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Towards environmentally compatible in situ leaching of mine waste using low concentration acids

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ABSTRACT

Conventional mining of metalliferous rock typically involves physical excavation followed by mineral processing. These are energy intensive and environmentally invasive processes which produce large amounts of wastes. In situ leaching of mine wastes with acidic lixiviants may provide an opportunity to recover additional metals and decontaminate residual material. However, the use of high concentration mineral acids (such as >1 M sulfuric acid) can be harmful to the environment and may necessitate post treatment to remove the acidity from the residual rock. The feasibility of using less aggressive lixiviants that may mitigate these risks was explored; 0.1 M citric and sulfuric acid were applied as lixiviants to determine the leaching behaviour of As and Cu from legacy sulfidic Cu/As mine waste. This was achieved via triplicate column upflow tests with a cumulative liquid-solid ratio of 31. Citric acid was more efficient than sulfuric acid for As recovery, with recovery (leaching efficiency) rates of 40.7 wt% and 35.2 wt%, respectively, but slightly less effective for Cu recovery: 33.8 wt% and 43.2 wt% of the total content, respectively. The comparable performance, despite citric acid being a weaker acid, is attributed to its affinity to form soluble As/Cu-citrate complexes. Numerical modelling of heap leaching of the mine waste at field scale was undertaken to allow exploration of scenarios for metal recovery versus time, lixiviant application rate and reagent consumption. This study highlights the suitability of applying lixiviants for the in situ leaching of metals from mine waste in low concentrations over a prolonged timescale. The work therefore provides a step towards unlocking a new paradigm of metal recovery and remediation for modern and legacy mine wastes with minimal environmental disturbance and energy input.

1. Introduction

Solid mine waste is humankind's largest waste-form by mass and is currently responsible for adverse environmental and human health impacts on a global scale, presenting a huge challenge to the social licence to operate (Hudson-Edwards et al., 2011). Mining operations worldwide are commonly linked to both sudden and long-term environmental hazards, including tailings dam failures, acid mine drainage and metal leaching (Helser et al., 2022). For example, in the UK, despite a cessation in metalliferous mining for several decades, legacy mine waste remains a major contributor to riverine metal and metalloid (hereafter metal) pollution (Hudson-Edwards et al., 2008). Similar situations exist worldwide, including the USA, Canada, Japan and Sweden, where approximately 35,000; 10,000; 5500 and 1000 respectively, legacy metal mines exist (Fields, 2003). To date, approximately 25,000 tailings storage facilities have been geo-located (mass in the order of 350 billion tonnes) (Franks et al., 2021; Oberle et al., 2020). Over the past 50 years, tailings dam disasters have caused more than 2000 fatalities and result in annual costs in the order of \$10 billion (Williams, 2021). Such active and legacy waste repositories can represent a major threat to human health and the environment and yet often contain metals approaching, or even exceeding, current ore grades. It is therefore necessary to rethink mine waste management practices and design new approaches for metal recovery which can be integrated into site rehabilitation (Crane et al., 2017).

Whilst there are examples of successful metal recovery schemes, many proposed projects remain unfeasible due to a range of economic, environmental, cultural and technological challenges. For example, Crane et al. (2017) demonstrated that 51 % of former metal mines in Wales and 84 % in England are co-located with at least one geological, environmental or cultural designation. The primary driver for intervention is often removal of pollution sources or pathways through

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remediation/rehabilitation. In such cases extraction of valuable metals and/or valorisation of residual minerals might generate revenue to offset the costs of such intervention. It is therefore necessary to explore new approaches to achieve this aim within the constraints posed by the site-specific environmental and/or economic constraints.

In situ leaching of mine wastes is a promising approach due to its ability to recover metals from the subsurface without excavation (Jenkin et al., 2024). A key technical challenge, however, which is currently limiting its widespread use, is the risk of secondary pollution due to any unintended loss of the lixiviant. Consequently, new approaches utilising more environmentally compatible lixiviant formulations and concentrations are required. Intermediate or high concentration (>0.5 M) mineral acids (typically sulfuric acid due to its low cost and efficacy) are commonly used for the leaching of sulfide and oxide ores (Bouffard, 2005; Kang et al., 2021; Liu et al., 2016). High acid strength is not optimal with respect to environmental performance where unintended lixiviant loss occurs (e.g., through pin-holes and tears in the liner). The environmental threat can also persist in solid residues (Catalan and Li, 2000; Rucker et al., 2017), particularly those deficient in fast-reacting neutralising minerals (e.g., calcite). Such waste requires long-term management in engineered facilities, posing a significant economic cost and environmental and/or human health liability. There is a consequent need to explore the applicability of low concentration and readily (bio)degradable lixiviants which may present a lower risk to the environment during, and post operation of a heap leach or other in situ leaching of mine wastes.

Citric acid is a weak acid and chelating agent that is a common natural component of soil (produced from the decay of plants, animals and microbial tissue), used in food manufacturing (Ghai et al., 2024), as a pH regulator and cleaning agent (Ghai et al., 2024). It is biodegradable under both aerobic and anaerobic conditions, and it is a highly versatile lixiviant (Reena et al., 2022). There is consequently, a growing interest within the academic literature in its potential use for metal recovery from geological materials (Crane and Sapsford, 2018; Crane and Stewart, 2021; Safari et al., 2024). Almost all empirical research studies in this area, however, have used batch leaching tests (e.g., Ettler et al., 2004). These do not adequately simulate the physicochemical conditions of most industrial scale leaching processes, which are typically either ex situ flow-through, heap or in situ (Garrabrants et al., 2021; Rosende et al., 2008). In such batch systems important hydrogeochemical conditions, such as redox gradients, mixing behaviour and liquid-to-solid ratios, are markedly different to industrial scale conditions, leading to under or overestimations of leaching efficiencies. In contrast, column tests provide more realistic simulation of field conditions (for both in situ or heap leaching scenarios) because they directly simulate percolation of the lixiviant. Therefore column test studies using novel lixiviants, such as citric acid are required to improve understanding of leaching efficacy.

The present study investigated the use of low concentration (0.1 M) citric and sulfuric acid for the long-term (104 days, liquid-solid ratio up to 31.1) assessment of the leaching of As and Cu from a legacy sulfidic copper mine tailings deposit. The aim is to provide insight into the potential applicability of low intensity hydrometallurgical schemes for metal recovery from mine wastes and ores (Sapsford et al., 2017, 2019, 2023; Mohammad et al., 2023).

2. Methodology

2.1. Site description, sampling and characterisation

Samples were collected from the tailings at the Devon Great Consols (DGC) mine (Devon, England). Primary ore at DGC comprised chalcopyrite (CuFeS₂) and arsenopyrite (AsFeS), which when the site was operational were processed onsite, resulting in two legacy tailings stockpiles with an estimated total volume of 246,500–302,000 m³ (Mighanetara, 2008). As a member of the UK mine water directive sites, it is known to be releasing ecotoxic metals into surrounding waters each year and is also a human health hazard due to the occurrence of such metals with dust emissions (Braungardt et al., 2020). A total of 17 samples were collected from 0.3 m depth (i.e., beneath the surface weathered zone) at equal distances around the base of the stockpile, using a stainless-steel trowel, following procedures of ASTM D6009 (2012). Each sample had a volume of 5 L with a mass typically between 6 and 8 kg, depending on bulk density. Each sample was split using cone and quartering and then mixed into a composite sample which was used for this study. Further detail on this sampling method and physical and chemical characterisation of the material is reported by Crane and Sapsford (2018).

2.2. Column leaching experiment

Saturated column leaching experiments (Fig. 1) were performed in triplicate as per USEPA-1314 (2017); key experimental parameters are summarised in Table 1. The average porosities of the materials in the citric and sulfuric acid exposed columns (hereafter Col-C and Col-S respectively) were 31.95 % and 26.45 %, respectively and bulk densities were 1.631 g/cm³ and 1.630 g/cm³ respectively. An acid concentration of 0.1 M was used, and all experiments were conducted at room temperature (21.0 \pm 1.5 °C). The columns contained multiple inlets along the base of the column (to limit lixiviant dispersion) and a 5 µm polypropylene filter paper (acid-washed: 5 % nitric acid, followed by deionised water, prior to use) was placed above and below the mine waste to ensure minimal loss of colloids. The columns were first saturated (initial volume was 202 mL and 168 mL for citric and sulfuric acid solutions, respectively), allowed to equilibrate for 24 h, and then fed with further lixiviant from the base, using a Watson Marlow 205S peristaltic pump at approximately 12 mL/h. Effluent samples from both columns were collected at the following times: 0, 6.0, 21, 54.0, 101.5, 214.7, 383.7, 861.0, 1537.0, 2041.0, and 2474.0 h and tested for solution pH, electrical conductivity (EC), and oxidation reduction potential (ORP) using a Metrohm i-unitrode pt1000 combination pH probe, Metrohm 907 Titrando equipped with a Metrohm 5 ring conductivity probe, and a SI-analytics[™] blueline platinum disk ORP electrode, respectively. Effluent samples were filtered using a 0.45 μ m PES syringe filter, acidified to 2 % nitric acid before being analysed using ICP-OES (Perkin Elmer Optima 2100 DV ICP-OES). The coefficients of variation for metal ion concentrations between the columns were calculated to identify presence of outliers between the columns as presented in Tables S1 and S2 (supplementary data). Data were plotted, fitted and visualised in Origin 2020 (USA). Statistical analysis and visualisation was performed using the Tidyverse package in R (Version 4.1.1).



Fig. 1. Schematic diagram of the column leaching experiment.

Table 1

Column leaching experimental parameters.

Parameter	Citric acid columns (Col-C)	Sulfuric acid columns (Col-S)
Cumulative	0.25, 0.33, 0.53, 0.94, 1.55,	0.26, 0.33, 0.54, 1.57, 3.03,
L/S ratio (L/	3.00, 5.09, 11.17, 19.55,	5.14, 11.08, 19.49, 25.89,
kg)	25.90, 31.10	31.11
Average sample	950.0	
mass (g)		
Sample	0, 6.0, 21.0, 54.0, 101.5, 214.7, 383.7, 861.0, 1537.0, 2041.0,	
Collection time	2474.0	
(h)		
Column inner	5.0	
dia. (cm)		
Column height	30.0	
(cm)		
Appox. flow rate	12	
(mL/h)		
Porosity (%)	31.95 ± 3.87	26.45 ± 1.89
Bulk density (g/	1.63 ± 0.03	1.63 ± 0.02
cm ³)		

2.3. Modelling of metal recovery from the saturated waste

The in situ leaching behaviour of a mine waste stockpile is dependent upon a range of factors including the lixiviant flow-rate, timespan and geometry of the waste pile. Numerical modelling of such leaching behaviour is an important consideration because it can be used to predict and plan numerous operational considerations, such as reagent consumption and leaching timescales.

Metal dissolution due to the interaction between a percolating lixiviant and a volume of permeable saturated waste can be expressed using Eq. 1 (CEN/TS 16637-3, 2016; Lee et al., 2017; Kim et al., 2018). Model assumptions include equilibrium being established instantly at the liquid solid interface and each particle being compositionally homogenous (Eq. 1).

$$U_{L/S_x} = U_{L/S_{lab}} \cdot \frac{1 - e^{-k(L/S_x)}}{1 - e^{-k(L/S_{lab})}}$$
(1)

where, U_{L/S_x} indicates predicted release content of the element of interest at L/S ratio achieved in a waste pile (L/S_x) as per Eq. 2.

kg), can be determined by,

$$U_{L/S_{lab}} = \sum_{i}^{p} C_{i} \cdot (L/S_{i})$$
(5)

where, p is the number of leachate fraction, C_i (mg/L) measured concentration in leachate fraction i, and L/S_i (L/kg) the L/S interval of leachate fraction (*i*).

The leaching rate constant k and $U_{L/S_{lab}}$ can be used to estimate $U_{L/S_x}(t)$ (in mg/kg) (refer to Eq. 1) to heap leach membrane or leachate collection layer over time (*t*) (year).

$$U_{L/S_x}(t) = U_{L/S_{tab}} \frac{1 - e^{-k\frac{tN}{dh}}}{1 - e^{-kL/S_{tab}}}$$
(6)

Finally, the % recovery with time has been calculated as.

$$R(t) = \frac{U_{L/S_{x}}(t)}{Total \ content} \ 100\%$$
⁽⁷⁾

The temporal variations of Cu recovery for both lixiviants were calculated at different percolation rates (1 to 20 mm/d) into an artificial heap of height 10 m and density of 1300 kg/m³. An in-situ density of 80 % of the density achieved in the laboratory was assumed in modelling, which is a conservative estimate to account for material compaction during column packing. Cu recovery (*R*) per unit area of a leach pad was modelled under different lixiviant percolation rates (total content in mine tailings = 1833 mg/kg).

3. Results and discussion

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3.1. Characterisation of the mine waste

The mine waste was recorded to contain a number of metals in appreciable concentrations as reported by Crane and Sapsford (2018). Bulk Cu and As concentrations (total acid digestion followed by ICP-OES) were 0.18 wt% and 1.9 wt% (dry basis) respectively with the former considered the most economically valuable component and the latter the most environmentally problematic. XRD indicates quartz (α -SiO₂) as the major crystalline component present with a minor contribution from muscovite (H₂KAl₃(SiO₄)₃), indicating a matrix that is

$L/S_x = \frac{Volume \text{ of lixiviant (i.e., citric acid or sulfuric acid) passed through the wastened total mass of wastened total wastened total mass of wastened total mass of wastened total wastened t$

If a unit cross sectional area of the waste deposit is considered then L/S_x can be expressed in terms of the time of percolation (t), rate of lixiviant percolation/pumping (N), density of waste (d) and target height of the heap or layer of interest (h), as Eq. 3.

$$L \bigg/ S_x = \frac{t \cdot N}{d \cdot h} \tag{3}$$

Further, in Eq. 1, $U_{L/S_{lab}}$ indicates experimentally determined release content of the metal of interest at L/S ratio achieved at laboratory (L/S_{lab}) and k is the leaching rate constant. The metal leaching behaviour from waste is expressed according to Eq. 4 (Kim et al., 2018; Lee et al., 2017). Here, k was calculated by achieving the least squared error between experimental leaching data and Eq. 4 by employing the solver add-in of MS Excel®.

$$C(L/S) = C(0) \cdot e^{-k(L/S_{lab})}$$
(4)

Total metal leaching in the laboratory column studies, $U_{L/S_{lob}}$ (mg/

recalcitrant to weathering and acid dissolution. The original primary ore minerals, arsenopyrite and chalcopyrite, however, were not detected. This was not unexpected given their low concentrations, which likely fall below the detection limit of the XRD instrument. SEM-EDX detected As and Cu as relatively uniformly distributed in the mine tailings but with some correlation with sulphur. This is in agreement with Carey et al. (2015) and suggests that it is likely that a proportion of the original ore minerals (chalcopyrite and arsenopyrite) remains, but that it may have also undergone environmental weathering to form Cu and Asbearing secondary (amorphous) minerals.

3.2. Column experiments

3.2.1. Changes in pH, EC and ORP

The pH, EC and ORP of leachate collected at each predefined sampling time for both Col-S and Col—C, is plotted in Fig. 2. It can be observed from Fig. 2(a) that at the start of the experiment, the pH of both leachates were similar at \sim 2.0. During the first 6 h (i.e., to L/S = 0.32), this increased to approximately 2.4. The pH of Col-S then decreased to a



Fig. 2. Variation of (a) pH, (b) EC and (c) redox with L/S ratios.

final value of 1.10 (which is the approximate theoretical value of the 0.1 M H_2SO_4 lixiviant as a monobasic acid), whereas it remained relatively constant for the Col-C system at approximately 2.3. This is attributed to the higher acid strength of the former lixiviant (pK_a 3.13, 4.76 and 6.40 for citric acid, -2.8 and 1.99 for sulfuric acid).

The EC of Col-S at the beginning of the experiment was higher (10.1 mS/cm) than Col-C (6.8 mS/cm). It decreased slightly to 7.7 mS/cm (up to L/S = 0.5) and then climbed to 36.80 mS/cm at the end of the experiment (Fig. 2(b)). Such high EC for Col-S could be due to the presence of high concentration of free ions, including H⁺. In contrast, the EC for Col-C decreased until L/S = 5.1 and then stabilised at ~2.7 mS/cm until the end of the experiment, indicating continued dissolution from the columns albeit as a lower rate than for Col—S. ORP decreased in both systems and then stabilised at approximately 430 mV and 300 mV for the Col-S and Col-C systems respectively. The lower ORP in the latter is attributed to its behaviour as a mild reducing agent.

3.2.2. Dissolved metal concentrations

Changes in the dissolved concentration of notable metals which eluted from the mine waste are plotted against L/S in Fig. S1, with their cumulative concentrations (in wt% total recovery) as a function of lixiviant L/S ratio plotted in Fig. 3. It can be observed that all metal concentrations increased with increasing L/S ratio; however, the rates and final cumulative percentages were different. Cr and Ti were only marginally leached (< 4 %) while they were significant (> 10 %) for all other metals analysed. In general, both lixiviants exhibited relatively similar metal leaching efficacy, despite the difference in strength of the acids (pKa 3.13, 4.76 and 6.40 for citric acid, -2.8 and 1.99 for sulfuric acid), and neither were particularly selective for metal dissolution indicating metal release is not simply a function of acid-driven dissolution. Col-S was slightly more effective for Al, Cr, Cu, Li, Mg, Mn and Zn, whilst similar efficacy was recorded for Fe. In contrast, Col-C was more effective for As, Cd and Ti leaching. Col-S exhibited maximum dissolution of 43.2 wt% Cu (compared to 33.8 wt% recorded for Col-C) with only 35.2 wt% As dissolution compared to 40.7 wt% for Col-C.

This relatively similar behaviour of Col-C and Col-S for certain metal (loid)s, particularly Cu, As and Fe, can be attributed to the additional capacity of citric acid as a chelating agent, which enables efficacy comparable to sulfuric acid, despite being a weaker acid. The chelating action is due to its O-donor asymmetric ligand, and thereby capable of forming relatively stable aqueous complexes; predominantly with divalent and trivalent elements in mono, bi- and polynuclear and bi-, triand multidentate complexes (Zabiszak et al., 2018). For example, Fe and Ni are known to form bidentate mononuclear complexes with two carboxyl acid groups, whereas Cu, Cd and Pb can form tridentate, mononuclear complexes (Zabiszak et al., 2018). Also, Slowey et al. (2007) reported that release of As from soils or sediments contaminated with tailings was dominated by organic acid (i.e., oxalic and citric acid) protonated dissolution or reductive dissolution of the host phase (i.e., ferric (hydr)oxide). The mobilisation of As is enhanced when citric acid is added in paddy soil due to ternary complex with As, Fe and organic matter and inhibition of As transformation, such as As(V) reduction and As(III) methylation (Liu et al., 2022). The only element that Col-C was markedly less effective at leaching was Ca (31.2 wt% compared to 75.3 wt% for Col-S), which can be attributed to the weaker tendency of citric acid to form complexes with alkaline and alkaline earth metals (Zabiszak et al., 2018).

Figure 4 displays a correlation matrix for geochemical measurements and metal concentrations in effluents. It can be observed that, Ca, Al, Mn and Cu exhibit strong positive correlations (>0.7) with pH for sulfuric acid and negative or weak correlations for citric acid, showing that the stronger acid leads to enhanced solubilisation of these elements from the gangue minerals. Furthermore, strong positive correlation was recorded between Fe and As for both acids, which corroborates with the findings of Slowey et al. (2007), that As is likely hosted within and/or sorbed onto Fe-containing phases.

3.3. Metal recovery from waste leaching

This study considers in situ leaching of mine waste as a potentially



Fig. 3. Cumulative recovery of different metals by two types of lixiviants with L/S ratio.



Fig. 4. Correlation matrix of the geochemical measurements and metal concentrations measured in effluents.

more environmentally compatible remediation approach than physical excavation followed by ex situ treatment. This paradigm requires lower concentrations of acids (preferably biodegradable) and low-cost metal recovery schemes, adapted from passive water treatment systems (e.g., permeable reactive barriers) to avoid costly site operations (see Sapsford et al., 2017, 2019, 2023). The intensity of such site operations is envisaged to be low yet long-term, with processing over years to potentially decadal timespans. It is therefore useful to consider how to

take column leaching results and apply them to long-term leaching scenarios in the field, to gain an understanding of the relative trade-offs regarding lixiviant application rate, recovery and reagent consumption. While column tests typically offer greater insights than batch tests, they are not without limitations. These include a lack of consideration for seasonal or long-term changes in geochemical, microbiological, or climatic conditions that occur in the field, as well as an inability to account for large-scale hydrogeological properties of mine waste, such as preferential flow (Sapsford et al., 2017). However, such modelling can still be useful for predicting the operational parameters under which the leaching operation will likely provide the greatest overall benefits, including economic return from valuable metal recovery and site rehabilitation through reduced mine waste ecotoxicity, when balanced against necessary resource inputs such as reagents, energy and labour.

Having determined the relationship between cumulative L/S and metal dissolution behaviour, it is possible to project (using Eqs. 5–7) the hypothetical leaching response at different lixiviant application rates for example scenarios, here for up to 10 years of leaching (Fig. 5 (c) and (d)). By fitting Eq. (4) $(R_{adj}^2 > 0.94)$, the leaching rate constant (k) for Cu is determined to be 1.02 and 1.09 kg/L for Col-C and Col-S, respectively. Based on Fig. 5 (c) and (d), it can be observed that metal recovery increases as the flow rate is increased from 1 to 20 mm/d for both lixiviants. However, large differences in the recovery can be seen for lower lixiviant application rates (below 10 mm/d). This low variation in total metal dissolution for higher lixiviant application rate (namely >15 mm/ d over the 10-year leaching time) suggests that the optimal flow rate is likely approximately 10 mm/d for such a scenario. Final recovery is modelled to be 32 wt% and 41 wt% for citric and sulfuric acid, respectively, after 10 years at an inflow rate 10 mm/d. Similar recovery can be achieved using a shorter time span (i.e., 5 years), however, if the pumping rate is increased by 50 % (i.e., 15 mm/d). For instance, if 10

mm/d and 15 mm/d pumping rate of citric acid is considered, Cu dissolution will be 26 % and 30 %, respectively, after 5 years. This implies that total acid volume will be increased from 18.25 to 27.4 m³ which is almost 50 % increase in consumption for only 4 % (of total content) increase in Cu recovery. In contrast, if 10 mm/d pumping rate is used for 10 years to recover maximum Cu (i.e., 32 % of total content, see Fig. 5a), the consumption of citric acid will be doubled (i.e., 36.5 m³).

The pumping rate of a typical commercial heap leaching operation can be as high as 250 mm/d (Decker, 2001). The modelling results suggest that best overall performance of the leaching of the Devon Great Consols mine waste stockpile could be the use of a considerably lower pumping rate but over a long time period (several years or decades). Such an approach could also lend itself to a range of other in situ legacy mine waste treatment scenarios where minimal environmental disturbance is also a key consideration.

Further work is required to explore this hypothesis and to account for complexity and scale through field trials and supporting empirical and numerical modelling. Important operational features to account for include: (i) the reusability and environmental degradation of lixiviants; (ii) changes in the permeability of the mine waste during leaching, such as due to the migration of fines and/or bioclogging; and (iii) the impact of site-specific heterogeneity in mineralogy, biogeochemistry and hydrogeology. For example, Kim et al. (2018) reported that column studies can often diverge from field conditions due to a range of factors, including: preferential flow, redox potential gradients, surface passivation and heterogenous saturation.

Despite such unknowns, physical modelling remains a powerful initial tool to inform broad application parameters for leaching operations and can be implemented more easily than geochemical models which are invariably more complex to construct and demand relatively intensive and expensive site characterisation, such as detailed



Fig. 5. Exponential decay fitting with experimental data of Cu for (a) citric acid and (b) sulfuric acid and temporal variation of Cu recovery for different inflow rate (1 to 20 mm/d) of (c) citric acid and (d) sulfuric acid.

determination of mineralogy, particle size distributions and hydrogeological boundary conditions (Lee et al., 2017).

4. Conclusions

The leaching characteristics of Cu and As bearing sulphidic mine waste when exposed to 0.1 M sulfuric and citric acids have been investigated herein using flow-through column experiments over 104 days and final liquid-solid ratio: 31.1. This study has demonstrated that both citric and sulfuric acid solutions are effective for target metal recovery, with 35.2 % and 40.7 % for As and 43.2 % and 33.8 % for Cu recorded respectively. The similar metal dissolution efficacy, despite their different pKa (3.13, 4.76 and 6.40 for citric acid, -2.8 and 1.99 for sulfuric acid), is attributed to the additional capability of citric acid as a complexing agent. Dissolution of non-target metals was also extensive. For example, dissolution of Fe, Mn, Cd, Pb and Zn was 39.1 %, 54.8 %, 33.9 %, 28.7 %, 24.2 % for sulfuric acid and 37.7 %, 39.7 %, 39.6 %, 34.7 % and 19.1 % for citric acid, respectively. Results therefore show that whilst such acids exhibit non-selective metal dissolution, this behaviour could prove beneficial depending on mine waste remediation and/or matrix valorisation constraints/targets.

As a contribution to a new paradigm of low-intensity leaching, over prolonged timescales, using less aggressive lixiviants mathematical modelling was used to upscale column testing results. Whilst this does not take into account the full range of field-scale complexity, it does allow an exploration of the impact of differential lixiviant application rate on the metal recovery expected as a function of time. Results demonstrate the relative trade-offs in leaching versus time and reagent addition rate. For example, a lixiviant application rate of 10 mm/ d would be expected to achieve a 26 % of Cu recovery after 5 years of operation.

Such an approach could prove particularly useful for on-site remediation applications (including heap leaching and in situ leaching) where rapidity and economics of metal recovery are not the sole driver for the intervention. The use of a low concentration and biodegradable organic acid, such as citric acid, may enable such remediation and/or resource recovery but with lower risk to the environment and be readily coupled with passive capture systems thus using dramatically less energy than conventional physical excavation and ex situ beneficiation of the material.

CRediT authorship contribution statement

R.A. Crane: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **A. Mohammad:** Writing – review & editing, Writing – original draft, Data curation. **F. Jin:** Writing – review & editing. **P. Cleall:** Writing – review & editing. **D.J. Sapsford:** Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare no conflict of interest.

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

Rich Crane reports financial support was provided by Natural Environment Research Council. Devin Sapsford reports financial support was provided by Engineering and Physical Sciences Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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