Element distribution in electrochemically treated mine wastewater for efficient resource recovery and water treatment

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Abstract

The feasibility of recovering major and critical elements from acid mine drainage using a pilot-scale electrochemical reactor (ECR) was investigated by assessing elements concentration and species distribution in the liquid and solid phase (sludge) in multistage tests. These were carried out at different electrical currents (18-22 amps) and thus, pH (8-12). The results showed that major metals Al, Cu and Fe were removed from the liquid phase at pH 5.9 while remaining the majority of Zn (57.2 ppm). On the other hand, at pH 7, the effluent was mainly composed of Mn (7.3 ppm). These results were confirmed by the simulation results using the PHREEQC model, which also identified the main chemical species in solution and the precipitates formed after the treatment (oxyhydroxides/sulfates/oxides). The ECR treatment led to sludges with targeted critical elements, some up to 20 times (Co, Be and Sb) higher than their earth's crustal abundance. At pH 10, rare earth elements in the sludge targeted Ce, followed by Nd and La. This study is one of the few studies carrying a detailed analysis of the behavioural distribution pattern of these elements at each pH, which opens the door for the potential of recovering these elements.

KEYWORDS: Electrochemical reactor; Acid mine drainage; critical elements, recovery; Rare earth elements

Introduction

Acid mine drainage (AMD) or acid rock drainage is a major problem in the mining industry, with the potential to harm ecosystems and communities if not managed correctly. It results from the oxidation of sulfidic rocks leading to mine drainage with acidic pH, high sulfate and dissolved metals (Amanda and Moersidik, 2019). While some of the dissolved metals are toxic, some have economic value. AMD has been identified in several studies as a promising source of elements commonly classified as 'critical', due to the scarcity of their economic concentrations and uneven global distribution (European Commission, 2020), including rare earth elements (REE) (Brewster et al., 2020; Pozo et al., 2017; Zhuang et al., 2015).

Conventional systems for managing AMD are based on linear economy thinking ('take-make-waste), with lime neutralization as the most widely used method to treat acid mine drainage. A major disadvantage encountered when applying lime is the production of large volumes of, difficult to dewater, sludge containing gypsum ($CaSO_4$) and metal hydroxides, incurring substantial operational expenditure concerning sludge handling and disposal costs (Macías et al., 2012; Rakotonimaro et al., 2017). An adequate AMD treatment based on a circular economy through the valorization of sludge has significant potential to overcome management costs, by recovering contained economic elements, thus reducing the pollution risk and generating economic profit (Kinnunen and Kaksonen, 2019; Masindi and Tekere, 2020; Rakotonimaro et al., 2017). For this, new cost-effective and sustainable AMD treatments are being developed but not yet adopted at the industry scale (Masindi and Tekere, 2020).

Electrochemical methods are an attractive alternative for the treatment of AMD in remote or legacy mine sites as they only use electricity that could be powered by off-grid solutions (e.g. generator, solar photovoltaic). In this technology, a controlled cathodic reduction reaction drives the pH and in turn, metals precipitate as hydroxide, oxide or sulfate (Bunce et al., 2001;

Chartrand and Bunce, 2003; Mamelkina et al., 2019). his allows chemical-free AMD neutralization and generates low sludge volumes containing targeted metals, thus allowing metals recovery from the sludge (Brewster et al., 2020).

In a previous study, metals distribution and optimal conditions for selective recovery in a lab-scale (38.4 cm^3) electrochemical reactor (ECR) were assessed. The results proved the successful removal of existing base metals in AMD from two mine sites, meeting Australian water drinking standards. The ECR also demonstrated the potential to produce metal-rich sludge with a targeted composition, including REE and yttrium (Brewster et al., 2020). From this experience, a pilot-scale ECR has been built with a processing capacity of up to 2000 L/d. In the scaling-up process, it is important to evaluate the robustness of the treatment upon variations in AMD composition, changes in electrode materials and current/potential, which can affect process efficiency (Mamelkina et al., 2019). In addition, the ability to predict the precipitates formed during and after treatment is useful for assessing the formation of compounds that either has an economic value or are pollutant concern. Given the amorphous nature of the precipitates, chemical equilibrium models such as MINTEQA2 and PHREEQC can help to predict the minerals and amorphous phases that make up the sludge. These models help to the decision-making for the selection of the optimal treatment conditions that target the recovery of specific elements/compounds or that can allow meeting discharge guidelines. PHREEQC for example has been used to complement laboratory-scale experiments evaluating the use of fly ash (Madzivire et al., 2011), nanofiltration (Andalaft et al., 2018) and an ECR (Brewster et al., 2020) to treat AMD.

In this work, we evaluated the feasibility of recovering major and critical elements and meeting discharge guidelines from the treatment of AMD using the developed pilot-scale ECR. This was done by monitoring the elements and species distribution in the liquid and solid phases (sludge) in multistage tests, through chemical analysis and modelling methods. A further

analysis was carried out by correlating the concentration of critical elements in the sludge with the estimated abundance in the earth's crust.

2. Materials and methods

2.1 Pilot scale ECR

The pilot scale ECR used in this study has a plate and frame assembly of 20 electrochemical cell pairs and consists of two stacks as shown in the orange cell to the right (Figure 1). The pilot scale ECR is 3 meters long by 1.2 meters wide and by 2.5 meters tall, weighs about 500 kgs and is skid-mounted (Figure S1). The ECR treats AMD by pumping it into the cathodic chamber of an electrochemical cell. Electricity is applied to draw sulfate anions from the AMD across an anion exchange membrane into the anodic chamber where they form sulfuric acid due to the transfer of hydrogen protons. Some other anions (e.g., chloride Cl^-) may also make their way into the anode cell and anolyte tank. As sulfate anions are drawn away from cathodic chamber, the pH of the AMD solution rises in the cathodic chamber, and metals precipitate out of solution, leaving clean water that is suitable for use or discharge.

2.2 Acid mine drainage

AMD from a mine site in Queensland, Australia, was used for this study. It was characterised physically and chemically within five days of collection. The determined parameter values are shown in supplementary table S1.

2.3 Reactor operational conditions

Multistage tests were carried out in the ECR at different electrical current values that allowed the pH to increase in steps to values of 1.8, 2.0, 2.5, 4.8, 5.9, 7.3, 8.8, 9.4, 10.9, 11.8, 12.2.

During the tests, the current density was kept between 18 and 22 amps, while cell voltage varied between 50 to 52 volts for an overall power use of about 0.9 to 1.2 kW per hour. This equated with a power use of about 1.1 kWh per 100L of processed AMD. After each pH increment was reached, the reactor was stopped, emptied and the liquid left to settle for at least 1 h. After this, samples of the liquid and solid phase were taken for chemical analysis. A second run of multistate tests was carried out in the ECR for analysis of trace elements such as REE in the produced sludges (Figure S2). The effluent pH increased in steps to pH values of 4.6, 6.5, 8.0, 10.0, and 11.9.

2.4 Chemical analysis

Samples from the multistage tests were collected and analysed for element and ion concentrations, and their respective redox potentials and total dissolved solids (TDS) were measured. This was carried out following the methodology outlined by Brewster et al. (2020). Briefly, the liquid and solid phase samples were separated by allowing the sludge to settle after reaching each pH target. Samples were filtered using a filtration system with Advantec GB-140 glass fibre filter paper (0.4 μm particle retention). The filter paper was dried at 105°C in a glass petri dish and weighed prior to filtering the sample. Dried filter paper with residue was transferred into a digestion tube with 1 ml HNO_3 and 25 ml milli-Q water, cap and placed on the Hot block at 90°C for 60 minutes until digestion was completed. After cooling the solution and top up the digestion tube to 50 ml total solution, 1:1 and 1:10 dilution of the digestion solutions, these were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES). The solid phase was analysed by inductively coupled plasma mass spectrometry (ICP-MS) after acid digestion to obtain the solid bulk composition.

Sludge samples of the second run of multistage tests were analysed with a new modified method developed for chemical analysis of AMD sludge, based on the previous experience on the development of a method for tungsten tailings (Han et al., 2021). The sample solutions

were left to settle down for 3 days. The supernatants were decanted into a sink. The residues were transferred into pre-weighed ultra-clean Teflon beakers and dried at 105 °C overnight. The dried samples were cooled in a desiccator to room temperature before re-weighing to calculate the dried residues. The dried residues were then digested in 1ml 15.8 N doubly distilled HNO_3, 10 drops of peroxide and 3 ml of hydrofluoric acid (HF) on a hot plate at 140 °C overnight. The digests were dried down to get rid of HF and re-dissolved in concentrated aqua-regia overnight. The solutions were dried down again and re-dissolved with 5 ml 10% HNO_3. An aliquot of each sample was taken to make a 10 ml solution in 2% HNO_3 for analysis. The elemental composition was determined by using the inductively coupled plasma mass spectrometry (Agilent 7900 ICP-MS) after acid digestion to obtain the solid bulk composition.

2.5 Modelling methods

The geochemical modelling software PHREEQC version 3 (Parkhurst and Appelo, 2013) was used to predict chemical speciation and solid-phase saturation at thermodynamic equilibrium by using the operational conditions during the multistage tests (e.g., pH, conductivity, redox potential) as input model conditions. The model predictions were assessed using primarily the SOLUTION_SPREAD function and the Minteq.v4.dat database.

The measured redox potential values (Eh) were used in the simulations once converted to pe using the Faraday equation. The simulation outputted the charge balance error, 100*(Cat-|An|)/(Cat+|An|), saturation indices (SI) of phases, and distribution of species. Phases with SI ranging between -1 and 1 were only considered as mineral phases between -1 and 1 are within close chemical equilibrium with water, meaning that these phases are within close range of either precipitating or dissolving based on pH change (Edraki et al., 2005).

2.6 Water and sludge quality comparison

This water and sludge chemical results were compared to discharge guidelines to determine if these satisfied the conditions for environmental discharge after the ECR treatment. The water chemistry data were compared against the Australian and New Zealand Environment and Conservation Council (ANZECC) water quality guidelines report (ANZECC, 2000) for both livestock and recreational purposes. The sludge data were compared against the 2013 Australian Health Based Investigation Levels of the National Environment Protection (Assessment of Site Contamination) (NEPM) guidelines for soil contamination (NEPC, 2013).

2.7 Resource recovery analysis

The elements found in the sludge after treatment listed as critical by the European Union (EU) (European Commission, 2020) and by Australia (Geoscience Australia, 2020) were further analysed. To determine which of these critical elements could be considered for recovery due to their concentration in sludge, the estimated abundance of these elements in the earth's crust in ppm was used as the threshold baseline (Course Hero, 2022).

3. Results and discussion

3.1 Removal of metals from the liquid phase

The results of the pilot-scale ECR treatment showed that the system was able to effectively control the pH (Table 1) allowing the precipitation and removal of specific metals from the liquid phase (Figures 2 and 3). The measured Eh value of the raw AMD showed an oxidising state (466 mV) consistent with the abundance of sulfate in the solution (Table S1). The pH value of the water increased from 1.5 to 12.3, while the Eh values changed from oxidizing to reducing states. The lowest measured Eh at -42 mV corresponded with a pH of 12.3 (Table S1). The redox conditions facilitated the precipitation of metals from the AMD solution with the increase in pH, as well as the reduction of the TDS, but the concentrations of each element

and the compounds formed depended on the water composition, pH as well as the redox conditions (Mamelkina et al., 2019).

A clear correlation of the pH with the removal of sulfate and chloride was observed (Figure 2a). While sulfate removal is a result of the anode reaction producing sulfuric acid, chloride removal can be also explained by the formation of its intermediates such as chlorine/hypochlorite and chloramines (Mamelkina et al., 2019). On the other hand, K^+ and N^+ concentrations remained similar at each pH tested, while Mg^+ and Ca^+, decreased with the increase of pH at 7 and at 12, respectively (Figure 2b), which confirms their migration to the cathode to maintain charge balance (Bunce et al., 2001).

The elements concentrations decreased with each increased step in pH level under the oxidizing environment (Figure 3). The results clearly showed a distinction between metals precipitating at each pH stage and confirmed that these differences can be used to target desirable compositions of the solid precipitates (Brewster et al., 2020). For example, at pH 5.87, Al, Cu and Fe were removed, while remaining the majority of Zn (57.18 ppm), along with some Mn (10.08 ppm), Si (10.28 ppm) and other cations at concentrations below 1 ppm. On the other hand, at pH 7, the effluent was mainly composed of Mn (7.25 ppm).

The range of pH for the precipitation of Fe, Al, Fe and Mn are similar to those for a typical titration with the addition of NaOH (Totsche et al., 2003), confirming, therefore, the efficiency of the ECR system and the potential role of hydroxides formed due to the pH increase, in the selective removal of these cations. However, unlike the previous study (Brewster et al., 2020) where Fe precipitation occurred at pH below 4, Fe precipitation predominantly occurred at pH above 5, pointing to the presence of air in the system that allowed re-oxidation and re-dissolution of Fe^{3+} (Bunce et al., 2001). This air intrusion is potentially a consequence of the ECR scaling up.

3.2 Water recovery analysis

In the AMD used in this study, 8 of 12 elements exceeded ANZECC water quality limits (Table 2). Other elements were either not exceeding the thresholds limits (e.g., As and Se) or did not have water quality limits in the ANZECC guidelines. After the pH increase due to AMD treatment in the ECR, all the metal concentrations were below the limits for both livestock and recreational uses. However, Cd and Mn as well as sulfate only achieved values below guideline limits at pH 8.76 and 12 respectively, which imposes a further pH adjustment step to meet the acceptable pH of 6.5 to 8.5 for livestock and recreational purposes, respectively (ANZECC, 2000).

3.3 Sludge characterization at different pH operation stages

Figure 4 shows the element concentrations in the solid phase at different pH stages. Elements at initial high concentrations (>1 ppm, Al, B, Ba, Fe, Cu, Mg, Mn, Si and Zn) are discussed separately from those found at lower concentrations (<1 ppm- Be, Cd, Co, Cr, Ni) and from Ca, K, Na, S and P. The concentrations of elements in the sludge can be explained either by the pH that allows the precipitation of cations as hydroxides or the affinity of cations for adsorption on Fe hydroxide (Younger et al., 2002). Comparing figure 4 with figure 3 shows that the majority of metal concentrations that were depleted in the liquid phase were ultimately precipitating into solid forms, although the mass balances did not completely close (data not shown). This could be either due to the acceptable levels of error for chemical analysis or the sorption of elements onto the minerals formed (Ifeoma Mary and Onyedikachi Anthony, 2019). In general, the elemental concentrations in the solid phase at high (Figure 2a) and low (Figure 4b) initial concentrations started increasing at different pH values depending on the element. Ba concentrations fluctuated and even decreased with the pH increment (Figure 4a) due to its moderate solubility in water (Don and Robert, 2008). At high initial concentrations, Al

concentration increased at pH ≥ 4.8, while Fe, Cu Mg, Mn, Si and Zn concentrations increased at pH ≥ 5.9 (Figure 4a). At low initial concentrations, Cr started precipitating at pH 4.8, followed by Ni and Co at pH 5.87 and Cd at pH 7.3 (Figure 4b). The similarity of the precipitation patterns of Ni, Co, Cd and Zn is the result of their close range of ideal pH for their adsorption on Fe hydroxide (Younger et al., 2002). The results of the remaining elements present in sludge showed low variations in concentration along the pH values tested, except for Na and Ca (Figure 4c), as these cations moved from the cathode to the anode at high current values (high pH) to maintain the charge balance (Bunce et al., 2001).

3.4 Geochemical modelling

The simulation results obtained at different pH values using the PHREEQC model allowed to identify the main chemical species in solution (Figure 5) and the precipitates formed (Figure 6) after the ECR treatment. The model results showed a similar distribution in the liquid and solid phases to the experimental results (Figure 3), however, the simulations at pH 12.2 and 12.3 exceeded the threshold charge balance error of 10%, which is probably due to the depletion of sulfate anions (Bunce et al., 2001).

Figure 5 shows only the main chemical species in solution for Al, Cu, Fe, Mg, Si and Zn outputted by the model simulation, although all the other elements shared similar outputs (data not shown). The initial concentrations of Mg, Cu, Fe and Zn in solution were dominated by free metal species (Mg^{2+}, Cu^{2+}, Fe^{2+} and Zn^{2+}), while for Cu, Fe, and Mg, the second most dominant species in solution were their sulfate compound forms (Figure 5b, c, d and f). The dominant species in solution for Al and Si were $AlSO_4^+$ and H_4SiO_4, respectively (Figure 5a and e). The sulfate compound forms resulted from the high sulfate concentration at lower pH, which follows the solubility order, with Al the most soluble among these elements (Don and Robert, 2008).

After treatment at each pH stage, a variety of minerals were formed as predicted by PHREEQC geochemical model. Dissolved minerals maintained in dissolved form throughout the pH values tested include gypsum ($CaSO_4 \cdot 2H_2O$) and anhydride $CaSO_4$, zincite (ZnO) and ZnO active, and SiO_2(am-gel) and SiO_2(am-ppt). Focusing only on phases which are close to equilibrium with the solution, i.e., SI close to zero, likely precipitates formed were oxyhydroxides, hydrous sulfates, sulfates, and oxides (Figure 6). At pH below 7, only Si-bearing mineral phases (chalcedony, quartz, cristobalite), along with barite ($BaSO_4$) were supersaturate. The latter remained supersaturated regardless the pH, in agreement with the Ba experimental results (Figure 4a). At pH 5 cuprite (Cu_2O) and Lepidocrocite (γ-Fe_3+O(OH)) precipitate, followed by ZnO and gibbsite ($Al(OH)_3$) at pH 9, Sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6H_2O$) at pH 10, and brucite ($Mg(OH)_2$) and tenorite (CuO) at pH 11.

3.4 Sludge characterisation

The chemical analysis of the sludge samples of the second set of experiments allowed to identify a) major (>1%), b) minor (0.1%-1%), c) trace elements (<100 ppm) and d) light REE and heavy REE (Figure 7), while the mineralogical examination of the sludge by quantitative XRD showed that the samples were amorphous (Figure S2). Overall, these results confirm that the sludge produced during the ECR treatment is a promising source of critical elements. However, from a contamination perspective, the sludge concentrations of Cd, Co, Cu, Mn, Zn are above Health Based Investigation Levels of NEPM (2013) guidelines for soil contamination (NEPC, 2013), whereas Be, Ni, As concentrations, on the other hand, are lower than the guideline values (Figure 7).

Although REE and other critical elements have been reported in AMD (Naidu et al., 2019), the sludge resulting from the ECR treatment allows for a concentration of these elements up to 20 times (Co, Be and Sb) which is higher than the reported crustal abundance (Table 3). It is

worth mentioning that even if the sludge also contains other major elements that must be removed to recover the high-valued elements, the energy required to separate the metals from the sludge is much lower as there is no need for crushing and grinding (Rankin, 2017).

Among the major elements, Mg and Ca had the highest concentrations in the precipitates, followed by Al and Cu (Figure 7a). Among the minor elements, Co, Cd and Sr stand out in terms of concentration, followed by Ce and Ni (Figure 7b). From this group of elements, Co and Ni displayed concentrations higher than crustal abundance (Table 3). Among the trace elements, Y and Li had the highest concentrations (Figure 7c), of which Li concentrations were higher than the crustal abundance at pH above 8.04 (Table 3).

The analysis of the REE concentrations in the sludge showed that Ce had the highest concentration at pH 10, followed by Nd and La (Figure 7d). Nevertheless, Nd, Pr, Tb and Dy had concentrations higher than their crustal abundance at pH 8.04, 10 and 11.93 (Table 3).

REE concentrated in the sludge may be adsorbed onto metal oxide/hydroxide colloids, mainly by Al, Mn and Fe oxyhydroxides, forming co-precipitates, or precipitating directly as rare earth-$(OH)_3$ (Naidu et al., 2019). To know this, future advanced studies revealing the possible mineral forms of REE in the sludge are needed, where geochemical modelling can be complementary. However, the current databases do not include all elements, particularly REE. Therefore, further works should also focus on the expansion of these databases.

4. Conclusion

This study demonstrated that the treatment of AMD using a pilot-scale ECR allows the separation and concentration of major and critical elements in the sludge while leaving treated water that could meet the water quality standards. The geochemical modelling simulation determined the thermodynamically favourable precipitates of the system in the sludge, mainly as oxyhydroxides, hydrous sulfates, sulfates, and oxides. Through the use of the pilot-scale

ECR, it was shown that extraction of REE is a viable goal, as the concentration of these elements was increased and even surpassed the crustal earth's abundance. Future studies may evaluate the composition and distribution of these elements. This is highly relevant as it helps to support avenues for the valorisation of AMD sludge enhancing circularity and closing loops in the mining industry.

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References

Amanda, N., Moersidik, S.S., 2019. Characterization of Sludge Generated from Acid Mine Drainage Treatment Plants. Journal of Physics: Conference Series 1351, 012113. https://doi.org/10.1088/1742-6596/1351/1/012113.

Andalaft, J., Schwarz, A., Pino, L., Fuentes, P., Bórquez, R., Aybar, M., 2018. Assessment and Modeling of Nanofiltration of Acid Mine Drainage. Industrial & Engineering Chemistry Research 57(43), 14727-14739. https://doi.org/10.1021/acs.iecr.8b03576.

ANZECC, 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality.

Brewster, E.T., Freguia, S., Edraki, M., Berry, L., Ledezma, P., 2020. Staged electrochemical treatment guided by modelling allows for targeted recovery of metals and rare earth elements from acid mine drainage. Journal of Environmental Management 275, 111266. https://doi.org/https://doi.org/10.1016/j.jenvman.2020.111266.

Bunce, N.J., Chartrand, M., Keech, P., 2001. Electrochemical Treatment of Acidic Aqueous Ferrous Sulfate and Copper Sulfate as Models for Acid Mine Drainage. Water Research 35(18), 4410-4416. https://doi.org/https://doi.org/10.1016/S0043-1354(01)00170-1.

Chartrand, M.M.G., Bunce, N.J., 2003. Electrochemical remediation of acid mine drainage. Journal of Applied Electrochemistry 33(3), 259-264. https://doi.org/10.1023/A:1024139304342.

Course Hero, I., 2022. Reading: Abundance of Elements in Earth's Crust. https://courses.lumenlearning.com/geology/chapter/reading-abundance-of-elements-in-earths-crust/#footnote-324-1. (accessed July 2022).

Don, W.G., Robert, H.P., 2008. Perry's Chemical Engineers' Handbook, Eighth Edition, 8th ed. / ed. McGraw-Hill Education, New York.

Edraki, M., Golding, S.D., Baublys, K.A., Lawrence, M.G., 2005. Hydrochemistry, mineralogy and sulfur isotope geochemistry of acid mine drainage at the Mt. Morgan mine

environment, Queensland, Australia. Applied Geochemistry 20(4), 789-805. https://doi.org/https://doi.org/10.1016/j.apgeochem.2004.11.004.
European Commission, 2020. Study on the EU's list of critical raw materials
Geoscience Australia, A.G., 2020. Australian Critical Minerals Prospectus Australian Trade and Investment Commission (Austrade), Canberra, p. 172.
Han, Z., Edraki, M., Nguyen, A.D., Mostert, M., 2021. Efficiency of acid digestion procedures for geochemical analysis of tungsten mining wastes. Geochemistry: Exploration, Environment, Analysis 21(3), geochem2021-2034. https://doi.org/10.1144/geochem2021-034.
Ifeoma Mary, U., Onyedikachi Anthony, I., 2019. Sorption of Heavy Metals on Clay Minerals and Oxides: A Review, in: Serpil, E. (Ed.) Advanced Sorption Process Applications. IntechOpen, Rijeka, p. Ch. 7. https://doi.org/10.5772/intechopen.80989.
Kinnunen, P.H.M., Kaksonen, A.H., 2019. Towards circular economy in mining: Opportunities and bottlenecks for tailings valorization. Journal of Cleaner Production 228, 153-160. https://doi.org/https://doi.org/10.1016/j.jclepro.2019.04.171.
Macías, F., Caraballo, M.A., Nieto, J.M., 2012. Environmental assessment and management of metal-rich wastes generated in acid mine drainage passive remediation systems. Journal of Hazardous Materials 229-230, 107-114. https://doi.org/https://doi.org/10.1016/j.jhazmat.2012.05.080.
Madzivire, G., Gitari, W.M., Vadapalli, V.R.K., Ojumu, T.V., Petrik, L.F., 2011. Fate of sulphate removed during the treatment of circumneutral mine water and acid mine drainage with coal fly ash: Modelling and experimental approach. Minerals Engineering 24(13), 1467-1477. https://doi.org/https://doi.org/10.1016/j.mineng.2011.07.009.
Mamelkina, M.A., Vasilyev, F., Tuunila, R., Sillanpää, M., Häkkinen, A., 2019. Investigation of the parameters affecting the treatment of mining waters by electrocoagulation. Journal of Water Process Engineering 32, 100929. https://doi.org/https://doi.org/10.1016/j.jwpe.2019.100929.
Masindi, V., Tekere, M., 2020. Innovative Routes for Acid Mine Drainage (AMD) Valorization, Recovery of Byproducts from Acid Mine Drainage Treatment. pp. 189-218. https://doi.org/https://doi.org/10.1002/9781119620204.ch7.
Naidu, G., Ryu, S., Thiruvenkatachari, R., Choi, Y., Jeong, S., Vigneswaran, S., 2019. A critical review on remediation, reuse, and resource recovery from acid mine drainage. Environ. Pollut. 247, 1110-1124. https://doi.org/https://doi.org/10.1016/j.envpol.2019.01.085.
NEPC, 2013. National Environment Protection (Assessment of Site Contamination) Measure 1999. https://www.nepc.gov.au/nepms/assessment-site-contamination. (accessed 30 November 2022).
Parkhurst, D.L., Appelo, C.A.J., 2013. Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, Techniques and Methods. Reston, VA, p. 519.
Pozo, G., Pongy, S., Keller, J., Ledezma, P., Freguia, S., 2017. A novel bioelectrochemical system for chemical-free permanent treatment of acid mine drainage. Water Research 126, 411-420. https://doi.org/https://doi.org/10.1016/j.watres.2017.09.058.
Rakotonimaro, T.V., Neculita, C.M., Bussière, B., Benzaazoua, M., Zagury, G.J., 2017. Recovery and reuse of sludge from active and passive treatment of mine drainage-impacted waters: a review. Environmental Science and Pollution Research 24(1), 73-91. https://doi.org/10.1007/s11356-016-7733-7.
Rankin, W.J., 2017. Sustainability – the role of mineral processing and extractive metallurgy. Mineral Processing and Extractive Metallurgy 126(1-2), 3-10. https://doi.org/10.1080/03719553.2016.1264164.

412 Totsche, O., Pöthig, R., Uhlmann, W., Büttcher, H., Steinberg, C.E.W., 2003. Buffering
413 Mechanisms in Acidic Mining Lakes – A Model-Based Analysis. Aquatic Geochemistry
414 9(4), 343-359. https://doi.org/10.1023/B:AQUA.0000029035.88090.eb.
415 Younger, P.L., Banwart, S.A., Hedin, R.S., 2002. Mine Water Hydrology, in: Younger, P.L.,
416 Banwart, S.A., Hedin, R.S. (Eds.), Mine Water: Hydrology, Pollution, Remediation. Springer
417 Netherlands, Dordrecht, pp. 127-270. https://doi.org/10.1007/978-94-010-0610-1_3.
418 Zhuang, W.-Q., Fitts, J.P., Ajo-Franklin, C.M., Maes, S., Alvarez-Cohen, L., Hennebel, T.,
419 2015. Recovery of critical metals using biometallurgy. Current Opinion in Biotechnology 33,
420 327-335. https://doi.org/http://dx.doi.org/10.1016/j.copbio.2015.03.019.
421

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423