Mitigating Rare Earth Element Contamination: A Geochemical Quantification of Sustainable Extraction Reagents

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Abstract

Rare earth elements (REEs) are crucial for future clean technologies, but the extraction process of REEs often causes environmental problems such as groundwater acidification and the release of toxic metals. Hence, it is crucial to compare and identify different reagents to find the optimal option that balances REE extraction efficiency, acidification of the resulting solution, and the extent of toxic metal release. This study compares five leaching reagents on six weathered soil (regolith) samples from three rare earth deposits in Southern China: hydroxylammonium chloride, GLDA, citric acid, sodium citrate, and ammonium oxalate with ascorbic acid. For each reagent, standard batch leaching procedure was performed for 16 hours, and REE extraction rate and toxic metal release rate were assessed using ICP-MS, along with pH changes measured using a pH meter. Hydroxylammonium chloride, being the conventional reagent, extracted the most REEs, but it was also the most acidic (mean pH 0.15) and released large shares of lead and other toxic metals. In contrast, GLDA recovered about 77% as many REEs as hydroxylammonium chloride while releasing about 9 times less of the measured toxic metals, making it the most promising option tested in terms of extraction efficiency and environmental performance. However, GLDA was strongly alkaline (pH 10.2), extracted almost no cerium from one deposit, and its performance varied substantially across deposits.

Introduction

Rare Earth Elements (REE) are essential for the development of clean technologies such as renewable energy systems and electric vehicles. However, current industrial extraction often relies on inefficient chemical leaching processes that generate 2000 tons of toxic waste per tonne of REE produced (Bicker 2025) and pose serious risks to local water systems and ecosystems (Xu et al. 2023). To meet the growing demand for REEs without exacerbating ecological damage, it is crucial to transition towards more sustainable mining methods. This Laidlaw research project aims to contribute to this environmental challenge by comparing different extraction techniques and identifying opportunities to minimize their environmental footprint.

The focus of this study is the comparison of five different extraction reagents used in REE extraction. Historically, strong reductive dissolution agents like hydroxylammonium chloride have been utilized for their extraction strength; however, they pose severe environmental risks, including the release of toxic metals (such as V, Zn, Pb, U and Th) that causes harm towards ecosystem and significant water acidification. In contrast, chelating agents such as tetrasodium

glutamate diacetate (GLDA), citric acid, and sodium citrate present potentially more environmentally benign alternatives. While these organic chelating agents may offer a greener approach, their limitations—such as the remarkably slow extraction rates of citric acid or the inability of sodium citrate to dissolve iron oxides independently—must be rigorously evaluated. By comparing these traditional reductive dissolution mechanisms with alternative chelation methods (including the use of ammonium oxalate combined with ascorbic acid), this research seeks to identify a balance between extraction efficacy and ecological safety.

Despite the growing interest in these alternatives, a direct quantification of their extraction efficiencies and corresponding environmental impacts has been lacking. Therefore, this study attempts to quantitatively evaluate these parameters to establish a data-driven framework for sustainable REE mining. In this study, a sustainable reagent will be considered based on the balance between (i) extraction efficiency, (ii) near-neutral pH condition after reaction, and (iii) release of low amount of toxic metals. Economic viability, such as reagent cost and the market value of the recovered REEs, is also essential for a sustainable process but is outside the scope of this study.

Methodology

Samples

Samples used in this study were LN-2-1-1, LN-2-8, BK17-C6, BK17-C7, ZK12-64-23, and ZK12-64-37, all provided by Dr.Martin Li. Samples were originally from Bankeng, Puxiong, and Zudong in Southern China, chosen since they are the sites of some of the largest REE deposits in the world. Complete REE concentration data of these samples were provided by previous studies of Li et al. (2019, 2020), Wang et al. (2024), to be used to compare the REE extraction efficiency of each reagent (Table 1).

Deposit	Sample ID	Source of bulk data
Zudong	LN-2-1-1, LN-2-8	Li et al. (2019)
Bankeng	BK17-C6, BK17-C7	Li et al. (2020)
Puxiong	ZK12-64-23, ZK12-64-37	Wang et al. (2024)

Table 1: Deposits and sample IDs

Reagents Considered

Reagents considered in this study, and their abbreviation throughout this paper are: hydroxylammonium chloride (HC), tetrasodium glutamate diacetate (GLDA), citric acid (Citric), sodium citrate (SC), ammonium oxalate + ascorbic acid (AA). Chemical reagents were chosen based on their wide usage in REE extraction schemes developed in the literature, and their pH changes before and after the extraction were recorded in order to understand the potential water acidification caused by the usage of these reagents. The molarity used for each reagent were designed so that they would theoretically react with the same stoichiometric amount of iron and manganese oxides, as determined on the basis of the below chemical reactions. Due to low aqueous solubility, ammonium oxalate + ascorbic acid was prepared in 0.25M + 0.125M and was compared accordingly in the data analysis process.

Two processes can release REEs bound to iron and manganese oxides. In reductive dissolution, Fe(III) and Mn(IV) are reduced to the more soluble Fe(II) and Mn(II), so the oxide dissolves and the REEs are released (Eq. (A1), (A2) for hydroxylammonium chloride, and the ascorbic acid part of Eq. (A6), (A7)). In chelation, a chelating ligand replaces the REE at the

surface, or binds Fe and Mn at the surface (for example X-O-REE + L → X-O-L + REE-L) and detaches them (Eq. (A3), (A4), (A5) for GLDA, citric acid, and sodium citrate, and the oxalate part of Eq. (A6)-(A7)).

Extraction by Batch Leaching

Rare Earth Element extraction plan was designed based on previous research on REE sequential leaching process, Denys et al. (2021); Rauret et al. (1999); Ruttenberg (1992); Wenzel et al. (2001), as they are common scheme used to distinguish REE hosts/distribution in geochemical research. 0.5g of sample was leached by 20ml of each reagent solutions. 'Blank' samples, which were the reagents without any samples, were prepared and went through the same extraction process to monitor any contamination or procedure error. pH values of all solutions were measured prior to the extraction process. Batch leaching extraction was done by mechanical end-over-end shaker of 120 ± 10 rpm overnight for 16 hours, and the samples were centrifuged at 3000rpm for 20 minutes Rauret et al. (1999). After this, the pH changes of each extracted solutions were measured, and the extracted solutions were then acidified to 2.2 mol/L HNO_3 using 3.33mL of 15.7 mol/L HNO_3 solution to preserve all REEs in solution.

Analytical detection

For ICP-MS, extracted solutions were diluted 50 times before the measurement to adjust the analyte concentration suitable for the measurement. The Agilent 8900 inductively coupled plasma mass spectrometer (ICP-MS) at Imperial College London was used to quantify the concentration of extracted REEs in the leaching solutions. Fe and Mn were not quantified because their concentrations in the leachates were expected to exceed the calibration range of the other elements.

The measured signal is converted to concentrations in ppb using a calibration curve generated from standards of known concentrations. A calibration curve was constructed using standard solutions prepared by serial dilution of a 10 ppm stock solution to concentrations of 1000, 100, 10, and 1 ppb, together with a DI water blank. The lowest calibration standard (1 ppb) corresponds to about 2.3 ug/g of sample (1 ppb x 50 x 0.023 L / 0.5 g); this is used here as the practical quantification limit, and values below the reagent blank were set to zero. 50 ppb Indium solution was used as an internal standard throughout the procedure to monitor the instrumental signal drift.

The solid residue was not analyzed, so the mass balance is checked by comparing the amount leached with the bulk content. 446 of 450 element recoveries are at or below 100%. The four above 100% (BK17-C6 with GLDA: Eu 116%, Tb 102%, Tm 135%, Lu 145%) are low-abundance heavy REEs, where the bulk values are less certain.

Data Processing

Leachate concentrations (C, in ug/L) were corrected for the reagent blank, C_{corr} = max(C - C_{blank}, 0), where the HC blank is the mean of two blanks. The amount released per gram of sample is m = C_{corr} x V / m_s (ug/g), with V the extraction volume (0.023 L) and m_s the sample mass (0.5 g). Moles per gram are n = m / A_r, with A_r the atomic mass. Recovery in mol% is the sum of n over the REEs in solution divided by the sum of n over the REEs in the bulk sample, multiplied by 100. Toxic metal release is expressed per mole of REE released, $\sum(n_{toxic})/\sum(n_{REE})$. Cerium is treated separately.

Result

Extraction efficiency

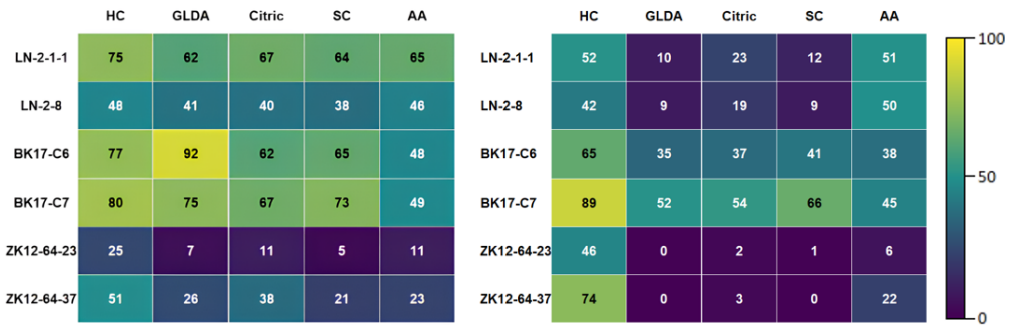

Figure 1: REE recovery (mass %) by sample and reagent: mean of total REEs with respect to the total concentration of the REEs in sample excluding Ce (left) and Ce (right) (%)

Table 2: Total REE recovery in moles (mol%, Ce excluded)

Deposit	**HC**	**GLDA**	**Citric acid**	**SC**	**AA**
Zudong	54	47	48	47	51
Bankeng	80	79	63	78	46
Puxiong	39	20	24	19	9
All	58	48	45	48	36

The overall recovery efficiency of rare earth elements ($\bar{R}$) of each reagent was evaluated to compare how much of the different REEs each reagent extracts. This was evaluated by taking the arithmetic mean of the extraction recovery rates across all individual REEs:

$$\bar{R} = \frac{1}{M} \sum_{i=1}^{M} R_i \tag{1}$$

where R_i is the extraction recovery rate (%) of the i-th individual REE, and M is the total number of evaluated REEs. Figure 1 (left) and Table 2 shows the average recovery of all REEs except cerium, which behaves differently and is discussed below. Averaged over the six samples, hydroxylammonium chloride recovered the most (59%), followed by GLDA (50%), citric acid (48%), sodium citrate (44%), and ammonium oxalate with ascorbic acid (40%). On a sample-by-sample basis, GLDA recovered on average about 77% of the REEs that hydroxylammonium chloride recovered from the same sample. The ammonium oxalate and ascorbic acid mixture was used at half of its designed concentration because of its low solubility, so its recovery cannot be compared directly with the others. Samples from Zudong and Bankeng gave recoveries of roughly 40-90% with every reagent, and in sample BK17-C6 GLDA (92%) even exceeded hydroxylammonium chloride (77%). Samples from Puxiong gave much lower recoveries. In ZK12-64-23, only hydroxylammonium chloride reached 25%, while the other reagents recovered between 5% and 11%; in ZK12-64-37 recoveries ranged from 21% to 51%. However, in terms of Ce recovery rate, the reagent mattered more than the sample, an apparent dip in the Ce recovery rate shown in almost every sample for GLDA, Sodium Citrate, and Citric acid (Figure 2).

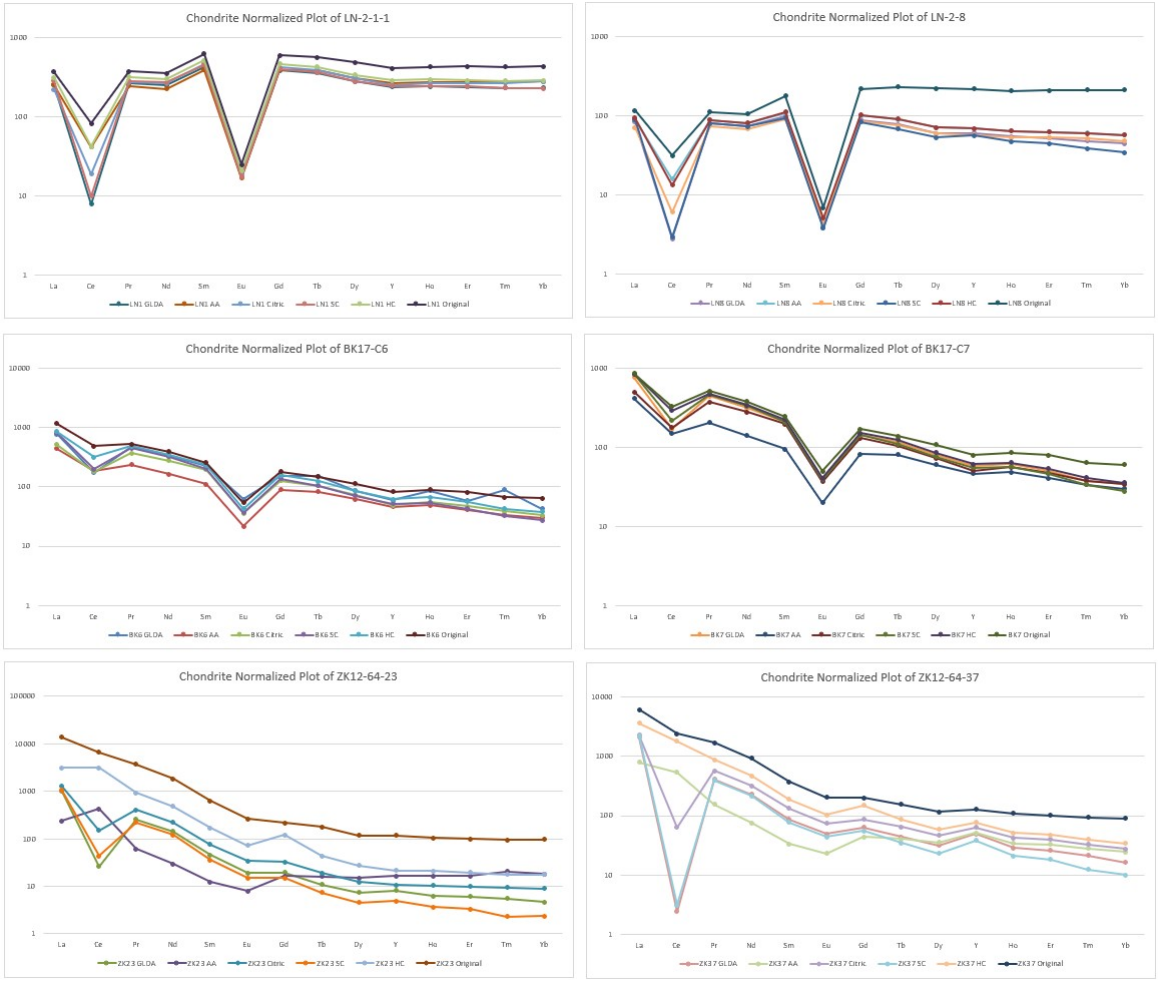

Figure 2: Chondrite normalized plot of each sample with different extraction reagents. Note that sample names and reagents' name are abbreviated in order to fit in the plot (e.g. LN-2-1-1 as LN1, Ammonium oxalate + Ascorbic acid as AA).

Cerium often occurs in soil as an oxide that is hard to dissolve unless it is first chemically reduced. Figure 1 (right) shows that the two reagents that act as reducing agents, hydroxylammonium chloride and ammonium oxalate with ascorbic acid, recovered the most cerium in most samples. The trend is more evident in Figure 2, where GLDA, citric acid and sodium citrate show low normalized concentration that results in a dip in the Ce datapoint. The difference was clearest in the Puxiong samples: hydroxylammonium chloride recovered 46-74% of the cerium there, whereas GLDA, citric acid, and sodium citrate recovered only 0-3%. In the Bankeng samples, however, the chelating agents also recovered a considerable amount (35-66%). (The hydroxylammonium chloride blank contained cerium, so its cerium values for the Zudong samples are less reliable.)

Table 3: **pH and proton (H^+) concentration before and after leaching**

Reagent	**pH before**	**pH after**	**ΔpH**	**[H^+] before** (mol/L)	**[H^+] after** (mol/L)	**H^+ released / REE** (mol/mol)
HC	0.47	0.15	−0.32	0.34	0.97	≈ 2500
GLDA	9.91	10.22	+0.31	1.2×10^{-10}	8.3×10^{-11}	< 0 (Net uptake)
Citric acid	1.55	1.32	−0.23	0.028	0.064	290
SC	6.38	6.60	+0.22	4.2×10^{-7}	2.9×10^{-7}	< 0 (Net uptake)
AA	3.40	3.37	−0.03	4.0×10^{-4}	4.7×10^{-4}	0.7

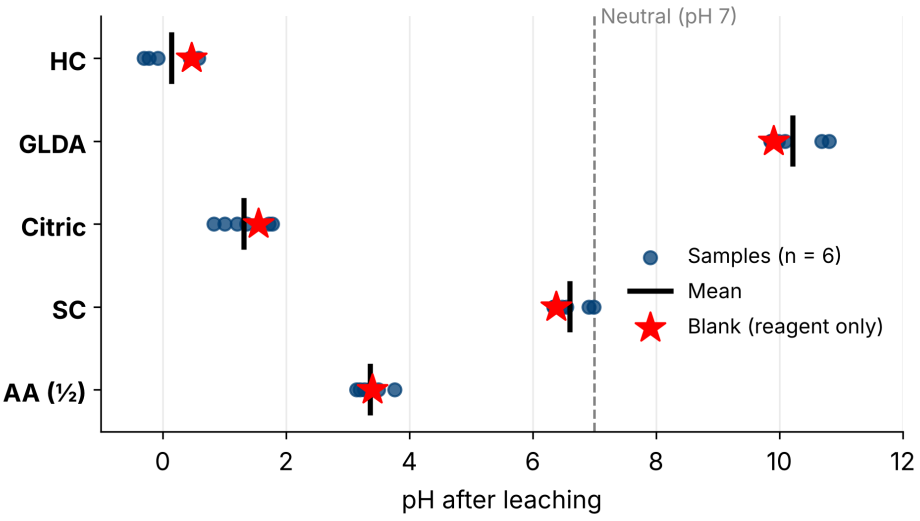

Figure 3: pH after leaching. Dots: individual samples (n = 6); black line: mean; red star: reagent blank (pH before leaching). AA was used at half concentration.

Proton release

pH difference before and after the leaching process was analyzed in order to assess the potential soil/groundwater acidification effect of each reagent. The acidity of the leaching solutions differed largely between reagents (Table 3, Figure 3). Among all 5 reagents, hydroxylammonium chloride was the most acidic reagent, with a mean pH value of 0.15. Citric acid was also strongly acidic (mean pH 1.32), followed by ammonium oxalate with ascorbic acid (3.37). Sodium citrate was closest to neutral (6.60). GLDA was the only reagent that showed the alkaline trend, the samples' mean pH being 10.22.

For every reagent, the pH after extraction stayed within about one unit of the reagent on its own (the blank). This shows that acidity or alkalinity is mainly a property of the reagent itself rather than of the sample.

The reactions in Appendix A show that dissolution consumes protons (they appear on the reactant side), so protons must come from the solution itself. Reagents with a low pH (HC, citric acid) therefore start with a large reservoir of protons, while GLDA (pH about 10) and sodium citrate (pH about 6.4) have almost none. For the high-pH reagents the reactions probably proceed by ligand exchange at the oxide surface rather than by proton attack. The pH after leaching shows that HC and citric acid became even more acidic (by 0.3 and 0.2 pH units), whereas GLDA and SC became slightly more alkaline; which reaction produces the extra protons is not resolved by these data.

Toxic metal release rate

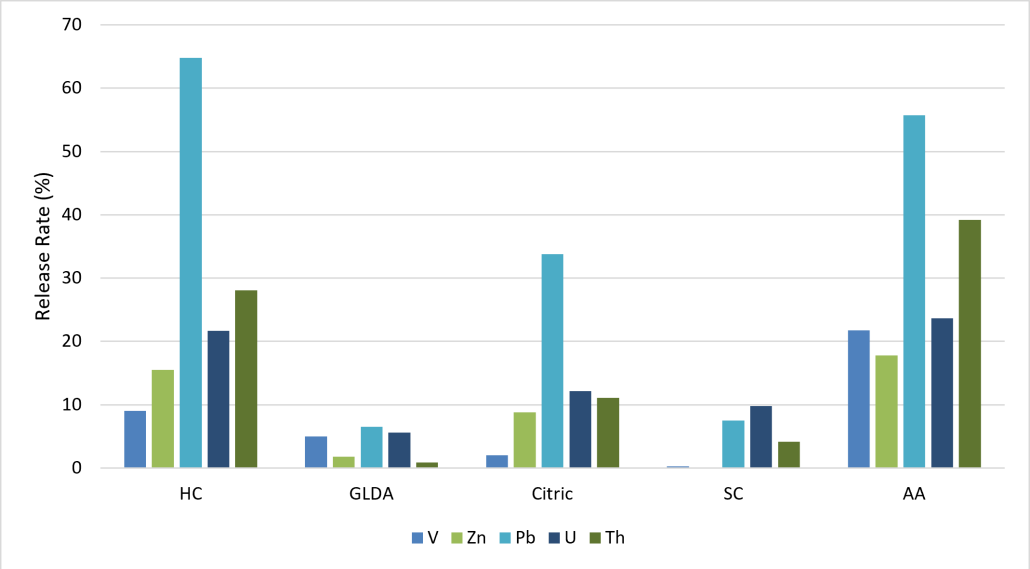

Figure 4: Toxic metal release rates of each reagent of Puxiong and Bankeng Samples after batch leaching for 16 hours (in mass %)

Table 4: Sum of V, Zn, Pb, U and Th released divided by total REE released (mol/mol). In brackets: grams of the five metals per kg of REE released.

Deposit	HC	GLDA	Citric acid	SC	AA
Zudong	0.13 (223)	0.03 (42)	0.13 (224)	0.02 (35)	0.15 (252)
Bankeng	0.09 (139)	0.02 (21)	0.09 (147)	0.03 (43)	0.18 (266)
Puxiong	0.26 (330)	0.02 (10)	0.35 (399)	0.01 (12)	1.24 (1513)

Toxic metal release rate was measured to quantify how much toxic metal is released together with each mole of REE. Figure 4 shows the percentage of each toxic metal in the sample relative to the regolith composition that was released (vanadium, zinc, lead, uranium, and thorium), averaged over the Bankeng and Puxiong samples; bulk values for these metals were not available for the Zudong samples. Table 4 shows that, per REE released, AA released the most toxic metal in all three deposits, followed by hydroxylammonium chloride and citric acid, which were similar. In contrast, GLDA and sodium citrate released the least amount of toxic metals in sum. Compared to ammonium oxalate and ascorbic acid, which released the most amount of

toxic metals per kg of REE released, GLDA released about 27 times less toxic metals. The difference was greatest in the Puxiong samples, where ammonium oxalate and ascorbic acid's toxic metal release rate was about 150 times more than GLDA's toxic metal release rate, and hydroxylammonium chloride's toxic metal release rate was about 33 times of that of the GLDA.

Discussion

The results show a clear trade-off among different reagents. Hydroxylammonium chloride extracted the most REEs, but it proved to be an extremely acidic solution with the release of large shares of lead and other toxic metals. These are exactly the kinds of conditions that raise concern for soil and groundwater around mining sites. At the other end, the more 'sustainable' reagents extracted fewer REEs. In terms of the mean of the individual recoveries (Figure 1), sodium citrate had the lowest recovery of the full-strength reagents (44%), although on a summed-mole basis (Table 2) it was similar to GLDA. Citric acid sat in between: it recovered nearly as much as GLDA, but it was strongly acidic (pH 1.3) and released about a third of the lead present in the samples. Ammonium oxalate with ascorbic acid cannot be judged fairly on efficiency because of its half concentration, but even at that concentration it released as much toxic metal as the conventional reagent. GLDA offered the best balance. It recovered about 77% as many REEs as hydroxylammonium chloride, did not acidify the solution, and released about 9 times less toxic metal in total than hydroxylammonium chloride. However, GLDA, like the other chelating agents, extracted almost no cerium from the Puxiong samples. In addition, the large differences between deposits show that no reagent will be best everywhere. The very low recoveries in the Puxiong samples, whatever the reagent, suggest that much of their REEs sits in minerals that none of these reagents dissolve well. A possible explanation is that these REEs are held in minerals other than iron and manganese oxides, but this could not be tested in this study because iron and manganese were not measured.

Conclusion

GLDA and sodium citrate released the least toxic metal per REE and did not strongly acidify; GLDA recovered about 48 mol% of the REEs against 58 mol% for HC. Recoveries were highest in Bankeng, lowest in Puxiong; no reagent was proved to be best everywhere, so extraction rate is deposit-dependent. Only hydroxylammonium chloride and ammonium oxalate and ascorbic acid extracted cerium from Puxiong. Determining the most sustainable reagent will further require considering economic value, i.e. reagent cost and the market value of the REEs recovered per tonne of processed material. Next steps are to repeat ammonium oxalate and ascorbic acid at full concentration, measure Fe and Mn, assess the impact of GLDA on soil and microorganisms, and relate results to the REE host mineral and to the value of the REEs recovered.

Appendix

REE Extraction equations for reagents considered in this study

Hydroxylammonium chloride (0.125M):

$$2\,Fe_2O_3 + 2\,NH_3OH^+ + 6\,H^+ \longrightarrow 4\,Fe^{2+} + N_2O + 7\,H_2O \quad \text{(A1)}$$

$$2\,MnO_2 + 2\,NH_3OH^+ + 2\,H^+ \longrightarrow 2\,Mn^{2+} + N_2O + 5\,H_2O \quad \text{(A2)}$$

Tetrasodium glutamate diacetate (GLDA) (0.25M):

$$Fe_2O_3 + 6\,H^+ + 2\,GLDA^{4-} \longrightarrow 2\,[Fe(GLDA)]^- + 3\,H_2O \quad \text{(A3)}$$

Citric Acid (0.25M):

$$Fe_2O_3 + 2\,C_6H_8O_7 \longrightarrow 2\,Fe(C_6H_5O_7) + 3\,H_2O \quad \text{(A4)}$$

Sodium citrate (0.25M):

$$Fe_2O_3 + 2\,{C_6H_5O_7}^{3-} + 6\,H^+ \longrightarrow 2\,Fe(C_6H_5O_7) + 3\,H_2O \quad \text{(A5)}$$

Ammonium oxalate + ascorbic acid (0.5M + 0.25M):

$$Fe_2O_3 + C_6H_8O_6 + 4\,{C_2O_4}^{2-} + 4\,H^+ \longrightarrow 2\,[Fe(C_2O_4)_2]^{2-} + C_6H_6O_6 + 3\,H_2O \quad \text{(A6)}$$

$$MnO_2 + C_6H_8O_6 + 2\,{C_2O_4}^{2-} + 2\,H^+ \longrightarrow [Mn(C_2O_4)_2]^{2-} + C_6H_6O_6 + 2\,H_2O \quad \text{(A7)}$$

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