the slurries were centrifuged (micro-centrifuge 13'200
145 rpm, 5 minutes). Each centrifugate was filtered (Whatman Puradisc polyethersulfone 0.45 μm
146 syringe filter, 13 mm), before pH and conductivity analysis of the supernatant (SI Table S2.2.).
147 Filtered fluid samples were stored refrigerated in micro-centrifuge tubes awaiting appropriate
148 dilution/acidification for ICP analysis.

149

150 **2.3.2. Through-flow column experiments.** Soil through-flow experiments were performed
151 using chromatography columns (Omnifit EZ-AA 25mm/400mm) with an internal diameter of
152 25 mm and two adjustable end-pieces fitted with 5 μm pore PTFE frits. Columns were pre-
153 conditioned by circulating, in a closed loop, a small volume (< 300 mL) of MQ water for >7
154 days (See SI.2.1.5. for filling and conditioning procedure used). Filled conditioned columns
155 were connected to a peristaltic pump tube (Tygon S3™ E-LFL, 0.1 or 0.06 mL min^{-1} flow rate)
156 clamped onto a fixed flow rate pump (Bran Luebbe). Flow rate was ultimately governed by the
157 balance of the input pressure and hydraulic pressure in the column (see the SI Table S2.3. for
158 the approximate flow rates achieved in each of the column experiments). Preliminary
159 experiments were performed on the more coarsely grained and presumably more permeable
160 0652 sample to test the system with lower hydraulic pressures and to gain insight into the pore
161 volumes of lixiviant required for extracted metal breakthrough. The systems were then
162 switched to the finer grained 0547 sample, where a low pore volume of lixiviant was passed
163 through the column before switching to a post-lixiviant low ionic strength solution. Small
164 variances were made with lixiviant pH for different columns to determine any effect of this
165 lixiviant property (details in SI Table S.2.4.).

166

167 **2.3.3. Oxalate precipitation experiments.** We investigated the potential for different lixiviant
168 cations to interfere with the precipitation of lanthanide oxalates, on the basis that this is a
169 typical initial concentration step in some industrial extraction process streams (ammonium
170 bicarbonate is also used; Vahidi et al., 2016; Chi et al., 2003). To obtain a loaded lixiviant
171 solution 50 g of soil 0547 was added to 500 mL of each of four salt solutions (1 M NH₄Cl,
172 NaCl, MgCl₂, CaCl₂). The resultant slurries were shaken on a table shaker for ~3 days then
173 left to stand for several weeks. The slurries were then centrifuged and the supernatant filtered
174 (0.45 µm polyethersulfone, Sartorius Minisart) and analysed for total dissolved concentration
175 of lanthanide elements (reported in SI.2.1.4). To triplicate 50 mL subsamples of each loaded
176 solution was added 50 mL of 0.6 M oxalic acid (Aldrich, purified grade ≥99.999% trace metal
177 basis). At several time intervals, up to 21 days, 1 mL subsamples were filtered (Whatman
178 Puradisc polyethersulfone 0.45 µm syringe filter, 13 mm) and immediately diluted 10-fold and
179 acidified with 200 µL of HCl (Honeywell-Fluka, ACS Reagent, ≥37%). This avoided further
180 precipitation of oxalate salts whilst solutions were awaiting analysis for total dissolved
181 lanthanide element concentrations.

182

183 **2.3.4. Chemical analysis of solutions.** Dissolved metals (Al and lanthanides) were analysed
184 using a Thermo Fisher iCAPQc or X-Series 2 ICP-MS following suitable dilution. Conductivity
185 and pH were measured with a Mettler Toledo Seven Excellence meter coupled to a pre-
186 calibrated conductivity probe InLab 752-6mm using a VWR Prolab 50000 µS/cm standard
187 (25°C, KCl) as a quality control, and a InLab Micro Pro-ISM pH electrode calibrated on the
188 hydrogen ion activity scale with three National Institute of Standards and Technology traceable
189 standard buffers (pH 4.00, pH 7.00, and pH 10.00). Typical detection limits were 1.7, 9.7, 5.5,
190 2.3, 6.1, 0.4, 0.4, 0.8, 0.4, 0.7, 0.4, 0.5, 0.4, 0.4 and 0.5 for Al, La, Ce, Pr, Nd, Sm, Eu, Gd,
191 Tb, Dy, Ho, Er, Tm, Lu and Yb respectively, units nmol L⁻¹ except Al as µmol L⁻¹.

192

193 **2.4. Geochemical modelling of experimental systems**

194 We compare the Al concentration data from column studies to the theoretical solubility of
195 gibbsite and kaolinite at equilibrium with the ionic composition appropriate matrix at 293 °K.
196 Modelling of solution and solid phase thermodynamic equilibria used the geochemical
197 modelling code PHREEQC (Parkhurst and Appelo, 2013), with the Lawrence Livermore
198 National Laboratory database (reviewed in Meeussen et al, 2009).

199

200 3. Results

201 3.1. Soil properties

202 The soil samples are predominantly kaolinite, with lower quantities of gibbsite and quartz.
203 Surface area (SA) and cation exchange capacity (CEC) analysis showed that the visually
204 coarser sample (0652) had the lowest values (SA 33.7 m² g⁻¹; CEC 3.7 meq 100 g⁻¹) with the
205 sample used for the batch and second phase of column experiments (0457) having the highest
206 values (SA 49.6 m² g⁻¹; CEC 7.1 meq 100 g⁻¹). Mineralogy does not significantly differ with
207 size fraction, except manganese oxide, which is present in greater quantities in the larger size
208 fractions (detailed results for soil properties are reported in SI3.1.).

209

210 3.2. Extraction efficiency with cation and anions in lixiviant

211 The general pattern in quantity of lanthanide recovery with lixiviant cation is NH₄⁺ ≈ Mg²⁺ ≈
212 Ca²⁺ > H⁺ > Na⁺. For anions the sequence is SO₄²⁻ > NO₃⁻ > Cl⁻, ClO₄⁻. However, where the
213 cation is NH₄⁺, Mg²⁺ or Ca²⁺ then high extraction rates are achieved and the counter-anion has
214 no additional effect. Figure 1 shows these trends, for total lanthanides, plotted against the
215 Gibbs free energy of solvation for the cations (other than ammonium). Less negative solvation
216 energy cations have lower total lanthanide extraction than more negative solvation energy
217 cations. Data for each individual lanthanide metal are shown in SI Figure S3.1.

218

219 The concentrations of co-extracted Al may affect the downstream lanthanide processing and
220 is therefore an important factor in choosing a lixiviant. The general pattern in recovery of Al
221 with different lixiviant cations follows the sequence H⁺ >> NH₄⁺ > Mg²⁺ ≈ Ca²⁺ > Na⁺. For anions
222 the trend was SO₄²⁻ > NO₃⁻ ≈ ClO₄⁻ ≈ Cl⁻ (Figure 2).

223

224 3.3. Oxalate precipitation of lanthanides in different matrices

225 Oxalic acid was added to lixiviant solutions loaded with dissolved lanthanide ions (using
226 chloride salts for all solutions) prepared from soil 0547. In the presence of the Ca²⁺ lixiviant
227 there was immediate precipitation of significant quantities of Ca oxalate with simultaneous
228 precipitation of lanthanides (>99%). Mg and Na lixiviants resulted in formation of some visible

229 Mg or Na oxalate salts but there was minimal precipitation of lanthanides after a 21 day period
230 (<5%). The NH₄Cl lixiviant resulted in no visible ammonium oxalate precipitation and
231 approximately 50% of the total lanthanides were precipitated from solution under the
232 experimental conditions (SI Figure S3.2.). Precipitation was not equal for all lanthanides, Sm
233 and Eu were the most depleted from solution with ~75% precipitated after 21 days. Lighter
234 and heavier elements then progressively had lower levels of precipitation, with La, Er, Tm, Yb
235 and Lu having >60% remaining in solution after 21 days (SI Figure S3.3.).

236

237 **3.4. Extraction in lixiviant through-flow systems**

238 Scoping experiments on the 0652 soil showed that the extraction of a large proportion (~80%)
239 of the lanthanides was realised after <0.3 pore volumes of lixiviant solution had eluted from
240 the column (Figure 3 and SI Figures S3.4., S3.5.), with breakthrough occurring at 1.3-1.4 pore-
241 volumes and the rapid desorption phase completed at 1.5-1.6 pore volumes. Further contact
242 with lixiviant resulted in limited further recovery, with <95% recovery with 12 pore volumes.
243 Results show that more than one pore volume of fluid is required to be passed through the
244 column before breakthrough of the lixiviant. This may be due to a combination of exchange
245 with inner pore waters, changes to the column packing properties after lixiviant injection,
246 and/or dead volumes in column input and output tubing. The typical profile of extraction in
247 each lixiviant fraction is shown in SI Figure S3.6., for each individual lanthanide. Only
248 lanthanum shows deviation in the extraction behaviour compared to other metals, with a
249 steeper initial breakthrough curve. A final bulk ion-exchange leach using CaCl₂ (performed in
250 a batch reaction on solids recovered from the column after approximately 8-12 pore volumes
251 of lixiviant through-flow) yielded 9-14% of the total La or Ce and 1-6% of other lanthanides.
252 The addition of acid to the CaCl₂ leach slurries reveals that some lanthanides are present at
253 significant concentrations only as acid-extractable forms (SI Table S3.6.). Acid extracted Ce
254 is 67% of the ion-exchangeable mass of Ce; Gd, Tm, Yb and Lu are 20, 22, 36 and 32%; with
255 other acid extracted metallic elements at lower amounts (5-17% of the ion-exchangeable).

256

257 Informed by the scoping experiments, further through-flow experiments on sample 0547 used
258 1 M NH₄Cl as the lixiviant, low lixiviant volumes (<0.5 pore volumes) and were followed by a
259 rinse solution (0.05 M NaCl or MQ water; informed by previous work revealing water content
260 trapped in leached material contained significant amounts of REE and residual lixiviant that
261 required thorough washing of the solid residue (Moldoveanu and Papangelakis, 2016)). In
262 replicate columns >95% of the ion-exchangeable lanthanides are extracted with the small

263 lixiviant injections (Figure 3 lower panel and SI Figures S3.4., S3.5). The final bulk ion-
264 exchange leaches yielded 1-6% of the total ion-exchangeable fraction for the lanthanide
265 metals. The addition of acid to the CaCl₂ leach slurries resulted in extraction of 24% more Ce
266 and 3-11% of the ion-exchangeable for other metals (SI Table S3.6.). Figure 4 details the
267 lixiviant analyte, pH, Al, and total lanthanide breakthrough curves for a typical column
268 experiment (the same experiment as Sample 0547, Column E in Figure 3). Chloride as the
269 conservative tracer, breaks through at the same stage as the marked decrease in pH and
270 increase in Al and lanthanides (for the breakthrough curves of other 0547 columns see SI
271 Figure S3.7.). The sum of the ion-exchangeable Al, converted to equivalent units for cation
272 exchange capacity, was 7.4 (\pm 1.5) meq 100 g⁻¹. The Al concentrations in the column eluent
273 fractions (post Cl breakthrough and when the pH is lower than 4.5) tends to follow the
274 theoretical solubility of Al oxide or hydroxide mineral phases in equilibrium with the matrix
275 solution (SI Figure S3.8.). The dataset for the column experiments is publicly available
276 (Stockdale and Banwart, 2021).

277

278 **4. Discussion**

279 We studied the extraction efficiency of lixiviants in terms of both cations and anions in the
280 lixiviant salt solution. When compared with the Gibbs free energy of solvation, cations with
281 less negative values have lower extraction efficiencies (Figure 1). Ammonium, together with
282 the divalent cations with the more negative solvation energies, exhibit the most complete
283 extraction. This is consistent with the proposed ion-exchange mechanism of Moldoveanu and
284 Papangelakis (2012). Their model states that cations with low negative hydration enthalpies
285 ($-\Delta H_{\text{hyd}}$), which are able to dehydrate completely at ambient temperature and reside directly
286 on the clay surface, establish a strong electrostatic bond. In contrast to cations with high $-\Delta H_{\text{hyd}}$
287 (such as REEs) that remain partially hydrated and thus establish weaker bonds with the
288 negative charge on the surface, thus making ion-exchange more energetically favourable for
289 cations with high $-\Delta G_{\text{solv}}$ values.

290

291 The counter anions in the lixiviant will affect desorption processes by shifting the equilibrium
292 of the aqueous REE ion complexes by reducing the activity of the free aquo ion, and thus in
293 turn, will result in some desorption from ion-adsorption sites in order to maintain aqueous
294 speciation equilibrium between the exchange surface and the bulk solution. For example, the
295 stability constants (log K, at 25 °C and ionic strength of 1) of the anions ClO₄⁻, Cl⁻, NO₃⁻ and
296 SO₄²⁻ for equilibrium with Ce³⁺ are 0.15, -0.04, 0.2 and 1.51, respectively (Martell et al., 2004).

297 Therefore, in lixiviants where the efficiency (in terms of surface desorption) of the cation is not
298 maximised, the anion can have a positive effect on extraction efficacy and this is directly
299 related to the potential for the anion to form complexes with the REE metal ions (larger log Ks
300 results in higher aqueous concentrations of anion complexes with the target lanthanide metal
301 ion). This is seen in Figure 1 for Na, which has a relatively weak selectivity for ion adsorption
302 and therefore cation ion exchange and where the sulfate ion results in a greater REE
303 extraction than nitrate, chloride or perchlorate by reducing the solution free-ion activity of the
304 REE.

305

306 The shape of the Al eluate concentration profiles (Figure 4 and SI Figure S3.7) and the
307 relatively slow kinetics of kaolinite (Wieland and Stumm, 1992) and gibbsite (Bloom, 1983)
308 dissolution indicate that the high concentrations in the eluate solution occur as a result of
309 desorption from ion-exchange sites. Occupation of ion-exchange sites is dominated by Al^{3+} in
310 these systems, consistent with the conclusions of Crawford (2019) on samples from the same
311 region. Nevertheless, eluate dissolved Al concentrations closely follow those calculated from
312 the theoretical solubility of gibbsite in equilibrium with the eluate solution (Figure S3.8). The
313 level of Al extraction is an important consideration in the recovery of REEs, relative to the
314 target metals; Al is present in large quantities and not of economic interest. It may also interfere
315 with downstream refining and processing. The choice of lixiviant directly influences Al
316 extraction from the soil. Divalent cations and ammonium tend to maximise REE extraction,
317 irrespective of the lixiviant anion. Therefore, selection of the counter anion can be based on
318 the Al extraction rates and the amount of extracted dissolved Al is therefore minimised with
319 chloride salt solutions (Figure 2). This will be related to the level of speciation of Al with anion
320 ligands (stability constants (log K, at 25 °C and ionic strength of 1) of the anions Cl^- , and SO_4^{2-}
321 for equilibrium with Al^{3+} are -1.0 and 1.48 , respectively; Martell et al., 2004). Sulfate species
322 in a 0.01 M $\text{Al}_2(\text{SO}_4)_3$ solution can represent 20% of total Al, in contrast to $\sim 5\%$ for nitrate
323 species in a $\text{Al}(\text{NO}_3)_3$ solution or $<3\%$ for perchlorate species in a $\text{Al}(\text{ClO}_4)_3$ solution (Urabe et
324 al., 2009). This is also consistent with the conclusions of Xiao et al. (2016), who reported lower
325 Al leaching in compound lixiviant mixtures (with sulfate and chloride salts) than with a sulfate
326 salt with the same cationic charge.

327

328 There are several methods developed for the recovery of REEs from aqueous solutions using
329 oxalate (e.g., Xia, 2018; Kasaini, 2015; and other patent applications cited therein). However,
330 this precipitation step is reliant on minimal interference from lixiviant cations. Dissolved ion

331 concentration at saturation with respect to oxalate salts follows the sequence $\text{NH}_4 > \text{Na} \gg \text{Mg}$
332 $\gg \text{Ca}$ (52, 36.1, 0.38 and 0.0061 g L⁻¹ respectively; Lide, 2005) and our results indicated that
333 in 1 M lixiviant solutions (0.5 M for Ca, Mg), the precipitation of lixiviant cation oxalate salts
334 occurred for all cations except NH_4^+ . Thus, where oxalate precipitation is used as a
335 downstream processing step other lixiviant cations will be ineffective and the potential for use
336 of compound lixiviants may also be constrained by the solubility of oxalate salts.

337

338 The patterns of precipitation of REE salts from loaded lixiviant solution after addition of oxalate
339 follow a similar trend to that of Weaver (1954), who reported preferential precipitation of Sm,
340 with lighter elements following in order of decreasing atomic number, and heavier elements
341 following Sm in order of increasing atomic number. Here, we found the amount of Eu
342 precipitated was slightly greater than that of Sm, and a slightly lower amount precipitated for
343 Lu compared to that for Yb.

344

345 Experiments (on sample 0547) examined the breakthrough curve profiles of eluate chemistry
346 under conditions where the soil is hydraulically saturated with fluid, followed by a relatively
347 small pulse of lixiviant and then followed by a prolonged washing phase. The lixiviant used
348 was NH_4Cl , optimised considering the results of previous experiments, i.e. to maintain high
349 extraction efficiencies, to reduce the Al extraction and considering the need to use NH_4^+ to
350 eliminate interference with oxalate precipitation. This is also consistent with the similar
351 extraction efficiencies of $(\text{NH}_4)_2\text{SO}_4$ or NH_4Cl lixiviants as revealed from the work of Xiao et al.
352 (2016).

353

354 Results from the scoping column experiments (on sample 0652) indicate that the number of
355 pore volumes of lixiviant required for a high rate of REE extraction is low relative to the volume
356 of soil. For sample 0547 in column experiments, 0.1 pore volumes of lixiviant will contain 3.2
357 ± 0.2 mmol of NH_4^+ per 100 g of soil, compared to a CEC of 7.1 meq 100 g⁻¹, suggesting that
358 ~ 0.25 pore volumes of lixiviant will be sufficient for complete exchange of all sorbed ions, and
359 this amount will be reduced where Al is not fully desorbed. We used ~ 0.4 (columns C, D and
360 F) to 0.6 (column E) pore volumes of lixiviant (based on Cl in eluent), indicating that significant
361 desorption can be achieved with lixiviant volumes around those required for saturation of ion-
362 adsorption sites. Results are also consistent with the finding of other studies that indicate fast
363 desorption kinetics (e.g., Moldoveanu and Papangelakis, 2012).

364

365 We identified several stages during lanthanide extraction in the column experiments (Figure
366 S3.9.). In the first stage total La's (T-La) concentrations increase as Al increases and there is
367 no ammonium breakthrough. In stage 2, Al reaches a peak breakthrough concentration but
368 there are no significant change in T-La concentration. For stage 3, ammonium breakthrough
369 occurs, Al concentration decreases from its peak value and there is a correlated increase in
370 the amounts of T-La extracted. In the final phases Al and T-La concentrations both decrease
371 as they are depleted from the column. Then, finally, the post-lixiviant wash results in a gradual
372 decrease in the ammonium concentration.

373

374 Moldoveanu and Papangelakis (2013b) reported that there is a beneficial effect of batch
375 leaching at lower pH, with slightly higher extraction levels being obtained at pH 3 versus pH 5
376 (86.5 vs. 82.1%). However, our column study indicates that pH variation of the lixiviant had
377 little effect on the recovery efficiency of REE extraction. The equilibrium pH of freshly prepared
378 0.1 M NH₄Cl was 4.8 (columns C and E); two other columns (D and F) used solutions adjusted
379 to pH 3 or 1. The pH changes in the column experiments during initial ion-exchange are driven
380 by the hydrolysis of desorbed Al releasing protons ($Al^{3+} + H_2O = AlOH^{2+} + H^+$). Following Cl
381 breakthrough, the pH in all columns was buffered to a value of ~3.2 irrespective of the input
382 solution pH. To restore the soil to the original porewater pH required 1-1.5 pore volumes of
383 flushing with low ionic strength solutions after lixiviant input. In columns with high throughputs
384 of lixiviant (>7 pore volumes, columns A and B, using sample 0652), the pH initially drops but
385 steadily increases towards the lixiviant equilibrium pH as the Al and REEs are desorbed from
386 the soil.

387

388 Our results show that heavier REE metals and Ce have significant amounts present as acid
389 extractable fractions that are not extracted by ion-exchange. For sample 0547 this phase
390 represents >9% above the ion-exchangeable concentrations for Sm and heavier metals and
391 24% for Ce. For the coarser grained 0652 sample, this phase represents 13-36% for Sm and
392 heavier metals and 67% for Ce. This is consistent with Estrade et al. (2019), who reported
393 higher light REEs extraction rates from leaching than for heavy REEs for samples from the
394 same deposit (from data based on more aggressive leaching procedures). Ce anomalies are
395 a well understood feature of these deposits, related to the very low reduction potential of
396 Ce(IV) to Ce(III) (Bard et al., 1985) promoting formation of cerianite (Moldoveanu and

397 Papangelakis, 2012). Reduction leaching has been investigated as a more efficient process
398 for extraction of rare earth oxides (Xiao et al., 2016b).

399

400 **5. Conclusions**

401 The results of this study are of potential value to industry in terms of extraction optimisation
402 and subsequent lowering of energy and lixiviant costs. Ammonium chloride appears to offer
403 benefits as a lixiviant over other salts with similar extraction efficiencies, as it minimises Al
404 mobilisation and yields less contamination of recovered REE-oxalate mineral precipitates. We
405 show that NH₄Cl solutions can be used to efficiently extract REE with relatively low lixiviant
406 volumes (compared to pore volumes) in a through-flow column system. The minimum relative
407 volume required is likely related to the cation exchange capacity of the ore deposit, which will
408 be closely associated with the exchangeable Al concentration.

409

410 **Acknowledgements**

411 Funding for this work was provided by the UK Natural Environment Research Council
412 (NE/M011232/2). AS acknowledges support from the University of Manchester during the data
413 analysis and manuscript preparation phases of this work.

414

415 **References**

416 Bard, A.J., Parsons, R., Jordan, J., 1985. Standard Potentials in Aqueous Solutions. Marcel
417 Dekker, New York.

418 Barnett, M.J., Palumbo-Roe, B., Gregory, S.P. 2018. Comparison of heterotrophic bioleaching
419 and ammonium sulfate ion exchange leaching of rare earth elements from a Madagascan ion-
420 adsorption clay. *Minerals*, 8, 236.

421 Bloom, P.R. The kinetics of gibbsite dissolution in nitric acid. *Soil Sci. Soc. Am. J.*, 1983, 47,
422 164–168.

423 Chakhmouradian, A.R., Wall, F. Rare earth elements: minerals, mines, magnets (and more).
424 *Elements*, 2012, 8 (5): 333–340.

425 Chi, R.A., Zhou, Z., Xu, Z., Hu, Y., Zhu, G., Xu, S. Solution-chemistry analysis of ammonium
426 bicarbonate consumption in rare-earth-element precipitation. *Metall. Mater. Trans. B* 2003, 34
427 (5), 611–617.

428 Crawford, A. Geochemical modelling of environmental processes in rare earth element mining.
429 2019, PhD thesis, University of Leeds. [<http://etheses.whiterose.ac.uk/id/eprint/23242>]

430 Estrade, G., Marquis, E., Smith, M., Goodenough, K., Nason, P. REE concentration processes
431 in ion adsorption deposits: Evidence from the Ambohimirahavavy alkaline complex in
432 Madagascar, *Ore Geol. Rev.*, 2019, 112, 103027.

433 Fernandes, A., Afonso, J.C., Dutra, A.J.B. Separation of nickel(II), cobalt(II) and lanthanides
434 from spent Ni-MH batteries by hydrochloric acid leaching, solvent extraction and precipitation.
435 *Hydrometallurgy*, 2013, 133, 37-43.

436 He, Z.Y., Zhang, Z.Y., Yu, J.X., Xu, Z.G., Chi, R.A. Process optimization of rare earth and
437 aluminum leaching from weathered crust elution-deposited rare earth ore with compound
438 ammonium salts. *J. Rare Earths*, 2016, 34, 413–419.

439 Josso, P., Roberts, S., Teagle, D.A.H., Pourret, O., Herrington, R., Albarran, C.P.L. Extraction
440 and separation of rare earth elements from hydrothermal metalliferous sediments. *Minerals*
441 *Engineering*, 2018, 118, 106-121.

442 Kanazawa, Y., Kamitani, M. Rare earth minerals and resources in the world. *J. Alloys Compd*,
443 2006, 408-412, 1339-1343.

444 Kasaini, H. Extraction of metals from metallic compounds. US patent application US
445 2015/035402.6 A1, 10th Dec 2015.

446 Kynicky, J., Smith, M.P., Xu, C. Diversity of rare earth deposits: The key example of China.
447 *Elements*, 2012, 8, 361-367.

448 Le Couteur, P.C. Geological Report on the Chambe Basin Area of Exclusive Prospecting
449 License EPL0325/11 Mulanje Massif, Southern Malawi, East Africa. 2011.

450 Lide, D.R. Ed. *Physical Constants of Organic Compounds*", in *CRC Handbook of Chemistry*
451 *and Physics*, 86th Edition, 2005, CRC Press, Boca Raton, FL, USA.

452 Martell, A.E. Smith, R.M., Motekaitis, R.J. *NIST Critically Selected Stability Constants of Metal*
453 *Complexes*, Database 46, Version 8, NIST, Gaithersburg, MD, 2004.

454 Meeussen, J.C.L., van der Sloot, H.A., Dijkstra, J.J., Kossen, D.S., 2009. Review of
455 thermodynamic and adsorption databases. Cementitious Barriers Partnership Publication
456 CBP-TR-2009-002.

457 Mentani, T., Ohmura, T., Watanabe, Y., Urabe, T. So-called ion-adsorption type REE deposits
458 found in weathered crust of ilmenite-series granite in northern Vietnam. GSA Denver Annual
459 Meeting. 2010.

460 Moldoveanu, G.A., Papangelakis, V.G. Recovery of rare earth elements adsorbed on clay
461 minerals: I. Desorption mechanism. 2012, *Hydrometallurgy* 117–118, 71–78.

462 Moldoveanu, G.A., Papangelakis, V.G. Recovery of rare earth elements adsorbed on clay
463 minerals: II. Leaching with ammonium sulfate. 2013, *Hydrometallurgy* 131–132, 158–166.

464 Moldoveanu, G.A., Papangelakis, V.G. Leaching of lanthanides from various weathered
465 elution deposited ores. *Can. Metall. Q.* 2013b, 52, 257–264.

466 Moldoveanu, G.A., Papangelakis, V.G. An overview of rare-earth recovery by ion-exchange
467 leaching from ion-adsorption clays of various origins. *Min. Mag.*, 2016, 80, 63–76.

468 Padrones, J.T., Imai, A., Takahashi, R. Geochemical Behavior of Rare Earth Elements in
469 Weathered Granitic Rocks in Northern Palawan, Philippines. *Resour. Geol.*, 2017, 67, 231–
470 253.

471 Parkhurst, D.L. Appelo, C.A.J. Description of input and examples for PHREEQC version 3—
472 A computer program for speciation, batch-reaction, one-dimensional transport, and inverse
473 geochemical calculations. US Geological Survey Techniques and Methods (Denver, CO)
474 Book 6, Chapter A43, 2013. [Available at <https://pubs.usgs.gov/tm/06/a43>; accessed June 19,
475 2018].

476 Rocha, A., Schissel, D., Sprecher, A., de Tarso, P., & Goode, J. Process development for the
477 Serra Verde weathered crust elution-deposited rare earth deposit in Brazil. Proceedings of the
478 52rd Conference of Metallurgists. 2013.

479 Sanematsu, K., Murakami, H., Watanabe, Y., Duangsurigna, S., Vilayhack, S. Enrichment of
480 rare earth elements (REE) in the granitic rocks and their weathered crusts in central and
481 southern Laos. *Bull. Geol. Surv. Jpn.*, 2009, 60, 527–558.

482 SRK Exploration Services Ltd. A Competent Persons Report on the Tantalus Project, Northern
483 Madagascar. 2013. [<http://www.tre-ag.com/~media/Files/T/Tantalus-Rare->

484 [Earths/Attachments/pdf/2013_01_21_ES7520_SRKES_Tantalus%20CPR_Final_English.pdf](#)
485 ; Accessed 14th March 2019].

486 [Dataset] Stockdale, A., Banwart, S.A., SoS Minerals Madagascar ion adsorption deposits,
487 inorganic leaching of rare earth elements. British Geological Survey - National Geoscience
488 Data Centre. 2021.
489 <https://webapps.bgs.ac.uk/services/ngdc/accessions/index.html?#item163345>

490 Stoltz, N.B. Geometallurgical investigations of ion adsorption clays. 2017. Thesis, Rheinisch-
491 Westfälischen Technischen Hochschule Aachen.

492 Urabe, T., Tsugoshi, T. and Tanaka, M. Characterization of aluminum species with nitrate,
493 perchlorate and sulfate ions in the positive and negative ion mode by electrospray ionization
494 mass spectrometry. 2009, J. Mass Spectrom., 44, 193–202.

495 USGS (U.S. Geological Survey). Mineral commodity summaries, rare earths. January 2020.
496 2pp. [<https://www.usgs.gov/centers/nmic/rare-earths-statistics-and-information>; accessed 13th
497 March 2020]

498 Vahidi, E., Navarro, J., Zhao, F. An initial life cycle assessment of rare earth oxides production
499 from ion-adsorption clays. Resour. Conserv. Recy. 2016, 113, 1–11.

500 Weaver, B. Fractional Separation of Rare Earths by Oxalate Precipitation from Homogeneous
501 Solution. Anal. Chem. 1954, 26, 479–480.

502 Wieland, E., Stumm, W. Dissolution kinetics of kaolinite in acidic aqueous solutions at 25°C.
503 Geochim. Cosmochim. Acta, 1992, 56 (9), 3339–3355.

504 Xia, C. Direct oxalate precipitation for rare earth elements recovery. International patent
505 application WO 2018/195642 A1, 1st Nov 2018.

506 Xiao, Y., Chen, Y., Feng, Z., Huang, X., Huang, L., Long, Z., Cui, D. Leaching characteristics
507 of ion-adsorption type rare earths ore with magnesium sulfate Trans. Nonferrous Met. Soc.
508 China, 2015, 25, 3784–3790.

509 Xiao, Y.F., Feng, Z.Y., Huang, X.W., Huang, L., Chen, Y.Y., Liu, X.S., Wang, L.S., Long, Z.Q.
510 Recovery of rare earth from the ion-adsorption type rare earths ore: II. Compound leaching.
511 Hydrometallurgy, 2016, 163, 83–90.

512 Xiao, Y.F., Feng, Z.Y., Hu, G.H., Huang, L., Huang, X.W. Chen, Y.Y., Long, Z.Q. Reduction
513 leaching of rare earth from ion-adsorption type rare earths ore with ferrous sulfate, J. Rare
514 Earths, 2016b, 34, 917–923.

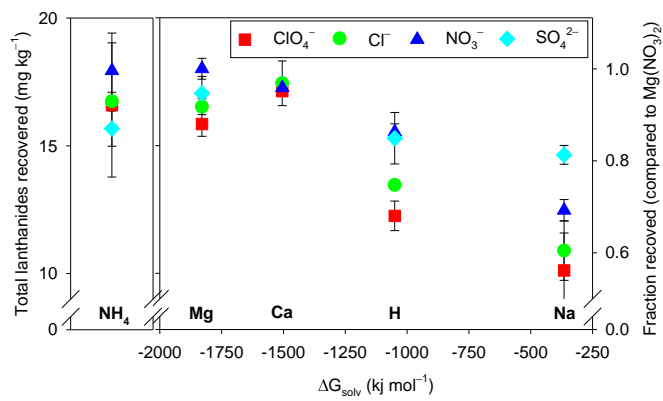
515 Xiao, Y.F., Lai, F.G., Huang, L., Feng, Z.Y., Long, Z.Q. Reduction leaching of rare earth from
516 ion-adsorption type rare earths ore: II. Compound leaching. *Hydrometallurgy*, 2017, 173, 1–8.

517 Yang, X. Zhang, J. Recovery of rare earth from ion-adsorption rare earth ores with a
518 compound lixiviant. *Sep. Purif. Technol.* 2015, 142, 203–208.

519

520 **Figures**

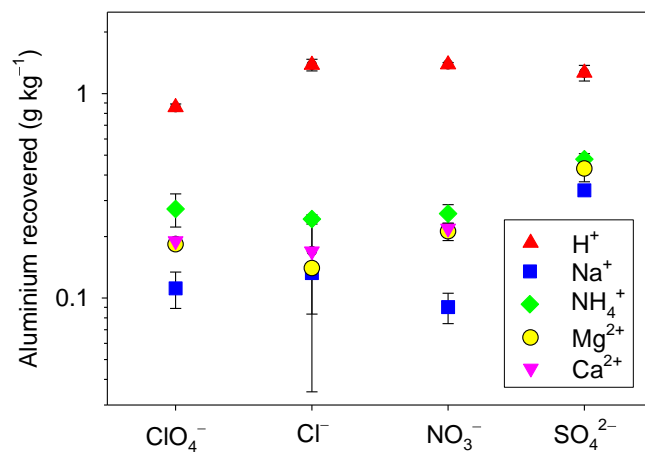
521 Figure 1.



522

523

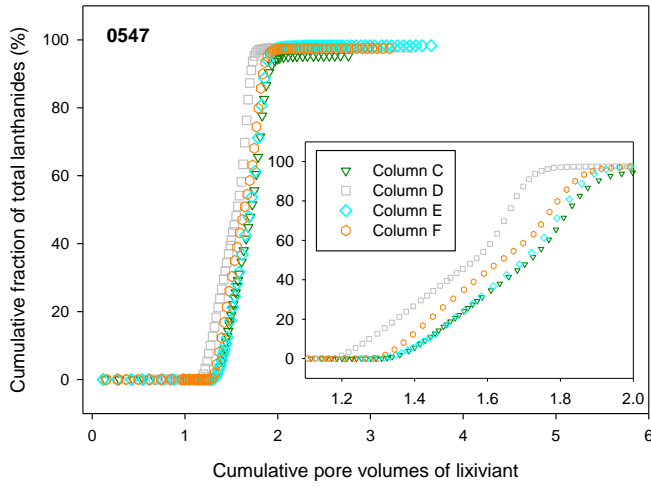
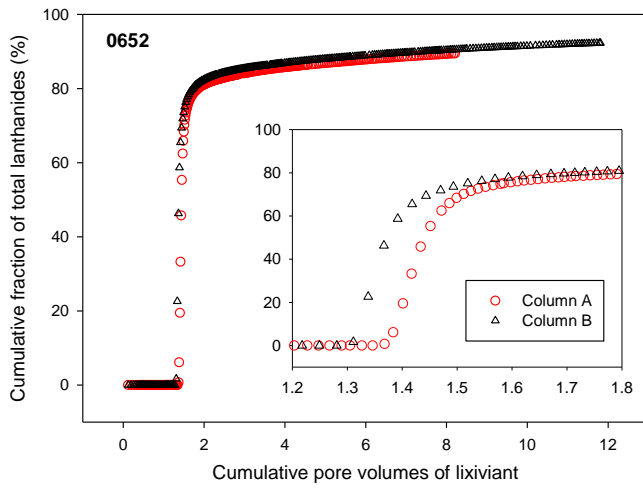
524 Figure 2.



525

526

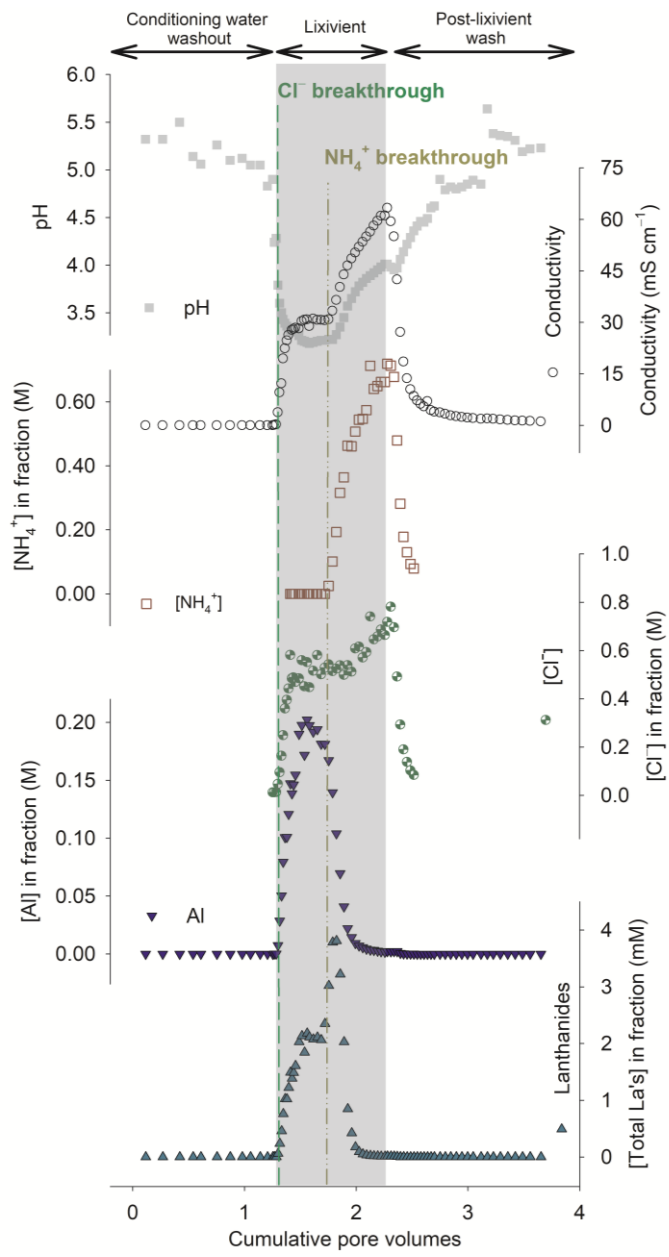
527 Figure 3.



528

529

530 Figure 4.



531

532 **Figure Legends**

533 Figure 1. Effect of lixiviant anions and cations on the extent of lanthanide leaching from an
534 ion-adsorption soil in a batch experiment. Lixiviant cations are plotted against their solvation
535 Gibbs free energies, except those for ammonium where data is not available so are plotted on
536 an independent axis to the left of the main panel. Experimental conditions were a 1:1
537 solid:liquid ratio and a concentration of 1 M (0.5 M for salts containing divalent cations or
538 anions). Error bars are two standard deviations from the mean of triplicate analysis.

539

540 Figure 2. Aluminium recovered from ion-adsorption soil using different lixiviant solutions.
541 Experimental conditions were a 1:1 solid:liquid ratio and a concentration of 1 M (0.5 M for salts
542 containing divalent cations or anions). Error bars are two standard deviations from the mean
543 of triplicate analysis.

544

545 Figure 3. Total lanthanide recovery in samples 0652 and 0547 as a fraction of the total
546 available from cation exchange leaching (column lixiviant flow and a final 1M CaCl₂ leach).
547 The inset shows data zoomed at the breakthrough of the lixiviant at the column outflow. The
548 equivalent data in molar concentration is shown in SI Figure S3.5.

549

550 Figure 4. Breakthrough curves for multiple analytes, for sample 0547 (column E). The
551 breakthrough points for Cl and ammonia are annotated as vertical lines. The lixiviant was 1 M
552 NH₄Cl (see Tables S2.2., S2.3. and S2.4. for other parameters). For columns C, D and F see
553 SI Figure S3.7. Arrows indicate the solution being eluted. The conditioning fluid that is in
554 equilibrium with the column before lixiviant injection is eluted first. This is followed by lixiviant
555 breakthrough (not reaching the ion concentrations of the input lixiviant due to mixing in the
556 columns and the low volume used). Then the lixiviant is washed out with the low ionic strength
557 wash solution (MQ water).

558

559