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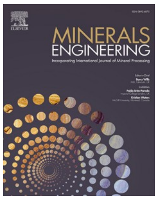

Electrodialytic extraction of copper, lead and zinc from sulfide mine tailings: Optimization of current density and operation time

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ABSTRACT

Re-mining unextracted metals from mine tailings can contribute to sustaining society's high demand for metals. Electrodialysis (ED) is a promising, yet underdeveloped, extraction technology for mobilizing and transporting particle-bound elements in a suspension slurry. This study investigated ED for extraction of copper (Cu), lead (Pb) and zinc (Zn) from Cu mine tailings (concentration of Cu: 2039 mg/kg, feldspar-dominant) and Pb-Zn mine tailings (Pb: 4469 mg/kg, Zn: 19417 mg/kg, dolomite-dominant). A multivariate experimental design was used to examine the effect of varying current density (1–5 mA/cm^2) and operation time (24–336 h) of 40 bench-scale experiments. The maximum extractions obtained were 70 % Cu from the Cu mine tailings and 97 % Pb and 88 % Zn from the Pb-Zn mine tailings. Depending on the tailing, the extraction was influenced differently by current density and operation time. In particular, carbonate minerals such as dolomite and calcite delayed acidification and thus the extraction due to their buffering capacity. However, as the carbonaceous tailings contained a larger proportion of soluble metals, likely to be bound in the carbonates themselves, overall higher metal extraction was obtained from these. Thresholds above, for which the increase of current densities did not increase extraction, were observed at 2 and 4 mA/cm^2 for the Cu and Pb-Zn tailings, respectively. The solubility of the remaining metals in the treated tailings increased significantly due to acidification by the EDR process and utilization of the treated tailings in construction materials therefore needs further investigation.

1. Introduction

Metals have gained critical importance in society (The European Commission, 2008). The increasing demand has resulted in the depletion of primary high-value resources and supply disruptions. Consequently, the extractive metal and mineral mining industry faces the challenges of working with complex, low-grade ores, resulting in larger land disturbances and increased waste generation (Rötzer and Schmidt, 2018; Nkuna et al., 2022). Notably, this industry is the largest global waste producer (IRP, 2020). One major waste product from metal and mineral processing is mine tailings, a fine-grained slurry of crushed ore, including critical metals in unprofitable concentrations. Approximately 5–7 billion tons of mine tailings are annually produced globally, in addition to the historically accumulated volumes in storage facilities (Edraki et al., 2014). Inadequate past management causes environmental and human health risks and incidents, including tailing dam failures (Owen et al., 2020; Schoenberger, 2016) and acid mine drainage generation (Simate and Ndlovu, 2014), highlighting the need to minimize waste generation of present mines (The European Parliament, 2006; European Commission, 2009) and develop measures to reduce the risks related to historical ones. To reduce harmful waste, using tailings in the construction sector could reduce the environmental risks related to mining while solving the increasing lack of raw construction materials (The European Commission, 2008; Spooren et al., 2020; European Commission, 2019; Martins et al., 2021; Kiventerä et al., 2020). However, historical mine tailings often contain residual metals, which could hinder utilization due to interference with hydration processes, leading to reduced performance (Gineys et al., 2010), or toxicological leaching reasons (Lu et al., 2016), which would be lost in the future if contained in constructions. Therefore, exploring techniques

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for re-mining previously discarded mine tailings prior to utilization is relevant (Lottermoser, 2011).

Electrodialysis (ED) is a separation technique capable of mobilizing elements adsorbed to particles such as soil, sediments, or bound in ashes (Ozkul et al., 2023; Ottosen et al., 2008). ED is driven by the application of an electric field to a suspension in an electrolytic cell, which drives charged ions towards the oppositely charged electrodes. The moved ions undergo electrolysis reactions at the electrodes. Anode oxidation causes water splitting, oxygen and proton (H^+) production, generating an acidic environment while cathode reduction cause hydrogen gas and hydroxide ion (OH^-) production to generate an alkaline environment. The acidification at the anode is vital for the mobilization and dissolution of ions from particles in the suspension, which promotes the movement of charged ions by electromigration towards the oppositely charged electrodes, while the alkalinity at the cathode results in cation precipitation and solid metal deposits. ED utilizes ion-selective membranes −cation-exchange membranes (CAT) and anion-exchange membranes- to selectively allow or block the passage of charged ions, enhancing the efficiency of ion transport and separation. The method has in some cases surpassed acid extraction methods (Jensen et al., 2012) and other metal extraction technologies (Juve et al., 2022; López et al., 2021) in heavy metal extraction extent from contaminated soils. The electrodialytic migration processes and the subsequent accumulation of cations in the catholyte, followed by their reduction and precipitation at the cathode, could potentially allow for a controlled and efficient resource extraction technique of solid deposits of valuable metals from sulfidic mine tailings (Juve et al., 2022).

The ED extraction of metals bound in the minerals of sulfidic mine tailings has also been documented (Jensen et al., 2016; Zhang et al., 2019; Hansen et al., 2008; Hansen et al., 2005). It was shown that a two-compartment setup offers faster acidification, favors cation extraction, and lowers energy consumption compared to a three-compartment setup when treating mine tailing materials (Kirkelund et al., 2019). In the two-compartment setup, the particulate material to be treated is suspended in the anode compartment and thus in direct contact with the anode.

Despite ED's documented potential, further research is essential before scaling up, particularly in optimizing the method to reduce energy consumption and processing time (Sun and Ottosen, 2012; Oliveira et al., 2019). Previous studies improved metal extraction from other materials by adjusting operational settings such as reduced stirring (Oliveira et al., 2019), adding extracting reagents (Hansen et al., 2005; Hansen et al., 2007; Hansen et al., 2005) or applying pulsed electric fields (in contrast to constant current) (Sun and Ottosen, 2012; Sun et al., 2013; Hansen and Rojo, 2007). Both operation time and current density proved to impact extraction significantly (Pedersen et al., 2015). In addition, material properties, such as particle size distribution and buffer capacity, also significantly affect extraction (Jensen et al., 2016; Zhang et al., 2019; Kirkelund et al., 2019; Pedersen et al., 2017; Ottosen et al., 2001; Jensen et al., 2022). For example, higher extraction efficiency was observed with decreasing particle sizes due to their larger surface area (Hansen et al., 2005; Sun et al., 2012). The acidification rate can be influenced by the material's buffer capacity, particularly from high contents of organic material and salts, which can retard the acidification process (Ottosen et al., 2001; Jensen et al., 2022). Material properties hence play a vital role in metal extraction.

Apart from offering increased recovery of metals from ore, the removal of toxic elements from tailings by ED may reduce the risk of leaching of toxic elements if tailings are utilized e.g. as a secondary resource in construction materials as has been researched for other ED-treated wastes (Ebert et al., 2021; Kirkelund et al., 2014).

The initial energy consumption during ED is high due to the low inherent conductivity of the tailings suspension. As acidification proceeds, the increasing ion concentration leads to decreasing ohmic resistance and thus voltage (Ottosen and Lima, 2021), while progressed acidification reduces the removal efficiency of target ions due to electromigration of the much more abundant hydrogen ions (Jensen et al., 2006; Viadero et al., 1998; Abou-Shady et al., 2012).

Through a multivariate experimental design, this study aims at optimizing ED extraction in a suspended two-compartment batch setup of copper (Cu), lead (Pb) and zinc (Zn) from two sulfide mine tailings (Cu and Pb-Zn mine tailings) with a focus on current density and operation time. The potential of utilizing the treated tailings in construction materials is evaluated on environmental and mineralogical aspects.

2. Materials and methods

2.1. Materials

Two sulfide mine tailings from metal-extracting mines were investigated:

- Tailings of a Cu (Mo, Ag, Au) mine in Chile working with sulfide ores (chalcopyrite, molybdenite, pyrite) in siderite and talc gangue minerals. The tailing sample originated from the processing outlet.
- Tailings of a Pb-Zn (Ag, Ge, Ga, Cd) mine in China working with sulfide ores (sphalerite, galena, pyrite, chalcopyrite, arsenopyrite, freibergite, pyrargyrite) in dolomite, calcite, and quartz gangue minerals. The tailing sample was collected from the reservoir.

After collection, the tailings were stored in closed buckets indoors.

2.2. Analytical methods

Metal concentrations (Cu, Pb, Zn) were analyzed by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) (Varian 720-ES) on triplicate samples (0.5 g) mixed with 10 mL concentrated HNO_3 and subjected to microwave-assisted nitric acid digestion according to EPA3051A (USEPA, 2007). Before ICP measurements, samples were filtered and diluted to 50 mL with deionized water. PlasmaCAL Calibration Standards for multi-elements from SCP Science were used for ICP calibration and verification. Quality control standards 1 and 2 from SCP Science were used for quality control. The limit of detection was 0.01 mg/l. The analysis was conducted on untreated and ED-treated mine tailings. Experiments EX 28 and EX 29 (168 h, 4.5 mA/cm^2) were chosen to represent high metal-extractable ED experiments.

Grain size distributions were determined on dry samples by a laser diffraction analyzer (Malvern Mastersizer 2000 laser diffractometer) (double determination).

pH and **conductivity** were analyzed on a pH- and conductivity-meter from Hach (Sension + MM 374) equipped with radiometer analytical electrodes on a 10 g sample with 25 ml deionized water and agitated for 30 min (triple determination).

The **solubility of metals in deionized water** was tested according to the standard batch leaching test EN 12457-1 (DS/EN 12457-1, 2002). The purpose was to obtain information on the potential mobility of metals if exposed to water. Mine tailing samples were mixed with deionized water in a liquid/solid ratio (L/S) of 2 and agitated for 24 h to reach equilibrium conditions for the metals present. After pH measurements (Radiometer analytical electrodes), the solid sample was filtrated through a 45 μm syringe filter, and the liquid was measured by ICP-OES. The test was performed (double determination). The analysis was conducted on untreated and ED-treated mine tailings.

The **pH-dependency of metal solubility** was investigated to understand how metal mobility shifted under acidic or alkaline conditions. In the test, a sample (5 g) was exposed to sodium hydroxide (25 mL NaOH) and nitric acid (25 mL HNO_3) in concentrations between 0.001–4 M, including a blind sample of deionized water. After 7 days of agitation, pH was analyzed (Radiometer analytical electrodes), and the sample was filtered and analyzed for metals by ICP-OES (double determination).

A four-step **sequential extraction method**, based on the modified three-step method by BCR (Rauret et al., 1999), developed for soil and sediment by Tessier et al. (1979) (Tessier et al., 1979) was engaged in providing information about the mobility of mine tailing metals at different environmental conditions (European Commission, 2009). Samples (0.5 g) were subjected to four extraction steps in triplicate, and the solutions were measured by ICP-OES. The analysis was conducted on untreated and ED-treated mine tailings. Since mine tailing phases differ from soil and sediments, the chemical phases should be interpreted differently (Table 1). Some interpreted the results as indicators of the strength of metal retention (Hansen et al., 2007), while this article shares the interpretation by Dold 2003 (Dold, 2003) who dedicated specific mineralogical phases in mine tailings to the operationally defined steps (Step 1–4) based on XRD analysis of Cu-sulfide mine tailings.

Powder X-ray diffraction (XRD) analysis was conducted in a PANalytical X'Pert Pro X-Ray diffractometer fitted with a Cu Kα radiation source with a wavelength of 1.54 Å. A crushed sample was back-loaded into sample holders and analyzed in a 2θ range of 5-70° (step size = 0.002° 2θ, sampling time per step = 24.8 s). A quantitative mineralogical estimation was conducted based on Reference Intensity Ratio (RIR)-values in X'Pert HighScore Plus software equipped with the International Centre for Diffraction Data (ICDD) database PDF-2 (2020). The analysis was conducted on untreated and ED-treated mine tailings.

2.3. Electrodialytic extraction experiments

The extraction of metals was investigated in a 2-compartment electrodialytic cell consisting of a 3.5 cm long electrolyte compartment (catholyte) and a 10 cm long suspension compartment containing 50 g mine tailing sample and 400 mL deionized water (L/S=8) and the anode (Fig. 1). Both compartments were made of plexiglass with an inner diameter of 8 cm. A cation exchange membrane (CAT) from Ionics (cation exchange membrane CR67 HUY N12116B) separated the two compartments. Pan World pumps circulated the electrolyte liquid $NaNO_3$ (0.01 M, 500 mL). Platinum-coated titanium electrodes were placed in each compartment and a constant direct current was supplied by a power supply (Hewlett Packard E3612A). The mine tailing suspension was constantly stirred by a glass rod with attached plastic wings connected to an electronic overhead stirrer (VWR VOS). The middle chamber's voltage, pH and electrical conductivity were monitored at least 3 times a day, and at each monitoring event, the catholyte pH was adjusted to below pH 2 by adding HNO_3 (5 M).

At the end of each experiment, the mine tailing suspension was filtered through a 45 µm filter. The solids were dried (40 °C) overnight before microwave-assisted acid digestion of samples according to EPA3051A (USEPA, 2007). The membranes and the stirrer were rinsed overnight in 1 M HNO_3 and the electrodes in 5 M HNO_3. Finally, the filtrate, the solutions from membranes, stirrer, and electrodes rinse, and the solution from the microwave-assisted acid digestion of the solid were analyzed for metals by ICP-OES.

2.3.1. Calculations

The current density was calculated as follows:

$$Thecurrentdensity[mA/cm^2] = \frac{Current[mA]}{Cationexchangemembranearea[cm^2]}$$

The metal mass balance of the cell experiment was calculated as follows:

$$Themassbalance[\%] = \frac{Initialmassofmetalintheminetailings[mg]}{\sum Finalmassofmetalinthecell[mg]}$$

The final mass of metal in the cell included the metal concentrations in the remaining mine tailing material, the suspension liquid, deposited on electrodes, in the catholyte solution and at the CAT after the experiment. Metals mass balances above or below 75–125 % were excluded. Supplementary Data (Table 4) provides a detailed overview, including excluded experiments.

The metal extraction included metals precipitated at the cathode, in the CAT and found in the catholyte, and was calculated as follows:

$$Themetalextraction[\%] = \frac{\sum extracted\ metal\ [mg]}{\sum \text{The final mass of metal in the entire cell system}[mg]}$$

The energy consumption of the experiments was calculated as:

$$\sum_{t=0}^{t} E[kWh] = V{*}I{*}dt$$

Where V is the voltage between electrodes (V), I is the current [A], and t is the operation time [h], as seen in Pedersen et al. 2019 (Pedersen et al., 2019). The energy consumption is further cumulated and normalized to the weight of the initial mine tailing sample used for each experiment (kWh/kg).

Table 1

The fractions, reagents and methods used for a 4-step sequential extraction method concerning metal-bound phases in soil and sediment (Tessier et al., 1979) and how they (WHO, 1994) are translated into mine tailing phases (Norgate and Jahanshahi, 2010).

Sequential extraction step	Reagent and method	Soil and sediment phase (Tessier et al., 1979)	Mine tailing phase (Dold, 2003)
Step 1: Ion-exchangeable/ weak acid-soluble fraction	Acetic acid (CH_3COOH 0.11 M, 20 mL, pH 3) for 16 h	Ion-exchangeable metals on, e.g., clay or carbonate-bound metals	Ion-exchangeable metals and metals soluble in weak acids such as bound in carbonate minerals, e.g., calcite, dolomite
Step 2: Reducible fraction	Hydroxyl ammonium chloride ($NH_2OH{\cdot}HCl$, 0.1 M, 20 mL, pH 2) for 16 h	Iron and manganese oxide-bound metals	Metals bound in iron and manganese oxide minerals, e.g., magnetite, hematite
Step 3: Oxidizable fraction	Hydrogen peroxide (H_2O_2, 8.8 M, 5 mL) for 1 h, followed by exposure to 85 °C for 1 h, followed by evaporation of liquid at 85 °C, followed by exposure to ammonium acetate (NH4OOCCH3, 1 M, 25 mL, pH 2) for 16 h	Organic matter-bound metals	Metals bound in organics and (secondary and primary) sulfides, e.g., covellite, galena
Step 4: Residual fraction	Nitric acid digestion (10 mL HNO_3)	Metals within the crystal structure of primary and secondary minerals, e.g., silicates	Residual, e.g. silicates

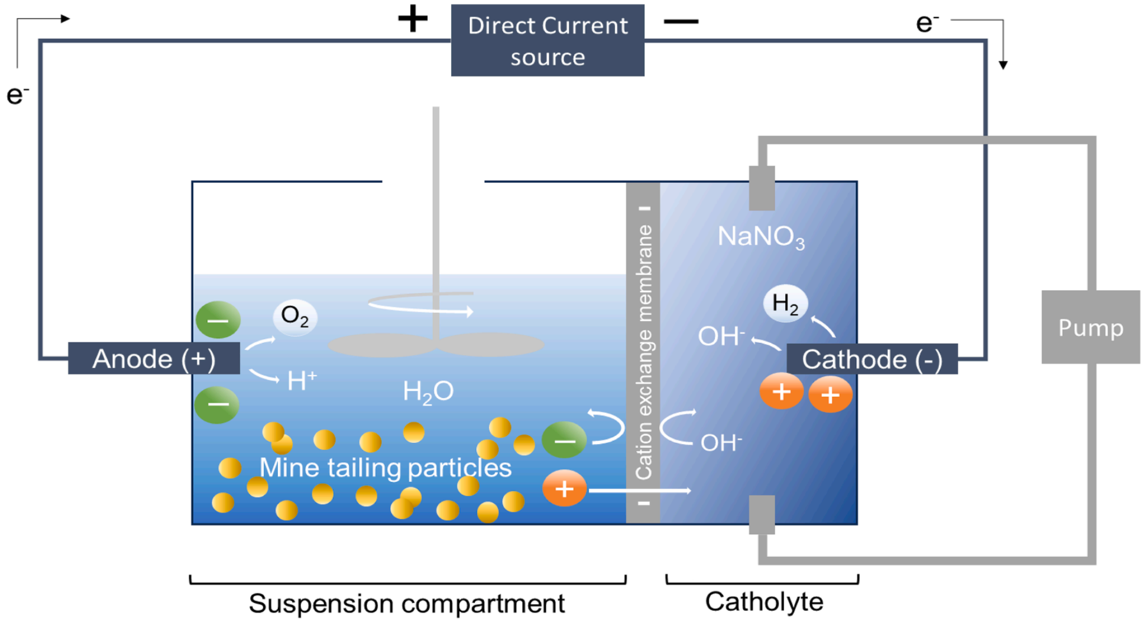

Fig. 1. A schematic illustration of the 2-compartment electrodialytic cell setup consisting of a stirred suspension of mine tailing particles and deionized water in the suspension compartment. A cation exchange membrane separated the suspension compartment from the $NaNO_3$-filled and circulated catholyte, allowing positively charged cations (exemplified by +) to pass while negatively charged anions (exemplified by −) were unable to pass. Applying a direct current generated reduction reactions at the cathode and oxidation reactions at the anode.

The energy consumption per material weight was calculated as:

$$Epermaterialweight[kWh/kg] = \frac{\sum E[\mathrm{kWh}]}{Initialweightofminetailingsample[kg]}$$

The energy consumption per extracted metal was calculated as:

$$Eperextractedmetal[kWh/kg] = \frac{\sum E[\mathrm{kWh}]}{\sum extractedmetal\,[kg]}$$

2.4. Multivariate experimental design

The settings of the 40 experiments in this study were determined based on a multivariate experimental design, examining current density, operation time and mine tailing material as variables, while all other key parameters (e.g. stirring, L/S-ratio, etc.) remained constant. The experimental design thereby used a $2^{(3-1)}$ fractional factorial design, resulting in 4 experiments for each tailing.

As the experiments progressed, the experimental domain expanded to optimize the extraction. An additional center experiment of the two continuous parameters, current density and operation time, was performed for validation (120 h, 2.0 mA/cm^2). The total experimental span ranged from 1-14 days (24, 48, 120, 168, and 336 h) and 50–250 mA (1.0, 2.0, 2.5, 2.8, 3.2, 4.0, 4.5, 5.0 mA/cm^2). Supplementary Data (Table 4) shows an overview of all experiments.

Table 2
Cu mine tailing and Pb-Zn mine tailing properties include pH, conductivity, LOI (organic matter), SSA (specific surface area) and D50 (mean particle size).

	pH	Conductivity [mS/cm]	LOI [550°] [%]	SSA [m^2/g]	D50 [μm]
Cu mine tailings	9.0 ± 0.0	2.5 ± 0.3	1.3 ± 0.1	0.48 ± 0.00	94 ± 0.1
Pb-Zn mine tailings	8.6 ± 0.1	32 ± 1	2.3 ± 0.2	0.12 ± 0.01	176 ± 10

3. Results and discussion

3.1. Characterization

3.1.1. Mine tailing properties

Table 2 displays key mine tailing properties earlier suggested to impact metal extraction significantly ED (Pedersen et al., 2017).

While both tailings shared characteristics regarding pH (slightly alkaline, 8.6–9.0) and organic content (1.3–2.3 %), they differed in mean particle size and conductivity. The Cu mine tailings had a smaller mean particle size (D50: 94 μm) and consequently a larger surface area (SSA) (0.48 m^2/g) compared to the Pb-Zn mine tailing (D50: 176 μm, SSA: 0.12 m^2/g). This smaller particle size in the Cu mine tailings could enhance extraction, as ED operates more effectively on a larger surface area (Zhang et al., 2019). In contrast, the higher conductivity in the Pb-Zn mine tailings indicated a higher presence of soluble ions accessible for extraction.

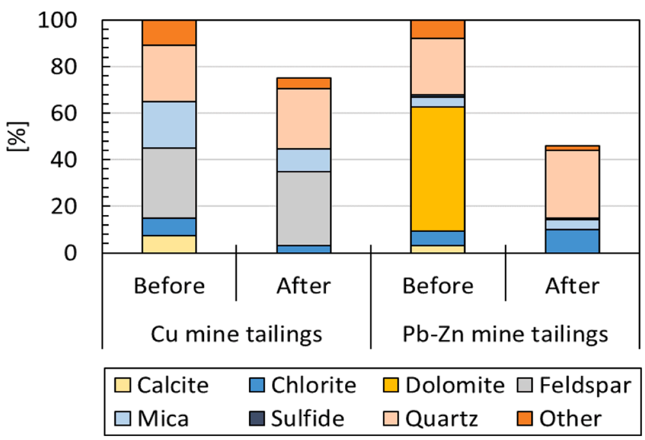

Fig. 2. Quantitative analysis [%] of Cu mine tailings and Pb-Zn mine tailing mineralogy before and after ED, including the mass loss after ED based on RIR-values.

Table 3
The nitric acid extractable metal content of Cu mine tailings and Pb-Zn mine tailings before and after ED treatment. The values are compared to mining production measures, EU criticality measures, stock exchange prices and solid limits for reuse or disposal of contaminated soil waste.

		Cu	Pb	Zn
Cu mine tailings	Before ED [ppm]	2039 ± 47	366 ± 9	509 ± 63
	After ED* [ppm]	952 ± 24	86 ± 6	154 ± 17
Pb-Zn mine tailings	Before ED [ppm]	404 ± 60	4463 ± 469	19417 ± 138
	After ED* [ppm]	360 ± 59	266 ± 22	6879 ± 478
	Continental crust abundance [ppm] (Zhan and Kirkelund, 2021)	25	15	65
	Global reserves [Mt] (U.S. Geological Survey, 2023)	890	85	210
	Global production in 2022 [Mt/y] (U.S. Geological Survey, 2023)	22	4.5	13
	Average ore grade used for profitable mining [ppm] (Norgate and Jahanshahi, 2010)	5000–20,000	50,000–100,000	100,000–300,000
	Criticality assessment (EU): Economic importance (European Commission, 2020)	5.3	4.0	5.4
	Criticality assessment (EU): Supply risk (European Commission, 2020)	0.3	0.1	0.3
	Stock exchange prices (November 2022) (EUR/kg)	7.13	1.85	2.15
	Solid limits for contaminated waste (EU) (European Union, 2017), soil wastes' reuse limit (DK) (Ministry of Environment and Food of Denmark, 1672) and soil quality criteria (DK) (Miljøministeriet, VEJ nr 9603 af 01/06/2006, 2006) based on WHO (WHO, 1994) and EU principles (European Chemicals Bureau, 2008) [mg/kg]	500	40	500

*High metal-extractable ED experiments with mine tailings (experiments EX 28 and EX 29: 168 h, 4.5 mA/cm^2) were chosen to represent the mine tailings after ED.

The results of a semiquantitative XRD analysis of key minerals before and after ED are shown in Fig. 2. Prior to ED, the Pb-Zn mine tailings were highly Ca-rich, containing 54 % dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$), whereas the Cu mine tailings contained only 8 % calcite in total. Both tailings contained chlorite, mica, and quartz minerals, while only the Cu mine tailings also contained feldspar minerals (albite, microcline) – 31 % in total. A small sulfide content was detected in the Pb-Zn mine tailings (1 %) but not in the Cu MT by XRD, despite the Cu mine tailings originating from a sulfide mine. The mine tailing properties after ED are discussed in section 3.5.

3.1.2. Metal content and mobility

The nitric acid extractable metal contents before and after ED are shown in Table 3. The mine tailings contained high levels of target and non-target metals compared to continental crust abundances (Hans Wedepohl, 1995). However, none of the mine tailings proved profitable for further extraction, considering the average ore grades currently required for profitable mining (Norgate and Jahanshahi, 2010). Except for the non-target metal, Cu, of the Pb-Zn mine tailings, all metal concentrations exceeded Danish and European limits for contaminated waste (European Union, 2017), materials to be reused for construction (Ministry of Environment and Food of Denmark, 1672), and soil quality criteria (WHO, 1994). Thus, additional metal processing could be relevant prior to eventual utilization, particularly to extract Cu and Zn, given their economic importance (European Commission, 2020), value and environmental toxicity.

The water-solubility of metals in the two mine tailings before ED is illustrated in Fig. 3A. Higher water-solubility of Pb (190 μ g/L) and Zn (127 μ g/L) was observed from the Pb-Zn mine tailings, compared to Cu mine tailings, exceeding the solute limits (Pb: 10 μ g/L and Zn: 100 μ g/L) for deposition of contaminated soil (Ministry of Environment and Food of Denmark, 1672). In contrast, despite the higher nitric acid extractable Cu concentrations of the Cu mine tailings (2039 ppm) (Table 3), the water solubility of Cu (24 μ g/L) was similar to that of the Pb-Zn mine tailings (22 μ g/L) and complied with the solute limits for reuse of soil waste (45 μ g/L).

The Pb and Zn in the Pb-Zn mine tailings consistently appeared more mobile than Pb and Zn of the Cu mine tailings with higher water solubility and more significant ion-exchangeable/weak acid-soluble fraction of Pb (42 %) and Zn (29 %), compared to the Cu mine tailings (Pb: 13 %, Zn: 15 %) (Fig. 3B–C). The difference may be attributed to the abundant carbonate phase.

Fig. 3D–E illustrates the pH-dependency of metal solubility. Metal extraction of Cu and Pb-Zn mine tailings initiated above pH 13 and below pH 6. For Cu mine tailings, 100 % Zn, 80 % Pb, and 60 % Cu were extracted at pH 2, while decreasing the pH to 0 caused Cu to increase extraction to 95 % and, surprisingly, Pb to decrease to 70 %. For Pb-Zn mine tailings at pH 2, 100 % Zn, 82 % Pb, and 73 % Cu were extractable, while decreasing to pH 0 caused Pb to reach 100 % extraction and Cu to 78 %. Overall, Pb-Zn mine tailings required less acidity for Pb and Zn extraction than Cu mine tailings, aligning with higher mobility of Pb and Zn in the water solubility and sequential extraction tests (Fig. 3A–C). Despite similar water-solubility and fractionation patterns for both tailings, Cu mine tailings reached higher Cu extractions when decreasing pH to 0 than Pb-Zn mine tailings, highlighting the complex relation between metal mobility, extraction efficiency, and pH conditions in distinct mine tailings.

3.2. Electrodialytic extraction

3.2.1. Mass balances of the experiments

The mass balance of the electrodialytic experiments varied among metals and mine tailings. The mass balances of the included experiments with Cu mine tailings were Cu (92 ± 8 %), Pb (97 ± 12 %) and Zn (107 ± 12 %), while those for Pb-Zn mine tailings were Cu (93 ± 11 %), Pb (91 ± 9 %) and Zn (95 ± 8 %). The mass balance variation was thus slightly higher for Cu mine tailings (77–123 %) than for Pb-Zn mine tailings (76–116 %). Supplementary Data (Table 4) shows an overview of all mass balances.

3.2.2. pH, conductivity, and voltage during the experiments

The development of the pH, conductivity, and voltage between the working electrodes during the ED experiments are shown in Fig. 4A–F for each current density (i.e., all experiments with the same current density are indicated with the same color despite their duration). For both tailings, the pH (Fig. 4A–B) generally decreased over time from a maximum of 9 to 0.5. The pH decreased slower in the Pb-Zn mine tailing suspension compared to the Cu mine tailings suspension. For example, the Pb-Zn mine tailings suspension reached pH 2 (marked by a dashed line) after approximately 40–130 h, depending on current density, while this occurred after 10–100 h for Cu mine tailings. Also, a larger proportion of long-term Cu mine tailings experiments ended with a lower final pH (pH 0.6–1.4) than the Pb-Zn mine tailings, which in turn showed greater pH variation depending on current density (pH 0.5–3.2), in accordance with Pb-Zn mine tailings' higher buffer capacity.

Besides causing a faster pH decrease, higher current density experiments generated higher conductivity for both tailings (Fig. 4C–D). While the conductivity of Cu mine tailings increased steadily for all experiments, Pb-Zn mine tailings showed lower current density experiments (1–2.5 mA/cm2) to increase slower while higher current density experiments (2.8–5 mA/cm2) increased more drastically. A larger portion of the Pb-Zn mine tailings ended with higher conductivity. For example,

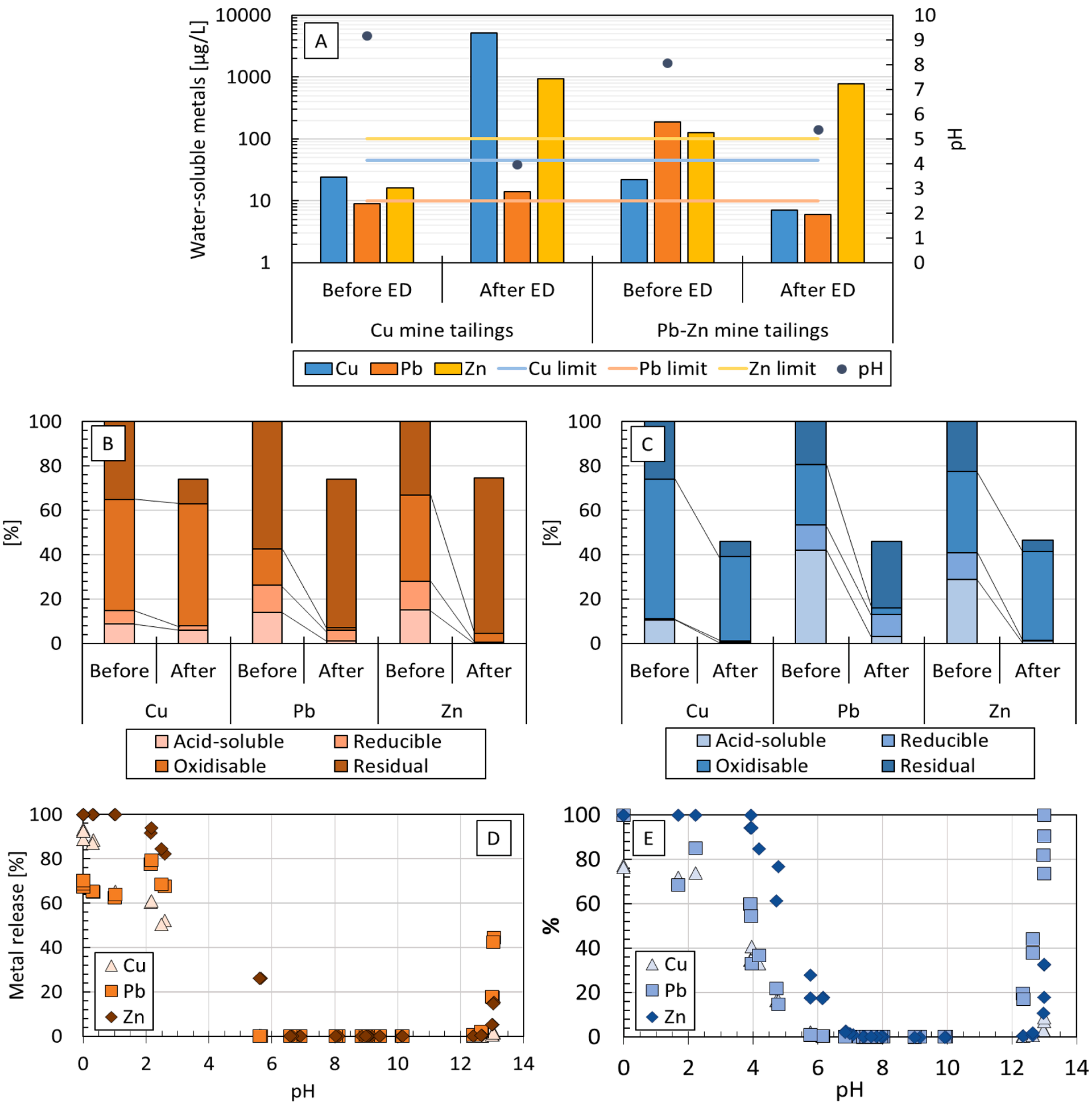

Fig. 3. A) Water-solubility of Cu, Pb and Zn of Cu and Pb-Zn mine tailings before and after ED with pH and limits for reuse and disposal of contaminated soil waste according to Danish legislation indicated, (B) metal fractions by a sequential extraction method for Cu mine tailings accounting for the mass loss after ED, (C) metal binding fractions by a sequential extraction method for Pb-Zn mine tailings, (D) metal release as a function of pH for Cu mine tailings, and (E) metal release as a function of pH Pb-Zn mine tailings.

from experiments above a current density of 2.8 mA/cm^2, the experiments ended with a conductivity above 62 mS/cm, while this only occurred for current densities above 4.5 mA/cm^2 for Cu mine tailings.

The voltage decreased for both tailings in Fig. 4E–F as conductivity increased during treatment. Significant voltage fluctuations occurred during all experiments, but once the pH of the electrolyte was adjusted, the voltage, in most cases, decreased. These non-permanent voltage increases have been excluded from the energy calculations' data in Fig. 4E and F, anticipating that continuous pH control would be implemented in a full-scale process. In the three Pb-Zn MT experiments at current densities of 2.8, 3.2 and 4.5 mA/cm^2, voltage remained high despite pH adjustments. These were included in Fig. 4F and energy calculations. Despite these deviations, pH decreased, conductivity increased, and metal extraction proceeded, as shown below. Increases in current density above five mA/m^2 were not pursued, as the observations demonstrated no additional metal extraction.

3.3. *Electrodialytic metal extraction*

3.3.1. *Metal extraction depending on current density and operation time*

The extraction of Cu, Pb and Zn by electrodialysis (ED) as a function of current density and operation time is shown in Fig. 5A–F. Metal extraction generally improved at higher current densities and operation times for both tailings. However, the extent of the extraction varied slightly depending on the specific metal and mine tailing. Fig. 5 provides guidance lines to facilitate the interpretation of short-term (48 h) and long-term (168 h) experiments.

Firstly, extraction increased with current density until reaching a plateau, where it stagnated, except for the long-term experiment (168 h) with Cu in Cu mine tailings, where extraction kept increasing. For example, during a long-term experiment with Pb-Zn tailing (Fig. 5F), 83 % Zn was extracted at a current density of two mA/cm^2, with a marginal extraction increase of 85 % at five mA/cm^2. The threshold, marking the

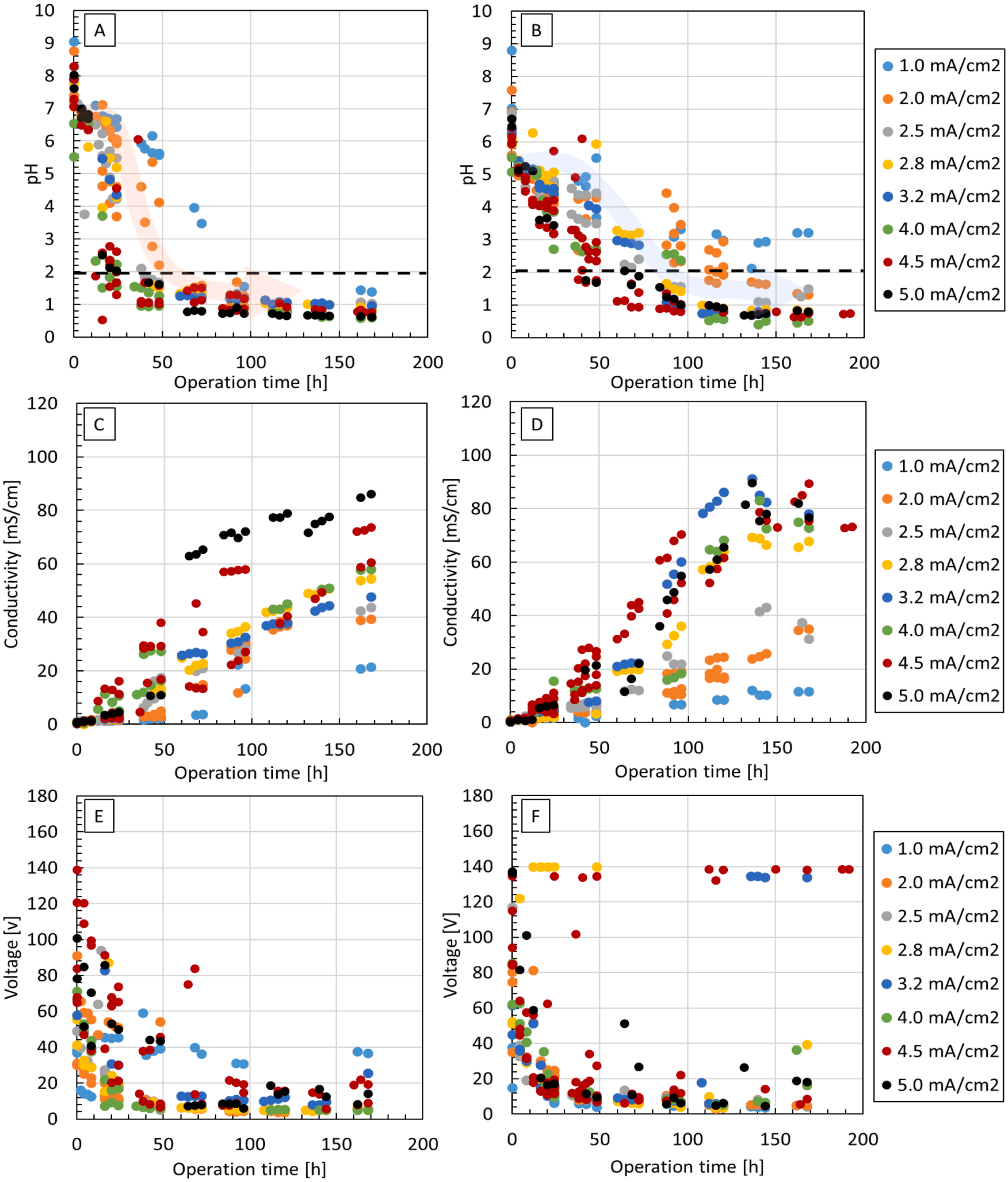

Fig. 4. Ph (a-b), conductivity (c-d) and voltage between the working electrodes (e-f) as a function of operation time of ed with cu mine tailings (left side: a, c, e) and pb-zn mine tailings (right side: b, d, f). guiding dashed lines at ph 2 are provided to illustrate the timing of the acidified suspension, and colored lines are used to ease interpretation.

point at which no significant additional extraction occurred with increasing current density, was found at approximately 2 and 2.5 mA/cm^2 for Zn in Pb-Zn mine tailings and all metals in Cu mine tailings and four mA/cm^2 for Cu and Pb in Pb-Zn mine tailings. This horizontal plateau could suggest a limiting current density of the membranes (La Cerva et al., 2018; Ottosen et al., 2000) or water splitting at the CAT (Ottosen et al., 2001; Abou-Shady et al., 2012; Ottosen et al., 2000).

For short-term (48 h) Cu mine tailing experiments, a steep increase in extraction occurred when increasing current density from 1-2.8 mA/cm, where it nearly reached the same extraction as the long-term experiments at current densities between 2.5–4 mA/cm^2, while the extraction leveled off or even decreased at higher current densities. For example, both short-term (48 h) and long-term (168 h) Cu mine tailing experiments at 2.5 mA/cm^2 extracted 47 % Cu (Fig. 5A), indicating that Cu mine tailings were more influenced by current density since no significant buffer capacity should be broken as seen for Pb-Zn mine tailings.

In contrast, extraction increased steadily with current density for the short-term experiments of Pb-Zn mine tailings, achieving maximum values of 60 % at a current density of 4 mA/cm^2, while the corresponding long-term experiments achieved 97 % extraction. This

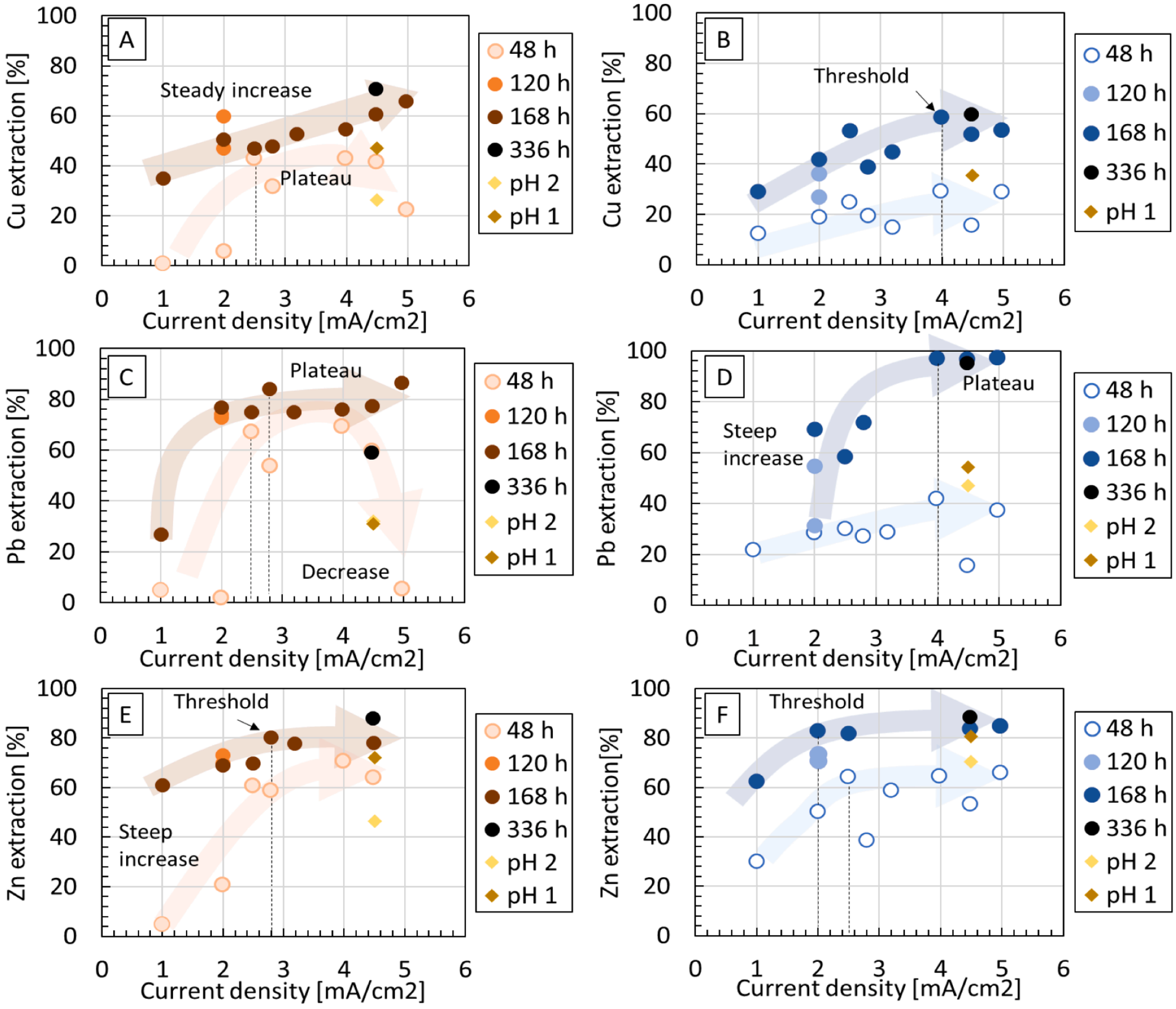

Fig. 5. Extraction of Cu (A-B), Pb (C-D) and Zn (E-F) by electrodialysis of Cu mine tailings (left) and Pb-Zn mine tailings (right) as a function of current density and experimental operation time. The two experiments marked by yellow show the effect of reaching pH 2 and 1, respectively. Guidance arrows are provided to ease the interpretation, and black dashed lines represent the threshold current density where no further increase in extraction could be obtained by further current increase. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

significant difference in extraction could indicate a higher dependency on operation time, related to the longer acidification time (Fig. 4A–B) due to the higher buffer capacity of Pb-Zn mine tailings.

The impact of operation time was investigated further to evaluate the metal extraction at a very long operation time of 336 h and a current density of 4.5 mA/cm^2. Cu extraction reached 52 % during long-term (168 h) treatment and only increased slightly to 60 % during a very long-term (336 h) treatment (Fig. 5B). Comparable trends of minimal or similar extraction levels were observed for Pb and Zn when extending the experiments to 336 h. However, Pb in Cu mine tailings achieved a markedly lower extraction level (59 %) at the corresponding current density for 168 h (78 %). The results illustrated the limited potential of increasing the operation time beyond 168 h.

3.3.2. *Metal extraction depending on specific metal*

The highest extractions were 70 % Cu from Cu mine tailings and 97 % Pb and 83 % Zn from Pb-Zn mine tailings (Fig. 5). The general order of proportional extraction for both tailings (Pb > Zn > Cu) aligns with previous observations for ED-treated mine tailings (Jensen et al., 2016; Zhang et al., 2019). The highest extractions were observed for the target metals of the mine tailings, with the highest nitric acid-digestible content (Table 3). The proportional extraction of metals by the ED, however, showed an opposite trend to the metal release as a function of pH (Fig. 3(D–E), where a higher proportion of Zn (100 %) was released than Pb (85 %) at pH 0. This suggested that factors other than suspension acidification are responsible for metal mobilization. The higher ED extraction of Pb compared to Zn, despite their reverse order of solubility product for sulfides (ZnS>PbS) (Peppicelli et al., 2018; Moncur et al., 2009), also suggests that sulfide solubility is not dominating the ED extraction.

Despite the two tailings' high difference in nitric acid-digestible Cu contents (Table 3), they encountered similar water soluble concentrations (22–24 µg/L: Fig. 3A), were both primarily bound in the oxidizable fraction (Fig. 3B–C) and showed lower metal extraction at acidic conditions (max 75 % at pH 0: Fig. 3D–E). In accordance, Cu showed a generally lower extraction by ED for both tailings (max 70 %) compared to Pb and Zn extraction.

3.3.3. *Metal extraction depending on pH*

ED experiments at high current density were terminated as they reached pH two and one. These experiments aimed to investigate the ED progress and extraction immediately following the significant pH decrease, indicating the collapse of the carbonate buffer capacity of the tailings and the beginning of the period of stagnant low pH during which aluminum and iron oxides likely induce the buffer capacity (Fig. 4A–B), as these phases previously have been shown to affect extraction

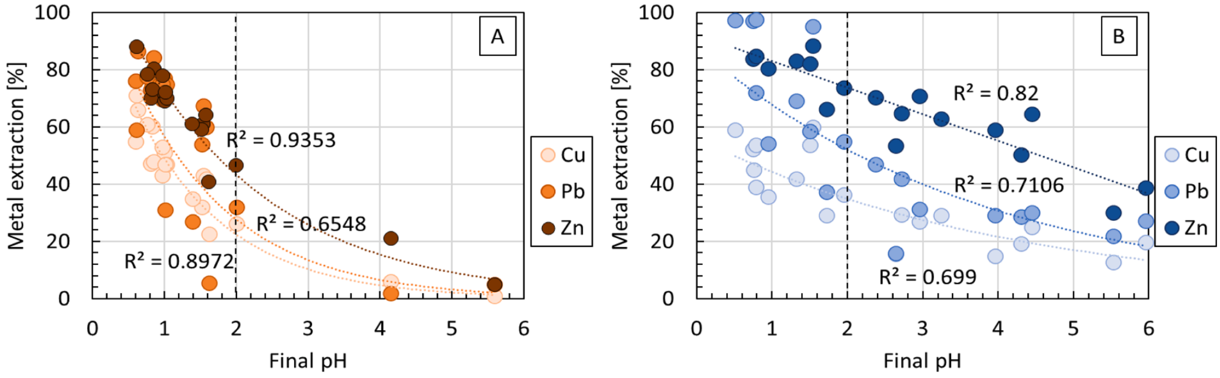

Fig. 6. Cu, Pb and Zn extraction by electrodialysis with A) Cu mine tailings and B) Pb-Zn mine tailings as a function of the final pH of the tailing suspension. Guiding dashed lines at pH 2 are provided to illustrate the acidified suspension.

efficiency (Jensen et al., 2006). For Cu mine tailings, pH reached two after approximately 24 h and one after 48 h (Fig. 5A, C, E), while for Pb-Zn mine tailings, these pH levels were attained after 48 and 72 h, respectively (Fig. 5B, D, F), both at a current density of 4.5 mA/cm^2. Fig. 5D and F showed Pb extraction of Pb-Zn mine tailings to increase from 47 % to 54 % and Zn extraction from 70 % to 81 % when pH was lowered from pH 2 to pH 1, which suggested a relation between metal extraction and lowering of the pH.

The relation between the final pH in the tailing suspension and metal extraction is presented in Fig. 6. The highest extraction is observed at the lowest pH, especially when the suspension's pH is below 2. Metal extraction of Cu mine tailings (Fig. 6A) exponentially increased with decreasing pH, while the relation of Pb-Zn mine tailings (Fig. 6B) was linear. The difference could stem from variations in carbonate content (Fig. 2) and metals bound in the ion-exchangeable/weak acid-soluble fraction (Fig. 3B–C). A previous study (Jensen et al., 2022) demonstrated metals' association with carbonates and can thus become mobilized as the carbonate dissolves during the ED process. Cu mine tailing metals were tighter bound, as shown by the predominant residual phase (Fig. 3B). In addition, similar to the metal extraction as a function of pH in Cu mine tailings (Fig. 3D), a limited number of ED experiments ended with a final pH between the 2–6 range, indicating rapid acidification of the material, likely due to its low buffer capacity.

Comparing the metal extraction by ED with the metal release in relation to pH (Fig. 3D–E), a higher proportion of metals could be extracted by exposure to acid than by ED treatment at pH 2 for both tailings. With pH decreasing further to pH 0.75, which was the minimum pH of the ED experiments, more Pb was extractable with ED processes for both tailings than by acid extraction (Fig. 3D–E), underlining the difference in metal behavior. Therefore, the main advantage of ED metal extraction of tailings is that it could potentially leave a smaller and much more concentrated volume of metal-containing liquid than acid washing.

3.3.4. The distribution of metals within the ED cell

The distribution of extracted and unextracted metals in ED cells in the short- (48 h) and long-term (168 h) ED experiments are shown for Cu mine tailings (Fig. 7) and Pb-Zn mine tailings (Fig. 8). Figs. 7-8 show that metals generally existed as cationic species (Cu^{2+}, Pb^{2+}, Zn^{2+}) due to the dominant abundance of metals at the cathode end (including dissolved metal in the catholyte and precipitates at the *cathode* and cation exchange membrane (*CAT*) (up to 80 %), compared to the anode (up to 35 %). Only Pb were present as anions in both tailings (e.g., oxides or hydroxides) (Fig. 7B, E and Fig. 8B, E). In short-term experiments (48 h) with Cu mine tailings (Fig. 7A–C), a high proportion of the metals remained in suspension in the *catholyte* + *CAT* compared to long-term

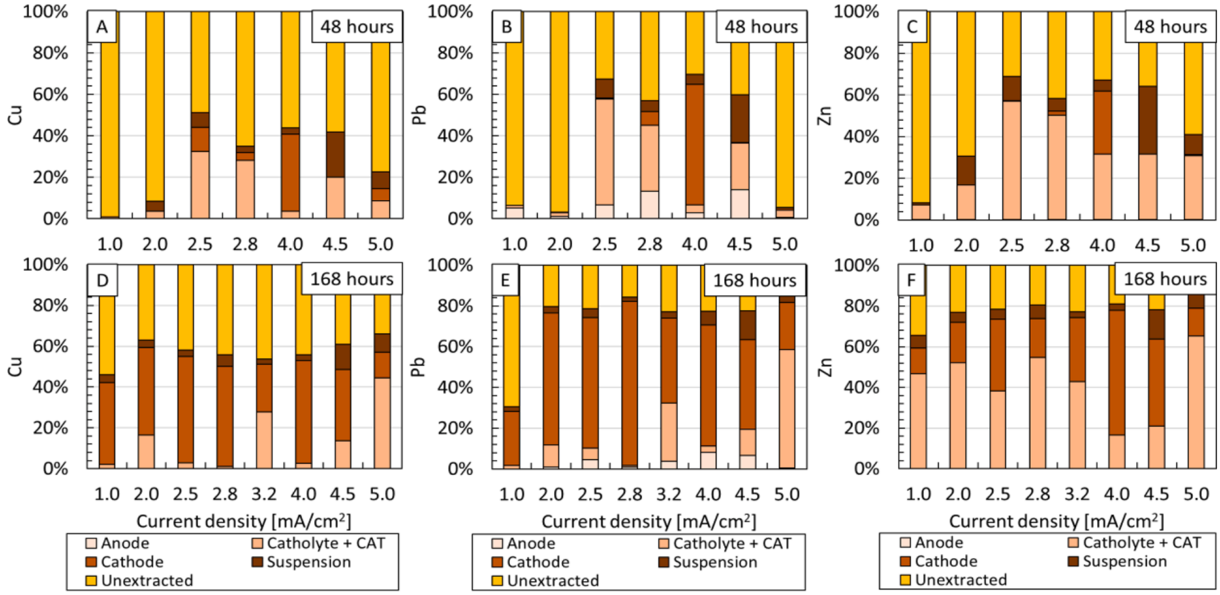

Fig. 7. Distribution of extracted (Anode, Catholyte + CAT (Cation Exchange Membrane), Cathode, Suspension) and unextracted (mine tailing material after ED) Cu (A, D), Pb (B, E) and Zn (C, F) according to current densities for ED experiments with Cu mine tailings for 48 h (upper) and 168 h (lower).

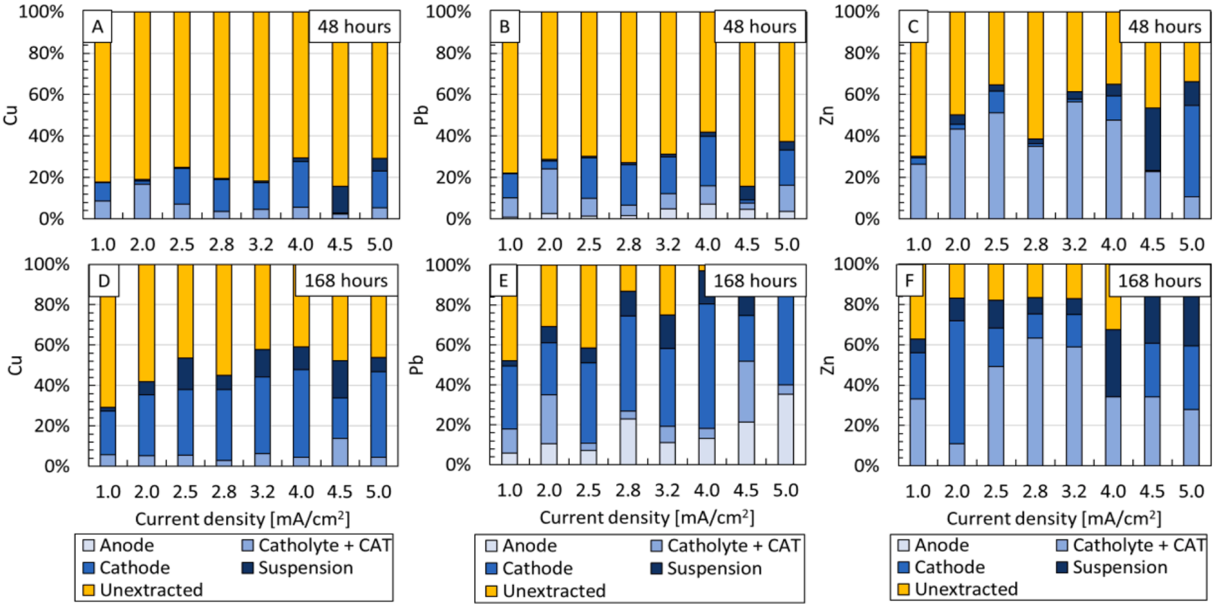

Fig. 8. Distribution of extracted (Anode, Catholyte + CAT (Cation Exchange Membrane), Cathode, Suspension) and unextracted (mine tailing material after ED) Cu (A, D), Pb (B, E) and Zn (C, F) according to current densities for ED experiments with Pb-Zn mine tailings for 48 h (upper) and 168 h (lower).

experiments (168 h) (Fig. 7D–F), where a higher proportion of Cu and Pb (Fig. 7D–E) was found on the *cathode*, illustrating time-dependent precipitation of metals. However, a high proportion of Zn stayed in the solution (*catholyte* + *CAT*) for long-term experiments. This is in accordance with previously observed soluble behavior of Zn in ED experiments with mine tailings (Jensen et al., 2016; Zhang et al., 2019; Peppicelli et al., 2018) and could relate to ZnS' higher solubility than especially PbS (Peppicelli et al., 2018; Moncur et al., 2009). For Pb-Zn mine tailings (Fig. 8), Cu and Pb generally precipitated faster and were found on the *cathode* in both short-term (Fig. 8A–C) and long-term (Fig. 8D–F) experiments. As observed for the Cu mine tailings, Zn favored a soluble state in contrast to precipitation on the cathode. Therefore, further processing and extraction of metals should also consider specific metal solubility when designing ED metal extraction, as, e.g., extraction of soluble Zn can require further processing.

3.4. *The energy consumption of the electrodialytic experiments*

The cumulated energy consumption of electrodialysis (ED) conducted on Cu mine tailings and Pb-Zn mine tailings are shown in Fig. 9A–B, which only considers the electricity used for electrodialysis. The results show that an increase in current density led to an increase in energy consumption, while Pb-Zn mine tailing experiments resulted in higher cumulated energy consumption, especially for experiments above current densities of 4.5 mA/cm^2. For example, Pb-Zn mine tailing experiments lower than 4.0 mA/cm^2 consumed less than 13 kWh/kg, while experiments above 4.5 mA/cm^2 consumed up to 25 kWh/kg. The high current density experiments often experienced increased voltage, accompanied by complications such as dissolved electrodes, frequent pH adjustments of the catholyte or osmotic processes transporting the suspension liquid to the catholyte. These complications and lack of electrode stability made the actual energy consumption uncertain and questioned the stability and accuracy of the results obtained from high current density experiments. In contrast, Cu mine tailings generally had a lower cumulated energy consumption (below 10 kWh/kg), except for one very high 4.5 mA/cm^2 current density experiment. Experiments with current densities above 4.5 mA/cm^2 for both tailings could illustrate a limit for applied current.

The energy consumption per mass of extracted metal is shown in Fig. 10A–F, which illustrates an increase in energy consumption with

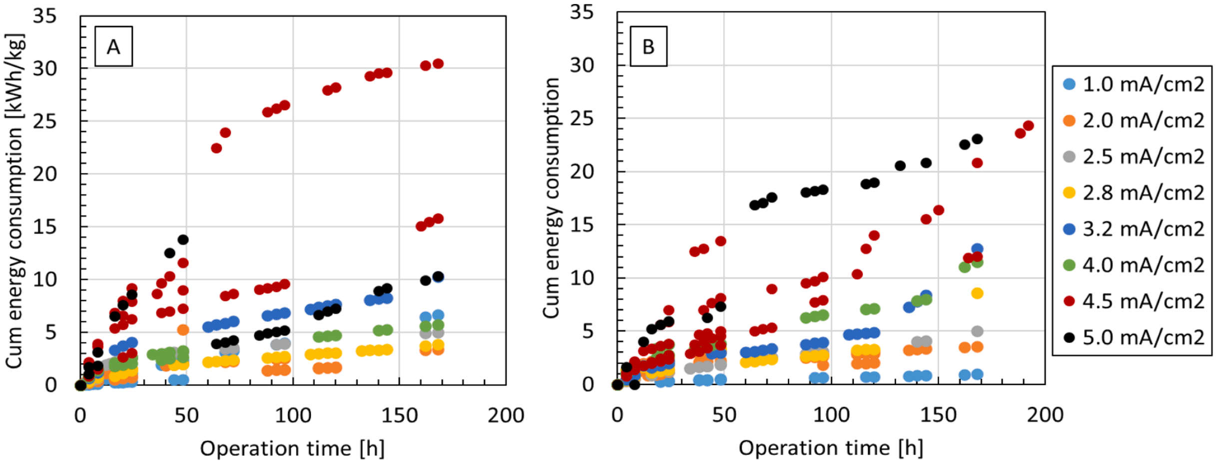

Fig. 9. Cumulative energy consumption per mass of tailing as a function of operation time with A) Cu mine tailings and B) Pb-Zn mine tailings. The experiments are divided into categories of current density. Guidance lines are provided to ease interpretation.

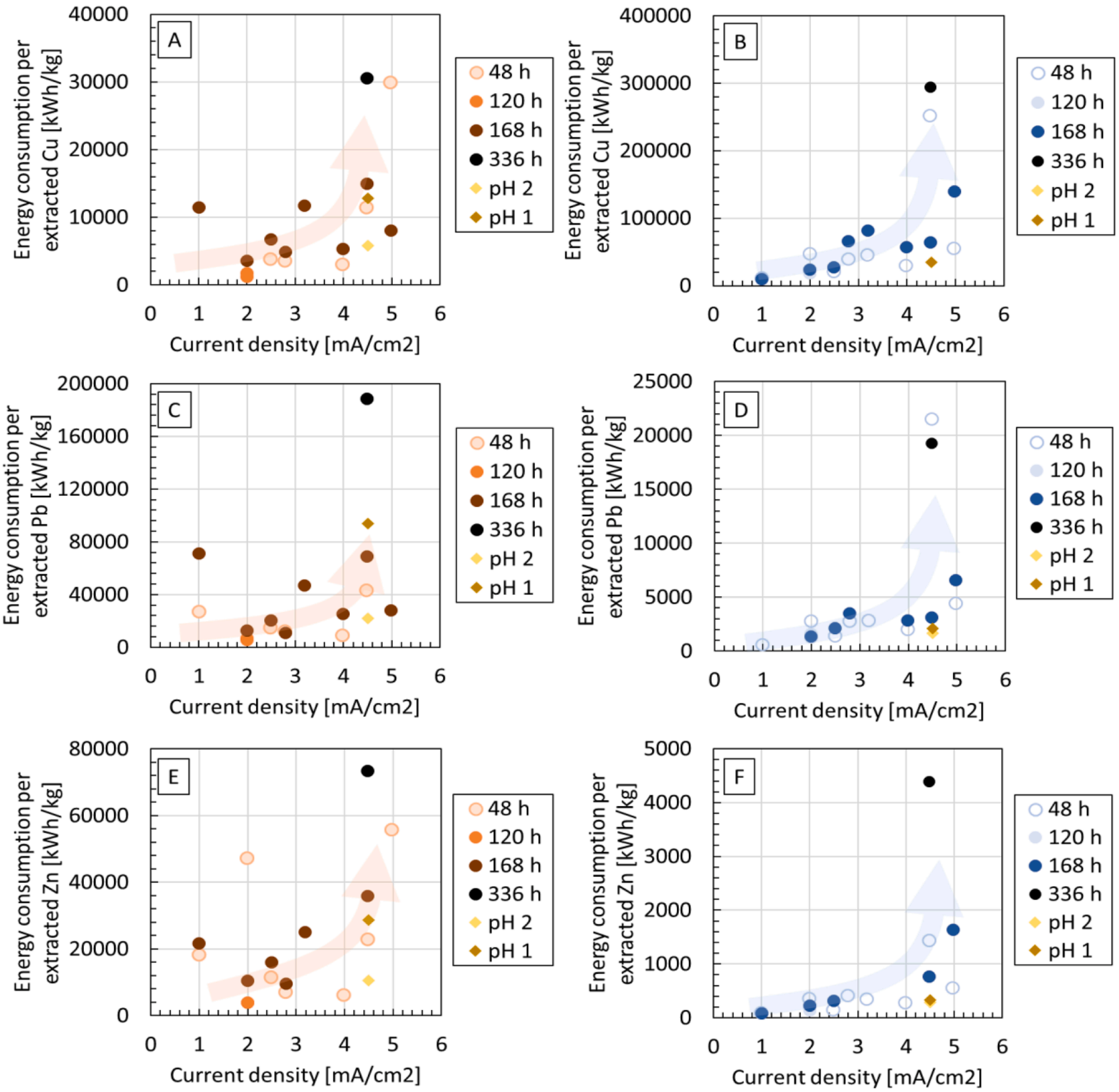

Fig. 10. The energy consumption [kWh/kg] per extracted Cu (A-B), Pb (C-D) and Zn (E-F) with Cu mine tailings (left side: A, C, E) and Pb-Zn mine tailings (right side: B, D, E) as a function of current density. The experiments are divided into categories of experimental operation time. Two additional experiments investigated the effect of before and after acidification of the suspension compartment when pH reached 2 and 1. Guidance lines are provided to ease interpretation.

increasing current density. Concerning specific metals, the energy consumption per extracted unit of Cu is the least for Cu mine tailings, whereas, for Pb and Zn, it is the least for Pb-Zn mine tailings. This is closely associated with the highest metal extractions observed in Fig. 5. Furthermore, long-term experiments (168 h) generally showed a slightly higher energy consumption per metal mass extracted than short-term experiments (48 h). These observations illustrated that while increasing operation time and current density increased metal extraction – to a certain limit, as seen in Fig. 5, the additional metal extraction reached by increasing current density is not necessarily feasible regarding energy consumption. Overall, a preference is given to experiments of lower current densities due to multiple operational challenges in high current density experiments, resulting in higher energy consumptions with limited additional metal extractions achieved.

3.5. *Mine tailing properties after electrodialytic experiments*

After ED, Cu and Pb-Zn mine tailings showed a considerable mass loss (Fig. 2) of 27 % and 57 %, respectively, coupled with a depletion in carbonate minerals (dolomite and calcite). The resulting tailings, rich in quartz, mica, and feldspar, could potentially qualify as aggregate or binder replacement materials in construction applications (Martins et al., 2021; Kiventerä et al., 2020; Simonsen et al., 2020). Rich in aluminum and silicon, these materials may possess pozzolanic or hydraulic properties in cementitious binders or serve as alumina and silica-rich precursors for alkali-activated materials (Kiventerä et al., 2020).

The Pb-Zn mine tailings retained 1 % of their sulfide content throughout the ED process (Fig. 2), indicating an undissolved fraction of sulfides inaccessible to ED. Cu mine tailings still showed undetectable sulfide levels. Although the mineralogical quantification method only provides a composition estimate, the persistent sulfide content could impede the use of the remnant material in construction materials. Sulfide oxidation and subsequent internal sulfate attack in the cement matrix or reinforcement corrosion can degrade concrete (Rodrigues et al., 2012).

ED treatment significantly reduced the remnant materials' nitric acid extractable metal content (Table 3). However, the metal contents exceeded the established limits except for Pb and Zn in Cu mine tailings, which were already below or close to the limits before ED. ED, furthermore, led to increased water solubility of metals by up to 214 times, except for Cu and Pb in Pb-Zn mine tailings (Fig. 3A), where the water solubility met limits for waste reuse. For Cu in Cu mine tailings and Zn in Pb-Zn mine tailings, the increased water solubility was coupled with an increased oxidizable fraction, accounting for 73 % and 82 % of the metal distribution, respectively (Fig. 3B–C). This could be attributed to the mobilization of the reducible phases by ED, while the less accessible phases (residual) were unaffected by the ED treatment (Zhang et al., 2019; Peppicelli et al., 2018). Previous studies have shown similarly increased water solubility of metal after ED (Zhan and Kirkelund, 2021), attributed to the significantly decreased pH, in alignment with decreased solution pH for Cu mine tailings (pH: 4.0) and Pb-Zn mine tailings (pH: 5.4) as shown in Fig. 3A. However, literature reports on alkaline cementitious materials' reduced metal leaching and ED-treated waste materials' improved mechanical performance in concrete products (Ebert et al., 2021; Kirkelund et al., 2014).

4. Conclusion

This study focused on Cu, Pb, and Zn from two sulfide mine tailings using ED in suspension, with optimization of current density and operation time. The findings can be summarized as follows:

- The maximum ED extraction was 70 % Cu from Cu mine tailings, 97 % Pb and 88 % Zn from Pb-Zn mine tailings. Cu extraction was lowest for both mine tailings, compared to Pb and Zn.
- Longer operation times (168 h) and increasing current density increased extraction from Pb-Zn mine tailings due to the breaking of the buffer capacity but reached a threshold for no significant further extraction between 2–4 mA/cm^2, depending on the material. Increasing the operation time beyond 168 h provided limited additional extraction. Cu mine tailings were less dependent on operation time due to a lower buffer capacity, as short and long-term experiments extracted similar contents.
- Although a longer electrodialysis (ED) operation time may be required, the higher levels of water- and ion-exchangeable/weak acid-soluble metals in Pb-Zn mine tailings could account for the increased metal extraction, highlighting the influence of material and metal properties on ED efficiency.
- While Zn exhibited the highest extraction in acidic conditions according to the pH-dependency of metal solubility test, Pb was more extractable with ED, suggesting that factors beyond acidification influence metal extraction with ED.
- The final pH of the tailing suspension showed a clear correlation with metal extraction, increasing with a lower final pH.
- Metal distribution in the ED changed with operation time, where Cu and Pb precipitate with time while Zn favors a soluble state, which may require further processing, highlighting the metal dependence on ED.
- The energy consumption increased with operation time and current density and could not equal the higher quantity of the metals extracted, which could support a limit for extraction regarding energy consumption. Cu mine tailings exhibited lower energy consumption due to their carbonate-poor composition.
- ED-treated mine tailings, particularly carbonate-reduced and Si- and Al-rich, could find use in construction applications. However, the presence of unoxidized sulfides, metal contents exceeding limits, increased water-soluble metals and pH reductions necessitate further testing for construction materials.

In summary, ED treatment of mine tailings offers a promising metal extraction technique, but careful consideration of factors such as mine tailing properties, metal content and mobility, experimental parameters, energy consumption, and potential applications of the treated materials is crucial. Further research and optimization are essential for fully realizing ED's potential in resource recovery.

CRediT authorship contribution statement

Anne Mette Tholstrup Bagger: Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Kristine Bondo Pedersen:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Formal analysis, Conceptualization. **Henrik Hansen:** Writing – review & editing, Validation, Resources, Formal analysis, Conceptualization. **Wolfgang Kunther:** Writing – review & editing, Validation, Supervision, Formal analysis, Conceptualization. **Pernille Erland Jensen:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mineng.2024.109023.

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