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Rare earth element (REE) and arsenic mobility in acid mine drainage (AMD) impacted soil

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ABSTRACT

The mobility of rare earth elements (REE) and arsenic (As) from acid mine drainage (AMD) impacted soil was investigated in a column leaching study. AMD impacted soils from prominent gold and coal mining regions in South Africa were eluted with a 1 μM $CaCl_2$ solution for 14 h and samples were collected at timed intervals corresponding to liquid to solid (L/S) ratios from 0 to 10. The results showed fast initial leaching ($L/S < 5$) leading to the leaching of 30–98 % of the total soil REE contents and 0.02–1.8 % of total soil As contents. The results show substantial indications of REE leachability and hence recovery from mining impacted soils. This has the potential to improve cost effectiveness of the remediation process. Conversely, As was found to be highly retained in the AMD impacted soils. This offers insights into the comparative conditions of leachability in AMD impacted soils. Further investigation into the mineral structures present in various AMD impacted soil media under leaching conditions is needed to fully explain the underlying geochemical factors responsible for the elements' release.

Acid mine drainage (AMD) is a form of environmental pollution arising from mining activity. It generates from the oxidation of sulfide-bearing minerals, predominantly pyrite (FeS_2), to produce dissolved sulfuric acid and Fe(III) (Nordstrom et al., 2015). The resulting, highly acidic solution contains a suite of metal(loid)s including critical elements rare earth elements (REE), arsenic (As) and others depending on the geologic conditions (European Commission, 2023; Migaszewski et al., 2016, Cheng et al., 2009). REE correspond to the lanthanide series of elements of the periodic table (z= 57–71) – lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) – and sometimes include the elements scandium (Sc) and yttrium (Y), which share geochemical similarities (Brioschi et al., 2013). The removal of REEs and As from AMD waste streams by chemical and electrochemical methods has previously been investigated. REEs have been removed for economic potential through re-mining and for offsetting the costs of remediation whilst As has been removed for pollution management. (Wang et al., 2003; Felipe et al., 2021). Many biogeochemical factors influence the speciation, stability, and mobility of As and REE in Fe rich soils. Their mechanisms of sorption to metal oxide and clay minerals present in AMD and soil conditions (and mineral structures) are well established and have been investigated through mineralogical techniques (Cheng et al., 2009; Ehlert et al., 2018; Borst et al., 2020; Gu et al., 2022). The affinities of As and REEs to Fe oxide and hydroxysulfate species lead to stable complexation and co-precipitation. The structural diversity of the mineral arising from different geochemical conditions at formation may, however, still be responsible for variations in As and REE mobility in the soil environment. This preliminary study serves to investigate that mobility and provide leaching data for As and REE (La-Lu, Y) in real-world, AMD impacted soils. This can inform the understanding of these variations in their context and their removal from AMD waste streams.

Approximately 500 g of surface soil (meaning 0 to 15 cm depth) was collected as a single grab sample at three AMD impacted sites in prominent gold and coal mining regions near Johannesburg, South

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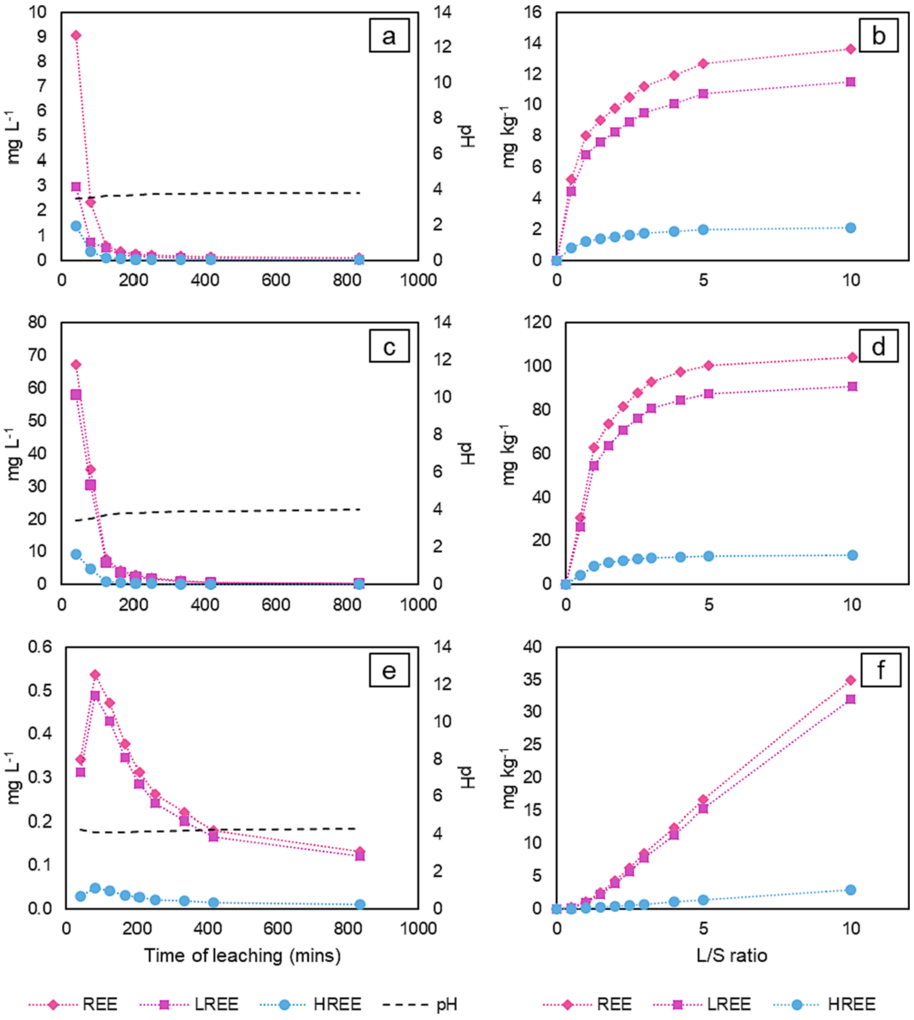

Fig. 1. Concentration of REE (La-Lu, Y), LREE (La-Eu), HREE (Gd-Lu, Y), and pH in eluate fractions (mg L^{-1}) over time of leaching in minutes (mins) and as accumulated leached contents per kg soil (mg kg^{-1}) over L/S ratio – data point indicates L/S end-point - for Witpoortje (**a**-**b**), Emalahleni (**c**-**d**), and Robinson Lake (**e**-**f**) soil columns.

Africa where AMD pollution has been prolific in groundwater and surface water (Thomas et al., 2023; Tutu et al., 2008). The soil collected from the sites, identified as Witpoortjie, Emalahleni, and Robinson Lake, had pH_{CaCl2} values ranging from 3.5 to 4.0, total carbon content < 2.5 %, cation exchange capacity < 11 cmol(+) kg^{-1}, and high sand (20–2000 µm) contents (85 %) (Thomas et al., 2023). Witpoortjie, Emalahleni, and Robinson Lake soil samples had total metal(loid) contents of 23, 4, and 360 mg kg^{-1} of As and 46, 106, and 70 mg kg^{-1} of REE (La-Lu, Y), respectively. For deeper soil characterisation and methods, please refer to Thomas et al (2023). Witpoortjie and Robinson Lake samples were from gold mining areas and the Emalahleni sample was from a coal mining area. Polyethylene columns (8.9 x 2.9 cm) were packed with the air-dried soil, sieved < 2 mm and gradually rewetted by an upward directional flow of eluent (1 µM $CaCl_2$) controlled by peristaltic pump (VC-360 Ecoline Pump, Ismatec, Denmark). The columns were equilibrated for 16 h, after which the eluent flow rate was set to 0.5 ml min^{-1}

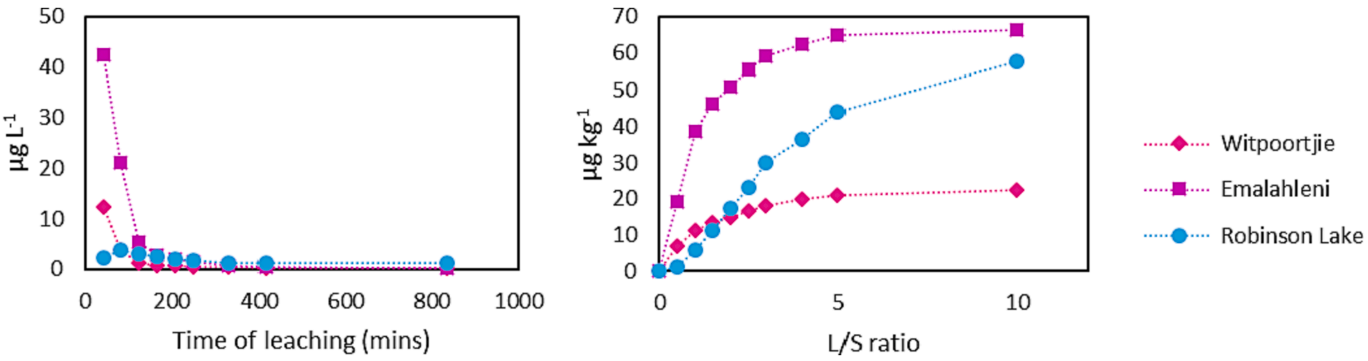

Fig. 2. Concentration of As in eluate fractions (µg/L) over time of leaching in minutes (mins) and as accumulated leached contents per kg soil (µg kg^{-1}) over L/S ratio – data point indicates L/S end-point - for Witpoortje, Emalahleni, and Robinson Lake soil columns.

and collection of 20 ml of eluate was completed at set time intervals corresponding to liquid to solid (L/S ratios) of 0–0.5, 0.5–1.0, 1.0–1.5, 1.5–2.0, 2.0–2.5, 2.5–3.0, 3.0–4.0, 4.0–5.0, and 5.0–10.0. Eluate samples was filtered by syringe and nylon top (0.45 μm). Subsamples of approximately 10 ml were acidified to 3.5 % HNO_3 and analysed by ICP-MS (Agilent Technologies) using multi-element calibration standards and analytical blanks, quality control samples and replicates were used to assess precision, accuracy, and detection limits. The remaining eluate solution was used to measure pH by electrode (Metrohm 914).

Fig. 1 shows pH, the concentration of total REE, light rare earth elements (LREE), and heavy rare earth elements (HREE) in the eluate fractions for Witpoortjie, Emalahleni, and Robinson Lake soil columns in mg L^{-1} and as the accumulated leached contents per kg soil (mg kg^{-1}).

The initial leached concentrations ($t < 417$ min, L/S ratio < 5) were higher for LREE than HREE in all soil columns, which is due to the lighter atomic mass of LREE and is expected from soils with acidic properties (i.e. podsols and spodosols) (Esser et al., 1991). Witpoortjie and Emalahleni (**a-d**) showed faster initial REE leaching compared to Robinson Lake, which neared equilibrium at the end of the experiment ($t = 835$ min), while Robinson Lake (**e-f**) showed a more gradual release of REE from the soil and increasing accumulated leached contents with increasing L/S ratio. The pH of the eluate from Robinson Lake ranged from 4.0 to 4.3 in comparison to Witpoortjie (3.5–3.8) and Emalahleni (3.4–4.0). Compared to the total REE soil contents of Emalahleni, Robinson Lake, and Witpoortjie soils, the columns leached 98 % (of 106 mg kg^{-1}), 50 % (of 70 mg kg^{-1}), and 30 % (of 46 mg kg^{-1}), respectively.

Fig. 2 shows the concentration of As in the eluate fractions collected from Witpoortjie, Emalahleni, and Robinson Lake soil columns in μg L^{-1} and the as the accumulated leached contents per kg soil (μg kg^{-1}).

Similar to the leaching behaviour of REE, Witpoortjie and Emalahleni showed faster initial leaching compared to Robinson Lake, which reached an equilibrium at $t = 417$ ($L/S = 5$). A higher amount of the total As soil content of Emalahleni was leached (1.8 % of 4 mg kg^{-1}) compared to Witpoortjie (0.1 % of 23 mg kg^{-1}), which points towards Emalahleni containing the highest fraction of dissolved and easily mobilised As species. In contrast, Robinson Lake showed a relatively slow release of As and did not reach equilibrium at the end of the experimental run time as the other two columns. At the highest L/S, the accumulated leached As content was equivalent to 0.02 % of the total As content of the soil (360 mg kg^{-1}), which was far lower than the leached contents of Emalahleni and Witpoortjie by factors of 5 and 90, respectively. The data indicates that As is highly retained in the AMD impacted soils despite showing variation in leaching rates and total concentrations.

The results show that the mobility of REE varies more than that of As in AMD impacted soil. The results also show that there is a relatively low environmental or human health risk of As leaching from a these mining impacted materials and that their mineral structures remain stable at the range of soil leaching conditions observed. While the eluate pH was within the range of what is considered conducive for As sorption to some Fe oxide minerals thus leading to lower As mobility (Burton et al., 2009), sandy soils are often associated with greater As mobility due to a negative surface charge of soil particles (Cheng et al., 2009). Further mineralogical analysis is necessary to distinguish whether the low As leaching is only due to Fe mineral structural stability or if there is an additional influence from potential amorphous oxide coatings on the sand fraction. It is also clear that the geochemical conditions of formation for stable As species are not the same for REE, given the high percentage of REE leached and the variation across the three soils. This variation indicates that recovery potential of REE for economic purposes (i.e. re-mining, resource recovery) is not the same for all AMD impacted materials, and that leachability may be more dependent on or relational to total concentrations than it was for As. These results support the conclusion that As and REE are not highly mobile under the same range of AMD impacted soil conditions which would be relevant for assessing methods of remediation or resource recovery. Through advanced microscopy techniques, future research could investigate the range of geochemical conditions for the selective removal of critical elements.

CRediT authorship contribution statement

Glenna Thomas: Conceptualization, Data curation, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. **Craig Sheridan:** Methodology, Supervision, Writing – review & editing. **Peter E. Holm:** Methodology, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Glenna Thomas reports travel was provided by Danish Agency for Higher Education and Science. Peter E. Holm, Craig Sheridan reports a relationship with Danida Fellowship Centre that includes: funding grants.

Data availability

Data will be made available on request.

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