# Selective leaching of ecotoxic metals from lime dosing plant metalliferous ochre using acid mine drainage and organic acids

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## Abstract

Lime dosing in a high-density sludge (LD-HDS) process is amongst the most widely applied acid mine drainage (AMD) treatment processes worldwide. It is effective and reliable, however, an intrinsic issue for metalliferous mining derived AMD is the formation of an ecotoxic metal(loid)-bearing (e.g. As, Pb, Ni, Cd and Sb) ochre waste product. Herein the efficacy and selectivity of AMD (pH 3.5; 1-500 g/L), citric and oxalic acid (0.01-1M) for ecotoxic metal(loid) dissolution from such ochre has been investigated. When AMD is applied at a low solid-liquid ratio (namely 1 g/L) or citric and oxalic acids are at low concentrations (namely ≤0.1M) such lixiviants are selective for certain ecotoxic metals which have been designated by BCR 4-step sequential extraction as "exchangeable" (namely: Sb, Cd, Cu and Ni) in preference to Fe. This suggests that they could potentially be integrated into the LD-HDS process in order to lower the ecotoxicity of the final ochre product and thereby valorise it for use in a wide range of commercial applications. Conversely when AMD is applied at a higher solid-liquid ratio (namely ≥100 g/L) ecotoxic metal precipitation occurred (due to the alkaline pH of the ochre). This suggests that the ochre could also be reused for AMD remediation.

**Key words:** arsenic, cadmium, acid rock drainage, citric acid, oxalic acid, hydrometallurgy, precipitation, remediation, upcycling

## 1. Introduction

Acid mine drainage (AMD) is an acidic solution created by the oxidation of sulphide minerals, typically associated with regions of metalliferous and coal mining [1],[2]. It is a widespread environmental issue and often ranked as one of the most formidable technical challenges which must be overcome in order for mining companies to maintain their social licence to operate [3],[4]. For example in the USA it is estimated that as much as 19,300 km of rivers and more than 180,000 acres of lakes and reservoirs have been damaged by AMD [5]. Consequently, the development of cost-effective AMD remediation schemes have been the subject of intense research for several decades. Lime dosing in a high-density sludge (LD-HDS) process is amongst the most commonly applied industrial scale methods and is widely regarded as highly effective and reliable [6]. It typically comprises a sequential process whereby the AMD is exposed to a lime slurry (often prepared using hydrated lime), air sparged and then a coagulant [7]. Lime dosing results in an increase in solution pH which induces metal and metalloid precipitation (hereafter metal), typically as hydroxides. Air sparging is then conducted in order to aid such precipitation and a coagulant (often a polyelectrolyte) added in order to induce flocculation of such precipitates. The net process is the near-total conversion of dissolved phase components into a ferruginous ochre sludge. An inherent issue for the treatment of AMD which also contains ecotoxic metals (e.g. As, Cd, Ni and Pb), such as those derived from metalliferous mines, however, is the formation of a chemically-mixed and ecotoxic ochre waste product [8]. This is in contrast to AMD derived from coal mine sites, which often contain lower concentrations of ecotoxic metals. Metalliferous mine derived ochre is therefore often classed as hazardous and therefore invariably requires storage in a purpose-built repository. This creates a long-term financial and environmental liability [9]. There is a strong consequent demand for the development of new technology which enables the selective recovery of ecotoxic and/or economically valuable metals from metalliferous mine derived ochre and thereby liberate it for use as a non-toxic raw material or product [10]. To date, there have been numerous studies on the reuse of AMD-derived ochre, including: as a pigment [11]; in water treatment [10],[12]; and in construction [13]. Most research output, however, has utilised ochre which has been derived from coal mining activity due to its aforementioned typically lower ecotoxicity. Within this LD-HDS derived ochre is an underexplored area [6]. There is consequent demand for further studies, such as herein, which investigate the development of novel chemical engineering processes in order to selectively remove ecotoxic metals from such ochre and thus liberate it for use as a non-toxic product or material. The alkaline nature of LD-HDS ochre (due to the lime dosing stage) also dictates that it may have some potential use in the neutralisation of acidic solutions, such as AMD (i.e. further recirculation within the LD-HDS treatment plant). Similarly its high calcite concentration may enable the material to be used as an additive in construction materials.

Herein metalliferous mine derived ochre, sourced from a LD-HDS treatment facility in Cornwall, UK, has been tested for its ability to be reused for AMD treatment. Different solid-liquid ratios of AMD have been investigated in order to both understand: (i) whether the ochre could potentially be reused/recirculated for the precipitation of ecotoxic metals from AMD (*via* pH neutralisation); and (ii) whether, under different solid-liquid ratios, the AMD could be used to selectively dissolve ecotoxic metals from the ochre and thereby liberate it for use as a non-toxic product (such as pigment or construction material [14]). In recent years certain organic acids, including citric and oxalic acid, have received widespread interest for their ability to selectively dissolve ecotoxic metals (e.g. As and Pb) from a wide range of substrates [15]. They are also typically more readily (bio)degradable than conventional mineral acids (such as sulphuric and hydrochloric acid) and as such could result in less long-term environmental harm if a containment breach within the ochre storage facility were to occur [16]. Both acids are also chelating agents and therefore demonstrated as able to exhibit selectivity for the dissolution of certain metals (compared to mineral acids) whilst also being able to operate at higher pH due to this additional chelating capability [17].

This study has therefore been established for the additional purpose of investigating whether such lixiviants could potentially be used to selectively dissolve ecotoxic metals from LD-HDS ochre. Such new approaches are urgently required in order to both prevent continued global stockpiling of hazardous ochre from metalliferous mine-derived LD-HDS facilities world-wide.

## 2. Methodology

### 2.1. Sample collection and preparation

AMD and ochre slurry (3 L of each) were collected from the Wheal Jane Mine Water Active Treatment Plant (Cornwall, UK) with assistance from Veolia Ltd. Samples were housed in polypropylene containers, filled without headspace in order to minimise oxidation, and refrigerated (at 4°C) within 1 hour. The ochre was transferred into an oven and dried at 45°C for 96 hours (with the weight monitored in order to confirm that full dehydration had occurred) and then stored in a desiccator. All subsequent experiments were performed within 4 weeks of collection and during this time the pH of the AMD was monitored in order to confirm that no major chemical change has occurred. The ochre was gently mixed using a stainless steel spatula prior to any subsampling. Unless specified otherwise triplicate AMD or ochre subsamples were used for all experiments and associated analytical measurements.

### 2.2. AMD characterisation

Immediately after collection, 25 mL of the AMD were filtered using a 0.45 µm cellulose nitrate filter, acidified and diluted using 2% $HNO_3$ for analysis using ICP-MS (Agilent 7700x). Duplicates, blanks and replicates of a Certified Reference Material (USGS: AGV-1 and DNC-1) were run every 10 samples. Calibration was performed using an Inorganic ventures ICP-71A multi-elemental standard. Solution pH and electrical conductivity (EC) was measured using a Hach sensION+ MM156 portable multi-meter.

### 2.3. Ochre characterisation

Ochre metal content was determined by 4-acid digestion (Garbe-Schonberg method [18]) followed by ICP-MS. Paste pH measurements were performed using ASTM D4972-13 [19] using a 1:1 solid-liquid ratio. Sequential extractions were performed using the BCR 4-step method [20],[21] which briefly comprised exposure of the ochre to 0.11M acetic acid, to extract “exchangeable” metals (Step 1), 0.5M hydroxylamine hydrochloride to extract all “reducible” metals (Step 2), 8.82M hydrogen peroxide and 1M ammonium acetate to extract all “oxidisable” metals (Step 3) and aqua regia to extract all “residual” metals (Step 4). A full description of this methodology is included in Appendix A. Particle size distribution (PSD) was determined using a FEG-SEM (Quanta 650F FEG-SEM) with ImageJ used to measure the diameter of particles identified. XRD analysis was performed using a Siemens D5000 Powder Diffractometer fitted with a Cu source (40 kV and 30 mA). XRF was performed using an Olympus Delta Professional HH-XRF analyser.

### 2.4. Exposure of ochre to the different lixiviants

Three different lixiviants were tested herein: citric acid, oxalic acid and AMD. Ochre samples (2.5 g) were first each placed into 50 mL centrifuge tubes and 25 mL of 0.01, 0.1 and 1M citric or oxalic acid were added. Alongside this 0.025 g, 0.25 g, 2.5 g and 12.5 g ochre subsamples were each placed in 50 mL centrifuge tubes to which 25 mL of the AMD was then added; representing 1 g/L, 10 g/L, 100 g/L and 500 g/L respectively. All samples then then mixed using a Grant-bio PTR-60 Multi-Rotator at 20RPM for 48 hours. Slurries were then centrifuged at 3000 RPM for 2 minutes in order to separate the solid from the supernatant. The supernatants were decanted and filtered using a 0.45 µm PTFE syringe filter and diluted using 2% $HNO_3$ for analysis using ICP-MS. The residual solid ochre was prepared for XRD analysis by heating at 50°C for 24 hours. Linear association (using the Pearson Product-Moment Correlation Coefficient: $R^2$) was performed for Fe, As, Pb, Cu, Sb, Cd, Zn, Ni, Co and Mn dissolution data in order to compare their concentrations in the “exchangeable” fraction (determined using sequential extraction) and when dissolved using the AMD, citric acid or oxalic acid.

## 3. Results and discussion

### 3.1. AMD characterisation

The AMD exhibited a pH of 3.51 and EC of 1501.11 mS/m. ICP-MS detected the following notable metals: 94.98 mg/L Fe, 0.29 mg/L Cu, 27.81 mg/L Zn, 0.25 mg/L As, 4.02 mg/L Mn, 0.22 mg/L Ni, 0.03 mg/L Cd, 0.003 mg/L Sn, 0.06 mg/L Pb, 0.13 mg/L Co, 0.005 mg/L V, 0.005 mg/L Cr and 0.002 mg/L Sb. The most notable metals in the AMD (in terms of potential ecological harm) therefore include: Fe, Zn, Mn, As, Ni, Cd, Pb and Sb.

### 3.2. Ochre characterisation

Table 1 displays wt.% concentration data for metals in the ochre using ICP-MS (following full acid digestion) or XRF. The most notable metals in the ochre include: Mg, Al, Ca, Al, Fe and Zn (in terms of potential economic value) and As, Ni, Cd, Pb and Sb (in terms of potential ecotoxicity). Paste pH was 8.22, confirming relatively strong alkalinity of the ochre. XRD analysis detected peaks at 23.16°, 29.48°, 36.1°, 39.54°, 43.28°, 47.22°, 47.66°, 48.62°, 56.74°, 57.56°, 60.82° and 64.84° which represent the emission spectra of calcite ($(Ca_{0.97} Mg_{0.03}) CO_3$) (Figure 1). Two broad and low intensity peaks were also detected within the range of 30°-40° and 55°-65° which are attributed to represent the broad peaks of 2-line ferrihydrite. SEM analysis recorded the majority of the ochre as comprised of a relatively amorphous nanomaterial that is typically <200 nm diameter (Figure 2), but most commonly within the range of 60-80 nm (Figure 2). Such nano-precipitates were interspersed with much larger particles (but still typically >1 µm) and often exhibiting well-defined rhombic, pentagonal prismatic and triangular prismatic crystalline structures. This well constrained and sub-micron PSD is significant because it suggests that the ochre could (once the ecotoxic metals have been removed) be valorised into a wide range of applications/products (such as pigments or in construction materials) and therefore elevate the economic value of the ochre beyond its raw scrap value.

Sequential extraction results (Figure 3) show Zn, Mn, Ni, Cd and Co as the most exchangeable, Fe, Cu, Zn, Mn, Cd and Co as the most amenable to dissolution *via* chemical oxidation/reduction and Sb, As and Pb as the most insoluble. This suggests that whilst it is likely that a mild (i.e. environmentally compatible) lixiviant (such as 0.11M acetic acid) would be effective at removing the ecotoxic metals: Ni and Cd, it is unlikely to be effective for Sb, As and Pb, which are likely held within more insoluble mineral phases. Given the fact that Fe is the principle metal component of the ochre (22.46 wt.%) the very low proportion (0.08 wt.%) of Fe in the “exchangeable” fraction is encouraging and suggests that the use of a mild lixiviant (assuming that it is not a strong oxidising or reducing agent) could be applied in order to dissolve certain ecotoxic metals (namely Ni and Cd) and leave Fe (i.e. ferrihydrite) for subsequent upcycling.

*Table 1. Wt.% concentration data for metals in the ochre using ICP-MS (following full acid digestion) or XRF.*

| | ICP-MS | XRF |
|---|---|---|
| Fe | 22.4656 | 22.43 |
| Cu | 0.0776 | 0.07 |
| Zn | 5.7418 | 5.27 |
| As | 0.1389 | 0.12 |
| Mn | 0.8605 | 0.72 |
| Ni | 0.0541 | 0.04 |
| Cd | 0.0074 | Not analysed |
| Pb | 0.0133 | 0.01 |
| Co | 0.0297 | Not analysed |
| V | 0.0012 | Not analysed |
| Cr | 0.0018 | Not analysed |
| Sb | 0.0007 | Not analysed |
| Mg | Not analysed | 13.92 |
| Al | Not analysed | 4.23 |
| Si | Not analysed | 2.67 |
| P | Not analysed | 0.18 |
| S | Not analysed | 0.77 |
| Ca | Not analysed | 10.44 |
| H – Na | Not analysed | 39.1 |

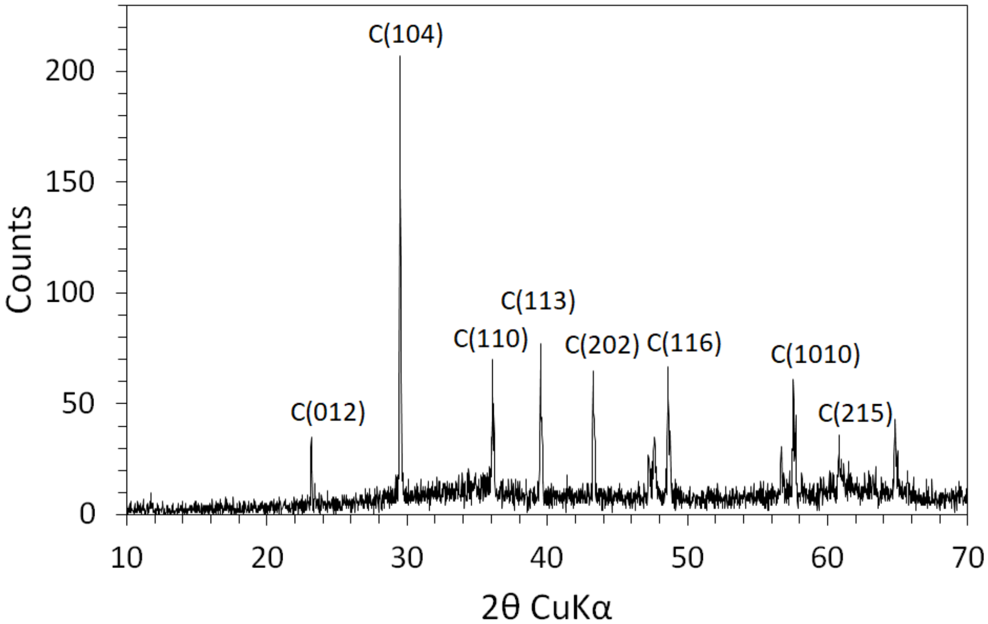

*Figure 1. XRD spectra of the dry ochre. C = calcite.*

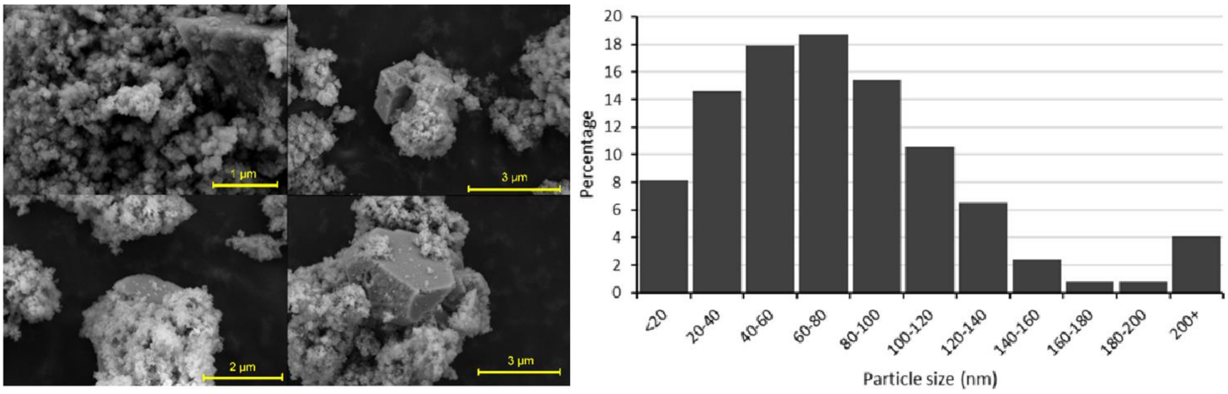

*Figure 2. LHS: SEM images of the ochre; RHS: Particle size distribution of the ochre. Number of particles analysed =123.*

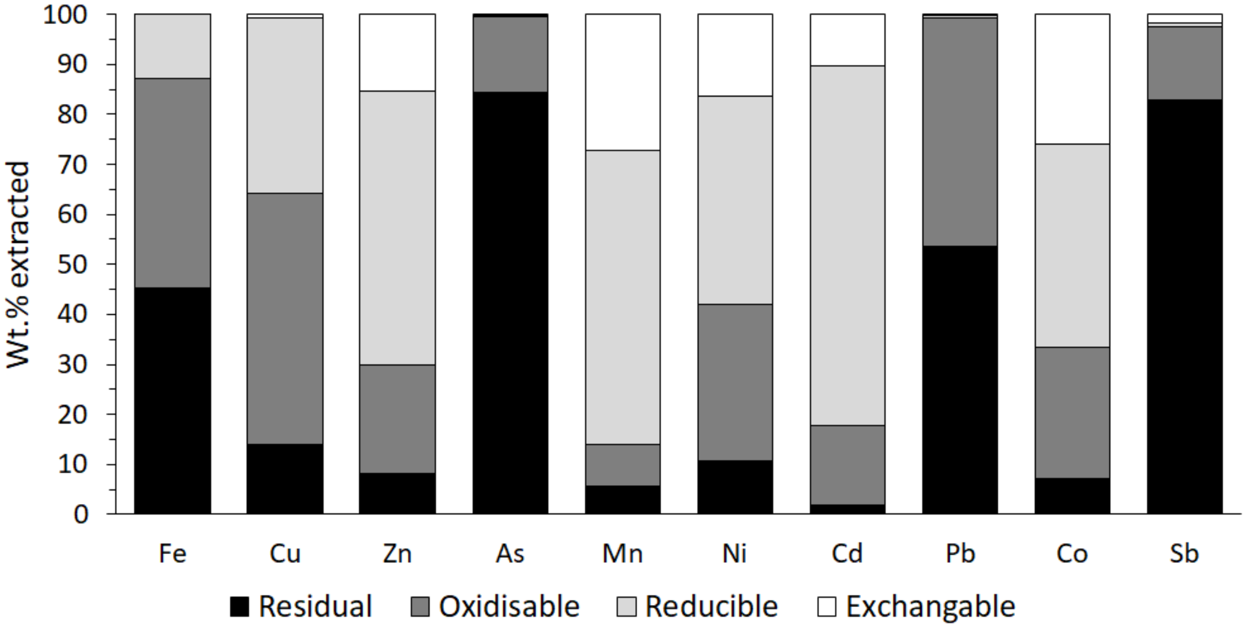

*Figure 3. BCR 4-step sequential extraction data for the ochre.*

### 3.3. Exposure of ochre to citric and oxalic acid

Figure 4 displays notable metal(loid) concentrations following exposure of the ochre (100 g/L) to 0.01-1M citric (LHS) and oxalic (RHS) acid for 48 hours. As expected, both acids display a positive correlation between their concentration and metal(loid) dissolution, however, this was more strongly exhibited by citric acid. When comparing such metal(loid) dissolution data against those recorded as “exchangeable” by BCR 4-step sequential extraction (Table S1) both acids exhibited very different metal dissolution behaviour with reasonably good correlation exhibited by 0.01 and 0.1M citric acid ($R^2$ = 0.48 and 0.58 respectively) with metal dissolution selectivity following the order of Sb>Pb>As>Co>Mn>Ni≥Cd>Cu≥Zn≥Fe and Co>Cd>As>Sb>Pb>Ni>Fe>Mn>Cu>Zn. In contrast the metals most amenable to dissolution by 1M citric acid were Fe and Cu (100.00 and 83.55 wt.% respectively) and all other metals except Mn were recorded to dissolve within the range of 41-59 wt.%. As such it can be concluded that the use of low concentrations of citric acid (i.e. <0.1M) yielded behaviour that can largely be predicted using an “exchangeable” BCR 4-step sequential extraction, whilst stronger concentrations exhibit more congruent dissolution behaviour. Instead, no clear correlation was exhibited by low concentrations of oxalic acid and the “exchangeable” fraction with $R^2$ of 0.03 and 0.01 exhibited by 0.01 and 0.1M respectively. In contrast to citric acid, a reasonable correlation was exhibited by 1M oxalic acid ($R^2$ = 0.57). Oxalic is also a reducing agent and as such was also recorded as exhibiting relatively significant dissolution of both Fe and Zn (which were the main components of the “reducible” BCR 4-step sequential extraction fraction), however, it was also selective for Mn, Ni and Co dissolution which were not denoted as “reducible” *via* sequential extraction. It is also important to note that whilst both acids exhibited near-total dissolution of Fe at 1M concentration, when citric acid was applied at 0.1M it dissolved Co, Zn, Mn, Ni and Cd at 24.3, 23.3, 20.3, 16.3 and 11.8 wt.% respectively with only 3.7 wt.% Fe dissolution – this high selectively for such ecotoxic metals (in preference to Fe) is highly advantageous in order to detoxify the ochre and thus yield a product of economic value. As such it can be concluded that 0.1M citric acid was the optimum concentration and acid type tested. XRD analysis shows that when both acids are applied at ≤0.1M the ochre remains as a mixture of crystalline calcite with possibly a minor concentration of ferrihydrite (Figure 5). In contrast when 1M concentrations were applied the residual crystalline component of the ochre was recorded to be quartz and weddellite/whewellite for citric and oxalic acids respectively, with the former therefore likely to represent the residual (insoluble) phase within the ochre and the latter a precipitate from the oxalic acid.

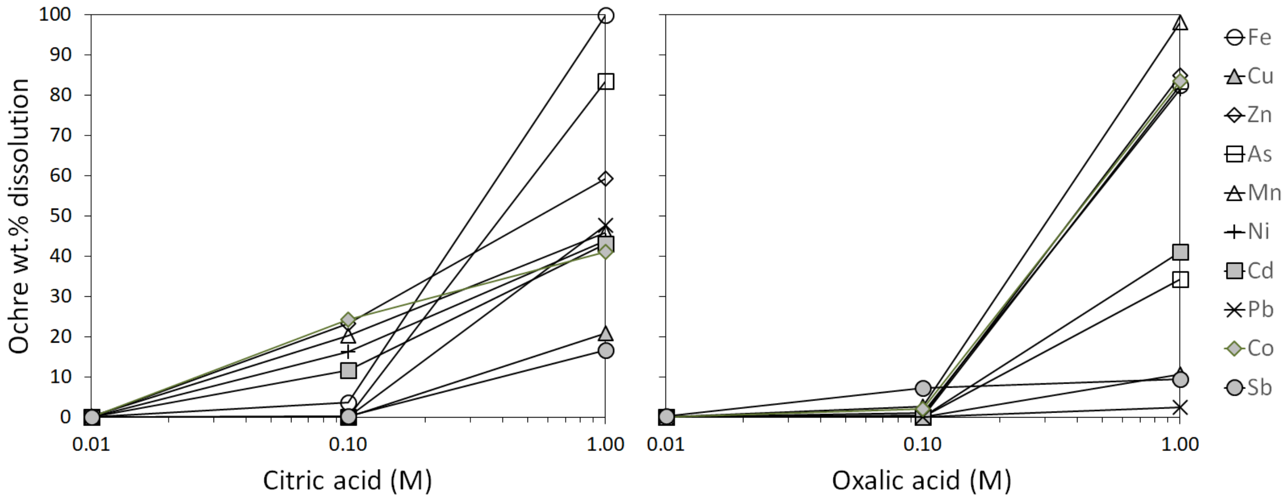

*Figure 4. Notable metal(loid) concentration following exposure of the ochre (100 g/L) to different concentrations of citric (LHS) and oxalic (RHS) acid for 48 hours.*

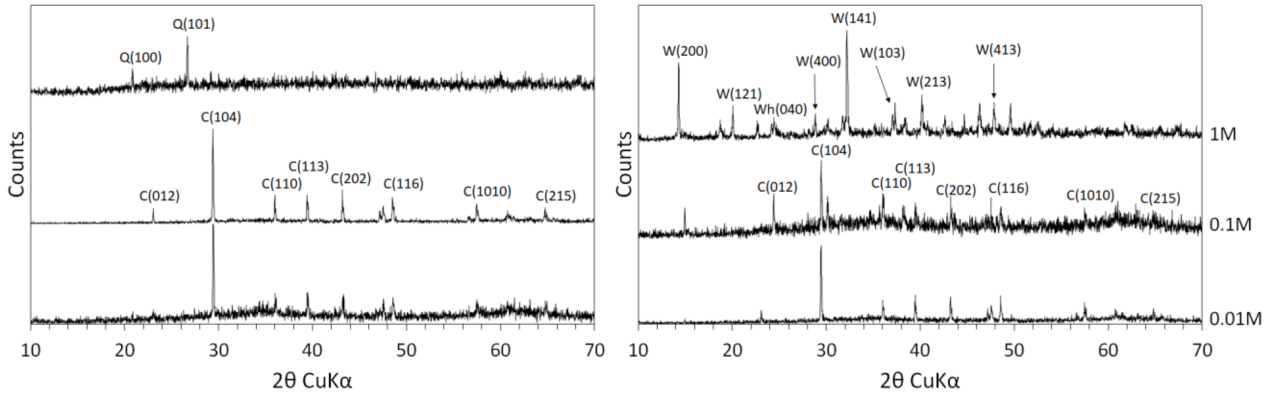

*Figure 5. XRD spectra for ochre exposed to citric (LHS) and oxalic (RHS) acid at 0.01, 0.1 and 1M. An ochre concentration of 100 g/L was used. C = calcite; Q = quartz; W = weddellite; Wh = whewellite*

### 3.4. Exposure of ochre to AMD

Figure 6 displays pH, EC and notable metal(loid) concentrations following exposure of the ochre to AMD at 1-500 g/L alongside corresponding data for the original AMD. Results demonstrate that when applied at a low solid-liquid ratio (namely 1-10 g/L) the ochre is amenable for dissolution, with such dissolution more strongly occurring at 1 g/L with metal(loid) (wt.%) dissolution comprising: Mn (100%), Co (68.84%), Ni (50.57%), Zn (42.82%), Cd (26.08%), Sb (2.56%), Cu (0.65%), Pb (0.63%), As (0.17%) and Fe (0.09%) (Table S1). Such dissolution shows very good agreement ($R^2$ = 0.96) with those recorded as "exchangeable" by BCR 4-step sequential extraction (Figure 3, Table S1). Similarly, whilst ochre dissolution was recorded as much lower by AMD at 10 g/L (Table S1) it still showed good correlation with the "exchangeable" metal(loid)s $R^2$ = 0.51.

When the ochre was applied at higher solid-liquid ratios (100-500 g/L) considerable metal(loid) precipitation was recorded (Table S2) with >70 wt.% removal of Fe, As, Pb, Cu, Cd and Zn from the aqueous phase exhibited by the 100 g/L system and Fe, Pb, Cu, Cd and Zn exhibited by the 500 g/L system. Both systems exhibited relatively low removal of Sb, Ni and Mn with 0.00, 4.91 and 0.00 wt.% removal recorded respectively for the 100g/L system and 15.33, 57.49 and 33.18 wt.% removal recorded for the 500 g/L system. This is in agreement with previous studies who have documented the relatively low removal of such metals as hydroxides due to precipitation and co-precipitation with Fe (e.g. [22], [23], [24]) with the latter system exhibiting greater removal of such metals due to its greater wt.% ochre concentration and subsequent greater pH increase. In contrast significantly higher As removal was recorded for the 100 g/L compared to the 500 g/L system (79.25 and 48.91 wt.% respectively) which is attributed to the differential precipitation-sorption behaviour of anionic As due to the likely establishment of negative zeta potential for the ochre under alkaline pH conditions and thereby promoting such As desorption-dissolution.

XRD spectra show that the 1 g/L system was predominantly comprised of ferrihydrite which the 10, 100 and 500 g/L systems comprised a mixture of calcite and ferrihydrite. This confirms that selective (likely incongruent) dissolution of the ochre had occurred in the 1 g/L system and that no major changes occurred in the 10, 100 and 500 g/L systems where metal removal from AMD was likely *via* pH driven precipitation and co-precipitation (as hydroxides and/or sulphides) and/or sorption.

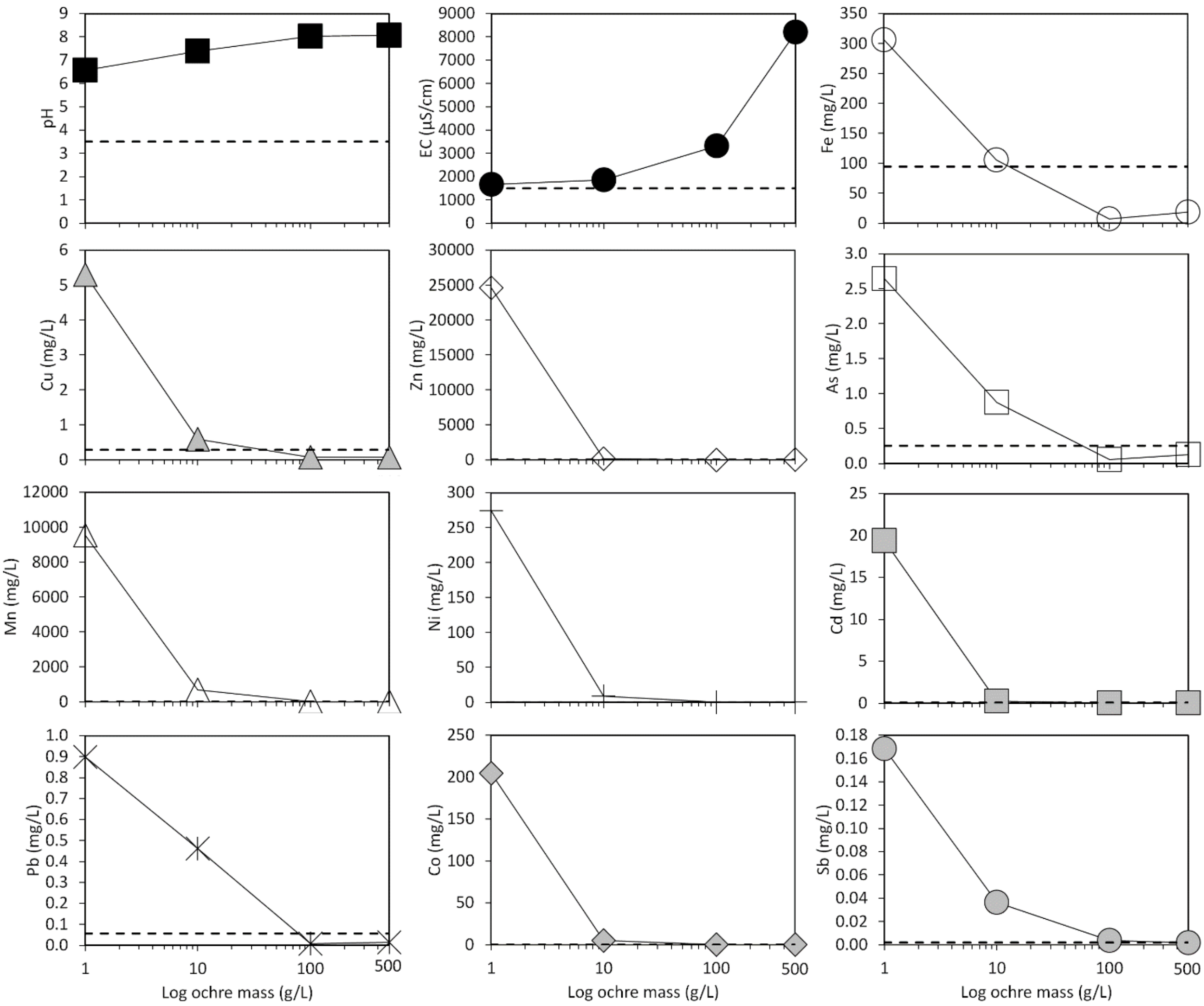

*Figure 6. pH, EC and notable metal(loid) concentrations following the exposure of the ochre to the AMD at 1, 10, 100 and 500 g/L. The dashed lines denote the pH, electrical conductivity or concentration of metal(loid) in the original AMD.*

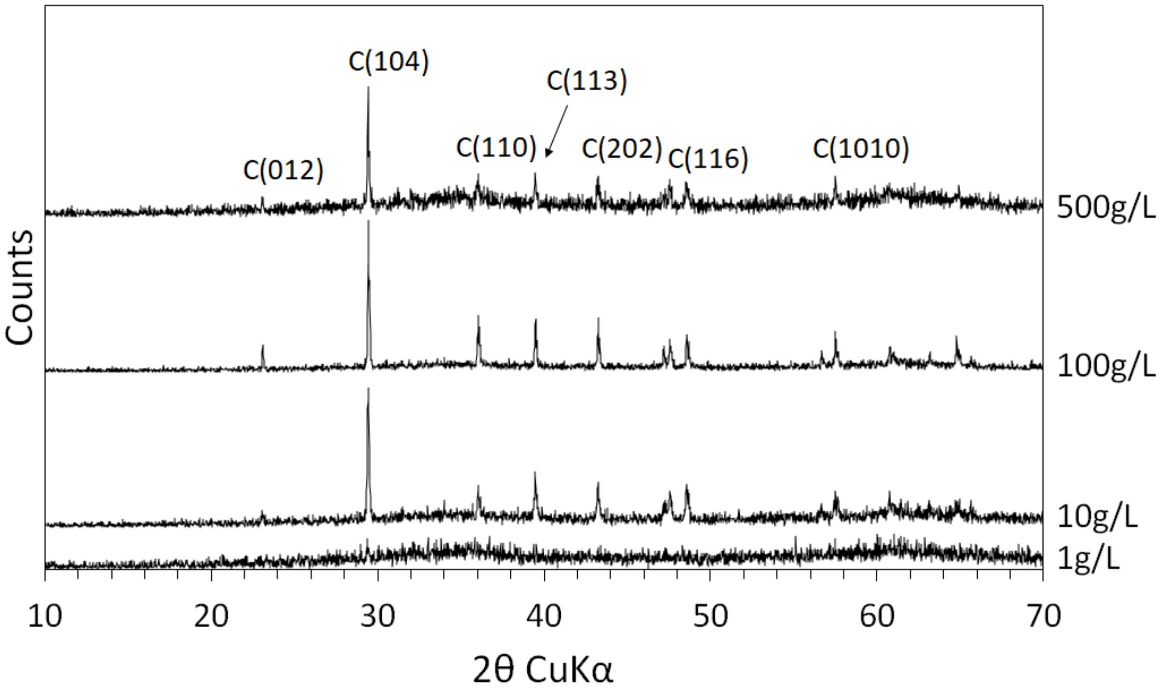

*Figure 7. XRD spectra for ochre exposed to AMD at 1, 10, 100 and 500 g/L. C = calcite.*

## 4. Environmental and industrial implications

There is currently a lack of cost effective and industrially scalable processes for the conversion of LD-HDS ochre into products of economic value. This issue is particularly acute for such ochre which has been derived from metalliferous mining leachates due to the co-association of ecotoxic metals (e.g. As, Pb, Ni, Cd and Sb). This study has determined that AMD, when applied at a low solid-liquid ratio (namely 1-10 g/L), is highly selective for the dissolution of certain ecotoxic metals from LD-HDS ochre (namely: Cd, Zn, Ni, Co and Mn) in preference to Fe (Figure 6). Similarly citric acid, when applied at low concentration (i.e. <0.1M), was selective for Cu, Zn, Co, Mn, Cd and Ni (Figure 4). Under both scenarios XRD determined that calcite (present in the LD-HDS ochre due to lime dosing) remained as the dominant crystalline phase (Figures 5 and 7). This suggests that such lixiviants are able to selectively remove a number of ecotoxic metals from the ochre without resulting in a major change in ochre mineralogy. An obvious target for utilisation of this (largely detoxified) calcite product therefore could be in the construction industry (namely as a raw material for concrete). Furthermore the majority of particles within this ochre product are in the nanometer scale (most commonly within the range of 60-80 nm, see Figure 2). This could prove advantageous because micron- and nanoscale calcite have been demonstrated as effective amendments to improve the physical and chemical properties of cementitious materials (e.g. for use in marine defence structures) [25], [26]. XRD also detected 2-line ferrihydrite, which has potential use in a wide range of applications, including as a pigment [11]; in water treatment [10],[12]; and in construction [13].

## 5. Conclusions

Herein the dual utility of: (i) using AMD or environmentally (bio)degradable acids, citric and oxalic, to selectively dissolve ecotoxic metals; and (ii) re-using the ochre to precipitate ecotoxic metals from AMD, have been studied. The following can be concluded:

1) When ochre is exposed to AMD at a low solid-liquid ratio (namely 1-10 g/L) it is amenable for dissolution, with such dissolution in reasonably good agreement ($R^2$ = 0.96 and 0.51 for 1g/L and 10 g/L systems respectively) with ecotoxic metals denoted as “exchangeable” by BCR 4-step sequential extraction. Optimum solid-liquid ratio was recorded to be 1 g/L which resulted in 26.08, 42.82, 50.57, 68.84 and 100 wt.% dissolution of Cd, Zn, Ni, Co and Mn respectively compared to only 0.09 wt.% recorded for Fe.

2) When ochre is exposed to AMD at high solid-liquid ratio (100-500 g/L) considerable metal(loid) removal from the aqueous phase occurs, with most significant removal (typically >70 wt.%) recorded for Fe, As, Pb, Cu, Cd and Zn and attributed to the (co-)precipitation of such metals as hydroxides and/or sulphides. In contrast relatively low (typically <50 wt.%) Sb, Ni and Mn removal was recorded due to their relatively higher solubility as hydroxides and/or sulphides.

3) Low concentrations of citric acid (i.e. <0.1M) yielded ochre dissolution behaviour that can largely be predicted using an “exchangeable” BCR 4-step sequential extraction ($R^2$ of 0.48 and 0.58 exhibited by 0.01 and 0.1M respectively) and exhibited high selectivity and efficacy for certain ecotoxic metal(loid)s (namely >20 wt.% removal of Cu, Zn, Co and Mn and >10 wt.% removal of Cd and Ni) in preference to Fe. In contrast, low concentrations of oxalic acid (i.e. <0.1M) were relatively ineffective (<8 wt.% dissolution of all metal(loid)s) and no clear correlation with “exchangeable” phases was exhibited ($R^2$ of 0.03 and 0.01 for 0.01 and 0.1M respectively).

4) High concentrations of both citric and oxalic acid (i.e. 1M) exhibited significant ecotoxic metal(loid) dissolution (often >50 wt.%) but also both dissolved >80 wt.% Fe.

As such it can be concluded that AMD (when applied at low solid-liquid ratios, such as 1 g/L) and citric acid (when applied at low concentrations, such as 0.1M) were both effective for selective ecotoxic metal dissolution (in preference to Fe) which is desirable in order to detoxify the ochre and thus yield a Fe-hydroxide product of economic value. Furthermore the results also suggest that when applied at high solid-liquid ratios (e.g. 100-500 g/L) the ochre can also be used to remove metal(loids) from the AMD and the selectivity of this process can be fine-tuned by modifying this solid-liquid ratio.

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