NOVA SCHOOL OF
SCIENCE & TECHNOLOGY

DEPARTAMENTO DE
ENGENHARIA CIVIL

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Mestre em Engenharia do Ambiente, Perfil de Engenharia Sanitária

DOUTORAMENTO EM ENGENHARIA CIVIL

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Recovery of mining residues for eco-efficient mortar production

To my family and friends,

"When you can't look on the bright side,
I will sit with you in the dark."

- Lewis Carroll -

Preface

This thesis is submitted as partial fulfilment of the requirements for the Doctoral Degree in Civil Engineering. The present Ph.D. project includes the results of the work performed from September 2017 to June 2021 at NOVA School of Science and Technology (FCT), NOVA University Lisbon (NOVA), and at National Laboratory for Civil Engineering (LNEC). The research work has been developed in collaboration with the Department of Civil Engineering (DEC) and the Department of Environmental Sciences and Engineering (DCEA, at RESOLUTION Lab, CENSE - Center for Environmental and Sustainability Research) from FCT NOVA, and the Department of Materials from LNEC. This Ph.D. work was supervised by Professor Paulina Faria (DEC-FCT NOVA), and co-supervised by Professor Alexandra B. Ribeiro (CENSE-DCEA-FCT NOVA) and Doctor António Santos Silva (Department of Materials, LNEC).

This research work is part of the EcoCoRe (Eco-Construction and Rehabilitation) Doctoral Program in Civil Engineering, sponsored by *Fundação para a Ciência e a Tecnologia*, Portugal (research grant PD/BD/135170/2017). The research was also supported by the European Union's Horizon 2020 project e.THROUGH - Thinking rough towards sustainability, from the Marie Skłodowska-Curie program (grant agreement 778045).

The work developed throughout this thesis is structured as follows:

Part I - The achievements from the appended publications are compiled to present the most important data and introduce the methodology developed. Part I contains a broad introduction and description of the Ph.D. project plan, the statement of the research goals and a summary of the main contributions attained from the scientific documents submitted and published during the research period. Part I also aims to sequentially present the topics dealt within the Ph.D. project, and clarify the existing links between the peer-reviewed scientific research works submitted or published.

Part II - The peer-reviewed scientific publications submitted or published during the Ph.D. project, including journal articles, book chapters and conference contributions, are presented following a sequence by the topic covered. As the first author of such publications, I hereby declare that I provided the major contribution to the research and experimental work developed, results interpretation, preparation and writing of the publications submitted during the Ph.D. project.

Monte da Caparica, 15th June 2021

Joana Almeida

Acknowledgements

> *"The secret, dear Alice, is to surround yourself with people who make your heart smile.*
> *It is then, only then, that you will find Wonderland."*
> *- Lewis Carroll -*

I would like to express my deep gratitude to my supervisors, Professor Paulina Faria, Professor Alexandra B. Ribeiro and Doctor António Santos Silva. I thank you for the constant encouragement and support throughout my research journey, which have helped me to a very great extent to accomplish all the tasks from my Ph.D. work plan.

As all the support and understanding is important in times of need, I am also grateful to several professionals that were essential to meet deadlines and to promote the development of the work. Hence, I would like to acknowledge:

- Engineer Manuel Pacheco, from Panasqueira mine, for the availability to provide the working samples of mining residues;
- Carla Rodrigues and Nuno Costa, from REQUIMTE, for the ICP-OES and GC-TCD analysis;
- Dora Soares, Ana Paula Menezes, Fátima Menezes and Idalina Silva, from the Department of Materials, LNEC, for their support in the laboratory work, TGA/DTA analysis and various administrative issues;
- Professor Luís Baltazar and Engineer Vítor Silva, from DEC-FCT NOVA, for the TGA/DTA analysis and the support during mortars campaigns, respectively;
- Professor José Mirão, from the Hercules Laboratory, for his assistance during XRD analysis;
- Doctor Eduardo Mateus from CENSE-FCT NOVA, for the help with analytical methodologies;
- Engineer António Galvão from CENSE-FCT NOVA, for the support with life cycle assessment procedures;
- Professor Susana Barreiros, Doctor Alexandre Paiva and Doctor Rita Craveiro, from the Department of Chemistry, FCT NOVA, for providing deep eutectic solvents mixtures and their characterisation;
- Doctor Olga Paredes, from SIMARSUL - Grupo Águas de Portugal, for sewage sludge samples and their characterisation.

This thesis was only possible with the willingness and continuous help of many people. Therefore, I would like to extend my sincere thanks to the RESOLUTION Lab team. A special thanks goes to Paula

Guedes, Nazaré Couto, Cátia Santos, Joana Dionísio, Flávia Freitas and João Brinco. I want to thank to Tânia Santos, Adriana Silva, Carolina Martínez Garcia, Alessandra Ranesi and Eleonora Cintura for all the insights and good mood during this period. Also, a special thanks goes to Frederico Martins for the support and availability. Moreover, I am deeply grateful to Cátia Magro. Her prompt inspirations, timely suggestions, kindness, enthusiasm and dynamism were a blessing during my Ph.D. journey.

A big thanks goes to my family and friends, for always supporting and stand by me.

The present work has received funding from the European Union's Horizon 2020 research and innovation program under Marie Skłodowska-Curie grant agreement No. 778045, and from *Fundação para a Ciência e a Tecnologia*, Portugal, through the support given to CENSE with the strategic project UIDB/04085/2020 and my Ph.D. fellowship PD/BD/135170/2017 from the EcoCoRe Doctoral Program. This research was anchored by the RESOLUTION Lab, an infrastructure at NOVA School of Science and Technology.

Abstract

Raw materials are essential for human well-being, although their production, consumption and end-of-life are causing increasing environmental burdens. The Panasqueira mine has been operating for more than one century, being the main threat to its activity and for the surrounding ecosystem the disposal of significant amounts of old mining residues that contain substances of environmental concern. On the other hand, tungsten, considered a critical raw material, can be recovered from Panasqueira mining resources. In the construction sector, cement is one of the main contributors for greenhouse gas emissions and is the main binder used in mortar and concrete production. Hence, a partial replacement of this binder by secondary mining resources may bring economic, social, technical and environmental benefits. Efficient technologies to remove and recover elements from environmental matrices may promote safe storage and reuse. The electrodialytic (ED) treatment has demonstrated successful results on the removal of inorganic and/or organic contaminants from a wide range of resources. Thus, to address the challenges in climate change and environmental degradation issues, in both mining and construction sectors, the present work aimed at assessing the feasibility of applying the ED technology to mining residues for (1) the recovery of critical raw materials and the hydrogen that is inherently produced; (2) the removal of harmful compounds; (3) the production of a suitable matrix for further reuse in cementitious construction materials, and (4) the minimization of environmental impacts in the materials life cycle. The main results of the work developed demonstrated that the reuse of mining residues can decrease the consumption of primary resources and promote improvements in the sustainability of the industries involved, without high investments. Through the ED treatment, tungsten could be recovered in 22%, while the removal of arsenic may achieve 63%. The hydrogen produced can be recovered with 74% of purity. The production of cement-based mortars, replacing cement by treated mining residues, revealed similar performances to conventional mortars. Although a higher cement substitution percentage (50% volume) have caused some deterioration in mechanical resistance, the mortars produced demonstrated compatibility with current applications, as bedding mortars and fired brick masonry walls. The life cycle analysis also proved that the mortars produced allow impact mitigation in several environmental categories, namely in global warming potential, supporting the circular economy of sustainable construction products.

Keywords: mining residues; electrodialytic treatment; critical raw materials; construction materials; life cycle assessment; circular economy

Resumo

As matérias-primas são fundamentais para o bem-estar humano, embora a sua exploração, consumo e fim de vida causem crescentes problemas ambientais. As minas da Panasqueira encontram-se em funcionamento há mais de um século, correspondendo a deposição de grandes quantidades de resíduos mineiros antigos, que contêm substâncias de preocupação ambiental, uma ameaça à sua atividade e ao ecossistema envolvente. Por outro lado, o tungsténio, considerado como matéria-prima essencial, pode ser recuperado dos recursos mineiros da Panasqueira. No setor da construção, o cimento é um dos principais responsáveis pelas emissões de gases com efeito de estufa, e o principal ligante utilizado na produção de argamassas e betões. Neste caso, a substituição parcial deste ligante por recursos mineiros secundários pode trazer benefícios económicos, sociais, técnicos e ambientais. Tecnologias eficientes para remover e recuperar elementos de matrizes ambientais podem promover um armazenamento e reutilização seguros. O tratamento eletrodialítico (ED) tem demonstrado resultados promissores na remoção de contaminantes inorgânicos e/ou orgânicos de uma ampla gama de recursos. Assim, para enfrentar os desafios das alterações climáticas e as questões de degradação ambiental no setor mineiro e da construção, o presente trabalho teve como objetivo avaliar a viabilidade da aplicação da tecnologia ED a resíduos de minas para (1) recuperação de matérias-primas essenciais e do hidrogénio que é inerentemente produzido; (2) remoção de compostos perigosos; (3) produção de uma matriz adequada para posterior reutilização em materiais de construção cimentícios e (4) minimização dos impactes ambientais no ciclo de vida dos materiais. Os principais resultados do trabalho desenvolvido demonstraram que a reutilização de resíduos de minas pode diminuir o consumo de recursos primários e promover melhorias na sustentabilidade das indústrias envolvidas, sem investimentos elevados. Através do tratamento ED, o tungsténio pode ser recuperado em 22%, enquanto a remoção de arsénio pode atingir os 63%. O hidrogénio produzido pode ser recuperado com 74% de pureza. A produção de argamassas com a substituição parcial do cimento por resíduos de minas tratados revelou desempenhos semelhantes às argamassas convencionais. Embora uma maior percentagem de substituição de cimento (50% volume) tenha provocado algum deterioramento nas resistências mecânicas, as argamassas produzidas demonstraram compatibilidade com aplicações atuais, como argamassas de assentamento e paredes de alvenaria de tijolo. A análise de ciclo de vida provou ainda que as argamassas produzidas permitem mitigar impactes em diversas categorias ambientais, nomeadamente no potencial de aquecimento global, apoiando a economia circular de produtos de construção sustentáveis.

Palavras-chave: resíduos mineiros; tratamento electrodialítico; matérias-primas essenciais; materiais de construção; análise de ciclo de vida; economia circular

Abbreviations

As	Arsenic
Al	Aluminium
Al_2O_3	Aluminium Oxide
BOD_5	Biological Oxygen Demand in 5 Days
$Ca(OH)_2$	Calcium Hydroxide
CO_2	Carbon Dioxide
COD	Chemical Oxygen Demand
CRM	Critical Raw Materials
Cu	Copper
DES	Deep Eutectic Solvents
DOC	Dissolved Organic Carbon
ED	Electrodialytic
EU	European Union
Fe	Iron
GC-TCD	Gas Chromatography - Thermal Conductivity Detector
H_2	Hydrogen
$H_2PO_4^-$	Dihydrogen Phosphate
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
KOH	Potassium Hydroxide
LCA	Life Cycle Assessment
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
Na_2SiO_3	Sodium Silicate
P	Phosphorus
SiO_2	Silicon Dioxide

Sn	Tin
SO_4^{2-}	Sulfate
TGA/DTA	Thermogravimetric Analysis/ Differential Thermal Analysis
Ti/MMO	Titanium/ Mixed Metal Oxide
TOC	Total Organic Carbon
W	Tungsten
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

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Part I

"Nothing in life is to be feared, it is only to be understood."

- Marie Curie -

1.Introduction

In the mining industry, during the extraction of ores and minerals, extremely fine particles are rejected from the grinding, screening or processing of the raw material. These residues are typically slurried into large impoundments [1]. Additionally, ore resources are gradually becoming limited. Tungsten (W) is one of the 30-critical raw materials (CRM) in the European Union (EU), once its scarcity started being felt throughout Europe [2]. W is used to produce hardmetal and metal carbide powder that can be further treated by powder metallurgical methods for hardmetal tools production [3]. In Portugal, the Panasqueira mine is the only operating unit where W extraction is still active [4].

The reuse of secondary mining resources can be the key for a sustainable construction sector facing overexploitation of primary resources, whilst contributing for a circular economy. This is encouraged due to the high amount of available mining residues and other related environmental risks [5]. Such approach also creates opportunities to recover CRM, save energy and provide a platform for innovative technologies, increasing Europe's competitiveness in the global marketplace. Secondary resources play a central role in the minimization of climate change effects, contributing towards a zero-carbon economy and climate resilient society [6].

Cement is the second most consumed substance on the planet, after water, and its exploration is one of the main causes of greenhouse gas emissions [7]. About 10% of the global emission of CO_2 is due to provision of construction materials of which cement accounts approximately 85% [8]. The production of cement releases emissions due to raw materials extraction, transport and calcination of raw marl for clinker production and milling [9].

Cement production in Europe has increased at an annual rate of 1.5% during the past decade [10]. To revert this impact, the European Commission targeted to reduce 90% of the emissions from the building sector until 2050, in line with the EU climate action and the European Green Deal [11]. This effort implies the reformulation of many building materials and products, whereby cement could be partially replaced with economic, technical and environmental benefits, according to the United Nations Sustainable Development Goals 9 (industries, innovation and infrastructure) and 11 (sustainable cities and communities) [12]. In particular, Portugal reported a cement consumption of more than 3,000,000 t in 2019 [13].

Advances in solid waste management resulted in new construction materials as a substitute to traditional materials and products, such as bricks, blocks, tiles, aggregates, ceramics, binders and timber [14]. The use of mining residues as secondary raw materials could have potential applications in the construction field, promoting recovery of CRM and channeling by-products back into the value chain. Nonetheless, secondary materials may have harmful compounds that must be removed or neutralized to avoid environment and public health risks. The electrodialytic (ED) technology has been developed to remove and recover a wide range of substances of environmental concern and economic interest, from liquid and solid matrices. This process is based on the application of a low-level direct current intensity, through pairs of electrodes, to promote the movement of species [15].

The most common cement application is in concrete production, being this product crucial for the resistance of several building structures, foundations and other constructions [16]. Nevertheless, mortars are also cement consuming and constitute important products to produce masonry walls, shape layers, set waterproof, regularization and finishing surfaces, in new constructions and in the rehabilitation of existing buildings [17]. One of the top leaders of the national cement market has two mortars facilities in Portugal with a full production capacity of 120,000 t/year [18].

Mortars can be applied as masonry mortars to produce concrete blocks, layer masonry units [19], to re-point masonry joints, to coat wall and ceiling surfaces, as plasters (applied indoors) or renders (outdoor applications) [20], and used on floors as screeds. The exposed applications are more prone to aging and, therefore, such mortars need frequent repairs and replacements when the coatings are no longer fulfilling their functions [21]. During the last decades, mortars' growth was not only caused by a large increase in production, but also due to the need to follow technological advances and final products requirements. The progress in mortars was leveraged by the implementation of new companies, the growth of existing markets and the diversification on products range [22].

The Portuguese mortar production has been mainly focused on traditional mortars (78%), followed by stabilized (20%) and dry (2%) mortars [22]. Traditional mortars are mainly formulated with mineral binders and aggregates. The formulation of mortars can involve more than one type of binder or aggregate and can also include additions and admixtures. The binder can be clayish earth, gypsum, lime or cement [23]. The most common gypsum construction product in Portugal is hemihydrate gypsum, produced at around 120 °C. Limes can have hydraulic properties or not, in the case of air limes, and are produced at approximately 900 °C. Limes release CO_2 during calcination of limestone but capture CO_2 during hardening by carbonation [24]. The most common cement used worldwide is Portland cement, although other cement types may be produced, all with heating temperatures higher than 1000 °C and low CO_2 capture when hardening, in comparison to lime [25]. Different binders produce mortars with distinct technical and environmental performance [26].

On the other hand, aggregates can be raw materials, from quarries, or residues from other industries [27]. Fillers and pozzolanic additions may be also included in formulations to increase mortar compactness, mechanical characteristics and durability [28]. Pozzolans are natural or artificial fine materials that in contact with water react with calcium hydroxide ($Ca(OH)_2$), acquiring hydraulic properties. These fine materials can partially replace the binder content in construction products. Examples of common artificial pozzolans are: fly ashes from thermoelectric plants, silica fume, rice husk ashes or thermally treated clays, such as metakaolin [29]. Nowadays, pozzolanic cement is one of the most commercialized type of cement and is produced adding a pozzolan, e.g. fly ashes [30]. However, as thermoelectric plants are closing, the cement industry is actively seeking for pozzolanic alternatives to fly ashes.

Climate emergency is a powerful motor for innovation and one of the main motivations in this Ph.D. project. Hence, this work aimed to develop an eco-efficient strategy to produce cement-based mortars by incorporation of Panasqueira mining residues as a cement replacer. Other by-products from the energy and minerals industry, that are currently disposed of as waste, have been the focus of research into reuse opportunities, namely as supplementary cementitious materials in concretes and mortars [31].

The novelty of the present work is the combination of the ED process with assisting agents to assess the recovery of CRM, the removal of substances of environmental concern and the clean energy production, during the treatment of mine tailings, and its reuse on eco-efficient cement-based mortars. In this sense, the study of a treatment approach with the ED process was carried out, aiming also the removal of harmful elements, CRM recovery and energy savings. The purpose of such strategy is to increase the added value of mining residues and turn them a suitable resource to be reused in the construction sector, with similar or improved properties compared to traditional materials.

In this context, on Part I, the research project is addressed outlining the interdisciplinary nature of the work, involving civil engineering, materials, chemistry and environmental sciences knowledge. First, an overview on mining residues applicability in construction materials production was conducted [32], and on the Panasqueira mine dynamics and its secondary resources potential [33]. Subsequently, regarding the ED technology and its sustainability, several electrochemical reactors designs for arsenic (As), W and other elements extraction were optimized [34], including the use of deep eutectic solvents as assisting agents in ED systems [35], hydrogen production and its recovery during the ED process [36], and wastewater resources enhancement for hydrogen production and CRM recovery [37]. Then, the study of the pozzolanic potential of treated Panasqueira mine resources [38], followed by the analysis of the effect of the incorporation of mining residues treated with the ED process, [39] or ED coupled with a thermal treatment in cement-based mortars [40], were discussed. Finally, the environmental benefits of mortars with mining residues [41], and the corresponding life cycle assessment evaluations were addressed [42]. This included analysis of data needed from raw materials acquisition to waste management scenarios [43], and discussion of the impacts related to mortar production from mining residues.

The study about the feasibility of the ED process to add value to mining residues and provide suitable matrices to reuse in construction materials, with improved or similar properties to traditional materials, justified the present research. This work aimed to develop an optimized strategy to produce eco-efficient mortars by incorporation of treated mining residues. At the same time, it also targeted the recovery of CRM and energy, and the removal of harmful compounds, by application of the ED technology. The Ph.D. work topics and goals are summarized in Figure 1.

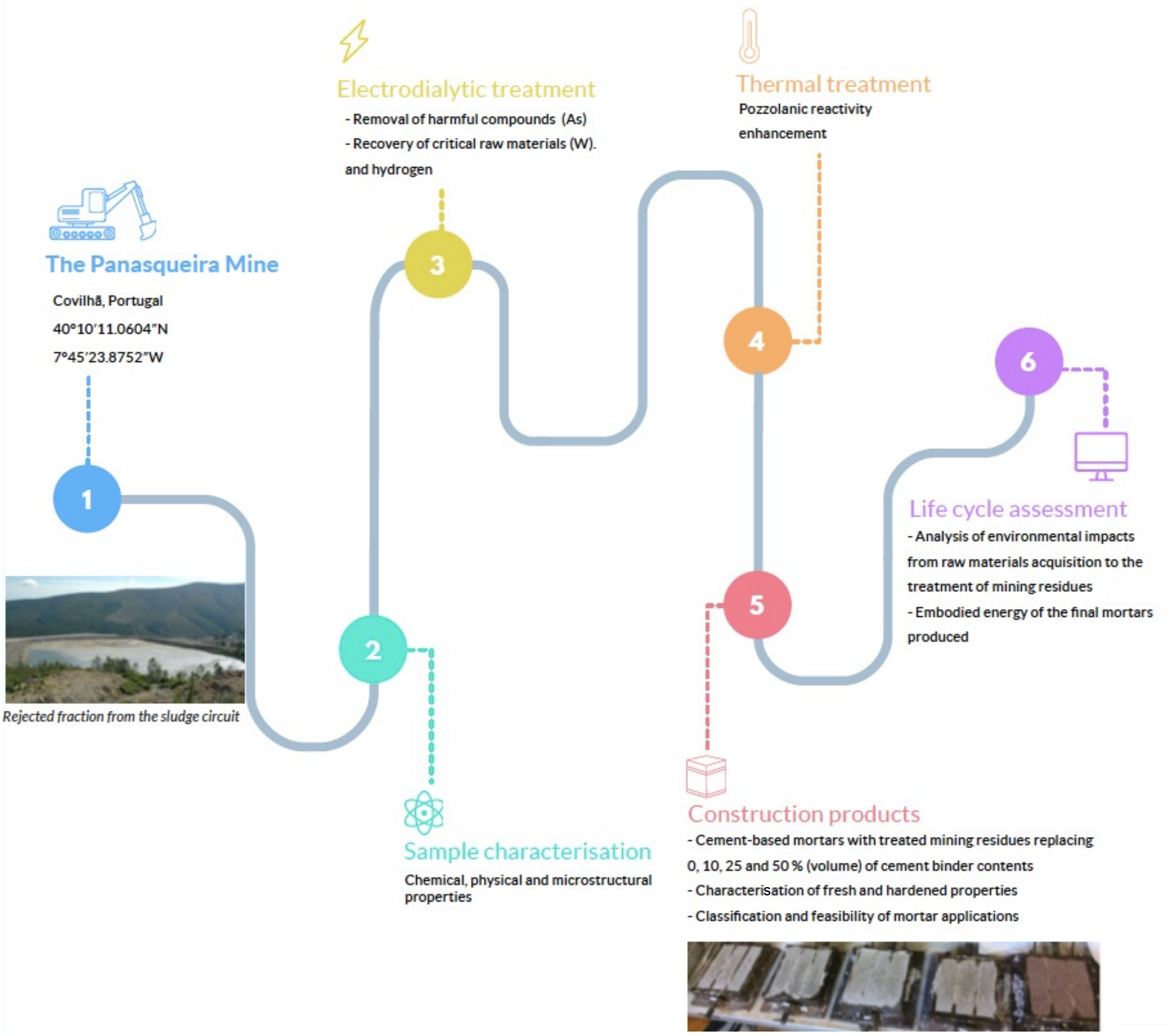

Figure 1. Topics addressed in the Ph.D. project and main goals.

Firstly, a characterisation of the raw samples was performed, using different analytical techniques to detect and quantify the existing minerals and elements. To assess whether the ED process is efficient for the recovery of CRM (namely the fraction with particles below 45 micrometer, that is the main challenge for the Panasqueira mine), and the removal of harmful elements from the matrix. Thus, ED studies were performed under different conditions, in order to optimize the highest As removal and W recovery.

Furthermore, mortars were produced with treated mining residues as cement binder substitutes, in different proportions (10%, 25% and 50% volume). After the initial characterisation of mining residues, mortar sample analysis was carried out to obtain data related to physical, mechanical and microstructural properties from the combination of mining residues with other constituents, as cement, sand and water. This analysis made it possible to conclude about the most efficient quantities of by-product to replace the original material and current feasible applications for the eco-mortars produced. To evaluate the technical potential of the mortars produced, parameters at both fresh and hardened state were studied: workability, porosity, density, compressive and flexural strength, dynamic modulus of elasticity, thermal conductivity, mineralogy and microstructure, water absorption by capillarity, drying capacity and lixiviate toxicity.

In parallel, strategies to turn the whole process more sustainable and to alleviate negative impacts were tested. Thus, the recovery of self-produced hydrogen and the use of assisting agents to enhance the ED process, as deep eutectic solvents and secondary resources from wastewater treatment, were considered and studied.

Finally, an evaluation of the environmental impacts of the processes involved from raw materials acquisition to mortar production was performed, according to ISO 14040 [44] and ISO 14044 standards [45].

Summing up, the main goals and contributions of the work presented herein were:

- To characterise relevant materials through their chemical, mineralogical and physical parameters;
- To deep the knowledge about the ED process and its potential for self-energy production, As removal and W recovery from mining residues;
- To find the most efficient constituents’ mixture and ratio of mining residues incorporation in cement-based mortars;
- To turn mortar production more sustainable, namely through the incorporation of ED treated mining residues to replace cement;

- To analyse environmental impacts of the processes involved and of the final mortars, through a life cycle assessment.

3.Research brief

A major problem in the construction sector is the overexploitation that primary resources are facing nowadays, combined with its significant impact in the environment, namely for global warming potential. Besides playing a central role in the minimization of climate change effects, secondary resources should be well characterised and properly managed for further applications. Applying mining residues in the production of construction materials alleviates waste disposal and use of primary resources. However, a main concern is the presence of hazardous compounds in secondary mining resources. These elements may leach or promote the occurrence of radioactive materials, which may present a threat to mining sites.

Additionally, mining residues contain contents of important raw materials. Since W is one of the 30-CRM considered in the EU [2], a prior W recovery would bring significant advantages. W recovery may contribute to decrease the exploitation of more mine ores and to reduce dependence from outside Europe countries. Also, the production of hydrogen, an enabler of the clean energy transition, and its recovery during the ED process, could be a way to decrease the energy drawbacks of this strategy and empower the maturity level of the ED technology. To promote construction and rehabilitation in benefit of sustainability, it is imperative to decrease the use of materials from primary resources.

The sequential methodology and the main results of the Ph.D. research are summarized in the four following subsections, 3.1 to 3.4.

3.1 Mining residues potential in construction products and resources availability

The reuse of secondary resources decreases waste generation, landfill disposal and primary resources overexploitation. These steps are crucial, not only to provide a cleaner production, but also to maintain a competitive EU industry by using resources efficiently and developing a circular economy [11]. Thus, to understand the potential of mining residues incorporation in construction materials, an overview was conducted and published in the Journal of Building Engineering [32], also addressing barriers for full-scale application (document A1 in Part II).

The research status on mining residues reuses in construction products, based on the Scopus platform (January 2020), demonstrated an increasing trend on scientific papers publication during the last decade. Up to date, there are more than a thousand scientific documents published on this matter since 1969. Generally, research has been mostly focused on energy-efficient construction products.

In this context, geopolymers were the base of many research studies performed for cementitious products due to the reduced amount of greenhouse gas emissions. Geopolymers, that result from the combination of an activator, aluminosilicates and water, also demonstrated advantages in stabilizing hazardous compounds in mixtures with mining residues, avoiding leaching phenomena [46].

The reuse of W mining wastes into innovative alkali-based materials for road pavement applications [47], red clay bricks [48] and light weight construction products [49] have also proved to be useful assets for the construction sector. Parameters like mechanical strength, thermal stability, chemical and fire resistance could be improved when mining wastes are combined in the products formulation. Cost comparisons also showed that alkali activated cementitious materials are one of the most cost-efficient repair solutions. However, the need of strong bases as reagents has been pointed out as the main environmental and economic constraint of this approach [50].

The development of innovative polymer-based composite materials from non-contaminated mining residues appears to be an important strategy, as referred in the literature review [51]. These materials demonstrated suitable properties and potential for conservation, restoration and/or rehabilitation of historic monuments, sculptures, decorative and architectural interventions or as materials for building coatings. Ceramic tiles can also be produced taking advantage of mining residues, namely with iron ore residues, due to its red-orange colour and other chemical and physical properties [52]. Iron ore residues can be applied as aggregates in manufacturing of unfired bricks, such as adobe, extruded or compacted earth blocks [53]. Mining residues have also been used to partially replace raw aggregates in road pavement applications [54].

In particular, the application of W mining residues as cementitious materials, activated by thermal and chemical methods, may improve chemical and structural stability of mortars. This technique is effective for stabilizing and solidifying heavy metals, particularly when used with commercial granulated blast furnace slag. However, minimal replacement percentages of cement by mining residues (5% by mass) were reported as effective for materials production [55].

Furthermore, construction products are exposed to environmental conditions during their lifetime and, consequently, may release harmful compounds. In the construction field, the ED process proved to be an efficient pre-treatment for hazardous elements removal in a wide-range of solid environmental matrices, and physical and chemical properties improvement [56]. The pre-treatment of mining residues using this technology may lead to chemical, physical and microstructural changes that could improve the final material and promote higher ratios of mineral binder replacement.

The significant mineral resources availability is the main strength for the reuse of mining residues in construction products. This represents an opportunity for the development of innovative eco-efficient methods in the construction sector. In this sense, regions rich in mineral resources play an important strategic role in Europe. Since the mining residues selected for the present work are from the Panasqueira mine, a review on this mine industry development, concerning W exploration and building materials production from Panasqueira resources, was published [33] as a book chapter in Electrokinetic Remediation for Environmental Security and Sustainability, edited by John Wiley & Sons, UK (document A2 in Part II).

The Panasqueira mine, located in the Central region of Portugal, begun W exploration in 1896 and is described as the largest tin (Sn)–W deposit (wolframite) of Western Europe. The W market downturns had influenced the dynamic of the plant over the years, regarding the optimization of mechanical processes. The current production is estimated in around 900 t of W with a concentrate grade of 75% WO_3, representing one of the best W products available on the global market [4].

The extraction and processing in the Panasqueira area has generated two types of residues: (1) coarse waste-rock tailings from rock blasting and (2) waste-mud tailings transferred into mud dams (Figure 2). These rejected fractions have been accumulated for a long time and it is estimated that 8,200,000 m^3 of mining residues are disposed of as waste. Besides landscape deterioration, the piles formed with mining waste are instable and prone to landslide, susceptible to be eroded and to leach harmful compounds [57].

Figure 2. Rejected fraction of the sludge circuit at the Panasqueira mine (Covilhã, Portugal).

Bearing in mind the high amount of local mining resources and their environmental impacts for the Panasqueira region, the production of construction materials started to be assessed. In particular, the W mine waste mud was used to produce geopolymeric binders with dehydroxylated mining waste, $Ca(OH)_2$, NaOH (as activator) and waterglass solutions [58].

The research on geopolymers optimization coupling the incorporation of other reagents and wastes was also conducted. W mining waste was combined with red clay brick waste, with improvements in compressive strength [48]. Together with W mining waste, waste glass and metakaolin, several precursors were tested to produce alkali-activated foams, such as aluminium (Al) powder [59]. Aiming the enhancement on compressive strength and microstructure of hybrid alkaline binders, W mining waste mud was combined with other mixtures, concentrations and liquid-solid ratios of alkaline activator solutions (e.g., Na_2SiO_3, NaOH, KOH and waste glass powder dissolved in NaOH).

The feasibility of reusing waste-rock piles from the Panasqueira mine was studied, aiming the development of a polymer-based composite material [51]. This type of material has potential for technical and artistic applications in rehabilitation as building coatings and conservation of sculptures. Panasqueira secondary resources as aggregates were successfully applied as refractory lining in foundry of non-ferrous metals [60]. Also, cementitious grouts for the road industry were formulated with milled glass and Panasqueira waste mud [61].

Generally, the Panasqueira mine resources were broadly tested in geopolymeric and alkali-activated products. Minimal research has been conducted considering the incorporation of the Panasqueira mining residues in other construction products. In this sense, the present work could be the beginning of further relevant alternatives for Panasqueira residues uses in construction materials.

3.2 Electrodialytic treatment of mining residues

3.2.1 Electrodialytic reactor assessment

W is a transition metal with density comparable to gold, being essential for the manufacture of a wide range of products. W presents high modulus of compression, wear resistance, tensile strength and thermal and electrical conductivity [62]. For these reasons, W is mainly applied for cemented carbide production in the mining, construction and metal-working industries. Other important W uses are alloying in steels [63]. However, W primary sources, ore bodies from scheelite and wolframite, are becoming gradually limited, being W included as a CRM in the EU list [2]. In Portugal, the Panasqueira mine has been active for around 130 years and is one of the largest Sn - W deposits in Europe, with 9,700,000 t of ore resources [64]. Therefore, the ED technology could have an important role in the removal and recovery of elements from Panasqueira residues (secondary resources), in particular below the 45 micrometer fraction that is a current challenge for the mine.

In this context, the ED process was primarily tested as a strategy to tackle the demand of W resources by their recovery from mining residues. Since the Panasqueira mine resources have considerable amounts of As and contents of other raw materials, as copper (Cu) and Sn, the extraction of these elements was also studied. Therefore, a preliminary approach to validate the applicability of the ED treatment to the Panasqueira residues was conducted, resulting in a Master thesis supervised by the candidate [65] and a paper [34] published in Science of the Total Environment journal (document A3 in Part II).

The ED experiments were performed using different ED cell design configurations, such as 2 and 3-compartment reactors (2C and 3C), current intensities between 50 and 100 mA, operation times from 4 to 14 days, and sample suspensions with NaCl or secondary treated effluent. Additionally, control experiments with no current application were carried out. Figure 3 presents a 2C ED system.

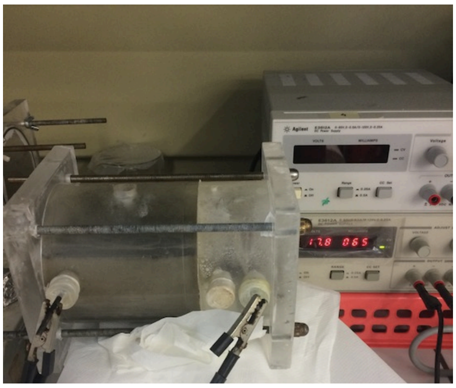

Figure 3. Electrodialytic treatment of mining residues in a 2-compartment reactor.

Regarding the target compounds on the Panasqueira samples, As, a harmful metalloid, presented the highest concentration, 3743 ± 471 mg kg^{-1}, compared to the contents of Cu, 1790 ± 202 mg kg^{-1}, Sn, 75 ± 8 mg kg^{-1}, and W, 488 ± 88 mg kg^{-1}. The presence of salts and other elements, namely Fe and SO_4^{2-}, may influence ions mobility due to uncharged complexes generation, affecting elements´ extraction by the ED process. Also, the presence of chlorides in the ED system may lead to the formation of active chlorine (oxidant agent). Generally, elements desorption from mining residues were higher at pH values below 2, due to their chemical speciation.

Mining residues are characterised by low conductivity (0.3 mS cm^{-1}). When a 2C reactor design was tested, the conductivity of the sample compartment tended to increase, due to the generation of free ions in the media, which was advantageous for current passage and, consequently, for the ED performance. A voltage decrease tendency was verified, due to the decrease of the internal resistance in the reactor along the experiments. When mining residues were placed in the central compartment (3C design), the current passage was not facilitated due to the low conductivity of the sample, being unfeasible to operate the process according to the time set. Considering this limitation, mining residues were treated in a 3C reactor design adding NaCl as supporting electrolyte. Also, 2C reactor designs were tested using secondary treated effluent instead of tap water for the preparation of the sample suspension.

After the 2C ED experiments, As presented the highest mobility, with predominant As extraction observed towards the anode (between 14 and 19%). The increment of the current intensity promoted As speciation. In the liquid phase, 60% of As was solubilized and traces of Cu (0.3%), Sn (0.3%) and W (0.1%) were detected. The results showed that a 3C reactor operating at 100 mA, with NaCl as supporting electrolyte, presented the highest extraction of Cu (13%), Sn (10%), W (13%) and As (63%).

The improvement of the ED performance targeting the Panasqueira mine residues was achieved by adding NaCl and secondary treated effluent, particularly to As. For Cu, Sn and W, other adjustments were studied to increase their extraction efficiencies (see Section 3.2.2).

3.2.2 Assisting agents

Deep eutectic solvents (DES) are natural extractants composed by a hydrogen bond donor and a quaternary ammonium or metal salt. They are considered the solvents of the XXI century, and successful results in the extraction of metals from environmental matrices have been reported. Advantages of using DES have been pointed out in relation to conventional ionic liquids, namely due to lower costs and toxic issues [66]. In this sense, the use of natural DES during the ED process was tested as a sustainable method to improve elements separation during the ED treatment, particularly for W. A study was published in Science of the Total Environment journal [35] (document A4 in Part II).

To screen W and As extraction efficiencies from mining residues, this study tested four DES with different physical and chemical properties: (1) choline chloride/ malonic acid (1:2); (2) choline chloride/ oxalic acid (1:1); (3) choline chloride/ latic acid (1:2) and; (4) propionic acid/ urea (2:1). DES containing carboxylic acids, as oxalic acid, malonic acid, lactic acid or propionic acid have a pH below 2, being more able to dissolve metals and metal oxides [67]. In addition, the application of current intensities of 50 and 100 mA was analysed in single and 2C reactors, during 4 days.

The addition of DES decreased the suspension pH to values below 2, promoting enough ionic conductivity (up to 2.0 mS cm^{-1}) to maintain the current intensity set for the period of 4 days. The results demonstrated that coupling natural DES in a 2C ED set-up could enhance the extraction of W from the Panasqueira mine secondary resources. DES with choline chloride presented the highest average extraction values, being choline chloride with malonic acid (1:2) more selective for As and choline chloride with oxalic acid (1:1) more effective for W.

DES composed by choline chloride may have promoted W complexation. In addition, the properties of the bidentate oxalate ion may have contributed to form oxalates complexes with W, since oxalic acid may react with the solubilized Fe^{2+} (that is in wolframite composition), promoting tungstate ions available in solution. Arsenic compounds may also be decomposed and stabilized by chloride ions. Comparing choline chloride/oxalic acid (pKa=1.46), the most acidic DES in the study, with choline chloride/malonic acid (pKa=2.8), the second has lower values of viscosity, which may have improved mass transfer phenomena in the As case. On the other hand, oxalic acid may had been consumed to form complexes with other elements (e.g., Cu, Fe), losing its buffer capacity and resulting in a faster/higher pH increase when compared to the pH behavior in the choline chloride/malonic acid case, that is faster with a current intensity of 100 mA.

The use of choline chloride with oxalic acid at 100 mA promoted the extraction from the matrix of approximately 22% of W and 35% of As. From the total W and As extracted, 77% and 82%, respectively, were successfully removed from the matrix compartment, as they electromigrated to the anolyte compartment. From the anode end, these elements can be further separated and potentiate circular economy.

Following the work developed for ED optimization in terms of CRM extraction, wastewater resources were introduced in the preparation of sample suspensions to assess element separation and decrease tap water uses. A study was published in the Water journal [37] using sewage sludge and secondary effluent during the ED treatment of mining residues (document A5 in Part II).

While mining residues have contents of W, sewage sludge can be regarded as a secondary resource of phosphorus (P), that is also included in the CRM EU list [2]. Secondary effluent has limited P contents (approximately 3 mg L^{-1}), since standards for wastewater treatment plants impose a removal above 75% of P for further disposal [68], contrarily to sewage sludge, that is enriched in P (around 66 mg L^{-1}). Mining residues also have amounts of P (approximately 37 mg kg^{-1}). Thus, the ED extraction was analysed for both P and W critical elements.

Sewage sludge showed a higher P content after the experiments. During tests, the pH turned to 6 in the central compartment at 50 and 100 mA, and in this range $H_2PO_4^-$ is the predominant form in suspension, being P more available in the media. Phosphorus availability can be limited by Fe and Al at acidic pH, reducing the amount of water-soluble P components, while increasing the amount of insoluble Fe and Al phosphates. At alkaline pH and in the presence of calcium, phosphates can form calcium phosphates and precipitate. When mining residues suspension were prepared with sewage sludge, there was a significant decrease of P in the final sample (32 mg P kg^{-1}; extraction of 71%). Phosphorus may form bonds with sulfur (phosphorus sulfides), chloride ions (phosphorus chloride) and calcium (calcium phosphates) that are present in the mining residues samples.

When mining residues suspensions were prepared with sewage sludge, W showed the highest extraction ratio (62%). This may have occurred due to W complexation with P (tungsten phosphides, WP) and calcium. This achievement can empower critical elements circular economy while mitigating environmental impacts of waste disposal from wastewater treatment plants and mining industries.

3.2.3 Hydrogen recovery

ED technologies are clean-up processes based on the application of a low-level direct current to produce electrolysis reactions and electrochemically-induced transport of contaminants [15]. As a consequence, these treatments inherently produce electrolytic hydrogen at the cathode compartment [69]. Hydrogen has currently a prominent role as an enabler of the clean energy transition, and technologies coupling hydrogen production may take advantage of the market expansion. Aiming to improve the overall sustainability of the ED process and regarding the EU targets defined for renewable energy share in energy consumption (up to 32% by 2030 [70]), the hydrogen produced during the ED treatment was studied. A proof of concept was developed and published [36] in Applied Energy journal (document A6 in Part II).

In this work, hydrogen production during the ED treatment in a 3C reactor, at 50 and 100 mA, was studied for three environmental matrices: (1) briny water; (2) effluent and; (3) mining residues. The rate of gases formed at the cathode compartment was measured until 30 mL and the hydrogen purity was analysed. Additionally, a proton-exchange membrane fuel cell was connected to the cathode, where energy conversion from chemical into electrical was assessed.

During the treatment of all matrices, hydrogen was produced, faster at 100 mA, with purities between 73 and 98%. Following these results, the electrical costs of the ED treatment could be reduced up to 7% (for the studied conditions). A proton-exchange membrane fuel cell evaluated the electrical energy generation from hydrogen production at the cathode, showing a stable output of approximately 1 V (maximum capacity of the fuel cell).

Following the work developed for the recovery of self-produced hydrogen during the ED process, the combination of wastewater resources with mining residues was also tested for hydrogen production. In this sense, the study published in Water journal [37] also considered the use of sewage sludge and secondary effluent for hydrogen production during the treatment of mining residues (document A5 in Part II).

Herein, the hydrogen produced during the ED treatment of sewage sludge and mining residues suspensions (coupled with secondary effluent or sewage sludge), at 50 and 100 mA, was also assessed in 3C reactors. The experiments demonstrated that hydrogen was generated in all tested cases, with purities between 33% (sewage sludge) and 71% (mining residues suspension with effluent). Competitive cathode reactions may affect the hydrogen purity in sewage sludge due to its complex composition.

A proton-exchange membrane fuel cell was connected to the cathode compartment and achieved an electrical energy generation from self hydrogen produced of 1.2–1.4 V in all experiments. The hydrogen generated can reduce electrical energy requirements from 5 to 8%, namely in terms of strategies concerning electrochemically induced transport. Additionally, if brine water is replaced by secondary effluent in mining residues suspension, the voltage of the proton-exchange membrane fuel cell increase, improving its stability. A higher conductivity was detected due to the higher amount of free ions in the system, that directly affects the fuel cell efficiency [69].

This research shows there are new possibilities for energy saving and hydrogen production for different purposes in the ED treatment, leading to an increase in the sustainability and applicability of electro-remediation or decontamination.

3.3 Treated mining residues as construction material

3.3.1 Pozzolanic reactivity

Pozzolans are natural or artificial fine materials that can partially replace cement in mortars and concrete. The high content on amorphous silica and/or alumina turn the materials able to react with calcium hydroxide ($Ca(OH)_2$) in the presence of water, generating products with cementitious properties [29]. Although the ED process and natural DES are well-documented clean-up processes for metals extraction from solid matrices, there is a research gap in their potential to improve the reactive properties of mining resources.

In this context, the modified Chapelle test, that is included in the French standard NF P 18-513 [71], was applied to measure the total quantity of fixed $Ca(OH)_2$ by amorphous siliceous or aluminosilicates constituents in 1 g of mining residues samples (Figure 4). The pozzolanic reactivity of mining residues was measured before and after the ED process, under several ED tested conditions, and a paper with the main achievements was orally presented at the Remine International Conference (RICON19) and published [38] in the KnE Engineering journal (document A7 in Part II).

Figure 4. Modified Chapelle test configuration applied to mining residues.

This study proved the feasibility of using different treatment steps to increase the pozzolanic reactivity of the Panasqueira mining residues. The amount of quartz and muscovite are an evidence of the abundant SiO_2 and Al_2O_3 presence in these mining residues, which corroborates the potential for the application of mining residues in the construction sector.

However, without pre-treatment, SiO_2 and Al_2O_3 are in a crystalline form and not able to react with $Ca(OH)_2$ to increase the reactivity and, consequently, the durability of the products. Thus, the possible role of the ED treatment and natural DES to increase the reactivity of residues from the Panasqueira mine was assessed. A milling step and a thermal treatment at 800 °C and 950 °C during 1 h, followed by cooling at room temperature, was also coupled.

The total amount of fixed $Ca(OH)_2$ by amorphous siliceous or aluminosilicates substances from 1 g of raw mining residues was reported as 8 mg. Mining residues treated with the ED process consumed 71 mg of $Ca(OH)_2$, and when ED was coupled with thermal treatment a total of 548 mg of $Ca(OH)_2$ was fixed. The results showed that it is possible to increase the reactivity of the initial sample, although the values achieved are still 17% under the limit stablished by the NF P 18-513 to be considered as pozzolanic [71].

The highest pozzolanic potential was obtained when the sample was treated in an ED system with choline chloride/malonic acid (1:2), followed by a milling step and a thermal treatment at 950 °C. Following this achievement, the treatment selected for the typology of mining residues incorporated in mortar production was a 2C ED reactor design with choline chloride/ malonic acid (1:2) at 50 mA, during 4 days.

3.3.2 Mortar production

Urban areas will face challenges in their sustainable development, once the world population is expected to reach 10,900 M by 2100 (from the current 7,000 M) and more infrastructures to serve inhabitants will be needed [72]. Concrete manufacture commonly involves Portland cement binders, as cement-based mortar production, that is one of the main contributors for greenhouse gas emissions [73]. In this sense, research has focused on the development of sustainable cementitious products to replace conventional cement uses.

To decrease primary resources uses within the construction industry, cement-based mortars with ED treated mining residues were produced. The study of their fresh and hardened properties was performed, and an article was published with the developed work [39] in the Cleaner Engineering and Technology journal (document A8 in Part II).

In this work, the application of ED treated mining residues in construction products, namely their effects on mechanical properties in comparison to raw residues and cement, was addressed. Mortars were produced with cement replacement percentages of 0, 10, 25 and 50% (volume), based on a proportion of binder, aggregate and water of 1:3:0.5, according to EN 196-1 [74]. The same water-binder ratio was maintained in all formulations to compare the effect of the water added on the mechanical and microstructural characterisation of mortars. A cement CEM II/B.L 32.5 N [75] was used in the formulations, since it is the most commercialized in Portugal. Mortar cure was performed in a water bath for 28 days, as presented in Figure 5.

Figure 5. Mortars produced with mining residues during the water cure.

Mining residues seemed to have permeability and surface properties that imply the requirement of higher amounts of water to achieve the same consistency as when using only cement. Once no adjuvants were applied during the formulation to maintain a similar workability as the reference, the mechanical performance was, thus, affected. Mechanical performance decreased between 11 and 30%, when 10% of mining residues were incorporated in the formulation. As expected, this decrease was more pronounced with the increase of mining residues content replacing cement. Furthermore, capillarity absorption and drying capacity were studied as a preliminary durability assessment. The increase on mining residues incorporation corresponded to a rise on capillary absorption, justified by mortar porosimetry, and that could be controlled by higher drying rates.

However, considering all the properties analysed, tested mortars showed mechanical and physical properties suitable for rendering, plastering, joint repointing, bedding masonry or screed uses. The use of the waste-based mortars, which have lower thermal conductivity, can result on building elements with higher thermal resistance. This can be attractive to applications as masonry bedding mortars, to shape layers in flat roofs or as renders (although with increasing influence with thickness). These applications are crucial to ensure comfort and decrease both energy consumption and related costs [76]. Considering the classification for rendering (and plastering) mortars from EN 998–1 [20], mortars with mining residues may be classified according to their compressive strength at 28 days as CS III for 25 and 50% of cement replacement (between 3.5 and 7.5 MPa) and CS IV for 10% of cement replacement (> 6 MPa). On the other hand, from EN 998–2 [19] (classification of bedding mortars for masonry units layering), mortars with mining residues can be classified in classes M5 (50% of cement substitution) and M10 (between 10 and 25% of cement substitution). In addition, considering screed applications and the classification from EN 13813 [77], mortars with mining residues range classes from C5 to C12 (between 5 and 12 MPa).

The results showed that the ED technology could be applied as a pre-treatment for mining residues since physical and mechanical mortars' properties were not deteriorated when compared with mortars formulated with raw mining residues. The use of the ED treatment promotes the previous removal of harmful compounds and recovery of CRM, providing a more sustainable working material. Mortars produced with ED treated mining residues are environmental friendlier and, considering the overall product lifecycle, can alleviate the negative impacts associated to their production, when compared to pure cement or cement-raw residues mortars.

Furthermore, the combination of different treatment steps may improve elements removal and changes in physical-chemical properties from mining residues. In this sense, and following the previous work, the incorporation of ED plus thermal treated mining residues in cement-based mortars was studied in terms of its technical and economic feasibility. The study of their physical, chemical and microstructural properties was performed and an article was published [40] in the Construction and Building Materials journal (document A9 in Part II).

Mining residues were treated combining the ED process with a thermal procedure, with a set temperature of 950 °C during 1 h and room temperature cooling. The thermal treatment parameters were defined based on previous tungsten mine sludge studies [78]. Herein, the cement content in mortars was also replaced in 0, 10, 25 and 50% (volume). A microstructural analysis of mortars was performed, as well as the study of their fresh and hardened state properties.

The mineralogical composition of mortars produced with ED plus thermally treated mining residues validated the compatibility of this material with cement mortars, and the removal of elements. Once more, the mortars were subjected to mechanical tests (Figure 6) and the same trend was observed, since the increase in the replacement level of cement by treated mining residues decreased flexural and, more pronounced, compressive strength. However, comparing to the reference mortar, this decrease was less accentuated when the residues incorporated were only submitted to the ED process (3 to 52% for flexural strength and 44 to 79% for compressive strength). Since most mortar applications require relatively low compressive strength, the studied mortars showed properties compatible with conventional contemporary concrete block and fired brick masonry walls.

Figure 6. Flexural strength test performed to the mortars produced with mining residues.

An improvement in the initial water absorption was observed when 10% of mining residues ED plus thermally treated were incorporated in mortars, since a similar asymptotic value to the reference was achieved, but at a slower rate. The cost effectiveness analysis also validated the feasibility of treated mining residues reuse in cementitious mortars, namely considering applications where flexural strength is a key factor.

Additionally, to complement the durability assessment, a leaching analysis of the mortars was performed according to EN 12457-1 [79], with slight modifications. The liquid-solid ratio was taken as 2, mixing 10 g of mortar (after milled) and 20 mL of deionised water. The suspensions were placed for 24 h on a shaking table, at room temperature. The suspensions were filtrated in vacuum through a 0.45 μm filter and the elements concentration in the filtrate were determined by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). The results are presented in Table 1. The As concentration in the leachate, that is the element of higher environmental concern, is lower than the acceptable limit of 1 mg L^{-1} [80], corroborating the safe applicability of mortars produced with mining residues. The mechanical mixture between cement and contaminated matrices, and heavy metals immobilization by encapsulation, sorption and precipitation, are the main mechanisms involved in solidification/stabilization by cement materials [81].

Table 1. Leachates results of mortars with mining residues.

		Leachates (mg L^{-1})			
Mortar	Cement replacement (% volume)	As	Cu	Sn	W
Reference	0	< D.L.	< D.L.	< D.L.	< D.L.
Raw mining residues	10	0.005 ± 0.002	0.063 ± 0.008	< D.L.	0.022 ± 0.008
	25	< D.L.	0.076 ± 0.002	< D.L.	0.018 ± 0.001
	50	0.003 ± 0.001	0.063 ± 0.006	< D.L.	0.017 ± 0.001
ED mining residues	10	0.005 ± 0.001	0.053 ± 0.013	< D.L.	0.014 ± 0.003
	25	0.003 ± 0.001	0.045 ± 0.005	< D.L.	0.019 ± 0.000
	50	0.002 ± 0.007	0.037 ± 0.005	< D.L.	0.015 ± 0.003
ED and TT mining residues	10	0.003 ± 0.007	0.045 ±0.017	< D.L.	0.013 ± 0.002
	25	0.002 ± 0.001	0.043 ± 0.007	< D.L.	0.015 ± 0.004
	50	0.002 ± 0.001	0.088 ± 0.011	< D.L.	0.092 ± 0.008

D.L. – Detection Limit; SD – Standard Deviation; ED- Electrodialytic treatment; TT-Thermal treatment

3.4 Life cycle assessment of processes and final products

3.4.1 Impacts of mining and electrodialytic processes

The current decrease on ore grade have prompted the assessment of existing mining resources, energy needs and mining residues environmental impacts in a life cycle overview. These approaches not only play an important role on supporting cleaner production, resources management and decision-making in the mining industry, but also in identifying new business opportunities. The ED process proved to be a feasible method to alleviate the impacts of rejected fractions from mining activities. Nevertheless, technologies already known in key sectors will need to demonstrate that they can work at a larger scale. Research and development will also reduce costs of breakthrough technologies and help new products to be competitive in the market [11].

In this sense, the trade-off between raw material extraction from secondary mining resources and the environmental harmfulness of mining residues after the ED process was studied through a life cycle assessment (LCA) approach. A research on potential environmental impacts resulting from the application of the ED technology to the Panasqueira rejected fraction was conducted and published [43] in the Sustainability journal (document A10 in Part II).

To assess the activities from the mining sector and gather data on technical and environmental issues, three waste management scenarios were considered for the rejected fraction from the W concentrate production at the Panasqueira mine: (1) ED treatment with DES as assisting agent (according to the findings reported in Section 3.2.2); (2) ED treatment with simultaneous hydrogen recovery (based on data from the work presented in Section 3.2.3); (3) ED treatment with sodium chloride as assisting agent (considering the results from the research work described in Section 3.2.1).

The major impacts of mining processes are due to material handling and grinding. These steps presented the highest energy consumption and, consequently, CO_2 release (0.35 kg t^{-1} ore). Regarding aquatic systems, the chemical parameters with higher impacts are chemical oxygen demand, COD (4.15×10^{-3} kg t^{-1} ore), biological oxygen demand in 5 days, BOD_5 (2.08×10^{-3} kg t^{-1} ore) and total organic carbon, TOC (1.54×10^{-3} kg t^{-1} ore).

Furthermore, an upscale approach of the ED reactor was developed. ED data obtained at a bench scale was used to estimate the potential environmental burdens involved in an ED plant conception. One of the main limitations in applying ED technology is energy consumption. However, the threats in the Panasqueira area are mainly related to resource management [82], where the ED technology could have a central role on its minimization, namely in terms of As content (63% of removal). The mine has a project for more 30 years [57], meaning that new market segments could be explored to keep the development and the requalification of the Panasqueira area. Considering a circular economy perspective, the recovery of W (22%) and the hydrogen self-produced (purity=74%) from the ED treatment of mining residues seemed to be relevant.

Additionally, based on the scenarios analysed, a sequential ED facility was presented, with a total investment estimated in approximately 51,000 EUR, increasing to 1 and 7 million EUR, respectively in the first and fifth year, due to maintenance and operational costs.

3.4.2 Mortars and materials embodied energy

Products demand will also depend on consumer choices driven by ongoing transformations, as environmentally friendly products. Data on carbon and environmental footprints of products should be more transparent to support consumers on their decision-making [11].

In this way, a simplified assessment on the environmental benefits of cement mortars produced coupling mining residues was submitted to the 2nd International Conference on Sustainable, Environmental Friendly Construction Materials - ICSEFCM 2021 and published [41] in the conference proceedings (document A11 in Part II).

The annual production of cement in Portugal reported in 2019 was around 3,000,000 t [13]. Considering the formulations tested in the present work, with properties more similar to the reference product, an estimate of cement production savings was determined based on the conservative 10% of cement replacement by mining residues. Thus, if hypothetically up to 10% of cement could be avoided due to the reuse of mining residues in cementitious products, savings in cement production of 300,000 t would be achieved in Portugal, whilst minimizing the same amount of mining waste disposal.

For the carbon footprint, the manufacture of 1 t of cement yields 0.471 t CO_2 [83]. Assuming this emission impact, a lower cement production (less 10%) would promote the decrease of 141,300 CO_2 t in Portugal, which is equivalent to 60,128 EU households annual electricity needs, considering that 1 EU house has a carbon footprint equivalent to an average of 2.35 t CO_2 [84].

On the other hand, LCA is an approach with few decades of development and application, although this methodology has matured over the years, being now an important tool to measure the impacts of construction materials [85]. In this sense, before applying an LCA methodology to determine the impacts of mortars produced with mining residues, a review to deepen the knowledge on the potential and drawbacks of LCA of mortars was conducted and published [42] in the Construction and Building Materials journal (document A12 in Part II).

The research status on mortar LCA, based on the Scopus platform (October 2020), demonstrated an increasing trend on scientific papers publication during the last decade. Up to date, there are more than 100 scientific documents published on this matter since 1998, focused mostly on cement-based composites.

LCA is a broad tool in terms of methodologies and quantification of impacts [86]. However, there is still lack of studies regarding the impacts of mortars. Typically, global warming potential is an impact category considered in many studies reviewed. Nonetheless, other impact categories such as ozone depletion, eutrophication and abiotic resource depletion potential are also frequently considered in LCA studies.

The use of alternative materials, namely secondary resources, as a replacement or addition to conventional raw materials in mortar manufacture, may represent an environmental benefit that can be quantified using LCA [87]. The LCA methodology presents drawbacks, namely the use of subjective criteria, limitations on scientific knowledge about impacts, lack of a consolidated method, data access and analysis difficulties. This could be overcome by the presentation of a clear and uniform LCA report with all the information needed to reproduce the study. The update and further development of specific databases for mortars with real data could improve LCA studies, while decreasing uncertainties and variabilities. In addition, an economic analysis could complement the assessment by addressing the cost-effectiveness of products.

Following these premises, the sustainability of mortars produced with mining residues was determined based on an LCA approach. The research conducted was published in Applied Sciences journal (document A13 in Part II).

The environmental impacts resulting from the production of 1 t of mortars with mining residues were determined based on: (1) abiotic depletion; (2) global warming; (3) ozone depletion; (4) photochemical ozone creation; (5) acidification; (6) eutrophication potential. A reference mortar (100% of cement binder) and mortars with cement volume substitutions in 10, 25 and 50% by raw, ED treated and ED plus thermal treated mining residues were used as study cases.

The environmental burdens were firstly analysed in terms of mitigation potential from mining residues applications, comparing to conventional mortar production with cement. The application of 50%

replacement ratios of cement by mining residues, as binder, could decrease the global warming potential in 49%, considering a release of 1.08 x 10^2 kg CO_2 eq. by the reference mortar.

The environmental pressures from mining residues disposed directly at mining sites, ED treated and ED plus thermal treated, before their reuse in mortars manufacture, were assessed. The application of a treatment to mining residues strongly contributed to alleviate ozone depletion, photochemical ozone creation and acidification potentials (up to 94%). In fact, the avoided mining residues discharges were key factors for such decreases, together with the lower use of cement in the mortar formulation.

Finally, the contribution of all mortar components and respective management scenarios for the mortar life cycle was evaluated. The aggregate fraction demonstrated higher impact in ozone depletion, where 2.55 x 10^{-7} kg CFC-11 eq. are released from the production of 1 t of mortars. On the other hand, the type of binder used demonstrated different environmental performances. ED mining residues showed higher percentual representativity (above 52%) in ozone depletion (3.03 x 10^{-7} kg CFC-11 eq.) and photochemical ozone creation (1.11 x 10^{-2} kg ethene eq.), whereas the combination of thermal treatment with ED mining residues contributed to the abiotic depletion potential in almost 100% (2.51 x 10^{-1} kg Sb eq.). However, the fossil fuels needed for the thermal treatment increased the resources required, promoting a higher impact for abiotic depletion than cement (1.58 x 10^{-4} kg Sb eq.).

Although other stages should be considered to a broader quantification of mortar embodied energy (e.g., construction, use and end-of-life phases), this study provided new insights on decision-making tools for future developments.

4.Conclusions

4.1 Final remarks

The climate emergency is a top priority in the European Green Deal. This ambitious set of action initiatives is playing a crucial role on the environmental balance of the planet, from cutting greenhouse gas emissions, to investing in leading-edge research and innovation. Raw materials recovery and recycling will be particularly important for the sectors where new dependencies might emerge, namely for high resources consuming industries. While research has mostly been focused on energy-efficient technologies, residues minimization and reuse strike as equally importance in a context of primary resources scarcity. In this sense, the development of sustainable systems accomplishing the valorization of secondary resources is now gaining attention in several fields.

Mining residues are characterised by their strong environmental pressures, namely due to the generation of high amounts of rejected fractions from concentrate production. Nevertheless, these mining residues can be regarded as a secondary resource of: (1) elements considered critical by the European Commission, as W, and (2) raw materials potentially reused in the construction industry.

In this Ph.D. project, the ED process was tested to improve the sustainability of the Panasqueira mining residues. The use of the ED process suggested new possibilities for the recovery of CRM and the removal of harmful compounds from secondary mine resources. The addition of assisting agents, as deep eutectic solvents and secondary wastewater resources, and the recovery of the hydrogen produced during the ED treatment, proved the economic and environmental feasibility of this strategy. The improvement in the extraction of elements from Panasqueira mine residues and energy savings during the ED process was achieved. Herein, renewable hydrogen can replace fossil fuels as a feedstock for industrial processes and improve the attractiveness of the ED technology in the market.

The use of mining residues in the manufacture of construction products can contribute to decrease primary resources consumption, as well as to improve the properties of the final products without high investments. The construction sector is seeking for innovative alternatives for material production, where new composites that can replace energy intensive materials are desired. Thus, in this work, cement-based mortars were produced with mining residues treated with an ED technology, also coupled with a thermal procedure. The thermal treatment was tested as a method to improve the pozzolanic properties of the residues and diversify their application, eventually as a pozzolanic material that could tackle fly ash scarcity, concerning cement and concrete industries.

In this context, mortars were produced replacing cement binder contents by treated mining residues in 10, 25 and 50% (volume). Extensive characterisation of physical, chemical and microstructural properties of the mortars was performed. The analysis of mortar behavior corroborated their compatibility with current applications, such as on contemporary concrete block and fired brick masonry walls, and also their economic feasibility.

By the incorporation of secondary resources in material production it will be possible to close loops and provide optimized, competitive, economic and lower embodied energy products. In this sense, the advantages and limitations of mortar production with treated mining residues concerning their environmental impacts were quantified based on a LCA approach. Mortars with mining residues demonstrated positive performances concerning the decrease of global warming potential (approximately 50 %), as well as in other environmental categories. These findings supported the reuse of secondary resources in the roll out of more sustainable construction products.

4.2 Future developments

Mining industries have been stimulated to operate in a more sustainable way, through the improvement of resources management. In this sense, continuous optimization of eco-efficient processes and alternative scenarios to direct waste disposal of rejected fractions are essential. Besides the cross-cutting edge topic of the research conducted in this Ph.D. project, there is still lack of knowledge that could and should be further investigated.

Considering the application of the ED process to mining residues, further adjustments on the ED system could overcome the low electromigration rate observed for raw materials, namely for Cu, Sn and W. The study of the complexes formed in the solution, that may inhibit the migration of the elements inside the reactor, should be deeply explored to support the development of an optimized ED set-up. Additionally, for the hydrogen self-produced during the ED treatment, the competitive cathode reactions and gases that may affect hydrogen purity should be analysed in future works.

The ED plant conception gives an overview on technical, environmental and economic aspects. However, there is not yet full understanding of its behavior at a larger scale. This conception should be based on a pilot study, since the upscaling effect of the strategy developed in the present Ph.D. work may improve the process, its cost and the market knowledge. Also, the heterogeneity of mine resources in terms of physical-chemical properties should be considered in the development of an ED facility.

Regarding the construction field, treated mining residues seem to have permeability and surface properties that imply the requirement of higher amounts of water to achieve mortars with the same consistency as when using only cement. In further studies, the influence of different water contents on the properties of mortars and on the corresponding types of applications should be addressed. To optimize mortar properties, expand the application range and increase mining residues replacement ratios, natural additives and admixtures (e.g., reused oils) could be tested. On the other hand, since ED plus thermally treated mining residues have demonstrated pozzolanic reactivity potential, water curing optimization may be needed to enhance the pozzolanic reaction in mortars. In future works, the influence of humid curing (without water immersion) should be studied as well as a broader characterization in terms of durability assessment.

Furthermore, the thermal treatment itself should be optimized to assess if pozzolanic properties can be improved. This could be particularly important to cement and concrete industries, since they are seeking for pozzolanic alternatives to fly ash from thermal plants, that are now scarce and tend to disappear in Europe.

A larger ED treatment facility would allow the treatment of higher volumes of secondary mining resources. The properties heterogeneity of mining residues from different areas of the Panasqueira mine after the ED treatment should be studied. This will also be important to enlarge the characterisation of mortars, namely in terms of further durability assessment.

The cost effectiveness analysis validated the feasibility of treated mining residues reuse in cementitious mortars. However, further studies should be conducted to assess more comprehensively the technical and environmental potential of using mortars with mining residues at an industrial scale, and to quantify more precisely the impacts of both ED and thermal treatment applications. In addition, to tackle water scarcity, the reuse of secondary liquid matrices to replace tap water usage in the manufacture of precast construction products, such as concrete blocks, could be studied.

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Part II

“Only those who attempt the absurd can achieve the impossible.”

- Albert Einstein -

Scientific journal article

A1 Overview of mining residues incorporation in construction materials and barriers for full-scale application

J Almeida, AB Ribeiro, A Santos Silva & P Faria

Published in Journal of Building Engineering (2020)

This article was published in Journal of Building Engineering, Vol 29, J Almeida, AB Ribeiro, A Santos Silva & P Faria, Overview of mining residues incorporation in construction materials and barriers for full-scale application, 101215, Copyright Elsevier (2020).

Journal of Building Engineering 29 (2020) 101215

Contents lists available at ScienceDirect

Journal of Building Engineering

journal homepage: http://www.elsevier.com/locate/jobe

Overview of mining residues incorporation in construction materials and barriers for full-scale application

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ARTICLE INFO

Keywords:
Construction product
Secondary resource
Alkaline activation
Artificial pozzolan
Electroremediation

ABSTRACT

Resources efficiency regarding the decrease of residues generation and disposal are important steps towards a cleaner production in the construction and mining industry. Minning processes generate huge amounts of residues, and some deposits have accumulated them over hundreds of years, causing environmental and public health problems. However, mining residues can be recovered as secondary supplies for construction materials production due to its physical, chemical and microstructural properties. This study presents a critical review on sustainable strategies researched to introduce mining residues in the construction sector. The gaps and barriers of these strategies and final products are discussed, concerning a safe and sustainable inclusion of mine residues in construction materials production.

1. Introduction

The importance of improving building energy performance for saving energy and enhancing construction sustainability has been widely recognized [1]. Urbanization has become an increasingly critical issue as 55% of the world population lives in urban areas and this figure is predicted to keep growing up to 68% by 2050 [2]. This scenario will imply a larger consumption of raw materials to produce construction products.

Traditional construction is commonly cement-based, such as concrete and some mortars. Concrete is the second most consumed substance on Earth, after water, and its exploration is one of the main causes of greenhouse gas emissions [3]. About 10% of the global emissions of CO_2 are due to construction materials production, where cement accounts approximately for 85% [4].

To revert this negative impact, the European Commission (EC) targeted to reduce construction sector emissions by 90% until 2050 [5]. A compulsory inclusion of a minimal percentage of residues replacing raw materials on constructions may be a feasible way to achieve EC goals. That means reformulating many construction products, depending on the region and type of applications. Cement contents and raw materials could be fully or partially replaced by secondary resources, turning the construction products eco-friendlier and with lower embodied energy.

In the mining sector, during the extraction of ores and minerals, residues such as extremely fine particles are rejected from the grinding, screening or processing of the raw material. These residues are typically slurried into large impoundments [6]. The reuse of these secondary resources is highly encouraged due to the amount of its generation and the economic and environmental costs associated to its management [7]. Furthermore, from these residues it may be possible to extract significant contents of (critical) raw minerals particularly from old mine residues that have been explored by aged technologies.

However, mining residues may contain harmful compounds, such as heavy metals that are commonly prone to leach [8]. Strategies to remove or neutralize these elements are also important to optimize the use of mining residues with different compositions. The literature dealing with mining residues' incorporation in the production of construction products is diverse in terms of the type of mining residues and its composition. Safe mine residues incorporation to produce construction products can become a key factor for a sustainable construction sector facing primary resources overexploitation, whilst contributing for research and innovation projects to the circular economy strategy empowered by the EC [9].

Climate change is a powerful motor for innovation in the field of raw materials replacement towards an eco-efficient production of construction products. The present work aims at reviewing the existing literature

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https://doi.org/10.1016/j.jobe.2020.101215
Received 21 October 2019; Received in revised form 23 January 2020; Accepted 23 January 2020

on construction products produced with mine residues, taking into account their physical, chemical and microstructural properties and also economic, social and environmental aspects.

2. Methodology

The research status on mining residues reuse in construction products was performed (January 2020) with the online version of Scopus. With the search words "construction", "material", "mining", "mine wastes", "tailings" and "residues", a total of 1,025 scientific papers were obtained from 1969 to 2020 (Fig. 1). The dominant research areas were engineering (25.7%), earth and planetary sciences (22.4%) and environmental science (20.6%).

This study focuses on analysing the methods of mine residues introduction in the construction industry. The mining residues from different types of mined ores are presented and differentiated as examples of incorporation in the construction sector. Features and drawbacks are presented, as well as environmental impacts of mining residues. The review is based on the available scientific literature.

3. Mining residues properties potential

The generation of rock residues by mining industries has accumulated over centuries into heaps and it is necessary to pursue new economic solutions that can contribute towards their reuse [10]. estimated that around 20 to 25 billion tons of solid mine residues are produced annually in the world, where 5 to 7 billion tons are fine mine residues [11]. According to other approximations, this value is up to 14 billion tons and tends to increase in the future due to the higher utilization of low-grade ores [12].

Mine residues are also composed by particles of crushed rock with particle sizes ranging from 0.01-1.0 mm, but up to 20% clay-sized particles (0.002 mm) can be found [13]. These variations are dependent on sedimentation, site and processing methods. The fine material contains chemicals and metals, which may be environmentally harmful when released in combination with water and air. These tailings can be described in soil mechanical terms and their geotechnical properties can partly be compared to natural materials. Their characteristics can diverge due to variations in origin and processing of the ore and deposition methods. The origin affects the size and the gradation of the grains, the internal friction angle and the particle density [13].

Mine wastes generally have high water content and porosity, low to moderate hydraulic conductivity and low plasticity when compared to soil. The shear strength has usually been rated low to moderate but found to be moderate to high in relation to the grain size compared to natural materials [13].

Focusing on iron, copper and gold mine residues, different properties can be seen, that affect the durability of a possible construction material produced.

[14] conducted laboratory experiments to analyse the static and cyclic characteristics of coarse and fine iron and copper tailings. Both coarse mine residues were classified as silty sand (SM) and both fine mine residues were classified as sandy lean clay (CL). Fine mine residues showed larger coefficients of compressibility (0,260 and 0,085 for iron and copper, respectively), lower permeability (void ratios of 1,41 and 1, 03 for iron and copper, respectively), lower strength and lower cyclic resistance, compared to coarse mine residues. When comparing iron and copper mine residues, iron mine residues demonstrated to have higher coefficients of compressibility, lower permeability, lower strength and lower cyclic resistance, both for the coarse and fine fractions [14].

Properties from gold tailings were investigated by Ref. [15]. These residues have been classified as alkaline silty materials of low plasticity with low organic contents (1.99–2.45%) and nitrogen contents (0.9–1.0 mg/kg). The cation exchange capacity range is between 6.0 to 7.5 meq/100 g and is dependent on clay content. The pH varies from 7.2 to 7.5, typical for soils with large amounts of calcium and magnesium. The major oxides present are silica (SiO_2), which form more than 50% w/w, alumina (Al_2O_3) with 9.6–14.6% w/w, iron (Fe_2O_3) with 10.4–17.5% w/w, and sulphur (SO_3) with 11.4–12.1% w/w [15]. Silica and alumina are relevant elements for the production of construction products. When submitted to a relatively low thermal treatment, silica and alumina state may change to an amorphous form. The material may acquire pozzolanic reactivity, potentiating the development of different construction products, namely by partial conventional binder replacement.

Only in Europe there are a wide range of mine ores, accounting at least 31 different deposits [16]. Table 1 shows some examples of mine deposits in Europe and their main specificities. Also, for the different ores explored, diverse toxic compounds are identified, such as arsenic, antimony, lead, nitrogen and sulphate. The risks of these elements for the region and for the production of construction products should be carefully addressed since it can compromise the durability of the product, the environment and public health. Nitrogen ending up in the water systems surrounded may cause eutrophication issues. Sulphates may also be accumulated in surface waters compromising water quality. Arsenic and antimony have harmful effects for public health, namely in cardiac and gastric systems, and also for the water ecosystems.

4. Construction products produced with mining residues

Mining residues have promised to be a sustainable and efficient alternative source for reuse in the construction sector. There are many studies regarding their application in different construction products and raw materials replacement.

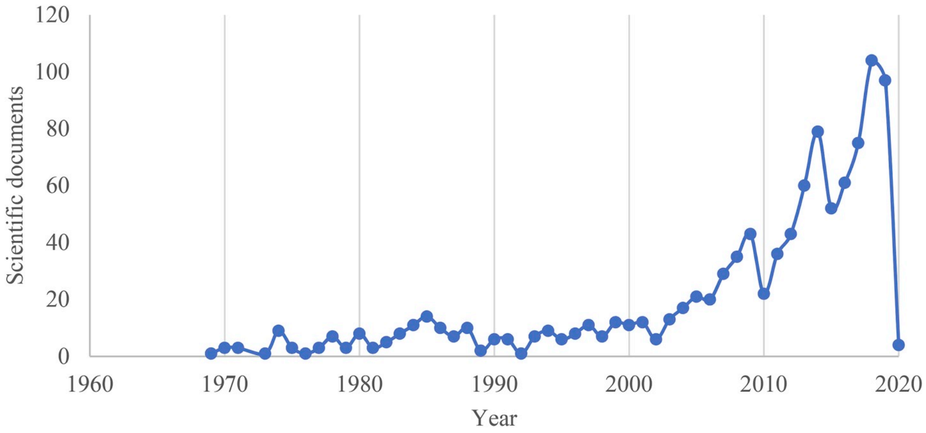

Fig. 1. Number of scientific documents by year related to mine residues in the construction materials production - SCOPUS, 2020, accessed in 6.01.2020.

Table 1
Examples of mine deposits in Europe and summary characterization.

Mine	Deposit type	Ore explored	Risks identified (compounds)	Reference
Evia, Greece	Epithermal- and porphyry	Nickel and Iron	-	[17]
Kiruna, Norrbotten, Lapland, Finland	Magnetite-apatite	Iron	Nitrogen	[18]
Kittilä, Lapland, Finland	Pyrite	Gold	Arsenic, Antimony, Sulphate and Nitrogen	[19]
Neves Corvo, Beja, Portugal	Volcanogenic massive sulphide (VMS)	Cooper, Lead, Zinc and Silver	Lead	[20]
Panasqueira, Covilhã, Portugal	Wolframite	Tungsten, Tin, Copper	Arsenic	[21]
Polkowice-Sieroszowice, Legnica-Glogów, Poland	Carbonate	Cooper and Silver	-	[22]
Pyhäsalmi, Pyhäjärvi, Finland	Bimodal-felsic	Zinc and Cooper	-	[23]

4.1. Alkali activated construction products

The reduced amount of greenhouse gas emissions made alkali activated construction products, also called geopolymers, one of the primary replacements for Portland cement [24]. Geopolymers (Fig. 2) are a class of inorganic polymers which have an amorphous structure of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$, generally produced by mixing a raw aluminosilicate source in the form of a powder with an alkaline silicate solution followed by curing [25,26]. Several aluminosilicate sources are applied for sustainable geopolymers production, such as metakaolin resulting from kaolin thermal treatment to achieve amorphous form [27,28], fly ash [29] and different types of slags and sludges [30,31].

Research focused on the reuse of residues (mining and quarrying) by integrating them into new construction products manufacture. Numerous works were developed with geopolymerization bases. Table 2 presents examples of mining residues incorporation in geopolymeric construction materials. Geopolymerization of mine wastes is mainly done through alkali-activation, which consists in the addition of a strong base to the mixture. Sodium hydroxide (NaOH) is the principal base selected for this purpose, although other reagents can be applied [21, 32–37]. The main drawback of this technique is the use of reagents, namely strong bases. The replacement for natural products or secondary alternatives would present benefits for the environment.

The reuse of tungsten mining wastes into innovative alkali-based materials for road pavement applications [38], red clay bricks [39,40] and light weight construction products [41] have proof to be a feasible strategy for the construction sector. For local communities, and since the mining sector is not stable along the time, the potential to reuse these secondary sources in different sectors may lead to an increase of the economic and social impact. Also, the durability of the products can be improved with the incorporation of mining residues comparing to the conventional products.

The properties of the final construction products are dependent on the components selection for the mixture and the incorporation rate of each raw material. According to Ref. [35]; when adding commercial granulated blast furnace slag (CGBF) as a co-binder to the alkali-activated tailings, parameters like strength, thermal stability, chemical and fire resistance tend to increase. However, lower density, micro/nano-porosity and shrinkage are obtained. Resistance to acid and sulphate attack has also been highlighted [37]. The incorporation of mine residues has reached 84% when fly ash is used as additive [34].

[21] developed a new alkali-activated binder by reusing mining wastes from Panasqueira tungsten mine, which showed good reactivity with alkaline activators and calcium hydroxide, for high alkali concentrations and curing at room temperature. The improvement on alkali-activation conditions was achieved by mixing mining clay residues with different sources of silica (river sand and amorphous ground glass residues) and cured at moderated temperatures.

The alkaline activation of other aluminosiliceous industrial by-products is known to yield binders, making their properties comparable or stronger and more durable than conventional Portland cement [42]. Cost comparisons show this alkali activated cementitious material is one of the most cost-efficient repair solutions [43]. The replacement of Portland cement by new alkali activated binders using mining residues was also studied by several researchers due to its enhanced environmental and durability performance [43,44].

Different combinations of mining sludge residues, grounded glass residues, Portland cement, metakaolin and expanded cork were mixed together with alkaline activators (sodium silicate and sodium hydroxide solution), as well as aluminum powder or hydrogen peroxide to produce foamed lightweight materials. Studies have shown the feasibility to produce improved lightweight foamed alkali activated materials incorporating expanded cork for applications in artistic, architectural, and historical heritage restoration [21].

Geopolymeric products are now gaining attention, since through the alkaline activation is possible to neutralize different mixtures, with

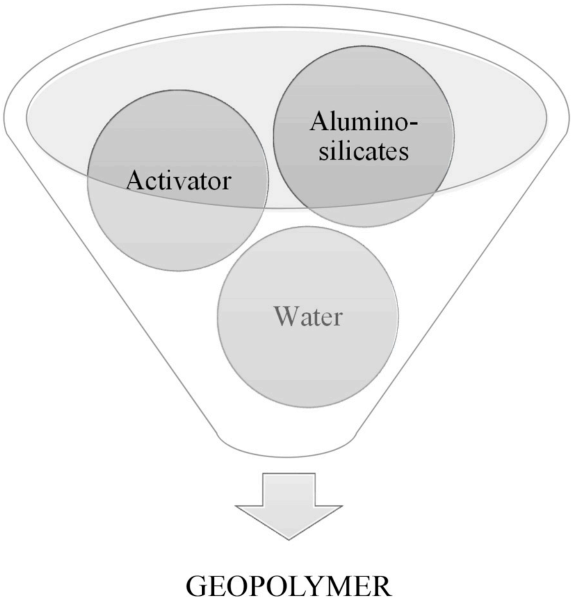

Fig. 2. Geopolymers' components for formulations.

Table 2
Examples of mining residues in geopolymeric construction materials.

Mined ores	Location	Final product/Goal	References
Copper	R.N.Macedonia	Fly ash-based geopolymers	[32]
Copper	Arizona, USA	Geopolymeric bricks	[33]
Iron	Western Hubei, China	Geopolymeric bricks	[34]
Gold	Finland	Raw material for construction industry	[35]
Gold, Copper	Musina, Limpopo, New Union, South Africa	Aggregates for conventional bulk manufacture	[36]
Tungsten	Portugal	Foamed lightweight materials	[21]

different resources incorporation. In terms of materials properties, it seems they are equivalent or better and with higher durability than conventional Portland cement, what makes this technique promising for the green movement of construction.

4.2. New-polymer based construction materials

The development of innovative polymer-based composite materials obtained from non-contaminated mine residues was also found an important strategy in the literature review. There is mechanical and physical potential for the reuse of Panasqueira aged rock-residues as new polymer-based construction materials in several applications [42]. These materials have shown great potential for conservation, restoration and/or rehabilitation of historic monuments, sculptures, decorative and architectural intervention or as materials for building coatings [42].

Different added value applications for reusing mining and quarrying residues are the production of compact composites, namely from marble or quartz residues. Compact composite products can be constituted by several sizes of particles/aggregates linked by a polymeric resin matrix. This aggregate/polyester matrix is optimized for mechanical and durability properties. The economic value of such composites depends principally on its aesthetic appeal (textures and colour scales) [45].

This is an innovative approach for reusing mining residues, as proposed by Ref. [45]; where new applications were developed for architectural, technical-sculptural and restoration process, by reusing residues of quarrying industry of Macael region, Spain. Different types of polymer-based mortars were produced incorporating fine residues, from dust to sand sized particles. Mortar properties and its potential for industrial applications is dependent on the texture and white colour scale of the residues [45].

It is possible to modify the original colours of natural quartz adding colour pigments and other compounds that confer high durability, resistance and consistency. The result is a large variety of designs, formats and finishes. Such advanced composite materials are compacted under intense vibration, vacuum, and pressure, resulting in dense and nonporous panels. Their appearance and properties differ according to the raw materials used. Besides quartz or granite, marble is also used in such composites, which can additionally incorporate residues from mining and quarrying industries [42].

New-polymer based products showed a great potential to provide personalized and original products for different purposes. The addition of different pigments makes possible to change the colour and also confer high durability to the products.

4.3. Ceramic tiles

[46] described a sustainable way of handling iron ore tailings by converting them into ceramic floor and wall tiles for building applications. The iron ore tailings were found to contain high percentage of silica and could be used up to 40% (by weight) as part of raw materials for ceramic floor and wall tiles production. Ceramic tiles from iron ore tailings were found to be superior in terms of scratch hardness and strength, while also keeping the essential properties of ceramic tiles made from conventional raw materials [46].

Amorphized tungsten tailings after magnetic separation demonstrated to have proper crystal structure and high performance to produce ceramic tiles. The gehlenite–hedenbergite glass ceramics repaired from tungsten mining wastes by controlled crystallization showed great potential [47].

The wastes from mining of boron-rich minerals, basalt rock and recycled soda-lime glass can be modified into a new product, between traditional ceramics and glass–ceramics, by using direct sintering at 1050 °C for only 30 min [48]. The surface porosity of the glass–ceramic body can be sealed by a glass–ceramic glaze, produced from the same starting mixture of residues and minerals [48].

Ceramic tiles can be produced in a superior way taking advantage of tailings, namely with iron, due to its colour (red-orange) and other chemical and physical properties.

4.4. Bricks

Several studies have shown the potential of mine residues to produce bricks in a more sustainable way. The possibility of applying tailings from Kolar Gold Fields, Karnataka, for brick fabrication was assessed by Ref. [49]. Since plasticity index of the tailings is zero it cannot be used directly for brick production. Thus, some additives that had plasticity or binding properties, such as Portland cement, black cotton soils and red soils were tested in the mixture with tailings from Kolar Gold Fields. According to the additives used, the bricks were termed as cement-tailing bricks or soil-tailing bricks. Bricks with 20% of cement and 14 days of curing were found to have suitable properties in terms of linear shrinkage, water absorption and compressive strength [49]. Also, bricks with high mechanical strength were produced with mine wastes from Jerada, Marocco [50,51].

Several works focused on iron ore mine residues incorporation to produce bricks. Different mixtures were carried out, adding to the mine residues components like soil, sand, cement, fly ash, gypsum and/or lime. The properties of the final product, such as compressive strength and water absorption, were found suitable for building products [52–57].

Studies demonstrated that iron ore residues can be also applied as aggregate in manufacturing of non-fired bricks, such as adobe, extruded or compacted earth bricks (respectively EEB and CEB), having a clear advantage in terms of low embodied energy products. However, as the incorporation of the residues reduces plasticity of the brick's mixture before moulding, for adobe and EEB may be a drawback since plasticity is an important factor. Therefore, additives such as mineral binders may be needed to improve its plasticity.

4.5. Aggregates for pavements and concrete

Aggregates are materials commonly applied in several products of the construction sector. Mine residues have been studied to partially replace raw aggregates in road pavement applications showing they have compatible physical properties (FHWA, 2016) and, therefore, presenting great potential for this application [58].

Hot mix asphalt (HMA) was developed containing mining waste as aggregates for making medium to low traffic roads. Kota stone was used to make bituminous concrete (BC) and dense bituminous macadam (DBM), replacing conventional basalt aggregates. Up to 50% replacement of conventional stone in BC mixes and 25% in DBM show satisfactory results for moisture susceptibility, resistance to rutting and low cracking temperature [59].

A lightweight aggregate was produced by sintering a mixture of Korean gold mine tailings, red mud and limestone [60]. However, the abrasion loss value of the aggregate was 290 mg, which exceeds the limit of 200 mg required in Korea. Heavy metals did not leach from the aggregate, despite the significant amounts of lead, arsenic and fluor existing in the residues. Although harmful elements present in the mine residues did not leach, other sources of pollution should also be assessed. The air indoor quality is also an important parameter since some elements can volatilize causing risks for the users.

The skid resistance and bond strength, together with physical properties of the reconstructed aggregate of the gold mine tailings were appropriate for use in bicycle lane construction, although the dissolution of calcium and the pH level of the leachate need to be controlled to protect aquatic ecosystems [60]. This will imply a hard and straight monitoring process, before, during and after the production, what in terms of costs could not compensate comparing to the conventional methods of aggregates production. Thus, the cost-benefit analysis is very important to support the feasibility of the mine residues incorporation in those cases.

Construction aggregates were also produced from a gold mine in Abitibi-Temiscamingue region, Quebec, Canada [61]. Rock residues samples containing 46% of coarse material have similar properties to common concrete. Depending on its composition, gold mine waste rocks show potential to replace almost 50% of the concrete needed, with a strong impact in an industrial scale.

[62] produced artificial lightweight aggregate (LWA) manufactured from recycled resources (mining waste, fly ash from an incinerator and heavy metal sludge from an electronic wastewater plant). LWA produced by sintering in tunnel kiln shows good vitrified surface, low water absorption rate (below 5%), and low cylindrical compressive strength (4.3 MPa). In addition, the study reported that only trace amounts of heavy metals were detected [62].

The presence of heavy metals is a parameter that authors are not addressing deeply. Although authors are awarded of the presence of harmful elements in the residues and, probably, in the materials formulated with them, no further tests show its influence in the surrounded ecosystems. If there are heavy metals, the monitoring process should be included since weather conditions and many other factors may influence its release in the atmosphere, apart from the influence on construction materials properties.

The use of mine tailings from a lead-zinc mine as a partial aggregate replacement in self-compacting concrete was also assessed [63]. The mine residues have no pozzolanic activity and their application in mortar and concrete can be made in the form of replacement of a certain percentage of aggregates. The results show that concretes with addition of 10% and 20% of mine residues achieved higher strengths when compared to a conventional concrete with 28 curing days.

Iron ore tailings may be used for complete replacement of conventional aggregates in concrete. An iron ore tailings aggregates concrete exhibited good mechanical properties, showing a compressive strength 12% greater than a conventional aggregates concrete [64]. However, due to the high content of fines in residues' aggregates, the indirect tensile strength is not superior when compared to the conventional concrete production.

Iron ore tailings were also tested to replace river sand in concrete [65]. Test results with 25%, 50%, 75% and 100% of replacement indicated that concrete workability was poorer, but strength and modulus of elasticity were consistently higher than for conventional concrete.

With the incorporation of mine residues for aggregates production and concrete aggregate replacement it is possible to improve properties as deformability and compressive strength. However, the workability may be affected. Also, the presence of heavy metals and other harmful compounds will imply the need of a straight monitoring process, since many factors may influence leaching and other release ways to the environment.

4.6. Mortars

Mortars are one of the most common construction products and can be constituted by only one or more types of mineral binders and aggregates. Mortars can also include additions, like pozzolans or fillers, and admixtures, such as plasticizers, in their formulation [66,67]. In this sense, mortars were also subjected to mining residues incorporation in several studies. Mortars are frequently studied instead of concrete since they constitute a concrete matrix without the coarser aggregates (Table 3).

[68] applied tungsten residues powders, activated by mechanical and chemical methods, as cementitious material in mortars. Garnet was the major group of silicate minerals present in the mine residues, which improved chemical and structural stability of the final mortar [68].

Conventional material for cement mortars was also replaced by tailings from a tungsten mine in Sangdong, Korea [69]. This technique was effective for stabilizing and solidifying heavy metals, particularly when used with commercial granulated blast furnace slag. This combination demonstrated acceptable properties for residues volumes up to 10% by mass.

Table 3
Examples of mining resources applications in mortars production and purposes.

Mining resource in mortar formulation	Purpose	References
Tungsten residues powders/tailings	Binder replacement	[68,69]
Iron mine residues	Aggregate/Binder replacement	[70,71]
Gold mine tailings	Additive	[50,72,73]
Bauxite mine residues	Binder replacement	[74]
Copper tailings	Aggregate replacement	[73,75]
Barite-fluorspar mine waste	Additive/Aggregate replacement	[76]

Iron mine residues were used to replace river sand as the adhesive mortar aggregate in the study of [70]. The results show that polymer–cement ratio and cement-mine residues ratio are important factors to the performance of the adhesive mortar. The adhesive strength did not decrease with the incorporation of the mine residues [70].

[72] studied the potential of Bergama gold mine tailings (Turkey) as an additive in mortars. Cement mortars were prepared with a mixture of Portland cement and dried gold tailings. According to the results, mine residues are suitable for mortar production, with an optimum gold mine residues incorporation mass ratio of 5%. Also, several studies reported that heavy metals and metalloids from gold mine waste may be immobilized in the concrete matrix [77].

[71] evaluated the technical feasibility of using iron ore mine tailings as construction material, for masonry layering, plastering and rendering mortars. Three types of mortars were produced: hydraulic lime conventional mortars, mortars with complete replacement of natural aggregate by mine tailings and mortars replacing the lime by mine residues in proportions from 10% to 100%. Mortars with iron ore mine residues show an increment in the content of mixing water, reduced levels of incorporated air, increased bulk density and improvement of mechanical properties when compared to conventional mortars [71].

Also [74], proved that up to 20% of red mud, from bauxite ore extraction to produce alumina, can be used as a cement substitute in mortars. In a calcination range of 450 °C and 650 °C, the red mud provides an acceleration of the hydration process while the workability decrease.

A technical comparison between stucco mortars (gypsum as binder) prepared with crushed conventional sand and with copper tailings was also carried out [75]. The best results were achieved for the stucco mortars containing mine tailings. The values of compressive strength (~14.7 N/mm^2), water retentivity (87%), and adherence (0.07 N/mm^2) in the stucco mortars prepared with copper tailings after 28 curing days improved in comparison to the values obtained with crushed sand (~0.57 N/mm^2, 62% and 0.02 N/mm^2, respectively). Therefore, the preparation of stucco mortars using copper tailings replacing conventional sand seems a feasible alternative for the construction industry. In addition, gypsum requires low temperatures for production, making this combination a very sustainable approach for plastering mortars production. Gypsum-based materials are commonly used for conservation and retrofitting projects [78].

Incorporation of barite-fluorspar mine waste (BFMW) as a fine aggregate additive has been investigated by Ref. [76] for its effect on the mechanical and shielding properties of cement-based mortars. Several mortar mixtures were prepared with different proportions of BFMW ranging from 0 to 30% as fine aggregate replacement. The results revealed that mortar mixtures containing 25% BFMW reached the highest compressive strength values, which exceeded 50 MPa. The use of BFMW aggregates increased attenuation coefficient by around 20% [76]. Mining residues can be used as partial replacement aggregate to improve radiation shielding and to reduce mortar (and concrete) costs.

Additionally, focusing on the use of mine tailings as a partial cement replacement, residues from Zinkgruvan (Sweden) and Nalunaq (Greenland) presented potential for partial cement replacement (5 and 10%) in cementitious mortars and showed indications of pozzolanic activity (Sigvardsen et al., 2018).

Therefore, the use of mine residues in mortars seems to be promised. The formulations may require the addition of additives (such as GBFS) that may help to immobilize the harmful elements, avoiding leaching phenomena and other contamination problems. At the same time, additives may also improve materials structural and chemical properties. Some mineral groups present in the mine residues may also potentiated the chemical and structural stability (e.g. garnet). However, some studies reported only an optimal replacement ratio of cement by mine residues of 5% by mass. Nevertheless, in an industrial scale, even only 5% will promote significant savings in raw materials for cement production and costs. Furthermore, this percentage may increase replacing fine aggregates by mine residues together with new techniques and strategies to make these residues more suitable for mortars. This will promote not only a drastic reduction of mine residues disposal but also will make countries less dependent of cement and energetic sources.

5. Environmental and social impacts of mining

As previously mentioned, mining activities affect the environment and associated biota through removal of vegetation and topsoil, displacement of fauna, release of pollutants and generation of noise [79]. Furthermore, the management of mining waste that are generated in the mining processes increase the negative impacts. Thus, finding ways to reuse this secondary source in order to reduce mine residues disposal is an important current issue.

The major impact of mining activities is related to water quality and availability in the area [80]. The potential for acid mine drainage is an important factor. When the walls of open pits and underground mines, mining residues, rock residues, and heap and dump leach materials are quarried and exposed to oxygen and water, acids can be formed. Acid formation occurs if iron sulphide minerals (e.g. pyrite) are abundant and if there are no neutralizing compounds [81]. Therefore, acids are prone to leach or dissolve metals and other harmful compounds present, forming acid solutions with high contents of sulphate and metals (e.g. cadmium, copper, lead, zinc, arsenic) [82,83].

Mineralogy is important for the ability of residues to neutralize acidity produced by sulphide oxidation. Iron carbonates in the form of siderite, ferroan dolomite and ankerite are less reactive and ultimately provide no net neutralization from the iron fraction of the carbonate due to subsequent Fe hydrolysis under oxidizing conditions. Whereas dissolution of other non-carbonate minerals (primarily silicates and aluminosilicates) can also provide some neutralization of acidic waters, the importance of such minerals in acid-generating environments is limited by low reaction rates [84].

Toxic constituents can leach even if acidic conditions are not present (e.g. arsenic, selenium, and metals). Elevated levels of cyanide and nitrogen compounds have been found in waters at mine sites, from heap leaching and blasting [79]. The impacts of wet mine residues impoundments can include contamination of water, since toxic substances can leach from these facilities, percolate through the ground and contaminate groundwater. Particulate matter from excavations, transportation of materials and stockpiles, may be transported by the wind. Emissions from cars, trucks and equipment increase the particulate levels [82].

The use of mining residues as construction materials for the production of construction products must comply with the requirements of safety at work during production and transport [85].

In an industrial scale, this aspect is crucial for the inclusion of mining residues in a safe and legal manner, although it has been rarely studied. Furthermore, safety during the lifetime of the construction product may be quite relevant, depending on the application. The construction product can be left exposed (uncoated) or applied as an intermediate layer. Also, depending if the final product will be applied indoors or outdoors, other interventions may be needed.

Construction products are in contact with several environments during their lifetime and, as a consequence of their contents, may release potentially harmful compounds [85]. Nevertheless, few studies have addressed this aspect when focusing on the development of construction products with the mining residues.

6. Discussion and research perspectives

Conventional construction products manufacture is under increasing pressure since the primary resources used have a strong impact for the sustainability of this sector. Thus, the use of alternative secondary resources appears to offer a promising way of alleviating this problem.

The industry workers' safety when handling with mining residues to produce construction products and the eventual toxicity of the residues may be one of the difficulties that companies face when considering the incorporation of mining residues in the production of construction materials.

However, broad types of mine residues have shown great potential for construction materials production. A common strategy applied is the previously mentioned alkali activation, such as geopolymerization. This strategy provides materials with suitable chemical and structural properties. Also, geopolymerization may be a key factor to stabilize hazardous compounds in mixtures with mining residues, avoiding leaching problems. This technique seems to be promising in Europe from an environmental, technical and economic perspective. However, although in-depth studied currently, commercially available geopolymeric products are still scarce.

Secondary resources may have latent pozzolanic reactivity [86]. A thermal treatment of mine residues may enrich their pozzolanic reactivity. After the thermal treatment, mine residues may be applied as a binder partial replacement for mortars and concretes, or for bricks production. Simultaneously, this process may be proficient to immobilize harmful compounds, preventing toxic risks for the environment. Further research on this topic should be addressed in order to expanse the application of mine residues in the construction field.

Mine residues have also the possibility to be reused from a secondary ore extraction. Since the EC identified 27 critical raw materials with high economic relevance and in risk of scarcity, alternative sources to recover are now being explored [87]. Various estimations of potential recovery of certain materials compared to their current demand have been done [88]. Thus, the application of a treatment before mine residues reuse could provide the recovery of critical raw materials and the removal or immobilization of harmful compounds, what would be advantageous in terms of economic and environmental perspectives.

Electroremediation has been studied for a wide range of liquid and solid environmental matrices to remove organic and inorganic contaminants. In the electroremediation process (Fig. 3), a low-level direct current is applied in a system with charged elements to remove the pollutants [89].

In the construction field, electroremediation proved to be an efficient pre-treatment for immobilization of heavy metals in solid environmental matrices and improvement of physical and chemical properties [90]: [91–93] and to remove salts in liquid environmental matrices [94], for matrices reuse in mortar production [94,95].

Other strategies, as desulphurization (oxidation of sulphide minerals in the presence of a sulphide activator) have shown potential to reduce the sulphide content from mine tailings [96]. The pre-treatment of mining residues with this technique may be also an important step for a greener incorporation of mine residues in construction materials. Also, it may lead to chemical, physical and microstructural changes that may improve the final material and promote a higher ratio of mineral binder replacement.

Metal ore processing activities generate significant quantities of residues at mining sites, causing environmental issues. The application

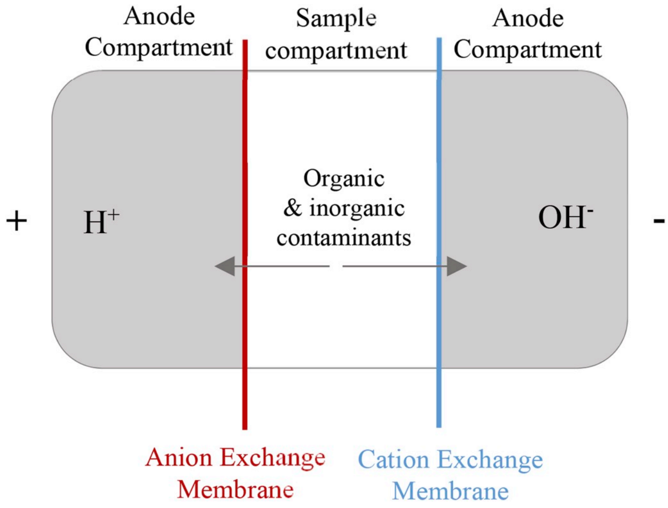

Fig. 3. Electrodialytic cell with 3 compartments.

of mining residues for the production of construction products is considered to be a key factor for the conservation of natural resources and reduction of environmental impacts, both for mining and construction industries. Incorporation of mining residues in construction products should provide competitive products, decreasing costs, resources consumption and mine residues discharge. At the same time, greener management of residues and production of construction products with lower embodied energy should be achieved. It is important to keep intensifying research in this topic in order to implement and improve optimized applications of mining residues in the construction field.

However, recovery processes can be highly energy dependent. Thus, environmental and land use aspects are also important to be considered. Availability of data and information on secondary materials and legislative framework within the EC is essential for the large-scale development of recovery practices [88]. Also, the development of a tool to assess climate protection and resources efficiencies, through indicators, will pursue the empowerment of innovative alternatives [97].

The valorization of tailings in the mining industry is slowly starting. One of the reasons is due to the limited knowledge of its contents and amounts. However, it is mandatory that this situation changes. In a circular economy perspective, the drawbacks related to the way that waste is managed and the conscience of industries to understand the potential of tailings as important and available materials are key factors to change from a linear economy model (take-make-use-dispose). This may promote the development of new business areas. Also, the implementation of taxation might change the profits, empowering the circular economy principles [98].

The comparative overview of the reviewed papers called up several promising prospects for future research. In this sense, a SWOT (strengths, weaknesses, opportunities and threats) analysis of the mining residues application in the construction sector is presented (Table 4).

Table 4
SWOT analysis of mining residues application in the construction sector.

STRENGHTS	WEAKNESSES
⇒ Huge mineral resources availability ⇒ Reduction of mining residues disposal ⇒ Reduction of primary resources exploration ⇒ Sample pre-treatment may not be necessary, depending on residues composition	⇒ Scale-up underdevelopment ⇒ Complex matrix may influence the replicability ⇒ Leaching of heavy metals or other harmful compounds may occur ⇒ An additional step can be needed for some residues: removal or immobilization of harmful elements ⇒ Additives may be necessary to enhance materials properties
OPPORTUNITIES	**THREATS**
⇒ Green methods development ⇒ Innovation in the construction sector ⇒ Increase knowledge on mining residues handling and products toxicity ⇒ Development of different products and application depending on their eventual toxicity ⇒ Critical raw materials recovery and harmful compound removal strategies from secondary resources	⇒ Percentage of raw materials replacement may not be significative in some cases ⇒ Heterogeneity of the mine residues may influence the results and limit industrial use ⇒ Importation and exportation of residues ⇒ Local politics ⇒ Residues classification and application constraints

7. Conclusions

The incorporation of mining residues into construction products manufacture can decrease consumption of primary resources in the construction sector, as well as improvements on the final products properties without high investments. While current research has been mostly focusing on energy-efficient construction products, residues minimization and reuse strikes as equally important in a context of primary resources scarcity. Thus, based on a literature review and showing several research examples of construction materials and products with mining residues, some gaps were presented, together with barriers that exist in the current literature. The diversity of available mine residues resources around the world, with specific problems, should be considered in further research. Nevertheless, it is clear the potential mine residues reuse can have to enhance eco-efficient construction materials and products.

Acknowledgments

This work has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No. 778045, as well as from Portuguese funds from FCT/MCTES through grant UID/AMB/04085/2019. J. Almeida acknowledges *Fundação para a Ciência e a Tecnologia* for her PhD fellowship PD/BD/135170/2017.

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Book chapter

A2 The electrokinetic recovery of tungsten and removal of arsenic from mining secondary resources: the case of the Panasqueira mine

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Published in Electrokinetic Remediation for Environmental Security and Sustainability, John Wiley & Sons UK (2020)

4

The Electrokinetic Recovery of Tungsten and Removal of Arsenic from Mining Secondary Resources: The Case of the Panasqueira Mine

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4.1 Introduction

Mining industries today are producing a larger volume of residues than ever. To access ore, waste rock needs to be removed, and other residues are generated in the process [1]. The accumulation of these residues in open pits leads to landscape problems and environmental deterioration. For example, the Panasqueira mine in Portugal has been active for more than a century and is one of the largest tin (Sn) – tungsten (W) deposits in Europe. The mining residues are low-grade secondary resources that contain not only W, from wolframite, but also elements of environmental concern, including arsenic (As) from arsenopyrite [2].

The electrodialytic (ED) process has been studied to remove metals and metal oxides from a wide range of porous solid matrices in the environment [3–7]. This process consists of applying a low-level direct current between pairs of electrodes. The electric field generated inside a reactor promotes the removal or separation of substances from contaminated matrices [8]. In addition, natural deep eutectic solvents are another strategy for extracting metals from environmental matrices and have economic and environmental advantages compared to conventional ionic liquids [9].

Natural deep eutectic solvents and/or ED processes were applied to secondary mining resources from the Panasqueira mine to remove or separate elements [10, 11]. Considering European Commission targets, the recovery of critical raw materials [12] and removal of harmful compounds from secondary resources contributes to close loops of by-products and move toward a circular economy [13].

Electrokinetic Remediation for Environmental Security and Sustainability, First Edition.
Edited by Alexandra B. Ribeiro and M.N.V. Prasad.

Additionally, worldwide, construction products have extremely high embodied energy and consume large amounts of raw materials. EU targets from 2021 to 2030 [14] call for reducing greenhouse gas emissions by 40% (comparing with 1990 levels) and improving energy efficiency by more than 32.5%. The valorization of residues as binder replacers or additions in cementitious construction products may be a sustainable alternative for the construction and mining sectors, alleviating primary resources needs and residue disposal.

Mining wastes from the Panasqueira mine have been successfully reused in the construction sector using different approaches [15, 16]. The introduction of Panasqueira W mining waste resources in construction products was assessed, emphasizing the advantages and drawbacks of the material's properties [17]. The feasibility of innovative technologies, namely the ED process, to remove and recover elements from secondary resources for subsequent use in construction product formulations was also studied.

4.2 Tungsten Mining Resources: The Panasqueira Mine

4.2.1 The Development of the Industry

The Panasqueira mine is located in the Centro region of Portugal and is described as the largest Sn–W deposit in Western Europe [18]. Tungsten market downturns have influenced the plant's dynamics over the years, regarding the optimization of mechanical processes and exploring alternative ores (Figure 4.1).

Panasqueira began W exploration in 1896, when the mining company Tungsten Mines Society of Portugal was founded. Wolframite ore was firstly extracted from Cabeço do Pião (now known as Rio). In 1904, the plant was improved, and 41 t of ore were produced by integrating a new mechanized treatment using the Zêzere river for a water supply. Although the first underground drifts were opened in Rio, mining activities decreased at this site due to richer veins in the Panasqueira area [19].

In 1911, Wolfram Mining and Smelting Company was formed and acquired all the rights and concessions of the previous company. Investments in machinery and equipment were made to increase ore production. From a social perspective, the need for more workers to manage the plant processes increased employment in the region. The production of wolframite concentrates was estimated to be 267 t of 65% WO_3 mined from 11 000 t of vein and 86 000 t of host rock [19].

During the World War I, the mining operation grew; production increased, and the plant facilities were enlarged. Also, the mine began to recover Sn from cassiterite. In 1928, the price of W fluctuated, which affected its exploration. To overcome the W "crisis," the recovery of Sn was intensified. The company reorganized itself and changed its name to Beralt Tin and Wolfram Company [19].

During the World War II, peak production of W was reported, and the price of W increased again in 1934. Manpower was also boosted from 750 workers in 1933 to 5800 in 1943. However, from the end of the war to 1950, the W market declined. The production of Sn was maintained, and Cu (copper) recovery was introduced to the

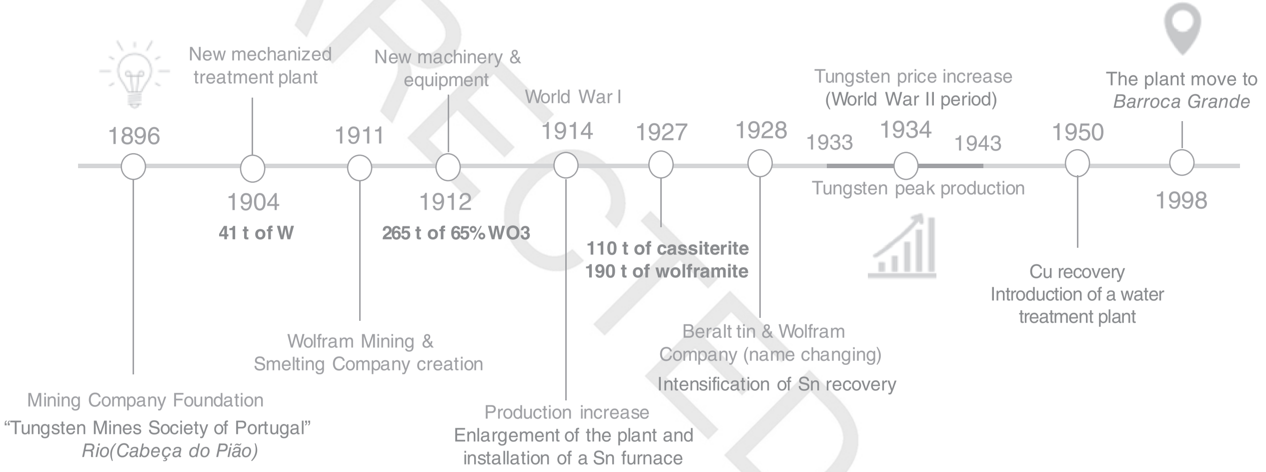

Figure 4.1 Highlights of the Panasqueira mine timeline.

plant to compensate for W depreciation. In addition, water treatment was integrated into the system to address water quality issues. The Zêzere river is one of Lisbon's water supplies, so constant water monitoring was necessary [18, 19].

Later, the company mechanized underground operations, reducing labor expenses. In 1998, the remaining plant at Rio was moved to Barroca Grande, where it is located today. The mine has a production plan for more than 30 years in the future [19].

4.2.2 Ore Extraction Processes

Tungsten is a high valuable transition metal that can be extracted from the two W minerals that are commercially mined: scheelite ($CaWO_4$) and wolframite ($(Fe, Mn)WO_4$) [20]. Panasqueira mine ore deposits are characterized by a series of sub-horizontal, stacked, and hydrothermal quartz veins that promote the mineralization of wolfram-bearing schists and shales. The mineralized area is 2500 m long, 400–2200 m wide, and 500 m deep. Wolframite, chalcopyrite, and cassiterite are extracted and recovered to produce concentrates of W, Sn, and Cu, respectively [21].

The current extraction technology is based on a room-and-pillar method, taking into account an analysis of the geomechanical and geological properties of the rock mass. The ore extraction process starts with a heavy media separation between fine and coarse fractions. This step removes 80% of the ore that does not contain W. Then, this pre-concentrated fraction is subjected to a conventional gravity concentration technique, followed by flotation (with sulfide) and dry magnetic separation [21].

4.2.3 Potential Risks

The final concentrate production procedures are carried out in the Barroca Grande plant. A huge tailings pile and two mud dams are currently in the area. One dam is still being filled with material (mud and coarse material) without W ore as a result of extraction operations [22].

More than 27 million t of rock were extracted in the first 50 years of mining. During this period, around 92 800 t of W concentrate, 4800 t of Sn concentrate, and 28 600 t of Cu concentrate were produced [22] (Figure 4.2).

Now production has been optimized and is estimated to yield 85 000–95 000 t of W concentrate per year, which is almost equal to the total W production during the first 50 years of Panasqueira mining. Currently, the W concentrate grade is approximately 75% WO_3, representing one of the best W products available on the global market [21].

Panasqueira extraction and processing generate two types of mine tailings: (i) coarse waste-rock tailings from rock blasting and (ii) waste-mud tailings transferred into mud dams. Panasqueira has accumulated these rejected fractions for a long time, and they now have enormous proportions. The total amount of accumulated residues is a problem: it is estimated that to date, 8 200 000 m^3 of mining waste have been disposed of. Even more concerning is the quantity of residue disposed of in

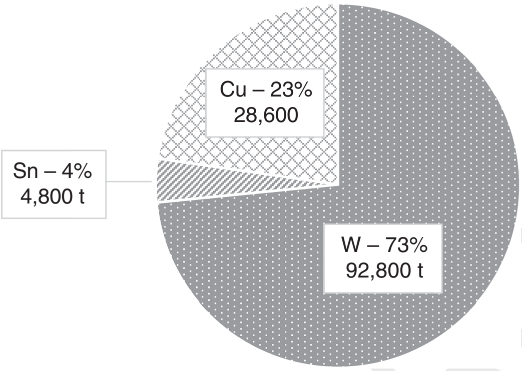

Figure 4.2 Tungsten, copper, and tin concentrate production in the first 50 years of Panasqueira mining.

open air impoundments, since only around 23% of the total mining waste estimated is effectively at dam facilities (1 924 919 m^3) [22].

Besides harming the landscape, the piles of accumulated mining waste are exposed to environmental conditions. Thus, these residue impoundments are unstable and prone to landslides, erosion, and leaching of harmful compounds. Waste mud contains high proportions of arsenic and other sulfide-related heavy metals, e.g. lead (Pb), copper (Cu), cadmium (Cd) and zinc (Zn). The oxidation of sulfides and their release from open impoundments are reported as the main threat to the Panasqueira area since they are associated with the migration and mobilization of metals/metalloids into the environment [23].

Although secondary resources from the Panasqueira mine have been successfully valorized in several applications, there are other potential risks. The presence of metals and metalloids, including arsenic (As), Cd, chromium (Cr), Cu, Pb, and Zn, has been reported in different streams (rhizosphere soils, irrigation water, road dust, and vegetables in local gardens). The mean concentrations exceed standards values and cause potential risks for habitants [24].

4.3 The Circular Economy of Tungsten Mining Waste

Europe's flagship initiative supports the shift to a resource-efficient, low-carbon economy to achieve sustainable growth. Reusing mining waste contributes to moving away from a linear economy model (take-make-use-dispose) and toward circular economic principles as set by the European Commission [13].

4.3.1 Panasqueira Old Slimes vs. Current Slimes

Reprocessing old tailings from Cabeço do Pião can be a solution to extract more ore concentrate and minimize the residues disposed of in the area [25]. However, research on old and current Panasqueira W slimes have shown varying efficiencies for the processes at the plant.

Panasqueira wolframite froth flotation (selective separation of hydrophobic from hydrophilic materials) has shown inconsistent results when comparing current tailings with old dam tailings. The old dam tailings have difficulty during flotation, which may be related to surface weathering. The finest wolframite is not effectively recovered by high-intensity magnetic separation (low to moderate fields) since the differential needed between wolframite, siderite, and other magnetic minerals is not achieved. With the application of higher fields, a substantial recovery of magnetic silicates and low-weight rejection is reported [26].

A three-stage gravity-separation process with a middle step of sulfide flotation can produce a wolframite concentrate of 55% WO_3. Tungsten minerals have extremely fine particles, and wolframite particles in Panasqueira mine tailings are less than 25 μm. Thus, the complex mineralogy and low-grade ore have led to the pursuit of a combination of enrichment techniques (e.g. flotation, magnetic, and gravity separation). The process for recovering ultrafine wolframite was optimized to enable efficient reprocessing of old mine tailings and current plant slime tailings from the Panasqueira mine [26].

4.3.2 Tungsten Recovery

Tungsten is both scarce and extremely important economically: it was reported as a critical raw material in the EU 2017 Critical Raw Material list [12]. Thus, alternative ways to recover W from secondary resources are now gaining attention. The Panasqueira mine has tons of accumulated secondary mining resources as a result of the extraction process, as reported in Section 4.2.3.

The electrodialytic process (ED) has been studied for removing organic and inorganic contaminants from liquid and solid environmental matrices by applying a low-level direct current to the system [27]. In the construction sector, ED has been demonstrated to be an effective pretreatment for immobilizing metals in solid matrices and improving the physical, chemical, and microstructural properties [28–31] for matrix reuse in mortars production.

Toward this end, research has been conducted to assess the feasibility of recovering W from secondary Panasqueira mining resources [10, 11]. Following the work of Almeida et al. [10], ED treatment was applied to W mining residues to (i) recover W contents, (ii) remove harmful compounds (As), and (iii) provide a suitable matrix for further reuse in the construction sector.

Tests also demonstrated the feasibility of adding biodegradable acid adjuvants – natural deep eutectic solvents – to the ED process [10]. The main goals of this combination were to improve the As and W extraction ratios and separate the extracted elements from the matrix.

Recovering W and removing As were assessed in a two-compartment ED cell (Figure 4.3). Tests were performed for four days at 100 and 50 mA. The electrolyte ($NaNO_3$ 0.01 M) was placed in the anode compartment, and the matrix was introduced in the cathode compartment in a water suspension (liquid-solid ratio of 9).

The tested conditions allowed the extraction of As (35%) and W (22%). Additionally, the conditions generated in the cell promoted the extraction and migration of

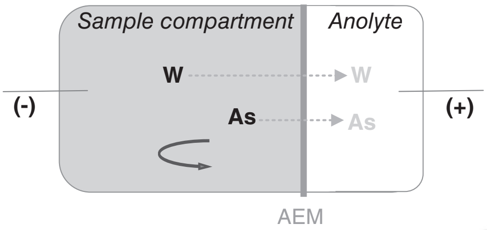

Figure 4.3 Two-compartment electrodialytic cell with an anion exchange membrane (AEM) interposed.

the studied elements. The elements extracted from the original matrix electromigrated into the anode compartment: 82% of the As and 77% of the W. Also, As and W can be further separated from the anolyte [10].

Simultaneously, research has been conducted for W recovery using other strategies. The hydrometallurgical recovery of W from minerals, tailings, and scrap involves several stages. Digesting and purifying these secondary raw materials allows the leaching of the concentrate and, consequently, extraction by the solvent. Tungsten from secondary scheelite can be processed through alkali leaching, where wolframite is dissolved in NaOH or Na_2CO_3 at temperatures between 125 and 200 °C or by high-pressure digestion. Then, silicates, phosphates, fluorides, As, antimony (Sb), bismuth (Bi), Pb, and cobalt (Co) can be selectively precipitated by other reagents. This purification step is accompanied by a W concentration step by either solvent extraction or ion-exchange resins [32].

However, the precipitation of contaminants leads to a loss of W. Therefore, direct solvent extraction of W from the alkaline medium was proposed with quaternary ammonium carbonate salts applied as extractants [32]. Trioctyl methyl ammonium chloride was transformed in quaternary ammonium carbonate and used as an extractant, removing almost all the impurities (e.g. phosphorus [P], As, silicon [Si], and Sn) [32].

Tungsten can also be selectively recovered from W-bearing scrap by biosorption. *Escherichia coli* and beer yeast have high uptake capacities for W biosorption (0.16 g W/g biosorbent and 0.29 g W/g biosorbent, respectively), comparable to ion-exchange resins [33].

Emulsion liquid membranes are another strategy for W recovery and consist of two consecutive steps: extraction and stripping. The emulsion membrane phase is based on (i) a homogeneous mixture of extractant, (ii) an organic diluent, (iii) an internal aqueous stripping phase, and (iv) a surfactant to stabilize the emulsion. Transporting the solute with the species through the liquid membrane is coupled with counter-transport of ions (H^+/OH^-) from the internal stripping phase to the external feed phase, which allows high enrichment concentrations. The enriched solute can be recovered by breaking the emulsion [34].

Recent developments in microprocess engineering have helped to intensify existing solvent extraction processes for various metals [35, 36]. Microextraction processes are designed for slug flow in a microchannel with alternating drops of the aqueous and organic phases, non-dispersively in surface-modified microchannels or with an extra membrane between the two phases [37].

4.3.3 Building Material–Related Applications

From the perspective of a circular economy, and in line with the EU desire to close secondary resources loops [13], mining residues from Panasqueira and other mines were broadly tested in construction material products [17].

Together with sources of alumino-silicates, alkali-activated binders can be obtained. Some examples are calcinated clays (e.g. kaolin) and other industrial byproducts. Alkali-activated binders, also known as *geopolymers*, are gaining increasing attention because their properties are in some instances superior to other cementitious products [38].

Tungsten mine waste mud was used to produce geopolymeric binders. Formulations were performed with dehydroxylated mine waste, CaOH, NaOH (as an activator), and water-glass solutions. Regarding fresh and hardened characterizations, the tests standards may not be appropriate to measure the benefits of introducing residues in the formulation. For instance, since the formulation includes a viscous residue (water glass), it may bond to metallic surfaces of the material used to measure consistency and, indirectly, workability, affecting the results [39].

In-depth research of geopolymer optimization coupled with the incorporation of other reagents and wastes has been conducted. Tungsten mining waste was combined with red clay brick waste. When higher amounts of red clay brick waste were added to the mixture, there was an increase in compressive strength from 25 to 59 MPa with 10 and 50% of red clay brick waste, respectively [40].

Together with W mining waste, waste glass, and metakaolin, several precursors were tested to produce alkali-activated foams. A foaming agent (aluminum powder) was added to the mixture. The compressive strength of the final foamed material can be enhanced by reducing the precursors' particle size [41].

Tungsten mining waste mud was also combined with other mixtures, concentrations, and liquid-solid ratios of alkaline activator solutions. Some examples are Na_2SiO, NaOH, KOH, and waste glass powder dissolved in NaOH, aiming to enhance the compressive strength and microstructure of hybrid alkaline binders. By adding ground granulated blast furnace slag to secondary resources from W mining, a compressive strength of 32.8 MPa was obtained in 28 days of cure. This strategy's major drawbacks are the alkaline activator solutions, which are the most expensive component to prepare a hybrid alkaline binder [15].

The feasibility of reusing waste-rock piles from the Panasqueira W mine was assessed, aiming to develop a polymer-based composite material. These materials have the potential for technical-artistic applications in rehabilitation as building coatings and for conserving sculptures, although polymer-based composite products are probably incompatible with the conservation of historical monuments [42].

Panasqueira secondary resources as aggregates were successfully applied as a refractory lining in a foundry of non-ferrous metals [43]. Also, cementitious grouts were formulated with milled glass and Panasqueira waste mud for the road industry [44].

The influence of sodium carbonate on the thermal reactivity performance of materials produced with Panasqueira mine waste mud was also assessed. Although compressive strength achieved 40 MPa in 28 days of cure, Na_2CO_3 did not lead to a stable structure or, consequently, enhanced thermal reactivity [45].

The potential of tungsten mine waste mud to repair ordinary Portland cement (OPC) concrete was studied. A geopolymeric binder formulated with W mining waste was used as a repair material. This geopolymeric binder showed excellent bond strength and was not affected by its low roughness. On the other hand, commercial repair products are characterized by low bond strength and are highly dependent on surface treatment roughness [46].

Additionally, W mine tailings were studied to determine their potential for use in commercial glass production. $CaCO_3$ and $NaCO_3$ were added since they are essential for glass manufacture. Tungsten mine tailings showed suitable properties for commercial glass manufacture and also retained toxic elements, preventing environmental deterioration [47].

4.4 Social, Economic, and Environmental Impacts

The impacts of mining activities involve social, economic, and environmental pillars. Mining residues can affect the environment as a result of their chemical and mineralogical composition, physical properties, volume and surface occupied, and need for waste disposal. As a consequence, water quality and availability may also be affected. The potential for acid mine drainage is high, since mine tailings, rock residues, and heap and dump leach materials are quarried and exposed to oxygen and water, increasing the probability of acids being formed due to the presence of sulfide minerals (pyrite) [48]. Toxic constituents can leach even if acidic conditions are not present. Elevated levels of cyanide and nitrogen compounds have been found in waters at mine sites, from heap leaching and blasting. Also, landslides can occur on high deposits [49].

Particulate matter is transported by the wind as a consequence of mining activities (e.g. excavations, blasting, transportation of materials, wind erosion). In addition, exhaust emissions from the vehicles involved in mining areas increase these particulate levels [49].

Current demand and metal prices have potentiated the interest in old mining waste. As mentioned before, this waste can be considered a secondary mining resource for critical/raw materials. The recycling of W has lower-energy negative impacts (below 6000 kWh t^{-1}) compared to virgin production (10 000 kWh t^{-1}), depending on the grade and cut-off. However, depending on the market conditions, energy savings associated with W recycling do not make recycling cheaper than conventional W production [50].

To overcome the drawback of recycling costs, innovative methods require lower processing energies, lower carbon emissions, and waste rock generation from excavation activities, wastewater, and leachates from mining operations. Also, new technologies should have an eco-friendly perspective for the W processing industry by reducing the reagents needed and/or the production of harmful/useless byproducts [50].

Future developments may consider redesigning models to optimize the environmental, social, and economic consequences of managing mining waste throughout the value chain. Orebody characterization, mine planning, processing, disposal, reprocessing, recycling, and reuse should be integrated. Economically, avoiding mining waste is at the top of the list, followed by reuse > recycling > recovery treatment > disposal. However, circular business models supported by public policies may have strategic importance [51]. To achieve social acceptance, special incentives may be provided to reward W producers or processors. These benefits should optimize the recycling management system to increase recycling rates [50].

4.5 Final Remarks

Reusing secondary mining resources may be a key factor in facing dependence on primary raw materials and improving sustainability in the industries that produce and reuse mine residues.

Although W mining wastes were reported as a feasible source to be reused, the presence of harmful elements may lead to potential risks. Applying a pretreatment before reusing secondary mining resources can recover critical raw materials, remove harmful compounds, and make it possible to safely reuse this matrix in other applications.

In the construction sector, geopolymerization proved to be able to stabilize hazardous compounds in formulations with W mining wastes for cementitious or clayish construction products. In addition to geopolymerization, other applications also seem feasible. Thus, W mining wastes are a valid secondary resource to empower a circular economy while mitigating primary resource needs in the construction sector without the loss of building materials' properties.

The imminent threat of climate change is a powerful motor for innovation in the field of raw material replacement for eco-efficient production of construction materials.

Acknowledgments

This work has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No. 778045. The authors acknowledge the Portuguese Foundation for Science and Technology (FCT) for the support given to CENSE and CERIS through the strategic projects UIDB/04085/2020 and UIDB/04625/2020, respectively, and for the J. Almeida PhD fellowship PD/BD/135170/2017 from the EcoCoRe Doctoral program. This work is anchored by the RESOLUTION LAB, a laboratory at the NOVA School of Science and Technology.

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Scientific journal article

A3 Electrodialytic treatment of secondary mining resources for raw materials extraction: reactor design assessment

J Almeida, C Magro, AR Rosário, EP Mateus & AB Ribeiro

Published in Science of the Total Environment journal (2020)

This article was published in Science of the Total Environment, Vol 752, J Almeida, C Magro, AR Rosário, EP Mateus & AB Ribeiro, Electrodialytic treatment of secondary mining resources for raw materials extraction: reactor design assessment, 141822, Copyright Elsevier (2020).

Science of the Total Environment 752 (2021) 141822

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Electrodialytic treatment of secondary mining resources for raw materials extraction: Reactor design assessment

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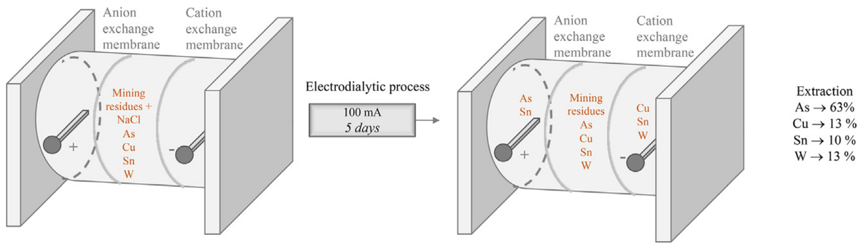
HIGHLIGHTS

- Electrodialytic extraction of arsenic, copper, tin and tungsten was assessed.
- Electrodialytic 2 and 3-compartment reactors were studied applying 50 or 100 mA.
- Effluent and NaCl were tested as enhancements on electrodialytic setups.
- The highest extractions occurred in a 3-compartment reactor with NaCl as enhancement.
- Copper, tin and tungsten extraction were 10–13% while for arsenic was 63%.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 31 May 2020
Received in revised form 13 August 2020
Accepted 18 August 2020
Available online 21 August 2020

Editor: Carlos Alberto Martinez Huitle

Keywords:
Mining residues
Electrodialytic treatment
Tungsten
Copper
Tin
Arsenic

ABSTRACT

The sustainability of mining activities is compromised due to the high amounts of mining residues generated that have to be disposed of, often in open dams, that may cause environmental deterioration, e.g. release of toxic elements to water supplies. These residues are, however, secondary resources of raw materials. In the case of Panasqueira mine, they even are a source of tungsten, considered a critical raw material. The present work aims to assess the electrodialytic process efficiency for raw materials extraction from Panasqueira mine residues. Experiments were performed with 2 and 3-compartment electrodialytic reactors, applying current intensities between 50 and 100 mA, from 4 to 14 days, and sample suspensions enhanced with NaCl or effluent. Additionally, control experiments with no current application were carried out. The results showed that a 3-compartment reactor operating at 100 mA, with NaCl as supporting electrolyte, presented the highest extraction of copper (13%), tin (10%), tungsten (13%) and arsenic (63%).

1. Introduction

The market of raw materials has increased the demand over the last few years across the globe (Mancini et al., 2019). Raw materials, constituents or substances used in goods primary production or manufacturing, are essential for human well-being and can influence the sustainable development. Their production, consumption and end-of-life is causing numerous environmental and social negative impacts (Mancini et al., 2019; Schreck and Wagner, 2017).

To tackle reliable and undistorted access to raw materials and improve growth and competitiveness of the EU economy, the European Commission (EC) launched the Raw Materials Initiative in 2008 (EC, 2008). In this context, EC has been presenting and updating the critical raw materials list, based on current raw materials economic

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https://doi.org/10.1016/j.scitotenv.2020.141822

relevance and supply risk (EC, 2017). Europe's transition towards a circular economy has been stimulated through secondary resources recovery, contributing to ‘close the loop’ of product life cycles (EC, 2020).

Mining residues are often a slurry of fine materials as a result of metals separation from mined ores. Their large production generates landscape and serious environmental problems. Besides the mining operation itself, the most significant impacts are waste rock dumps and residues disposal (Almeida et al., 2020a).

Panasqueira mine (Centro Region, Portugal) has been working for more than a century, being on the top list of the largest tin (Sn)-tungsten (W) deposits in Europe (Candeias et al., 2014a). The well-known tungsten trioxide (WO_3) production from wolframite, with grades up to 75%, is one of the best quality W products worldwide (Yang et al., 2016). Additionally, Panasqueira mine has a secondary production of copper (Cu) from chalcopyrite and Sn from cassiterite (Yang et al., 2016).

Panasqueira area is occupied with piles of mining residues and mud dams, nearby small villages and Zêzere river (Coelho et al., 2014). The presence of sulfides, such as arsenopyrite, presents severe risks for the surrounding ecosystem, namely for water resources. Secondary products are discharged to dams with 30% of arsenic (As) contents, that are prone to be released into various environmental compartments (Candeias et al., 2014b). According to Portuguese legislation (Diário da República, 2017), As concentration in water for public consumption must be below 10 μg As/L. Due to its characteristics, mining activities, and consequently their residues, have been one of the focus for the sustainable development goals (Mancini et al., 2019).

Research and technology have empowered the reuse of mining secondary resources, particularly focusing in construction products (Almeida et al., 2020a). However, the pH conditions may affect the leachability of As from a cement matrix (Randall, 2012). To assure safety requirements and to tackle primary resources over exploitation, versatile technologies are needed for harmful substances and raw materials extraction, namely critical metals.

The electrodialytic treatment (ED) is used to remove inorganic and organic contaminants from liquid or solid matrices (Ribeiro and Rodríguez-Maroto, 2006). When a low-level direct current is applied between pairs of electrodes, the movement of charged contaminants is promoted (Guedes et al., 2014). Three main mechanisms are responsible for contaminants´ transport: electromigration, electroosmosis and electrophoresis. Ion exchange membranes are used to separate the contaminated matrix and to control the electrolyte conditions. The water electrolysis at inert electrodes generates an acidic media at the anode (H^+) and an alkaline media at the cathode (OH^-) (Ribeiro and Rodríguez-Maroto, 2006).

The ED process has long been applied to mining resources aiming the extraction of materials (Hansen et al., 2007), namely from sulfidic reserves (Zhang et al., 2019). Furthermore, strong acids and acidic salts such as H_2SO_4, HNO_3 and NH_4Cl, have been used to assist the process and improve the extraction ratios (Hansen et al., 2007; Ortiz-Soto et al., 2019). The implementation of green chemistry principles would promote the sustainable growth of ED technologies (Chen et al., 2020) for this application. In this sense, due to their low volatility and toxicity, natural deep eutectic solvents (DES) were applied on the extraction of metals and alloys, as As and W (Almeida et al., 2020c). Additionally, the reuse of available liquid secondary resources, as effluent from wastewater treatment plants, could also be an alternative for ED enhancing purposes. This would decrease effluent discharges and tap water consumption needed for sample suspensions preparation (Almeida et al., 2020b).

The present work aimed to assess the feasibility of Cu, Sn, W and As extraction from Panasqueira mining residues through the electrodialytic process. Several reactor setups and experimental conditions were tested to understand raw materials behavior and optimize a bottom-line treatment strategy.

2. Experimental

2.1. Materials

Mining residues mud was directly sampled from the sludge circuit output of Panasqueira mine (Covilhã, Portugal, 40°10′11″N, 7°45′24″ W). Typically, this mud contains fines with particle sizes lower than 2 mm diameter (Castro-Gomes et al., 2011). The annual production of W at Panasqueira mine is estimated in around 90,000 t with concentrated grades of approximately 75% WO_3 (Franco et al., 2014). Panasqueira samples were dried at 20 °C for 48 h in a fume hood, before starting the experiments. Effluent was collected from the secondary clarifier (May 2019) of a wastewater treatment plant located in Lisbon (Portugal) and all the experiments were performed with samples from the same batch.

2.2. Elements extraction analysis

The concentration of As, Cu, Sn and W in the sample was determined after a pre-treatment in accordance with EPA3051A (USEPA, 2007): 0.5 g of dry sample, 9 mL of HNO_3 (65%) and 3 mL of HCl (38%) were placed in a vessel and extracted in a Microwave (Milestone Ethos, Bergamo, Italy). The microwave program was set to reach 175 °C in 15 min, and to keep the temperature for the next 15 min. After, the samples were collected and filtered through a 1.2 μm MFV3 glassmicrofibre filters (Filter lab, Barcelona, Spain) and stored until analysis. Liquid samples (electrolyte and suspensions liquid phase) were also filtered through a 1.2 μm MFV3 glassmicrofibre filters (Filter lab, Barcelona, Spain) and stored until analysis. As, Cu, Sn and W contents were measured in an Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP–AES), Varian 720-ES. For Cl^- and SO_4^{2-} quantification, 5 g of mining residues were mixed with 25 mL deionized H_2O and placed in a shaking table for 24 h, at room temperature. The samples were prior filtered by vacuum, using 1.2 μm MFV3 glassmicrofibre filters (Filter lab, Barcelona, Spain) and further analyzed by ion chromatography (DIONEX ICS-3000 equipment, Waltham, USA), equipped with conductivity detector and a Thermo Ionpac AS9-HC AG9HC column (250 × 4 mm). The eluent used was Na_2CO_3 (8 mM) at a flow rate of 1 mL/min. The sample injection volume was 10 μL at 25 °C.

2.3. pH desorption tests

To determine the pH influence in As, Cu, Sn and W desorption, 2.5 g of mining residues were suspended in 12.5 mL of different concentrations of HNO_3 and NaOH, as well as in deionized H_2O, in order to have solutions with pH between 1 and 14. The suspensions were placed in a shaking table for one week, at room temperature. At the end, pH was measured with an EDGE, electrode meter (HANNA Instruments, Rhode Island, USA). The suspensions were filtered by vacuum using 1.2 μm MFV3 glassmicrofibre filters (Filter lab, Barcelona, Spain) and As, Cu, Sn and W concentrations were determined by ICP-AES.

2.4. Electrodialytic laboratory reactor

The experiments were carried out in a 2-compartment (2C) and 3-compartment (3C) ED reactor (Fig. 1). The reactors had an internal diameter of 8 cm and were separated by commercial anion and/or cation exchange membranes, from Ionics (AR204SZRA and CR67, MKIII, Blank, respectively). The compartment where the mining residues were placed had a length of 10 cm in the 2C configuration, and of 5 cm in the 3C setup. The electrolyte (anolyte or catholyte) compartment had a length of 5 cm. A pair of electrodes were placed in the reactor according to its design. The platinized titanium, with a 0.3 cm diameter and a length of 5 cm (Bergsøe Anti Corrosion A/S, Herfoelge, Denmark), were selected for the system due to its performance reported in other ED studies (Ferreira et al., 2018; Magro et al., 2020). A power supply (Hewlett

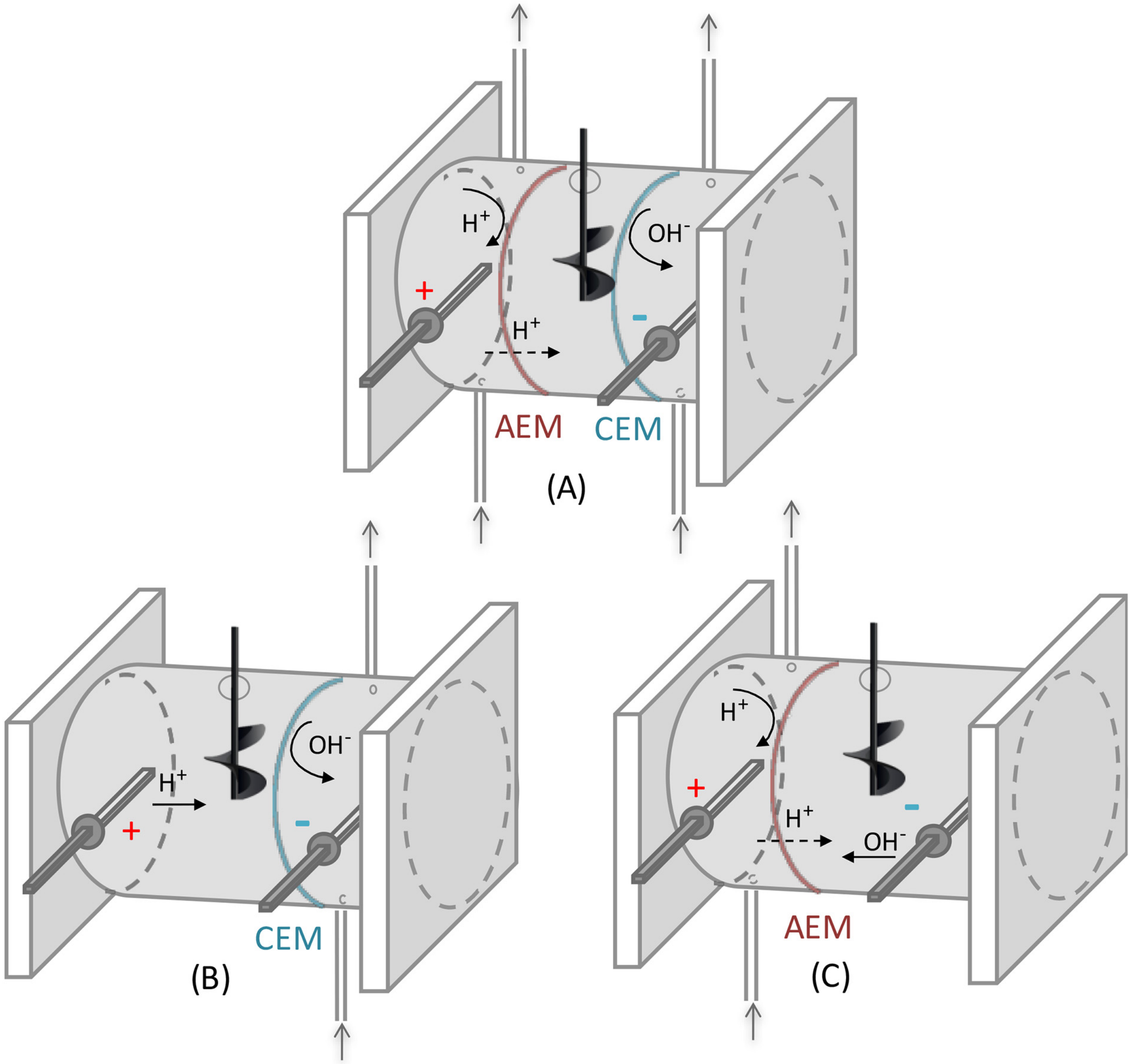

Fig. 1. Schematic design of the electrodialytic laboratory tested reactors: (A) 3-compartments, 3C; (B) 2C with CEM - cation exchange membrane, and (C) 2C with AEM - anion exchange membrane.

Packard E3612A, Palo Alto, USA) was used to maintain a constant direct current and voltage drop was also monitored (Kiotto KT 1000H multimeter). The electrolyte, 0.01 M $NaNO_3$ (PanReac Appli Chem ITW Reagents, Germany), was recirculated by means of a peristaltic pump (Watson-Marlow 503 U/R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK), with one head and two extensions.

2.5. Electrodialytic experimental conditions

In total, ten experiments were performed with constant and sequential current intensities, different reactor setups, operation times and enhancing agents (Table 1). E1-E3 experiments were performed under regular ED conditions (no enhancement agent), BW, EF1-EF3 experiments were performed adding NaCl or effluent to the sample compartment as enhancing agents, and C1-C3 were conducted with no current applied, working as control tests.

In the 2C reactors, the sample compartment was filled with 39 g of mining residues and 350 mL of deionized H_2O or effluent (EF), while in the 3C setup 22.2 g of sample were added to 200 mL of deionized H_2O, both with a Liquid/Solid (L/S) ratio of 9. For the experiment with 3C configuration, in order to ensure enough conductivity to test this design, a brine solution was created by adding 11 g of NaCl to the deionized H_2O present in the sample suspension compartment (BW experiment).

The electrolyte was recirculated using a flow rate of 3 mL/min in the electrolytes' compartments. To guarantee the suspension of the mining residues, a magnetic stirrer was used in the sample compartment. All the experiments were performed in a fume hood at room temperature.

2.6. Statistical analysis

Statistically significant differences among samples for 95% level of significance were evaluated through ANOVA tests using GraphPad Prism software (version 8). Statistical differences were analyzed for pH and conductivity variations in the reactor compartments, and for elements extraction considering: (1) same element, different experiments, and (2) same experiment, different elements. The notation selected to present statistically significant differences among the results

Table 1
Electrodialytic experimental conditions.

Experiment	Setup	Membrane	Current (mA)	Sample compartment	Running days
ED experiments ($n = 2$)					
E1	2C	CEM	100	Anode	14
E2	2C	AEM	100	Cathode	14
E3	2C	AEM	50	Cathode	8
Enhanced ED experiments (BW $n = 2$; EF $n = 1$)					
BW	3C	AEM and CEM	100	Central	5
EF1[b]	2C	AEM	50	Cathode	4
EF2[b]	2C	CEM	50	Anode	4
EF3[b]	2C	AEM	65-55-45-35[a]	Cathode	4
Control experiments with no current ($n = 2$)					
C1	2C	AEM	0	Cathode	10
C2	2C	CEM	0	Anode	10
C3	3C	AEM and CEM	0	Central	10

BW – Brine water; EF – Effluent; AEM – Anion exchange membrane; CEM – Cation exchange membrane.
n – number of experiments performed.
[a] Sequential decreasing current intensity.
[b] Effluent was placed in the sample compartment.

obtained was lower case letter versus same capital letter. Thus, data with lower case letter is statistically significant different from the data with the same capital letter, with 95% confidence interval.

3. Results and discussion

3.1. Initial characterization

Table 2 presents the initial composition of mining residues by ICP-AES method. Regarding the target compounds, As presented the highest concentration (3743 ± 471 mg/kg), comparing to the contents of Cu (1790 ± 202 mg/kg), Sn (75 ± 8 mg/kg) and W (488 ± 88 mg/kg) in the sample. The presence of salts and other elements, namely Fe (7250 ± 318 mg/kg) and SO_4^{2-} (217 ± 5 mg/kg), may influence ions mobility due to uncharged complexes generation, affecting elements extraction by ED (Almeida et al., 2020b).

3.2. Electrodialytic experiments

During the ED treatment, pH fluctuations occurred due to electrode reactions (described later in Eqs. (1) and (2)). Accordingly, desorption tests were performed before the remediation process to understand As, Cu, Sn and W concentration in the aqueous phase as function of pH (Fig. 2).

Table 2
Composition of mining residues.

Parameter	mg/kg
ICP-AES analysis	
As	3743.2 ± 471.0^{a}
Ca	$97.3 \pm 44.8^{A,b}$
Cu	$1790.3 \pm 202.3^{A,B,c}$
Fe	$7250.2 \pm 318.4^{A,B,C,d}$
P	$46.6 \pm 12.7^{A,C,D}$
Sn	$75.11 \pm 8.6^{A,C,D}$
W	$487.8 \pm 87.5^{A,C,D}$
IC analysis	
Cl^-	$5.0 \pm 2.3^{A,C,D}$
SO_4^{2-}	$217.0 \pm 4.6^{A,C,D}$

ICP-AES, Inductively Coupled Plasma - Atomic Emission Spectrometer.
IC - Ion Chromatography.
Statistical analysis was carried out at $p < 0.05$ (95% confidence interval). Data with lower case letters are statistically significantly different to data with the same capital letter.

The solubility of compounds, namely oxides, hydroxides, carbonates or mineral forms, is highly dependent on the media pH. Also, cationic/anionic constituents are related to solid residues through adsorption/desorption on mineral or organic surfaces with a pH-dependent charge. Dissolution and sorption processes provide a pH-dependent leaching trend where the release of cations increases in low pH media and the release of anions increases towards high pH solutions (Król et al., 2020).

Generally, elements desorption from mining residues were higher at pH values below 2 (Fig. 2) due to the chemical speciation of the studied elements, where the release of cationic species was more pronounced. Only As showed a second desorption peak at pH above 11. At high pH, $HAsO_4^{2-}$ is the dominant As species, followed by AsO_4^{3-} considering an oxidizing media. These anions can react with Ca^{2+} to form amorphous or crystalline arsenate (Vempati et al., 1995). This means that during the ED process the sample should be theoretically placed at the anode compartment, where an acidic pH (below 2) is promoted and, as a consequence, higher desorption rates are expected. Considering the ED system, it is foreseen that the most common forms of As, Cu, Sn and W, in extreme acidic conditions and with soluble forms at pH below 2 are, respectively, H_3AsO_4/H_3AsO_3 (Chen et al., 2014), $Cu^{2+}/Cu(OH)^+$ (Cuppett et al., 2006), $Sn^{2+}/Sn(OH)^{3+}$ (Dulnee and Scheinost, 2015) and WO_3 (Cao and Guo, 2019). Nevertheless, the mobility of these elements during ED experiments may be limited due to eventual complexation with other substances present in the media (Almeida et al., 2020b).

In a first stage, the ED process was applied considering 2C and 3C reactors at 50 and/or 100 mA. The pH behavior of the sample compartment during the treatment is presented in Fig. 3a.

Generally, after the ED process, sample pH decreased when mining residues were placed in the anode compartment (Fig. 1b), while the opposite was verified when the matrix was at the cathode compartment (Fig. 1c). Sample pH increased in E2 and E3 tests and decreased in E1 test. This was expected due to water electrolysis phenomena occurrence at the electrode compartments. Herein, H^+ is generated at the anode (Eq. (1)) while OH^- is formed at the cathode end (Eq. (2)), promoting an acidic and alkaline pH media, respectively. Also, the presence of chloride in the ED system may lead to the formation of active chlorine, which is an oxidant agent (Eq. (3)).

$$H_2O\ (l) \longrightarrow \frac{1}{2} O_2\ (g) + 2H^+ + 2e^- \quad (1)$$

$$H_2O\ (l) + e^- \longrightarrow \frac{1}{2} H_2\ (g) + OH^- \quad (2)$$

$$Cl_2\ (g) + 2e^- \longrightarrow 2Cl^- \quad (3)$$

As the pH in the residue suspension decreases, a higher dissolution of the residue is expected (Fig. 2). Fig. 3(b) and (c) also shows the conductivity behavior and the voltage variation on the sample compartment during the experiments, respectively.

Conductivity in the media has to be assured to promote current passage and electrochemically-induced extraction of substances. Typically, mining residues are characterized by low conductivity values, with an average of 0.3 mS/cm (Almeida et al., 2020c; Almeida et al., 2020b; Magro et al., 2019). The initial electrical conductivity of the suspension was in average approximately 1 mS/cm (Fig. 3). When a 2C reactor design was tested (E1, E2 and E3), the conductivity of the sample compartment tended to increase (Fig. 3b), due to the generation of free ions in the media (Eqs. (1) and (2)), which was advantageous for current passage and, consequently, for the ED process performance. This increase was more pronounced at the end of E1 (9.8 mS/cm) and E2 (4.9 mS/cm), where 100 mA were applied. However, there are oscillations in the conductivity, namely in E1. This may be explained by CEM

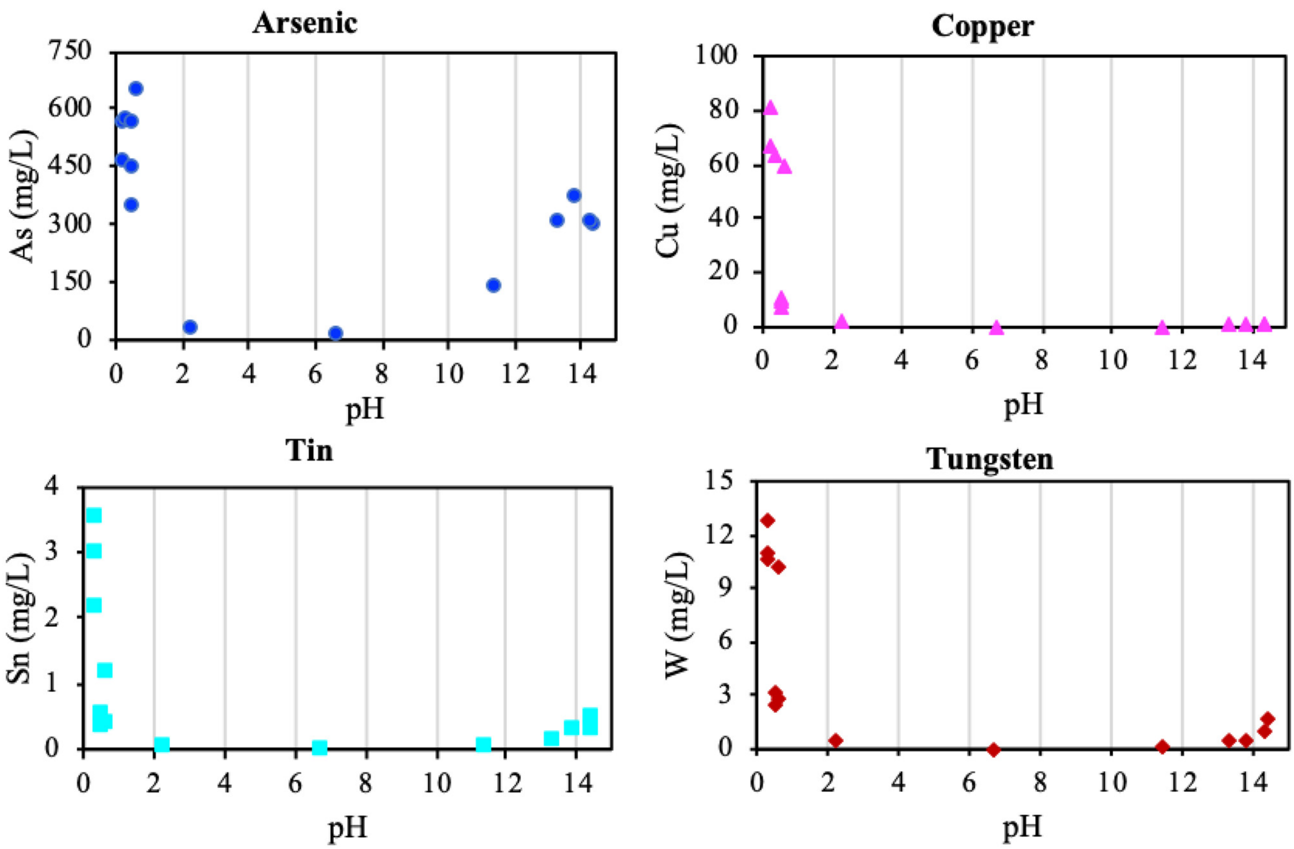

Fig. 2. Arsenic, copper, tin and tungsten pH desorption at different concentrations of HNO_3 and NaOH solutions with pH between 1 and 14.

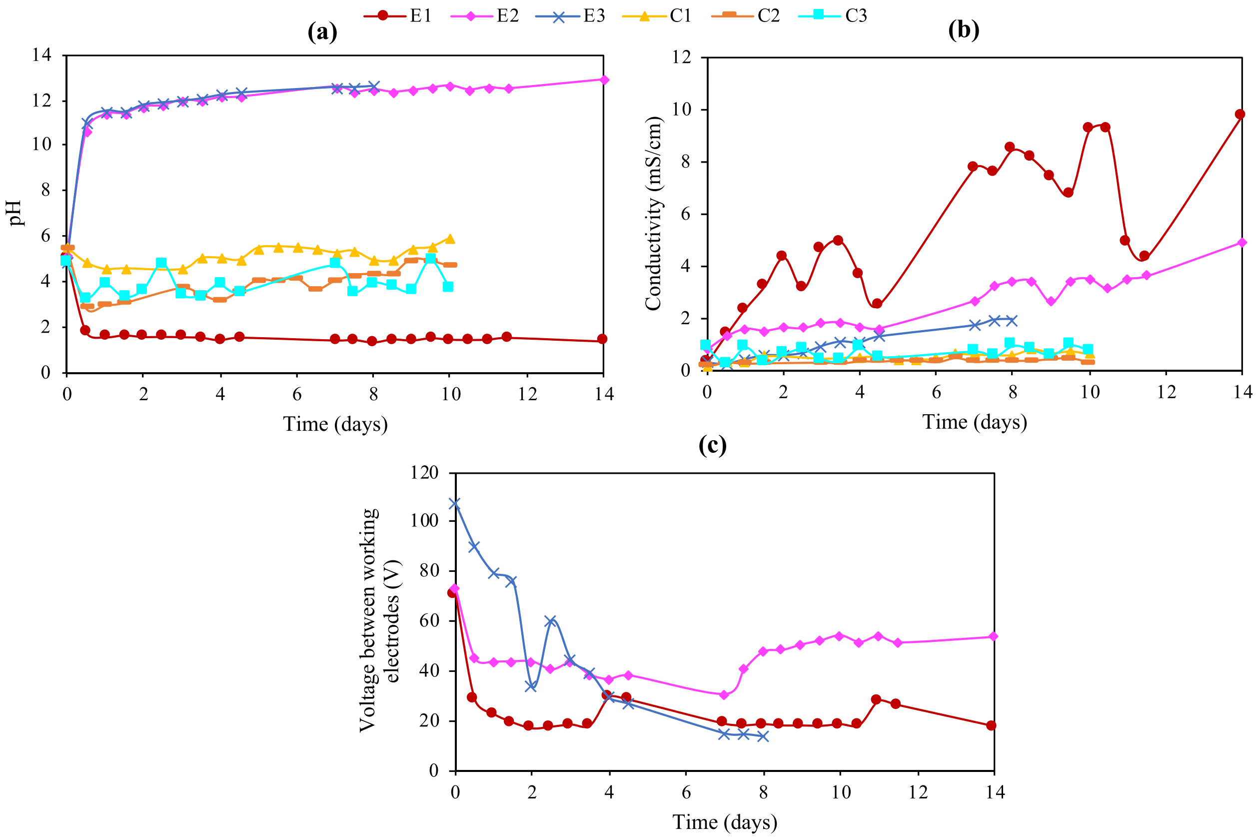

Fig. 3. Mining residues: (a) pH, (b) conductivity and (c) voltage between working electrodes during the electrodialytic experiments. E1-CEM,100 mA; E2-AEM, 100 mA; E3-AEM, 50 mA; C1-control AEM; C2-control CEM; C3-control AEM and CEM.

properties, since sulphonation is required to maintain good conductivity, ion exchange capacity and permselectivity on the system. A high degree of sulphonation may have caused instability (Shukla and Shahi, 2019).

A voltage decrease tendency was verified (Fig. 3c), due to the decrease of the internal resistance in the reactor along the experiments, based on Ohm law (Eq. (4)):

$$\mathrm{I} = \frac{V}{R} \tag{4}$$

where I is the current intensity (in amperes), V is the voltage (in volts) and R the resistance (in ohms) applied.

Moreover, when the current was applied, the pH at the anolyte compartment decreased to around 2, while the pH at the catholyte compartment increased until approximately 10 (Table S1, in Appendix A). In all experimental setups, conductivity increased at the end of the experiments, from approximately 1 to 4–6 mS/cm. This was predictable due to the increment of free ions, corroborating the generation of ions by the electrodes and the electromigration of substances from the sample to the electrolyte compartments.

Furthermore, when mining residues were placed in the central compartment (3C reactor case, Fig. 1a), the current passage was not facilitated due to the extremely low conductivity of the sample, being unfeasible to operate the process according to the time set for the experiments, without the addition of adjuvants. Electrokinetic effects promote non-homogenous slipping flows over charged surfaces, which may impact hydrodynamics of tight porous materials, as mining residues (Karaca et al., 2017). Regarding the transport of ionic solutions, both hydrodynamic and electrokinetic transport are expected. However, the transport due to electric fields (e.g. electroosmosis) is more prominent in tight pores where electrical diffuse layer is not negligible (Godinez-Brizuela and Niasar, 2020).

In fact, the ED 3C reactor could not perform properly without adding enhancing agents, to assure enough conductivity in the media and avoid operation problems, such as pressure fluctuations inside the reactor during the operation time. Considering this limitation, mining residues were treated in a 3C reactor design adding brine water (BW), and in 2C reactor designs using effluent (EF) as enhancing agents (Table 1). Whereas NaCl was added to the sample compartment only to assure enough conductivity, effluent was tested as an eco-friendlier alternative, comparing to water, in both 3C and 2C reactor designs. Additionally, the application of decreasing current intensities was tested in solid matrices (Guedes et al., 2016). Thus, a sequential decreasing current intensity was applied to an effluent experiment to test their feasibility on ED experiments, aiming to improve the process efficiency and the overall stability of the ED system.

Table 3 presents pH, conductivity and voltage behavior on enhanced ED experiments with EF and BW.

The same pH, conductivity and voltage trends verified on Fig. 3 were observed in enhanced experiments. The sample pH decreased to around 2 when mining residues were placed at the anode, and increased to approximately 12, when the sample was at the cathode compartment. Concerning the BW experiment (performed in the 3C reactor), the pH at the central compartment decreased from 5.3 to 4.5, once the anion exchange membrane has limited permselectivity (Ribeiro and Rodríguez-Maroto, 2006). Only protons (H^+) are able to cross this membrane, promoting the decrease of the pH in the central compartment, during the experiment. Conductivity dropped about 70% in the central compartment at the end of experiment, due to the electromigration of charged species towards the electrolyte compartments. Thus, a conductivity increase was verified in the cathode (6.3 ± 1.6 mS/cm) and anode (13.5 ± 1.6 mS/cm) compartments, where the second was more pronounced (Table 3).

On experiments performed with 2C reactors, using effluent as an enhancing agent, the pH at the anode compartment decreased to around 2, while the pH at the cathode compartment increased until approximately 12. The conductivity at the end of the experiments in the sample compartment increased in all experiments. The experimental behavior was similar to E1, E2 and E3 experiments (Fig. 3), corroborating that water replacement by effluent to perform the liquid suspension did not significantly affect the ED system balance.

Electrochemical reactions that occur at the anode and cathode (oxidation and reduction) may contribute to the increase of conductivity in the media. The removal process may cause the presence of more ions in solution (free ions), and consequently higher conductivity at the end of the experiments. As expected in all tested cases, the voltage values decreased as electrical conductivity increased, which is in line with Ohm's law. BW voltage decrease from around 29 to 16 V; EF1 from 21 to 15 V; EF2 from 23 to 8 V and EF3 from 32 to 12 V (Table 3).

3.3. Elements extraction

After the ED process, As, Cu, Sn and W final distribution in the reactor compartments was assessed. Fig. 4 presents the amounts of each studied element detected at the anode (anolyte), cathode (catholyte) and sample (solid sample and liquid phase) compartments, for all experiments performed.

Generally, after the ED experiments (E1, E2 and E3), As demonstrated the highest mobility since As was detected in the anolyte on experiments E2 (19%) and E3 (14%). Thus, predominant As extraction was observed towards the anode, where the rising current intensity promoted its speciation. Also, 60% of As was solubilized in the liquid phase on E1. Only trace amounts of Cu (0.3%), Sn (0.3%) and W (0.1%) were detected in the solid sample at E1. Copper was detected at the cathode compartment and in the liquid phase in E1, while Sn and W where mainly detected in E1 at the catholyte (Sn = 0.3%; W = 0.01%) and in E2 in the liquid phase of the sample suspension (Sn = 0.02%; W = 1.1%).

Table 3

Initial and final pH, conductivity and voltage values in the reactor's compartments, on enhanced ED experiments.

Experiment	Compartment	pH		Conductivity (mS/cm)		Voltage between working electrodes (V)	
		Initial	Final	Initial	Final	Initial	Final
BW (3C)	Cathode	6.8 ± 0.2	3.5 ± 0.5	0.7 ± 0.1^{b}	6.3 ± 1.6^{d}	29.2 ± 9.1	16.2 ± 1.4
	Central (sample)	5.3 ± 0.7	4.5 ± 1.0^{a}	12.6 ± 1.6^{B,c}	3.8 ± 1.2^{e}		
	Anode	6.8 ± 0.2	1.5 ± 0.1^{A}	0.7 ± 0.1^{C}	13.5 ± 1.6^{D,E}		
EF1 (2C)	Cathode (sample)	7.5	12.4	1.6	2.2	20.5	14.5
	Anode	8.0	1.9	1.1	5.0		
EF2 (2C)	Cathode	7.6	12.4	0.7	1.9	22.7	8.4
	Anode (sample)	4.82	2.2	0.8	1.5		
EF3 (2C)	Cathode (sample)	7.6	12.7	0.7	3.2	32.3	11.8
	Anode	4.8	2.7	0.8	1.6		

Statistical analysis was carried out at $p < 0.05$ (95% confidence interval). Data with lower case letters are statistically significantly different to data with the same capital letter.

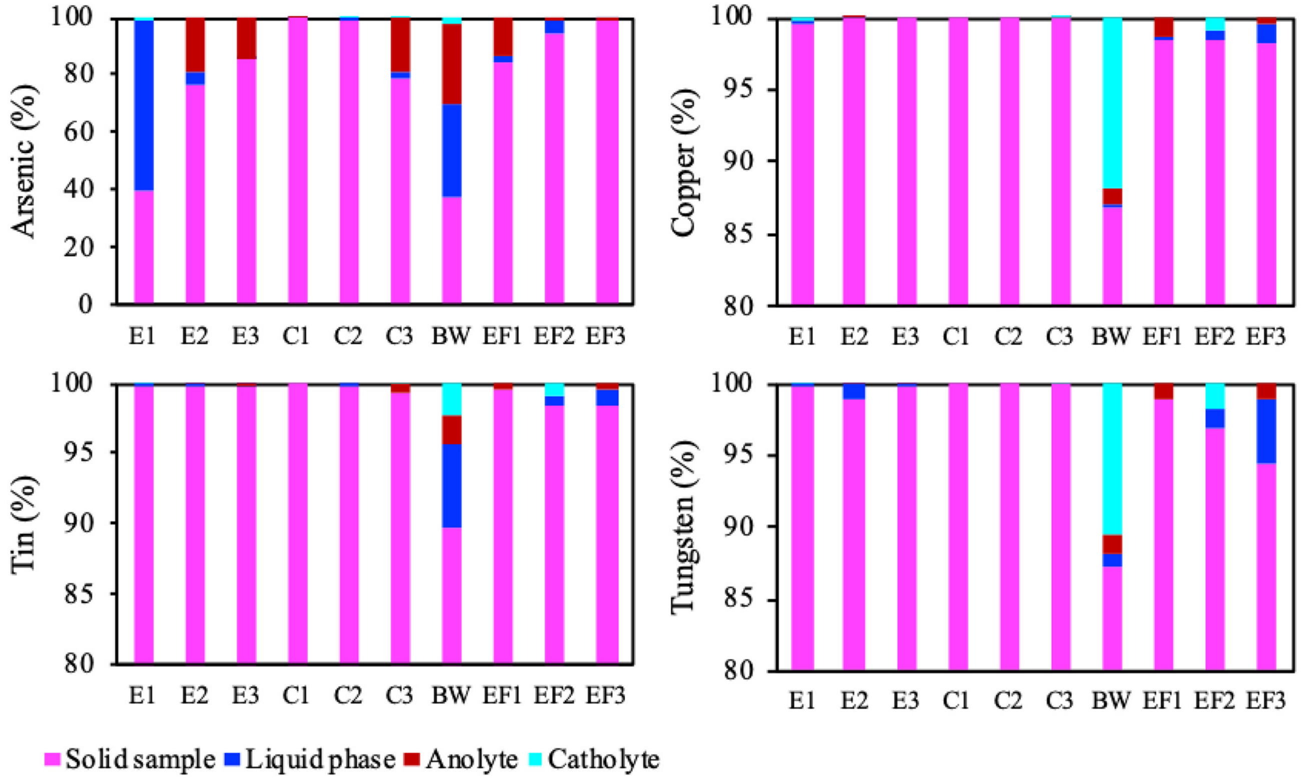

Fig. 4. Arsenic, copper, tin and tungsten distribution in the ED reactor after the ED experiments. E1-CEM, 100 mA; E2-AEM, 100 mA; E3-AEM, 50 mA; C1-control AEM; C2-control CEM; C3-control AEM-CEM; BW-AEM-CEM, NaCl, 100 mA; EF1-AEM, 50 mA; EF2-CEM, 50 mA; EF3-AEM, 65-55-45-35 mA (sequential current intensity).

Contrarily, enhanced experiments (BW, EF1, EF2 and EF3), demonstrated an increase on elements extraction. BW showed the highest electromigration rates, since elements were detected in the anode and in the cathode compartments. Arsenic was detected in the anolyte (28%), while Cu (12%) and W (11%) were mainly detected at the anode end. Tin was detected in both electrolyte compartments in the same proportion (2%). Regarding effluent experiments, advantages namely for Cu, Sn and W extraction were observed, when compared to E1, E2 and E3 experiments. Copper, Sn and W were detected in higher percentages at the anode on EF1 and at the cathode on EF2. The solubilization of Cu (1%), Sn (1%) and W (5%) was obtained when the ED experiment was performed with a combination between effluent and the application of a sequential decreasing current intensity (EF3), that may improve ED efficiency and stability. Thus, the combination of the three tested setups could present advantages for the extraction of Cu, Sn and W.

The possible complexation of metals with substances present in the media may have hindered the extraction and electromigration rates towards the electrolytes compartments. At lower pH, As can form insoluble complexes with Fe oxides as $AsFeO_4$, since high levels of Fe are present in the sample (7250 ± 318 mg/kg, Table 2). Thus, arsenate species may react in an easier way with ferrous ions, inhibiting at the same time Fe reaction with other species, also present in solution (Guan et al., 2011). This type of As, associated to insoluble complexes, is immobile. However, in the reduction state, arsenite is predominant and the complexes formed are mobile (Yang et al., 2015). The presence of Ca (97 ± 45 mg/kg) in the sample may promote the generation of $Ca_3(AsO_4)_2$ as well (Mahapatra et al., 1984). Copper complexation may also occur in presence of As ($Cu(OH)AsO_4$) (De Pedro et al., 2011), Fe ($CuFe_2O_4$) (Satheeshkumar et al., 2019) or SO_4^{2-} ($CuSO_4$) (Xi et al., 2019), limiting Cu extraction. Additionally, Sn complexes may also be formed in the presence of Cu, as Cu_6Sn_5 or Cu_3Sn (Liu et al., 2016).

The W most common form is WO_3, which is present in solution at pH below 2. In addition, SO_4^{2-} presence (217 ± 5 mg/kg, Table 2) may promote the formation of $WO_2(SO_4)_3^{4-}$. These species also blocks oxygen reduction reaction, which is already low in cationic dissolution in electrochemical processes (Lassner and Schubert, 1999). $CaWO_4$ may also be formed in the present conditions (Yekta et al., 2016), complicating W extraction.

In lower proportions, due to the Cl^- presence in the initial sample (5 ± 2 mg/kg, Table 2), $AsCl_3$ (Cazzoli et al., 1978), $[CuCl_2]^-$ (Cotton et al., 1974), $SnCl_3^-$ or $SnCl_4^{2-}$ (Sherman et al., 2000) and $[W_2Cl_9]^{3-}$ (Rollinson, 1973) may also be formed. However, when NaCl was added to the sample suspension in BW (11 g) and also during effluent experiments, which is also reach in Cl^- (193 mg/L, Table S2 in Appendix A) (Magro et al., 2020), the increase in Cl^- content may have potentiated the formation of the species mentioned, promoting at the same time their extraction.

The summary of the extraction of the studied elements from the original matrix is presented in Table 4.

According to Table 4, As showed the highest extraction ratios, compared to the other studied elements. A maximum of 63% of As was successfully extracted from the matrix in the BW experiment, whereas Cu, Sn and W extraction reached 13, 10 and 13%, respectively. Arsenic may have been solubilized from the solid to the liquid phase of the sample compartment due to the pH changes that lead to its speciation. The changes in As oxidation states may have generated a “mobile phase” of this element, potentiating its electromigration to the anolyte/catholyte compartment. Moreover, As extraction is statistically significantly different (p value < 0.0001) compared to As extraction in other experiments, and to Cu, Sn and W in the same experiment (E1 and BW).

4. Conclusions

Generally, secondary mining residues are stable matrices with low conductivity, implying changes both in the ED reactor design and in the process itself. From the results obtained it was observed that an ED 3C reactor might be the most suitable setup for raw materials

Table 4
Arsenic, copper, tin and tungsten extraction from mining residues after ED experiments.

Experiment	Extraction (%)			
	Arsenic	Copper	Tin	Tungsten
E1	60.1 ± 24.1^{a}	0.6 ± 0.5^{A}	0.3 ± 0.1^{A}	0.1 ± 0.1^{A}
E2	$23.4 \pm 3.9^{A,b}$	0.1 ± 0.1	0.3 ± 0.2	1.1 ± 0.3
E3	$14.3 \pm 0.5^{A,c}$	n.d	0.4 ± 0.1	0.4 ± 0.1
BW	$63.2 \pm 28.3^{B,C,d}$	13.4 ± 1.7^{D}	10.2 ± 6.7^{D}	12.6 ± 3.6^{D}
EF1	15.1	1.6	0.4	1.2
EF2	5.8	1.5	1.6	3.1
EF3	1.5	1.7	1.6	5.6
C1	$0.5 \pm 0.2^{A,D}$	n.d	n.d	n.d
C2	$1.1 \pm 0.3^{A,D}$	n.d	0.2 ± 0.2	n.d
C3	$21.0 \pm 0.6^{A,D}$	0.1 ± 0.1	0.7 ± 0.3	n.d

n.d – not detected.
Statistical analysis was carried out at $p < 0.05$ (95% confidence interval). Data with lower case letters are statistically significantly different to data with the same capital letter.
E1-CEM, 100 mA; E2-AEM, 100 mA; E3-AEM, 50 mA; C1-control AEM; C2-control CEM; C3-control AEM-CEM; BW-AEM-CEM, NaCl, 100 mA; EF1-AEM, 50 mA; EF2-CEM, 50 mA; EF3-AEM, 65-55-45-35 mA (sequential decreasing current intensity).

extraction, comparing to ED 2C systems. The conductivity increases by the addition of NaCl on the sample compartment improved the current passage, and consequently, the species extraction (As = 63%; Cu = 13%, Sn = 10% and W = 13%).

At the studied conditions, the ED process potential for Cu, Sn and W extraction from the mining residues is lower than for As, due to the poorer solubilization and migration rate of species to the electrolyte compartments.

Arsenic was successful extracted from the initial sample during the tests performed due to its conversion into mobile forms. Contrarily, raw materials ED extraction was mainly affected by the presence of other compounds in solution, where the formation of complexes inhibited the migration of the elements inside the reactor. However, the development of different treatment stages can overcome the electromigration low rate.

The application of enhancements could be a key factor to improve elements extraction ratios from the mining residues. Additionally, ED operation time could be optimized, promoting savings in terms of labor and energy costs.

Summing up: The improvement of the ED performance targeting the Panasqueira mine residues was achieved by adding eco-friendly enhancements as NaCl and effluent, particularly to As, as mobile forms were obtained with the generated pH changes. For Cu, Sn and W, further adjustments have to be studied in order to increase their extraction efficiencies.

CRediT authorship contribution statement

J. Almeida: Conceptualization, Methodology, Writing - original draft, Visualization, Writing - review & editing, Software, Investigation. **C. Magro:** Conceptualization, Methodology, Writing - review & editing, Investigation. **A.R. Rosário:** Conceptualization, Methodology, Investigation. **E.P. Mateus:** Validation, Resources, Writing - review & editing. **A.B. Ribeiro:** Validation, Supervision, Writing - review & editing, Funding acquisition, Resources.

Declaration of competing interest

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

Acknowledgments

This work received funding from the European Unions Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No. 778045, and from Portuguese funds from FCT/MCTES through grant UIDB/04085/2020. J. Almeida acknowledges *Fundação para a Ciência e a Tecnologia* and EcoCoRe Doctoral program for her PhD fellowship PD/BD/135170/2017. The authors acknowledge Carla Rodrigues and Nuno Costa from REQUIMTE for the ICP and IC analysis, and Eng. Manuel Pacheco from Panasqueira mine for providing the mining residues. This research is anchored by the RESOLUTION LAB, an infrastructure at NOVA School of Science and Technology.

Appendix A

Table S1
Initial and final pH and conductivity values in the electrolytes' compartments on regular and control ED experiments. E1-CEM, 100 mA; E2-AEM, 100 mA; E3-AEM, 50 mA; C1-control AEM; C2-control CEM; C3-control AEM-CEM; BW-AEM-CEM, NaCl, 100 mA; EF1-AEM, 50 mA; EF2-CEM, 50 mA; EF3-AEM, 65-55-45-35 mA (sequential current intensity).

Experiment	Electrolyte	pH		Conductivity (mS/cm)	
		Initial	Final	Initial	Final
E1	Catholyte	6.1 ± 0.4	9.8 ± 1.2^{a}	1.2 ± 0.1	4.5 ± 4.3
E2	Anolyte	5.2 ± 0.6	$1.6 \pm 0.1^{A,b}$	0.7 ± 0.5	6.3 ± 1.6
E3	Anolyte	5.3 ± 0.6	$1.8 \pm 0.4^{A,c}$	0.9 ± 0.1	4.1 ± 0.5
C1	Anolyte	6.1 ± 0.3	4.9 ± 0.1^{A}	1.2 ± 0.4	1.1 ± 0.1
C2	Catholyte	6.1 ± 0.3	$4.1 \pm 0.6^{A,d}$	1.2 ± 0.4	1.0 ± 0.1
C3	Anolyte	5.7 ± 0.9	$1.9 \pm 0.1^{A,e}$	1.4 ± 0.1	3.1 ± 0.6
	Catholyte		$8.2 \pm 1.8^{B,C,D,E}$		1.3 ± 0.1

Statistical analysis was carried out at $p < 0.05$ (95% confidence interval). Data with lower case letters are statistically significantly different to data with the same capital letter.

Table S2
Effluent initial characterisation.

	Total suspended solids (mg/L)	Cl^{-}	NO_3^{-}	SO_4^{2-}
Effluent*	< 15	193	82	28

* Data from (Magro et al., 2020)

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Scientific journal article

A4 Electrodialytic removal of tungsten and arsenic from secondary mine resources — deep eutectic solvents enhancement

J Almeida, R Craveiro, P Faria, AS Silva, EP Mateus, S Barreiros, A Paiva & AB Ribeiro

Published in Science of the Total Environment journal (2020)

This article was published in Science of the Total Environment, Vol 710, J Almeida, R Craveiro, P Faria, AS Silva, EP Mateus, S Barreiros, A Paiva & AB Ribeiro, Electrodialytic removal of tungsten and arsenic from secondary mine resources — deep eutectic solvents enhancement, 136364, Copyright Elsevier (2020).

Science of the Total Environment 710 (2020) 136364

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Electrodialytic removal of tungsten and arsenic from secondary mine resources — Deep eutectic solvents enhancement

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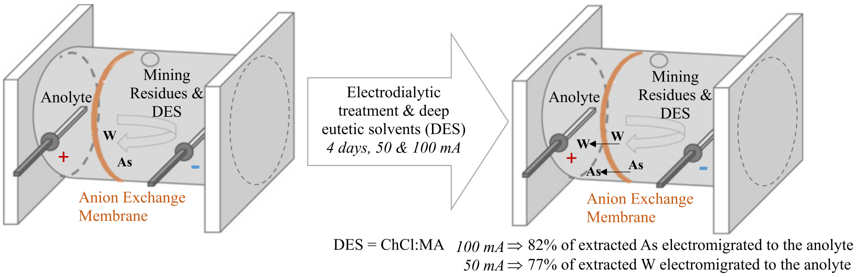
HIGHLIGHTS

- Proof of concept in coupling DES + ED for As and W removal from mining residues
- Best As and W extraction achieved with ChCl:MA (1:2) and ChCl:OA (1:1).
- DES and electrical current use improved extraction for As (22%) and W (11%).
- From total As and W extracted, electromigration achieved 82% for As and 77% for W.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 September 2019
Received in revised form 29 November 2019
Accepted 25 December 2019
Available online 30 December 2019

Editor: Maria Loizidou

Keywords:
Critical raw material
Harmful compound
Secondary resource
Electro-based technology
Choline chloride/malonic acid
Choline chloride/oxalic acid

ABSTRACT

Tungsten is a critical raw material for European and U.S. economies. Tungsten mine residues, usually considered an environmental burden due to e.g. arsenic content, are also secondary tungsten resources. The electrodialytic (ED) process and deep eutectic solvents (DES) have been successfully and independently applied for the extraction of metals from different complex environmental matrices. In this study a proof of concept demonstrates that coupling DES in a two-compartment ED set-up enhances the removal and separation of arsenic and tungsten from Panasqueira mine secondary resources. Choline chloride with malonic acid (1:2), and choline chloride with oxalic acid (1:1) were the DES that in batch extracted the average maximum contents of arsenic (16%) and tungsten (9%) from the residues. However, when ED was operated at a current intensity of 100 mA for 4 days, the extraction yields increased 22% for arsenic and 11% for tungsten, comparing to the tests with no current. From the total arsenic and tungsten extracted, 82% and 77% respectively were successfully removed from the matrix compartment, as they electromigrated to the anolyte compartment, from where these elements can be further separated. This achievement potentiates circular economy, as the final treated residue could be incorporated in construction materials production, mitigating current environmental problems in both mining and construction sectors.

Abbreviations: W, tungsten; As, arsenic; ED, electrodialytic; DES, deep eutectic solvents; ChCl:OA, choline chloride/oxalic acid; ChCl:MA, choline chloride/malonic acid; ChCl:LA, choline chloride/latic acid; PA:U, propionic acid/urea.

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https://doi.org/10.1016/j.scitotenv.2019.136364

1. Introduction

Tungsten (W) is a critical raw material with a wide range of uses, being the largest in cemented carbides production, followed by mill products, alloys and steels (Cuesta-Lopez, 2017). China owns 82% of the world's W mine production (U.S. Geological Survey, 2019). In addition, other W primary ores commercially mined, such as scheelite ($CaWO_4$) and wolframite ($(Fe,Mn)WO_4$), are becoming gradually limited (Yang et al., 2016). The European Union and the United States of America recognized W, respectively, as one of the 27 Critical Raw Materials (European Comission, 2017), and as one of the 35 mineral commodities considered critical to U.S. National Security and Economy (U.S. Geological Survey, 2018). Tungsten deposits have typically a grade of <1% $WO_{3.}$ Additionally, due to the waste rock that needs to be removed to access the ore, W mines produce volume-wise more waste than has originally been mined. The accumulation of residues in open pits generates serious landscape and other environmental problems (Schmidt et al., 2012).

Panasqueira mine (located in the *Centro* region of Portugal) has been active for more than one century and is one of the largest tin (Sn) - W deposits in Europe, with estimated 9.7 Mt of ore resources (Candeias et al., 2014). These mining residues are low grade secondary resources that contain not only W, but also other elements of environmental concern, as arsenic (As) from arsenopyrite (FeAsS) (Candeias et al., 2014), an element which toxicity strongly affects the individuals exposed (Coelho et al., 2014).

The electrodialytic (ED) process is a treatment technology, that has been studied over the last three decades, to remove heavy metals from several environmental matrices: (1) soil (Ribeiro and Mexia, 1997), (2) sludge (Guedes et al., 2015), (3) fly ash (Ferreira et al., 2005), (4) timber waste (Ribeiro et al., 2000) and (5) mine tailings (Hansen et al., 2008, 2007; Zhang et al., 2019). When a low-level direct current is applied between a pair of electrodes, the removal or separation of substances from polluted matrices is promoted (Ribeiro et al., 2016). Despite promising data, the technology readiness level (TRL) remains far from being introduced as an efficient process into the market (Lacasa et al., 2019).

Deep eutectic solvents (DES) have been considered the solvents of the XXI century, having successful results in the extraction of metals from various sources (Abbott et al., 2017, 2015, 2011, 2005; Schaeffer et al., 2018; Söldner et al., 2019; Su et al., 2018). DES are now a feasible option for scale-up purposes, since they are composed by inexpensive and abundant raw materials, and their formulations are simple and reproducible (Smith et al., 2014; Zhang et al., 2012). DES are a mixture of hydrogen bond donors and hydrogen bond acceptors. When mixed at a certain molar ratio, the melting point of the mixture becomes significantly lower than that of the original components (Abbott et al., 2003). Additionally, tuning the water content and composition of DES can change their properties, favoring their versatility for several applications. Through the use of strong acids, as sulfuric and nitric acids, the yields in metals extraction could achieve up to 97% (Gong et al., 2019; Pena-Pereira and Namieśnik, 2014; Shen et al., 2018). However, their negative impacts are also widely recognized (Shen et al., 2019). The use of natural DES offers advantages in terms of costs, toxicity and biodegradability (Pena-Pereira and Namieśnik, 2014).

To the best of our knowledge, the use of DES to enhance the ED process removal/separation yield has not been reported. Mining residues can be treated with ED technologies via stirred suspensions mixtures (Zhang et al., 2019). In these cases, critical raw materials recovery and harmful compounds/elements removal may be extremely attractive. The decrease of primary sources needs and toxic risks in an industrial scale application can be reduced coupling ED and DES.

If a successful recovery of the critical raw material W and the removal of As from secondary mine resources is achieved, it will contribute to close loops, in a circular economy perspective. Secondary resources re-integration provides a platform for the study of new concepts and application of technologies, business models, and policy for sustainable circular economy approaches in several industrial sectors (Velenturf et al., 2019). Furthermore, alternative strategies to recover secondary resources in EU and US will decrease their resources dependency from other countries.

Additionally, in the construction sector, innovative alternatives for materials under basic conditions are now increasing attention since they are less prone to leach hazardous elements and their durability may not be conditioned by physical, chemical and microstructural properties changes. This opens the possibility for treated mining residues with ED and DES be further reused in construction materials, alleviating the need of primary resources.

This work aimed to: (1) assess efficient DES for W and As extraction, (2) combine the use of DES in the ED process, and (3) perform a proof of concept of the feasibility to couple ED treatment and DES to separate W and As from the matrix, into a different compartment.

2. Materials and methods

2.1. Materials

Mining residues were collected at Panasqueira mine, Covilhã, Portugal (40°10′11.0604″N, 7°45′23.8752″W). The plant produces ~900 t WO_3/year, and the collected residues corresponds to the rejected fraction from the sludge circuit, directly pumped into a dam. The collected mining residues were filtered by vacuum with filter paper 42 (Whatman, Germany) and left to dry for 48 h at room temperature. All the experiments were conducted with filtered and dried residues.

Deep eutectic solvents were prepared with choline chloride (ChCl) CAS 67-48-1 (≥99%, Sigma-Aldrich, Germany), malonic acid (MA) CAS 141-82-2 (99%, Sigma-Aldrich, Germany), oxalic acid (OA) CAS 144-62-7 (≥99%, Sigma-Aldrich, Germany), propionic acid (PA) CAS 79-09-4 (99%, Sigma-Aldrich, Germany), urea (U) CAS 57-13-6 (≥99.5%, Merck, Germany) and DL-lactic acid (LA) CAS 50-21-5 (≥85%, Tokyo Chemical Industry, Japan). For water content measurements, Hydranal Coulomat AG CAS 67-56-1 (Honeywell, Germany) was used.

2.2. Experimental set-up

Twelve experiments were carried out in duplicate, according to the conditions presented in Table 1. Due to the heterogeneity of the sample, high standard deviations on the results may be expected. A liquid/solid (L/S) ratio of 9 was selected for the experiments, since ratios between 7 and 12 allow the suspension of the sample, improving extraction efficiencies (Nystroem et al., 2005).

Experiments were designed according to the following objectives:

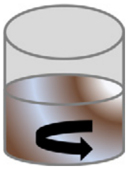
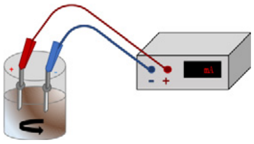
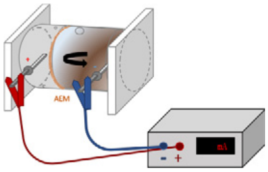
1) To access the best DES combination for As and W extractions

a. Experiments: 1–4
b. Mixture: 2.2 g of mining residues with 20 mL of DES

2) To study the influence of the current intensity with DES on As and W extractions

a. Experiments: 5–8
b. Mixture: 11.1 g of mining residues within 98.5 mL of deionized water and 1.5 mL of DES
c. Set-up: a power supply was connected to a pair of electrodes, and the cathode and the anode ends were placed inside a beaker, in order to

Table 1
Experimental conditions: with DES extraction; DES and current intensity extraction; and DES and electrodialytic separation.

Experiment	Code	Liquid solution proportions	Duration (days)	Current intensity (mA)	Set-up
DES extraction					
1	ChCl:MA	100 % Choline Chloride:Malonic Acid (1:2)	10	-	
2	ChCl:OA	100 % Choline Chloride:Oxalic Acid (1:1)	10	-	
3	ChCl:LA	100 % Choline Chloride:Latic Acid (1:2)	10	-	
4	PA:U	100 % Propionic Acid:Urea (2:1)	10	-	
DES + electrical current					
5	ChCl:MA 50	5 % Choline Chloride:Malonic Acid (1:2) + 95 % Deionized water	4	50	
6	ChCl:OA 50	5 % Choline Chloride:Oxalic Acid (1:1) + 95 % Deionized water	4	50	
7	ChCl:MA 100	5 % Choline Chloride:Malonic Acid (1:2)+ 95 % Deionized water	4	100	
8	ChCl:OA 100	5 % Choline Chloride:Oxalic Acid (1:1) + 95 % Deionized water	4	100	
DES + ED					
9	ChCl:MA 50 ED	5 % Choline Chloride:Malonic Acid (1:2) + 95 % Deionized water	4	50	
10	ChCl:OA 50 ED	5 % Choline Chloride:Oxalic Acid (1:1) + 95 % Deionized water	4	50	
11	ChCl:MA 100 ED	5 % Choline Chloride:Malonic Acid (1:2) + 95 % Deionized water	4	100	
12	ChCl:OA 100 ED	5 % Choline Chloride:Oxalic Acid (1:1) + 95 % Deionized water	4	100	

generate an electric field.

d. Current intensities: 50 and 100 mA

3) To test the feasibility of coupling DES with the ED process in order to increase As and W extraction and allow their later separation in a different compartment.

a. Experiments: 9–12
b. Mixture (cathode compartment): 39 g of mining residues (1.18 g/cm^3) with 345 mL of deionized water and 5 mL of DES
c. Anode compartment: 250 mL of 0.01 M $NaNO_3$ (anolyte)
d. ED set-up: two-compartment cell, as seen in Fig. 1A

The level of the two compartments in the ED set-up is different. The anode compartment is full, and the cathode compartment was filled up to ~400 mL out of a 500 mL capacity (not completely so that no overflow would occur during the stirring), which may potentiate osmosis phenomena from the anode to the cathode compartment during the treatment.

The two-compartment ED set-up (Fig. 1) was an acryl XT cell (RIAS A/S, Roskilde, Denmark) with an internal diameter of 8 cm, and compartment lengths of 5 cm and 10 cm, respectively, for the anolyte compartment and for the sample compartment. An anion exchange membrane, AR204SZRA, MKIII, Blank (Ionics, USA) separated the two compartments. The electrodes were Ti/MMO Permaskand wire with a diameter of 3 mm and a 50 mm length (Grønvold & Karnov A/S, Denmark). A power supply E3612A (Hewlett Packard, Palo Alto, USA) was used to keep a constant current in the cell. A magnetic stirrer at 250 rpm maintained the mixture in suspension into the sample compartment.

2.3. Methods

2.3.1. DES preparation and properties determination

DES were prepared by accurately weighing the amounts of the respective components in screw capped flasks, according to the appropriate molar ratios of each DES, in a Kern 770 weighing scale. The mixtures were then stirred and heated, until a clear homogeneous liquid was obtained (~24 h). When different percentages of distilled water were added, DES were also accurately weighed in order to obtain the desired water content (wt%).

The water content of the DES prepared was measured by Karl-Fischer (KF) titration, using an 831 KF Coulometer from Metrohm, with a generator electrode without diaphragm, and Hydranal Coulomat AG as reagent. The water content values obtained in weight percentage (wt%) are an average of at least three measurements for each DES.

DES viscosities and densities were determined using an SVM 3001 Viscometer (Anton Paar). The samples were submitted to a temperature scan, varying between 20 and 40 °C, in 10 °C intervals.

2.3.2. Experiments control, elements extraction and analysis

In all experiments, pH and conductivity were measured daily, respectively using a Radiometer pH-electrode EDGE (HANNA, USA) and a Radiometer Analytic LAQUA twin (HORIBA Ltd., Japan). Mining residues pH and conductivity were measured in a water suspension (L/S = 9). When an electric field was applied to the experiments, the voltage was also daily measured.

Total concentrations of As and W were determined by Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES) (HORIBA Jobin-Yvon Ultima, Japan), equipped with generator RF (40.68 MHz), monochromator Czerny-Turner with 1.00 m (sequential), automatic sampler AS500 and dispositive Concomitant Metals Analyser. Also, initial As and W concentrations were determined by a TRACER 5 X-ray fluorescence equipment (XRF) (Bruker, Germany) considering a semiquantitive analysis. To quantify the elements in the solid matrix, aqua regia extraction was carried out mixing 0.5 g of mining residues with 3 mL of HCl (37%) and 9 mL of HNO3 (65%). The vessels were set in a shaking table for 48 h at 140 rpm. Then, the samples were filtered by vacuum with 0.45 μm MFV3 glass microfibre filters (Filter lab, Barcelona, Spain) in order to separate any rest of solid present in the liquid to be further analyzed. Finally, the samples were diluted in a volumetric proportion of 1:25 with deionized water. Liquid samples (anolyte and liquid phase) were also filtered in the referred conditions, and all the samples were analyzed by ICP-OES in duplicates.

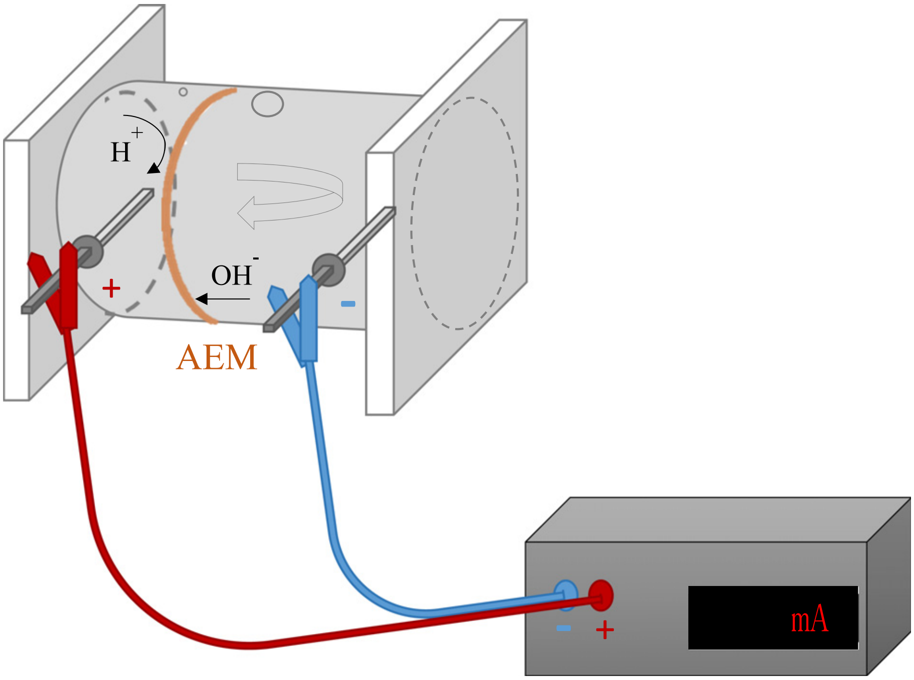
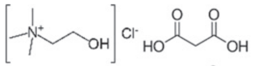
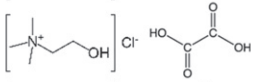
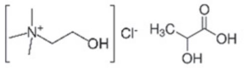
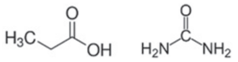


Fig. 1. Electrodialytic two-compartment cell, with stirrer and anion exchange membrane (AEM), connected to a power supply.

Table 2
Identification of the selected DES, molar ratio, designation, water content and molecular structure.

DES	Molar ratio	Designation	Water content (wt. %)	Molecular structure
Choline Chloride:Malonic Acid	(1:2)	ChCl:MA (1:2)	3.0	
Choline Chloride:Oxalic Acid	(1:1)	ChCl:OA (1:1)	0.23	
Choline Chloride:Lactic Acid	(1:2)	ChCl:LA (1:2)	0.74	
Propionic Acid:Urea	(2:1)	PA:U (2:1)	0.78	

2.3.3. Data treatment and analysis

To determine the percentage of As and W that was removed (Eq. (1)), separated (Eq. (2)) and electromigrated (Eq. (3)) in the ED process, the following equations were applied with the elements As/W (El) quantification data at the end of the experiments:

$$\text{El removal }(\%) = \frac{El_{liquid\ suspension}(mg) + El_{elecrolyte}(mg)}{El_{liquid\ suspension}(mg) + El_{elecrolyte}(mg) + El_{mining\ residues}(mg)} \times 100 \quad (1)$$

$$\text{El separation }(\%) = \frac{El_{liquid\ suspension}(mg)}{El_{liquid\ suspension}(mg) + El_{elecrolyte}(mg) + El_{mining\ residues}(mg)} \times 100 \quad (2)$$

$$\text{El electromigration }(\%) = \frac{El_{elecrolyte}(mg)}{El_{liquid\ suspension}(mg)} \times 100 \quad (3)$$

The statistical data from all experiments were analyzed using the software GraphPad Prism version 7.0e. Statistically significant differences among samples for 95% level of significance were calculated through ANOVA tests. The samples were compared according to the following criteria: (1) same element, same current, different DES; (2) same element, different current, same DES, and (3) different elements, same current, same DES.

3. Results and discussion

3.1. Matrix characterization

Mining residues were characterized using XRF and ICP-OES. The XRF results (Fig. A in supplementary data) show that Si (silicon) represents 67.6% of its total composition. The ICP results show the presence of high contents of As and W, 1675 and 130 mg/kg, respectively, but also of other elements, as Cu (71 mg/kg) and Fe (75,150 mg/kg).

The high amount of Si is explained by the presence of quartz, among other silicate minerals in the ore (Candeias et al., 2014). The presence of silica is important once it can be turned into a pozzolanic/reactive material, increasing its durability and thus promoting a broad range of materials with application in the construction sector (Matias et al., 2014).

The pH of the mining residues, in water suspension, is slightly acid (5.3) and their conductivity is extremely low (0.8 mS/cm). Conductivity is an important variable for the experiments, where a current intensity was applied, in order to allow current passage and enable the electrolysis reactions. The addition of DES to all the experiments decreased the suspension pH to values below 2 and promoted sufficient ionic conductivity (up to 2.0 mS/cm, Figure D and Figure F in supplementary data) to maintain the current intensity applied during the selected period of 4 days (see Section 3.2).

3.2. DES characterization and selection

DES have different water contents when compared to their individual initial components. A summary of the DES selected and their water contents is presented in Table 2, where it can be observed that water contents vary between 0.23 and 3%. The data suggests that hydrogen bond network is maintained together with their properties as it is expected for DES with water contents bellow 40 or 50 wt% (Dai et al., 2015; Hammond et al., 2017).

Density and viscosity are DES properties, directly related to their water content and composition that influence the efficiency of their applications. DES extremely viscous normally show lower extraction yields. Viscosity affects the solubilization/extraction yield of elements from solid matrices since mass transfer phenomena are dependent on DES viscosity.

Additionally, for the mining residues application, the DES pH's also influence the solubility of the metal species and the extraction itself. DES containing carboxylic acids, as oxalic acid, malonic acid, lactic acid or propionic acid have an acidic pH (below 2), being more able to dissolve metals and metal oxides (Söldner et al., 2019). Concerning the carboxylic acids, the higher number of carboxyl and hydroxyl groups, as well as a shorter hydrocarbon chain, will result in higher DES viscosity values (Table A in supplementary data).

Preliminary tests were performed by adding four DES with different physico-chemical properties to mining residues, in order to screen their extraction efficiencies for As and W (Table 3). The best extraction yields were obtained with ChCl:MA for As (average: 16.2%), and with ChCl:OA for W (average: 8.8%). Table A (in supplementary data) presents the viscosities data for all experimental DES at room temperature, where viscosities of ChCl:OA and ChCl:MA were ~15,000 and ~4000 mPa·s, respectively. Regarding W and As chemical properties, the extraction efficiency for each element is dependent on the used DES combination.

Table 3
Arsenic and tungsten extraction percentages from mining residues obtained with different DES.

Experiment	Code	As extraction (%)	W extraction (%)
1	ChCl:MA	16.2 ± 5.9^{A}	4.4 ± 0.8^{a}
2	ChCl:OA	6.0 ± 0.9^{a}	8.8 ± 0.3
3	ChCl:LA	4.0 ± 2.4^{a}	0.9 ± 0.1
4	PA:U	7.7 ± 1.7	5.5 ± 0.9

Statistical analysis: multiple comparisons were statistically performed at $p<0.05$ (95% confidence interval); data with capital letter is statistically significantly different from the data with the same lowercase letter.

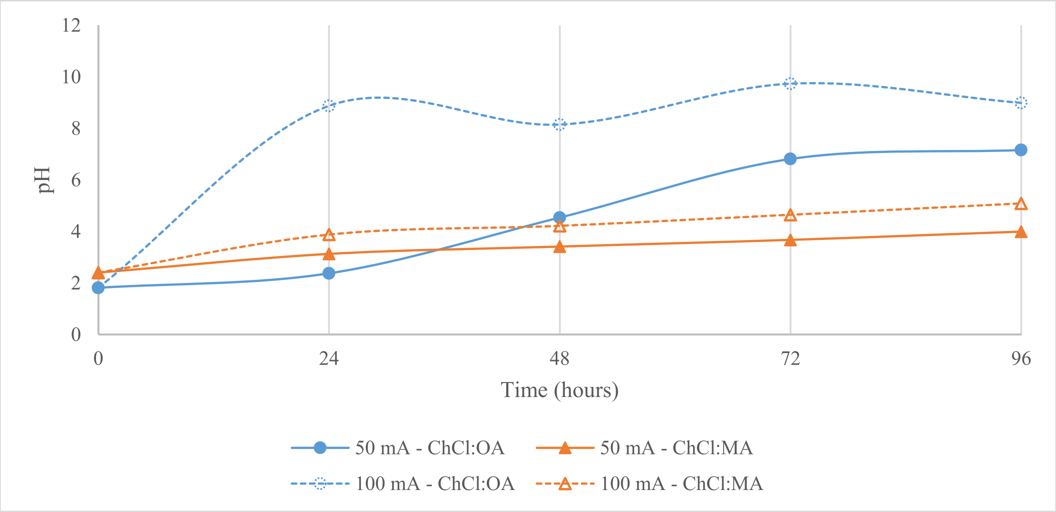


Fig. 2. pH behavior in the cathode compartment during experiments 5–8, corresponding to DES with an applied current intensity.

DES composed by choline chloride may enhance W complexes release, since when high concentrations of chloride ions are available in solution, W may complex and form $[W_2Cl_9]^{3-}$.

The properties of the bidentate oxalate ion may have promoted the formation of complex oxalates with metals (Krishnamurty and Harris, 1961). Once W is in the form of $(Fe,Mn)WO_4$, oxalic acid may react with the solubilized Fe^{2+}, making WO_4^{2-} available in solution.

Arsenic compounds may also be decomposed and stabilized by chloride ions, forming $AsCl_3$. Contrarily to W, a very stable element, As can be solubilized in extremely acidic conditions. On one hand, DES containing carboxylic acids, such as oxalic acid, malonic acid, lactic acid or propionic acid have an acidic pH (below 2). Comparing ChCl:OA, the most acid DES in the study, with ChCl:MA, the second has lower values of viscosity, which may have improved mass transfer phenomena in As case.

3.3. DES and electrical current combination

The combination of a current intensity (50 or 100 mA) with DES to enhance As and W extraction from the sample was tested. ChCl:MA and ChCl:OA were the selected DES for experiments 5–8, since they previously show to be the most efficient in As and W extraction, respectively (Section 3.2 data). For these experiments, a power supply was connected to a pair of electrodes, and the cathode and the anode ends were placed inside a beaker, in order to generate an electric field. The current promoted the alkalization of the media along the time, more evident with ChCl:OA (Fig. 2).

The media alkalization was faster for both DES when a current intensity of 100 mA was applied, achieving ChCl:OA a pH of 9.0 ± 4.3 and ChCl:MA a pH of 5.1 ± 0.8 at the end of the experiments (Fig. 2). Both ChCl:OA and ChCl:MA provided an extremely acidic pH (below 2) to the initial sample. However, during the experiments the pH tends to increase. ChCl:OA is more viscous than ChCl:MA. Also, pKa from OA (1.46) is higher than MA (2.8), which means OA is more acid than MA. Thus, OA may had been consumed to form complexes with other elements (e.g. Cu, Fe), losing its buffer capacity. The result was a faster/higher pH increase when compared to the pH behavior in the ChCl:MA case, that is faster with a current intensity of 100 mA. In some cases, the pH may increase when temperature rises (Skulcova et al., 2018). The electric field generated inside the beaker may also have contributed to increase the temperature and, consequently, the pH overtime.

On the other hand, DES increased mining residues' conductivity, which allowed the passage of the current during the whole experiment time (Fig. B in Supplementary data). The conductivity of ChCl:OA (6.7 ± 3.8 mS/cm) was higher than ChCl:MA (2.0 ± 0.3 mS/cm) at the beginning of the experiments. However, ChCl:MA showed a stable conductivity along the time, with a slight variation (~8%). Contrarily, ChCl:OA decreased drastically its conductivity after 24 h, faster at 100 mA (to 2.1 ± 0.4 mS/cm), maintaining it stable in the remaining time. Oxalic acid may have reacted with elements present in solution, such as Fe (Mashaly et al., 2004) and Cu (Royappa et al., 2016). Complexes may have been quickly formed, lowing ions (e.g. Cl) in solution and, consequently, decreasing the media conductivity in 24 h. Also, since ChCl:OA is more viscous (Table A in supplementary data), ions transport may have been hindered (Craveiro et al., 2016).

Table 4 presents As and W extraction percentages obtained at the end of experiments 5–8. The average extractions were higher in experiment 8, with ChCl:OA at 100 mA (~28% for As and ~16% for W). Comparing the elements extraction between experiments with electrical current and with no electrical current application (Fig. 3), there is an extraction yield upgrade in almost all cases. The highest improvements achieved were ~22% for As extraction (ChCl:OA 100 mA) and ~11% for W extraction (ChCl:MA 100 mA).

The combination of DES and electrical current may help to accelerate tungsten dissolution, since its chemistry is characterized by slow reactions. Paratungstates are the most important species by the progressive acidification of normal tungstate solutions in the pH range of 5–9, while metatungstates are stable in the pH range from 2.0 to 4.0. According to Nguyen and Lee (2016), WO4^{2-} is predominant when pH is higher than 9, which corroborated the data obtained with experiment 8 (ChCl:OA 100 mA).

3.4. ED separation of As and W

Experiments 9–12 were carried out in the two-compartment ED cell (Fig. 1). When the ED process was tested without DES, under the same experimental design and current intensities, the extraction of W was

Table 4
Arsenic and tungsten extraction percentages with ChCl:MA and ChCl:OA, at 50 and 100 mA.

Experiment	Code	As extraction (%)	W extraction (%)
5	ChCl:MA 50	18.2 ± 15.8	5.4 ± 2.8
6	ChCl:OA 50	5.0 ± 5.9	11.2 ± 9.5
7	ChCl:MA 100	10.6 ± 10.2	15.1 ± 9.6
8	ChCl:OA 100	27.6 ± 26.3	15.6 ± 11.5

There are no statistically significantly differences in the results presented at $p<0.05$ (95% confidence interval).

Fig. 3. Improvement percentages of arsenic and tungsten extraction with a current intensity of 50 mA (experiments 5, 6) and 100 mA (experiments 7, 8) compared to the experiments with no current (experiments 1, 2).

<1%. Thus, DES and mining residues were placed in the cathode compartment to assess the potential of extracted As and W to electromigrate into the anolyte, where they can later be separated. Once more, ChCl:MA and ChCl:OA were the selected DES, for the reasons previously explained.

The pH of the anolyte decreased to ~2 (Fig. E in Supplementary data), which was expected due to the water electrolysis generating H^+ at the anode. At the cathode compartment, during the first 24 h for both DES at 100 mA, an abrupt increase of pH to ~12 occurred, suggesting OH^- generation by the water electrolysis at the cathode dominated (Fig. C in Supplementary data).

Table 5 presents the removal percentages of As and W (extracted from the matrix and determined according to Eq. (1) in Section 2.3.3), and the separation percentages of As and W (extracted from the mining residues and that electromigrated into the anode compartment, determined according to Eq. (2) in Section 2.3.3). The highest simultaneous removal of As (35.0 ± 4.8%) and W (22.1 ± 1.8%) was observed with ChCl:OA (experiment 12). However, regarding the separation percentages, for As the highest was registered in experiment 11, with ChCl:MA (21.0 ± 1.2%), while for W was in experiment 12, with ChCl:OA also (7.2 ± 3.1%). Arsenic can be solubilized under acid conditions. Although the pH of the sample compartment increased during the experimental time, the anion exchange membranes separating the anode compartment from the cathode compartment does not work as a perfect rectifier, showering but allowing the passage of H+ to the cathode compartment. Thus, this passage of H+ to the cathode compartment may have contributed for the extraction and separation of As when the pH of the sample compartment turned to basic.

Table 5
Removal and separation percentages of As and W obtained at the end of experiments coupling DES with ED.

Experiment	Code	As (%)	W (%)
		Removal/separation	Removal/separation
9	ChCl:MA 50 ED	10.8 ± 1.6^{b}/4.9 ± 0.5^{e}	1.6 ± 0.38/0.6 ± 0.1
10	ChCl:OA 50 ED	9.2 ± 2.7^{a}/5.6 ± 2.8^{f}	7.4 ± 3.7^{c}/5.4 ± 2.2
11	ChCl:MA 100 ED	25.4 ± $1.1^{B,d}$/21.0 ± $1.2^{E,h}$	7.2 ± 1.2^{D}/4.3 ± 0.1^{H}
12	ChCl:OA 100 ED	35.0 ± $4.8^{A,c}$/17.0 ± $4.6^{F,g}$	22.1 ± $1.8^{C,d}$/7.2 ± 3.1^{G}

Statistical analysis: multiple comparisons were statistically performed at $p<0.05$ (95% confidence interval); data with capital letter is statistically significantly different from the data with the same lowercase letter.

Considering the analytes percentage extracted from the matrix (Table 5), the ratios of As and W that electromigrated into the anode compartment (anolyte) were determined according to Eq. 3 (in Section 2.3.3) and presented in Table 6. The high migration percentages were obtained with ChCl:MA at 100 mA for As (82.3 ± 1.3%) and 50 mA for W (76.5 ± 8.6%). This supported the hypothesis that As and W were in anionic forms and were able to cross the anion exchange membrane in the ED cell and hence to electromigrate into anolyte. Also, since ChCl:MA is less viscous, it may have facilitated the movement of species between compartments, improving the migration ratios.

These results proved the feasibility of coupling DES and ED to isolate As and W from mining residues in the anode compartment, from where they can be recovered. At the same time, the treated mining residues in the cathode compartment may be further used in construction materials, replacing conventional raw materials with economic and environmental benefits. Although the final residue is still not free of pollutants, leaching phenomena of harmful elements may be avoided with the studied treatment since the elements can be encapsulated. Also, there are emerging innovative strategies able to immobilize the remain contents of toxic metals in construction materials production, such as alkali activation (Kiventerä et al., 2018).

Table 6
Percentages of extracted As and W that electromigrated to the anolyte.

Experiment	Code	As migration (%)	W migration (%)
9	ChCl:MA 50 ED	49.8 ± 20.0	76.5 ± 8.6^{A}
10	ChCl:OA 50 ED	58.4 ± 12.9	32.1 ± 11.4^{a}
11	ChCl:MA 100 ED	82.3 ± 1.3^{B}	33.6 ± $2.9^{a,b}$
12	ChCl:OA 100 ED	46.0 ± 2.0	58.6 ± 11.4

Statistical analysis: multiple comparisons were statistically performed at $p<0.05$ (95% confidence interval); data with capital letter is statistically significantly different from the data with the same lowercase letter.

4. Conclusions

The experimental results proved the feasibility of coupling DES and ED to recover tungsten (W) and arsenic (As) from mining residues.

The study assessed the use of different deep eutectic solvents for the extraction of W and As from Panasqueira mine secondary resources on the tested experimental conditions. Their extraction efficiency was DES dependent. DES with choline chloride presented the higher average extraction yields, being ChCl:MA more selective for As (16%), and ChCl:OA for W (9%).

The study on current intensity influence with DES on As and W extractions (4 days experiments) showed an increasing in As and W extraction efficiencies, when compared to the tests with no current. The best average extractions were registered with ChCl:OA at 100 mA (28% for As and 16% for W), although with no statistically significant differences ($p < 0.05$).

A proof of concept of coupling DES with a two-compartment electrodialytic set-up was accomplished. The use of ChCl:OA at 100 mA for 4 days extracted simultaneously ~35% of As and ~22% of W from the matrix. The conditions generated in the cell sample compartment promoted the extraction and migration of As and W from the mining residues. A maximum of ~82% of As and ~77% of W extracted from the original matrix successfully electromigrated into the anode compartment, from where they can be further separated. The data support the applicability of electroremediation processes for this purpose.

Summing up, the experimental data suggests new possibilities for the recovery of critical raw materials and the removal of harmful compounds and elements from secondary mine resources that will contribute to circular economy and to increase sustainability in both mining and construction sectors that are seeking for innovative alternatives for materials production.

Declaration of competing interest

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

Acknowledgments

This work has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No. 778045, as well as from Portuguese funds from FCT/MCTES through grant UID/AMB/04085/2019 and by the Associate Laboratory for Green Chemistry- LAQV UID/QUI/50006/2019. J. Almeida and A. Paiva acknowledge *Fundação para a Ciência e a Tecnologia* for, respectively, her PhD fellowship PD\BD\135170\2017, and for the project IF/01146/2015 attributed within the 2015 FCT researcher program. The authors acknowledge Carla Rodrigues from REQUIMTE for the ICP-OES analysis. This research is anchored by the RESOLUTION LAB, an infrastructure at NOVA School of Science and Technology.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.136364.

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Supplementary data

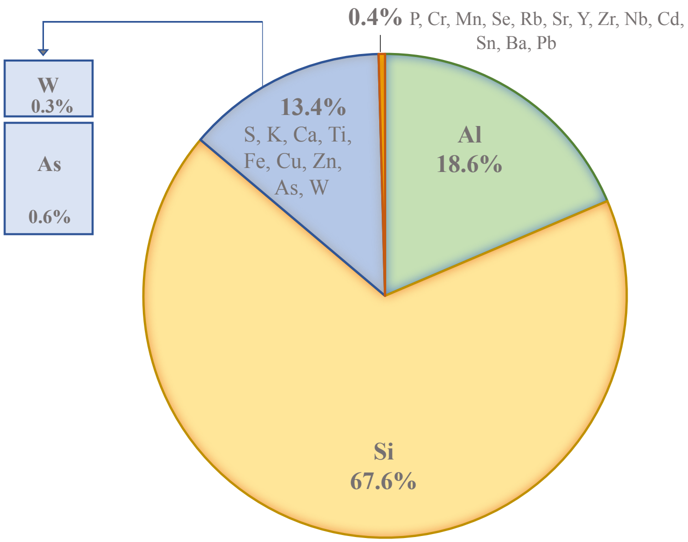

Figure A. Elements distribution in the mining residues, obtained by X-ray fluorescence (Semiquantitative data, wt. %).

Table A. Deep eutectic solvents dynamic viscosity between 20 and 40 ºC (mPa.s).

	mPa.s			
Temperature (ºC)	**ChCl:MA**	**ChCl:OA**	**ChCl:LA**	**PA:U**
20	3,891	14,683	257	22
30	1,251	5,020	137	14
40	538	2,007	78	9

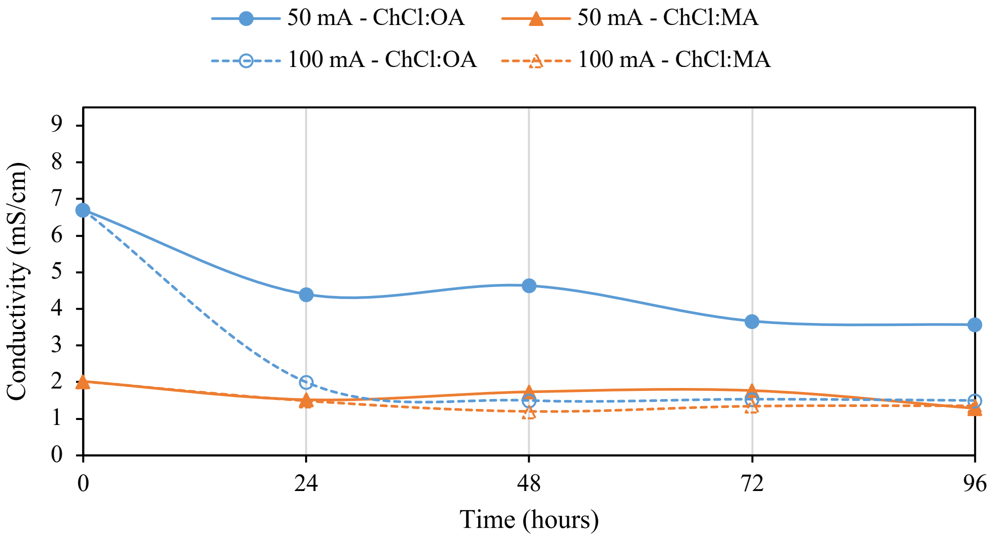

Figure B. Conductivity behavior during experiments 5-9, corresponding of DES with an applied current intensity.

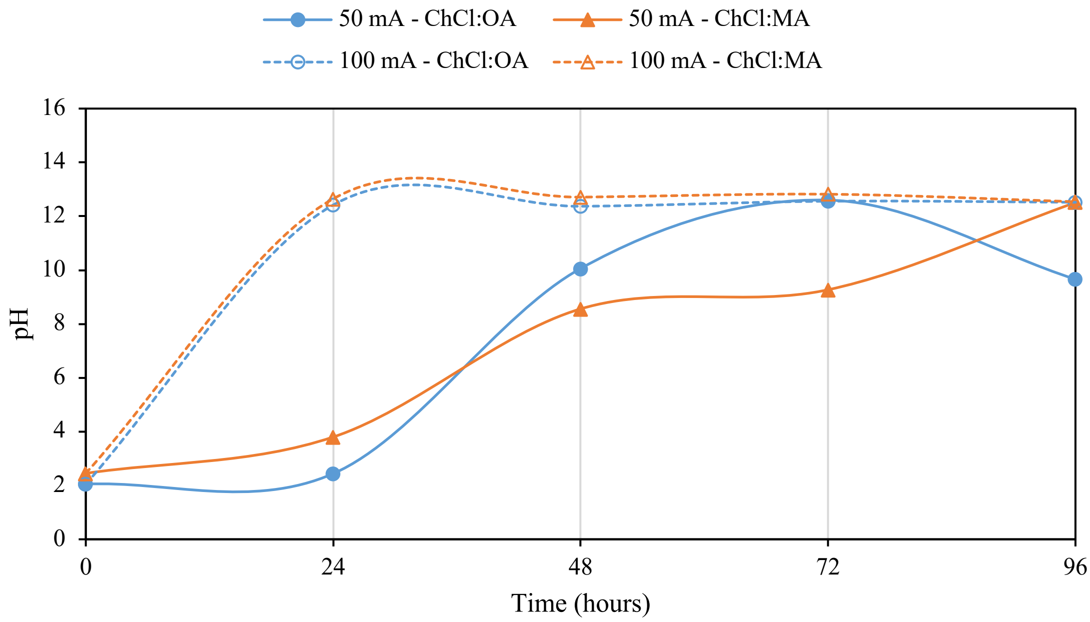

Figure C. pH measured at the cathode compartment of the ED set-up during the experiments 9-12, corresponding to DES + ED.

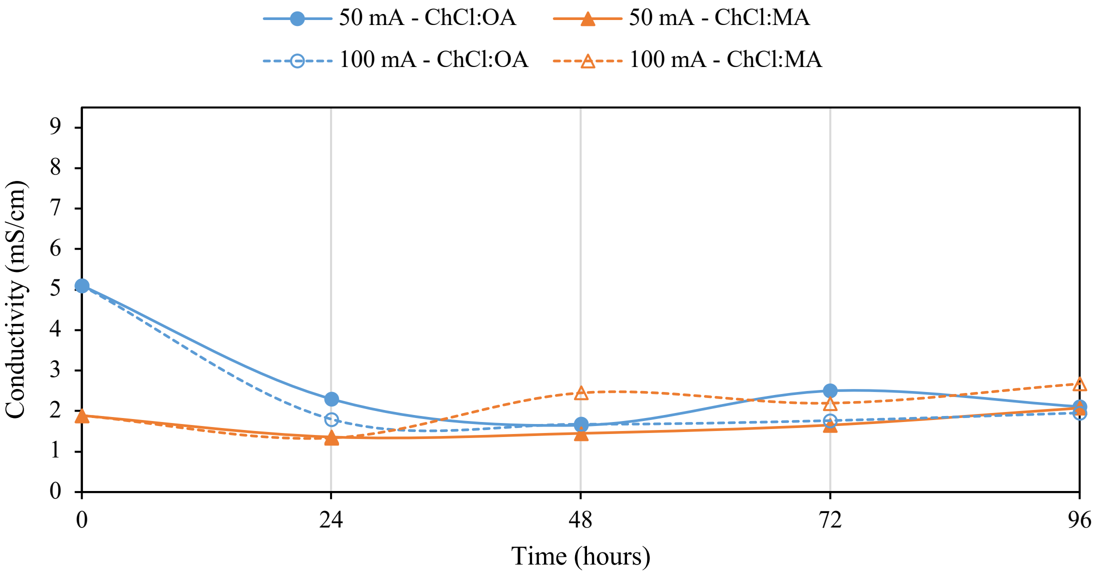

Figure D. Conductivity at the cathode compartment of the ED set-up during the experiments 9-12, corresponding to DES + ED.

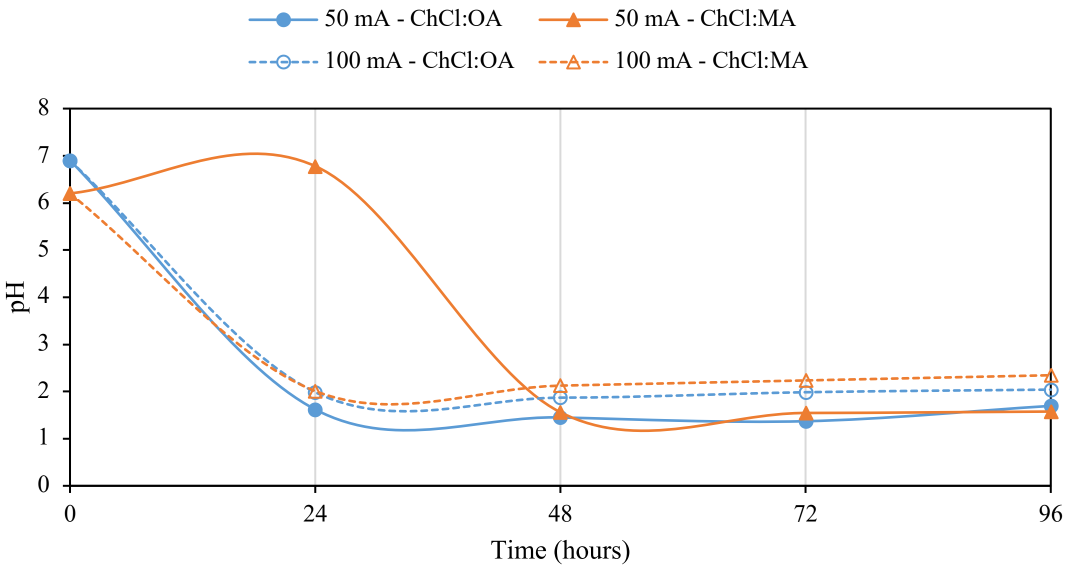

Figure E. pH measured at the anode compartment (electrolyte)of the ED set-up during the experiments 9-12, corresponding to DES + ED.

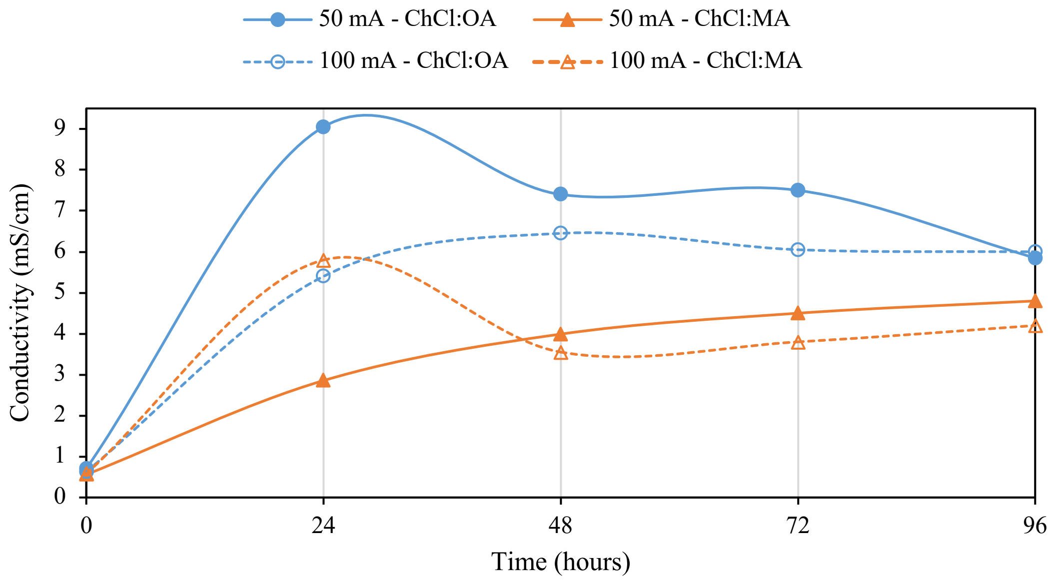

Figure F. Conductivity at the anode compartment (electrolyte) of the ED set-up during the experiments 9-12, corresponding to DES + ED.

Scientific journal article

A5 Electrodialytic hydrogen production and critical raw materials recovery from secondary resources

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Published in Water journal (2020)

This article was published in Water, Vol 12(5), J Almeida, C Magro, EP Mateus & AB Ribeiro, Electrodialytic hydrogen production and critical raw materials recovery from secondary resources, 1262, Copyright MDPI (2020).

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Article

Electrodialytic Hydrogen Production and Critical Raw Materials Recovery from Secondary Resources

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Received: 30 March 2020; Accepted: 27 April 2020; Published: 29 April 2020

Abstract: Electrodialytic technologies are defined as treatment processes that promote the removal/recovery of substances in a matrix, based on the application of low-level current intensities. Additionally, along these processes hydrogen is self-generated, allowing them to operationally produce clean energy. This energy carrier is produced due to electrolysis reactions occurring at the cathode end of the electrodialytic reactor, when using inert electrodes. Herein, hydrogen production during the electrodialytic treatment of sewage sludge and mining residues suspensions (coupled with effluent or sewage sludge), at 50 and 100 mA, was assessed. During the electrodialytic treatment of sewage sludge, hydrogen purity production achieved 33%. When effluent or sewage sludge were used as enhancements in mining residues suspensions, hydrogen purity reached 71% and 34%, respectively. Furthermore, a proton-exchange membrane fuel cell was connected to the cathode compartment of the electrodialytic reactor. The electrical energy generated from self-hydrogen produced at 100 mA achieved ≈1 V in all performed experiments. Simultaneously, critical raw materials extraction, namely phosphorus and tungsten, was evaluated. When the process was applied to mining residue suspensions combined with sewage sludge, the highest extraction ratio of phosphorus (71%) and tungsten (62%) was observed.

Keywords: electrodialytic technology; hydrogen production; proton-exchange membrane fuel cell; energy; phosphorus; tungsten

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1. Introduction

Raw materials are crucial to the European Union's economy and, as the population grows [1], more resources are needed to meet the demand. Raw materials are the main base to produce a broad range of goods and applications for the quotidian life and modern technologies. However, the unhindered access to certain raw materials is raising awareness across the globe. Regarding the high economic importance and scarceness of certain raw materials, in 2017, the European Commission presented a list with 27 critical raw materials to emphasize the need to find reliable alternative suppliers [2].

Simultaneously, the targets presented by European Commission for the period of 2021 to 2030 also comply the reduction of greenhouse gas emissions in more than 40% (regarding 1990 levels) and energy efficiency improvements above 32.5% [3].

Seeking for technology developments on clean energy production through non-fossil resources, its storage and further uses called for new and integrated strategies [4]. Thus, coupling the recovery of critical raw materials from secondary resources with the empowerment of clean energy production will move towards circular economy principles [5].

Technologies based in the electrodialytic process have proved their potential to remove/recover a wide range of contaminants/substrates from environmental matrices [6–8]. Electrodialytic technologies consist on the application of a direct or alternate low-level current density (mA/cm^2) and low potential gradient (V/cm), between a pair of electrodes. Herein, ion-exchange membranes allow a selective separation of cations and anions in concentrated electrolytes' solutions [9]. In this sense, electrodialytic technologies are being shaped for critical raw materials upturn, namely phosphorus (P) from sewage sludge [8] and tungsten (W) from secondary mining resources [10].

Treated effluent and sewage sludge are by-products from wastewater treatment plants (WWTP). Sewage sludge can be regarded as a secondary resource of critical raw materials, e.g., due to its high P content, when compared with effluent. However, treated effluent have also shown feasible reuses in building products [11] and irrigation purposes [12], making electrodialytic treatment also attractive. Sewage sludge can be applied in soil fertilization/remediation if a pre-treatment promotes a product with high quality standards. Moreover, sewage sludge can be used as an energy resource for power and heat by conventional/emerging technologies through the use of biogas and biofuels. The reuse of sewage sludge can, therefore, be economically appealing and sustainable, preventing its disposal as waste in landfills [13].

On the other hand, mining industries produce extremely high quantities of residues due to the low ore grade concentrates [14]. Additionally, the disposal of these residues in open pits can cause severe landscape issues and environmental deterioration. Located in the central region of Portugal, Panasqueira mine has been active for more than one century, representing one of the largest tin (Sn)—W deposits in Europe. Mining residues disposed in Panasqueira area can also be a source of critical raw material, although their low ore grade in W, from wolframite [15].

Despite of promising results in substances removal and separation from a wide range of solid and liquid environmental matrices, energy requirements for electro-based technologies operation are still one of the main operational drawbacks of these treatments. Regarding current low-carbon economy principles [16], this topic was addressed in a proof-of-concept work presented by Magro et al., 2019 [17]. The use of hydrogen produced during the electrodialytic process due to water electrolysis reactions was studied. The experimental reactor was coupled to a proton exchange membrane fuel cell (PEMFC), at the cathode end. Water was reduced to hydrogen gas, with purity levels up to 97% (mol/mol) and promoting the generation of ≈1 V electrical energy throughout the course of wastewater treatment. However, many factors may decrease hydrogen cleanliness, namely the typology of the process, the experimental matrix, and the presence of contaminants, involving competitive redox reactions at the electrodes (e.g., chlorine gas, metals deposition) [17].

Sewage sludge and mining residues suspensions have in common high disposal rates and critical raw materials contents, making them particularly attractive for electrodialytic technologies. Coupling the self-hydrogen production and exploitation with the recovery of P and W, may lead to the decrease of primary energy consumption while decreasing costs, particularly in a full-scale perspective. In addition, treated matrices may be further applied for different purposes, such as in the construction industry [11,18,19], promoting the much needed closed loop systems.

In the present work, the experimental set-up of a three-compartment electrodialytic reactor was operated at 100 and 50 mA, for 1 h and 2 h, respectively. The aim was to compare hydrogen production and purity rates during the electrodialytic treatment of effluent, sewage sludge, and mining residues suspensions, with or without sewage sludge and effluent enhancements. In parallel, the recovery of P and W from all matrices under treatment was assessed.

2. Materials and Methods

2.1. Materials

Secondary effluent (Lisbon, Portugal) and sewage sludge (Sesimbra, Portugal) samples were collected from the secondary clarifier of the respective wastewater treatment plants. Mining residues suspensions were prepared with a rejected fraction from the sludge circuit from Panasqueira mine (Covilhã, Portugal).

2.2. Experimental

The experimental set-up is presented on Figure 1. A three-compartment electrodialytic reactor acryl XT (RIAS A/S, Roskilde, Denmark), with an internal diameter of 80 mm and unitary compartment lengths of 50 mm was used. Anode and cathode compartments were separated from the central sector by an anion exchange membrane, AR204SZRA, MKIII, Blank (Ionics, Ringwood, NJ, USA) and a cation exchange membrane, CR67, MKIII, Blank (Ionics, Ringwood, NJ, USA), respectively. Electrodes composition were Ti/MMO Permaskand wire, with a diameter of 3 mm and a length of 50 mm (Grønvold & Karnov A/S, Copenhagen, Denmark). A power supply E3612A (Hewlett Packard, Palo Alto, USA) was connected to the electrodialytic reactor for constant current. A magnetic stirrer was used in the central compartment to maintain the mixtures in suspension (Figure 1).

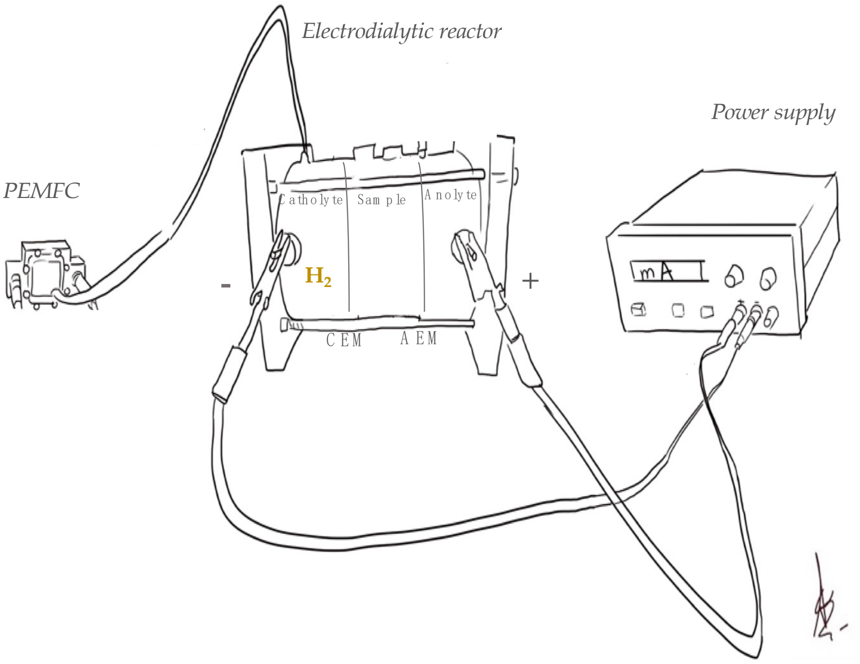


Figure 1. Schematic electrodialytic reactor coupled with a proton-exchange membrane fuel cell (PEMFC). CEM—Cation Exchange Membrane; AEMAnion—Exchange Membrane.

Sewage sludge tests were performed adding 200 mL of sample to the central compartment. Suspensions with effluent or sewage sludge and mining residues were prepared at the same L/S (9), adding 22.2 g of solid sample to 200 mL of liquid sample. Both anolyte and catholyte compartments were filled with 250 mL of 0.01 M $NaNO_3$.

Six electrodialytic experiments were carried out with three matrices and two current intensities (50 and 100 mA), in duplicate: Sewage sludge, mining residues with effluent, and mining residues with sewage sludge. The data from these experiments was compared with the effluent and mining residues data from [17], and ten electrodialytic experiments were evaluated (Table 1).

The hydrogen produced at the reactor cathode was collected in a storage cylinder with 30 mL of capacity (Horizon Fuel Cell Technologies, Singapore). The gas volume was measured every 10 min. For hydrogen purity analysis, the cathode compartment exit vent was connected to a 500 mL tedlar sample bag with a single polypropylene septum fitting (SKC, Cerritos, CA, USA) for 6 h. The gas was analyzed by Gas Chromatography with Thermal Conductivity Detector (GC-TCD). Finally, for electrical power generation, the cathode compartment was directly connected to a 32 mm × 32 mm × 10 mm PEMFC, with a nominal voltage of ≈1 V (Horizon Fuel Cell Technologies, Singapore).

Table 1. Electrodialytic experiments conducted and used to compare gas capture and critical raw materials recovery.

Code	Operation Time (min)	Current Intensity (mA)	Matrix
E50 *	120	50	Effluent
E100 *	60	100	
SS50	120	50	Sewage Sludge
SS100	60	100	
MR50 *	120	50	Mining Residues and Briny Water
MR100 *	60	100	
MRE50	120	50	Mining Residues and Effluent
MRE100	60	100	
MRSS50	120	50	Mining Residues and Sewage Sludge
MRSS100	60	100	

E—Effluent; SS—Sewage sludge, MR—Mining residue. * Data from [17].

The electrodialytic reactor and the fuel cell open circuit voltage were monitored every 10 min using a multimeter KT1000H (KIOTTO, Lisbon, Portugal) [17].

2.3. *Methods*

At the beginning and at the end of every electrodialytic experiment performed, pH and conductivity were measured in central and electrolytes compartments by means of pH (EDGE, HANNA, Providence, RI, USA) and conductivity meters (LAQUA twin, HORIBA Ltd., Kyoto, Japan).

Total concentrations of arsenic (As), calcium (Ca), cooper (Cu), potassium (K), magnesium (Mg), sodium (Na), P, sulfur (S), Sn, W and zinc (Zn) were determined by Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES) (HORIBA Jobin-Yvon Ultima, Kyoto, Japan), equipped with generator RF (40.68 MHz), monochromator Czerny-Turner with 1.00 m (sequential), automatic sampler AS500 and dispositive CMA-Concomitant Metals Analyzer.

Sample preparation for elements´ quantification was performed through acid extraction of solid matrices (dried for 48 h at ≈20 °C): 0.5 g of solid sample with 9 mL HNO_3 (65%) and 3 mL HCl (37%) were placed on a shaking table at ≈125 rpm for 48 h. Finally, the samples were diluted in deionized water (1:25), filtered by vacuum through 0.45 µm MFV3 glass microfiber filters (Filter lab, Barcelona, Spain) and analyzed by ICP-OES.

Hydrogen purity was determined by GC-TCD on a Trace GC Ultra (Thermo Electron Corporation, Beverly, MA, USA), using a Carboxen 1010 plot column (0.32 mm of diameter, 30 m of length). The analytical process was performed in isothermal mode at 35 °C for 50 min. A gastight syringe (vici precision sampling, Baton Rouge, LA, USA) was used to inject a volume of 250 µL on the GC system. The injector was set at 200 °C and the detector/transfer line at 120 °C.

Data statistical analysis was performed with GraphPad Prism software (version 7.0e). The statistically significant differences between samples for 95% level of significance were assessed with ANOVA tests.

3. Results and Discussion

Table 2 presents the initial concentrations of elements in the studied effluent, sewage sludge, and mining residues.

Table 2. Initial characterization of elements in the studied matrices.

Element	Matrix		
	Effluent (mg/L) *	**Sewage Sludge (mg/L)**	**Mining Residues (mg/kg) ***
As	n.d.	0.06 ± 0.01	218.57 ± 132.31
Ca	51.74 ± 18.34	158.98 ± 48.21	91.11 ± 27.08
Cu	0.04 ± 0.00	1.90 ± 0.48	76.82 ± 39.30
K	47.80 ± 29.10	25.51 ± 1.30	n.d.
Mg	118.00 ± 137.17	14.87 ± 3.35	n.d.
Na	524.55 ± 532.55	23.63 ± 0.07	n.d.
S	84.89 ± 65.27 ^{a}	78.35 ± 17.45^{b}	789.59 ± 214.13 ^{A,B}
Sn	n.d.	0.17 ± 0.04 ^{c}	1.95 ± 0.53 ^{C}
Zn	0.07 ± 0.06 ^{e}	7.20 ± 0.99 ^{E}	n.d.
Cl^-	908.1 ± 1013.7	81 $^{\#}$	5.6 ± 2.3

* Data from [17]; n.d.—not detected. $^{\#}$ Value provided by the wastewater treatment plants (WWTP). Statistical analysis performed through multiple comparisons at $p < 0.05$ (95% confidence interval). Data with capital letters are statistically significantly different from the data with the same lower-case letter.

3.1. Characterization of Electrodialytic Experiments

Table 3 presents the pH and conductivity values at the beginning and at the end of the electrodialytic experiments. As expected, the initial pH of the effluent (7.67 ± 0.16), sewage sludge (6.68 ± 0.02), and mining residues suspensions (4.57 ± 1.74) presented different levels. The combination of effluent or sewage sludge with mining residues (pH slightly acid), promoted the neutralization of the matrices (pH of 7.24 ± 0.12 and 7.18 ± 0.04, respectively). Sufficient conductivity on the media has to be guaranteed to assure the passage of the current, and consequently, the removal of elements. The effluent was the matrix with higher conductivity values (2.41 ± 2.12 mS/cm), enhancing the conductivity of mining residues when suspensions were mixed with effluent (from 1.82 ± 0.54 to 2.55 ± 1.92 mS/cm).

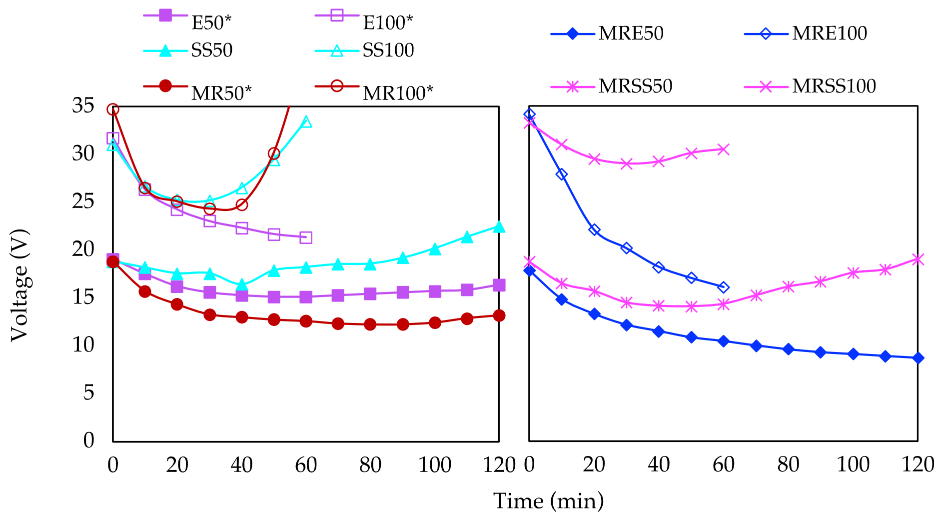
After the electrodialytic process, almost all tested matrices turned slightly more acid (Table 3). This occurred due to the anion exchange membrane permselectivity, which allows the passage of H^+ to the sample compartment and, consequently, the pH tends to decrease. In the anode and cathode compartment, pH values reached ≈2 and ≈12, respectively. This was expected since water electrolysis promotes the generation of H^+ at the anode and OH^- at the cathode compartment. In addition, conductivity in the sample compartment decreased after the experiments, suggesting the electromigration of ions to the anolyte or to the catholyte.

The electrodialytic reactor voltage decreased along the time (Figure 2) and was faster during the experiments performed at 100 mA. Ohm's law defines an inverse relation between resistivity (or conductivity) and voltage, when current intensity is maintained constant. Thus, the increase in conductivity from 0.54/0.90 mS/cm to 0.94–4.0 mS/cm in the anolyte and to 0.91–2.5 mS/cm in the catholyte (Table 3) are related to the voltage decreased in the central compartment. The conductivity in the central compartment is dependent on the matrix and, since the matrices are highly heterogeneous, high standard deviations are observed to the parameters monitored. The experiments operated with sewage sludge and mining residues suspensions showed a voltage increase in the final minutes of the experiments (Figure 2). As an example, when sewage sludge experiments where conducted at 100 mA, the voltage inside the reactor decreased from ≈31 V to ≈25 V after 30 min and increased until ≈34 V in the following 30 min of experiment. The reduction of ions and the energy efficiency decrease related to ohmic losses may have contributed for the oscillations observed.

Table 3. Initial and final pH and conductivity values in the reactor compartments.

Experiment	Compartment	pH		Conductivity (mS/cm)	
		Initial	Final	Initial	Final
E50 *	Anode	6.46 ± 0.55	2.20 ± 0.02	0.90 ± 0.06	2.70 ± 0.00 ^{j}
	Cathode		12.21± 0.01 ^{a}		2.45 ± 0.2^{1}
	Sample	7.67 ± 0.16	4.54 ± 2.55	2.41 ± 2.12	1.80 ± 0.86
E100 *	Anode	6.46 ± 0.55	2.21 ± 0.04	0.90 ± 0.06	2.85 ± 1.06 ^{k}
	Cathode		12.11 ± 0.01 ^{b}		1.94 ± 0.23
	Sample	7.67 ± 0.16	2.85 ± 0.20 ^{o}	2.41 ± 2.12	1.49 ± 0.15
SS50	Anode	7.54 ± 0.38	2.27 ± 0.19	0.54 ± 0.06	1.24 ± 0.14 ^{l}
	Cathode		11.77 ± 0.13 ^{A,c}		0.97 ± 0.02
	Sample	6.68 ± 0.02	5.96 ± 0.18	0.81 ± 0.02	0.37 ± 0.01
SS100	Anode	7.54 ± 0.38	2.15 ± 0.11	0.54 ± 0.06	0.94 ± 0.17 ^{K}
	Cathode		11.51 ± 0.08 ^{B,d}		1.06 ± 0.21
	Sample	6.68 ± 0.02	5.86 ± 0.14	0.81 ± 0.02	0.30 ± 0.01
MR50 *	Anode	6.46 ± 0.55	2.02 ± 0.11	0.90 ± 0.06	3.25 ± 0.21 ^{L}
	Cathode		12.30 ± 0.01 ^{C,e}		2.40 ± 0.14
	Sample	4.57 ± 1.74	5.91 ± 0.45	1.82 ± 0.54	1.41 ± 0.49
MR100*	Anode	6.46 ± 0.55	1.99 ± 0.04f	0.90 ± 0.06	2.55 ± 0.07
	Cathode		12.21 ± 0.25 ^{D,g}		2.08 ± 0.46
	Sample	4.57 ± 1.74	4.42 ± 1.33	1.82 ± 0.54	0.24 ± 0.16
MRE50	Anode	6.46 ± 0.55	2.00 ± 0.02	0.90 ± 0.06	2.70 ± 0.14 ^{n}
	Cathode		12.31 ± 0.02 ^{C,h}		2.12 ± 0.54
	Sample	7.24 ± 0.12	6.50 ± 0.22	2.55 ± 1.92	1.17 ± 0.60
MRE100	Anode	6.46 ± 0.55	2.08 ± 0.01	0.90 ± 0.06	4.00 ± 0.99
	Cathode		12.25 ± 0.03 ^{D,i}		2.20 ± 0.14
	Sample	7.24 ± 0.12	7.51 ± 0.12 ^{O}	2.55 ± 1.92	1.68 ± 0.32
MRSS50	Anode	7.54 ± 0.38	2.36 ± 0.11	0.54 ± 0.06	1.00 ± 0.50 ^{J,N}
	Cathode		11.65 ± 0.16 ^{A,E,H}		1.12 ± 0.28
	Sample	7.18 ± 0.04	6.38 ± 0.23	0.65 ± 0.01	0.61 ± 0.37
MRSS100	Anode	7.54 ± 0.38	2.47 ± 0.18 ^{F}	0.54 ± 0.06	1.05 ± 0.30 ^{K}
	Cathode		11.57 ± 0.11 ^{B,G,I}		0.91 ± 0.04 ^{M}
	Sample	7.18 ± 0.04	6.31 ± 0.01	0.65 ± 0.01	0.43 ± 0.01

E—Effluent; SS—Sewage sludge, MR—Mining residue. * Data from [17]. Statistical analysis performed through multiple comparisons at $p < 0.05$ (95% confidence interval). Data with capital letters are statistically significantly different from the data with the same lower-case letter.



(a) **(b)**

Figure 2. Voltage variation during the electrodialytic treatment: (**a**) effluent, sewage sludge, and mining residues suspensions; (**b**) mining residues suspensions with effluent or sewage sludge, at 50 and 100 mA. E—Effluent; SS—Sewage sludge, MR—Mining residue. *Data from [17].

3.2. Critical Raw Materials Extraction

Sewage sludge and used mining residues can be considered secondary resources of critical raw materials, namely for P and W, respectively. Table 4 presents the initial contents of P and W in all matrices and studied suspensions. Effluent has limited P contents (3.21 ± 0.04 mg/L) since standards for WWTP impose a P removal above 75% for further disposal [20]. On the other hand, sewage sludge is enriched in P (65.83 ± 19.60 mg/L). Additionally, the amount of P in mining residues (36.57 ± 18.74 mg/kg), could potentially be recovered when suspensions are prepared with sewage sludge (108.66 ± 38.34 mg/kg).

Table 4. Matrices' initial and final critical raw materials content, at 50 and 100 mA.

Experiment		Phosphorus		Tungsten	
		Initial	**Final**	**Initial**	**Final**
E50 *	mg/L	3.21 ± 0.04 ^{a}	2.84 ± 0.51 ^{b}	nd [#]	nd [#]
E100 *			3.30 ± 0.14 ^{c}		nd [#]
SS50	mg/L	65.83 ± 19.60	156.97 ± 30.73 ^{B,d}	nd [#]	nd [#]
SS100			146.83 ± 0.25 ^{C,e}		nd [#]
MR50 *	mg/kg	36.57 ± 18.74	20.73 ± 23.81 ^{D}	5.30 ± 1.56	5.64 ± 0.43 ^{f}
MR100 *			30.29 ± 4.88 ^{E}		4.88 ± 1.58 ^{g}
MRE50	mg/kg	39.80 ± 20.61	4.22 ± 0.64 ^{D}	5.30 ± 1.56	3.89 ± 0.13 ^{h}
MRE100			17.81 ± 22.15 ^{E}		3.76 ± 0.27
MRSS50	mg/kg	108.66 ± 38.34 ^{A}	29.59 ± 1.11 ^{D}	5.30 ± 1.56	1.71 ± 0.41 ^{F,H}
MRSS100			33.51 ± 0.66 ^{E}		1.63 ± 0.02 ^{G}

E—Effluent; SS—Sewage sludge, MR—Mining residue; * Data from [17]; [#] nd—not detected. Statistical analysis performed through multiple comparisons at $p < 0.05$ (95% confidence interval). Data with capital letters are statistically significantly different from the data with the same lower-case letter.

After the electrodialytic treatment, differences on the final content of P and W were observed (Table 4). Sewage sludge showed a higher P content after the experiments. Regarding phosphoric acid speciation, for pH of suspensions between 2 and 6, $H_2PO_4^-$ is dominant. When pH increases from 6 to 10, HPO_4^{2-} is the main specie present [21]. Thus, since pH turned to ≈6 in the central compartment at 50 and 100 mA, $H_2PO_4^-$ is the main form in the suspension, being P more available in the media and contributing for the increased P amount detected. Phosphorus availability can also be limited by iron and aluminum at acidic pH and calcium at alkaline pH [22]. Sewage sludge has 158.98 ± 48.21 mg/L of calcium (Table 2). When pH is above 5.5, phosphates can react with calcium to form calcium phosphates. Considering sewage sludge eventual contents on aluminum [23], when pH is below 5.5 it may react more readily with phosphates, reducing the amount of water-soluble P components while increasing the amount of insoluble aluminum phosphates [24].

On the other hand, when mining residues suspension were prepared with sewage sludge, there was a significant decrease of P in the final sample (≈32 mg W/kg; extraction ≈71%). P may form bonds with sulfur (phosphorous sulfides), chloride (phosphorus chloride) ions and calcium (calcium phosphates) [25]. Considering mining residues composition (Table 2), there are high contents of sulfur (789.6 ± 214.1 mg/kg) and, in lower quantities, chloride (5.6 ± 2.3 mg/kg). The formation of other chemical species and the removal of Al, Ca and Fe by the electrodialytic process may had promoted the solubilization of P and increased P extraction/removal from the sample inside the reactor central compartment.

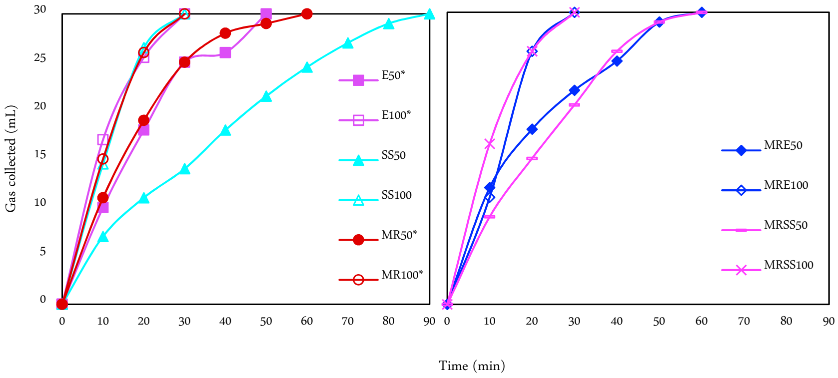
Mining residues have tungsten in the form of (Fe, Mn) WO_4 (wolframite), and contents of W (5.30 ± 1.56 mg/kg). When mining residues suspension were electrodialytic treated with briny water [17], the extraction of W was not significant for both current intensities applied: 5.64 ± 0.43 at 50 mA and 4.88 ± 1.58 mg/kg at 100 mA (Table 4). Monomeric tungstate ion is only stable in neutral/alkaline solutions (pH > 6.2), which may explain the differences of dissolved tungsten concentrations [26].

Contrarily, when mining residues suspensions were prepared with effluent, the extraction of W was higher, meaning lower contents of W in the final sample (≈4 mg W/kg; extraction ≈25%). This may have occurred due to complex formation, which promotes the extraction of W from mining residues. Effluent is rich in calcium (Table 2), where W can form complexes such as $CaWO_4$ [27]. When mining residues suspensions were mixed with sewage sludge, W extraction showed the highest extraction rate. Less than ≈2 mg/kg of W (W extraction ≈62%) remained in the final sample (Table 4), which may be caused due to W complexes formation with P (tungsten phosphides, WP) together with W calcium complexes [28].

Coupling mining residues with effluent and sewage sludge promoted a final pH range of the suspension ≈6.3–7.5. In the absence of complexing substances, W in aqueous solution mainly exists under the soluble form of tungstic ions $(WO_4)^{2-}$ that are stable at neutral and alkaline pH (higher solubility at alkaline pH). The W insoluble/slightly soluble species WO_2 and W_2O_5 are stable between pH 5 and 6.5, while WO_3 is stable below pH 5 throughout all the oxidizing conditions [29,30].

3.3. Hydrogen Generation and Purity

Figure 3 presents the gas produced at the cathode compartment during the electrodialytic experiments. A maximum of 30 mL was collected in all experiments due to the reservoir capacity. The hydrogen flow rate production during electrodialytic treatments can be affected by the matrix itself, competing cathode reactions, and the current intensity applied [17].



(**a**) (**b**)

Figure 3. Gas collected during the electrodialytic treatment from the cathode compartment: (**a**) effluent, sewage sludge, and mining residues suspensions at 50 and 100 mA; (**b**) mining residues suspensions with effluent or sewage sludge, at 50 and 100 mA. E—Effluent; SS—Sewage sludge, MR—Mining residue. * Data from [17].

At 100 mA, effluent, sewage sludge, and mining residues with or without wastewater resources, showed similar rates of gas production (≈1 mL/min). However, at 50 mA, the gas production rates were lower and more variable, from a minimum of 0.33 mL/min on sewage sludge compared to a maximum of 0.68 mL/min on effluent [17] (Table 5).

Table 5. Hydrogen flow rate (slope), its R-square and purity.

Experiment	**Hydrogen**		
	Flow mL/min (Slope)	**R-Square (Slope)**	**Purity *w/w* (%)**
E50 *	0.68	0.97	-
E100 *	1.13	0.96	90.4 ± 0.3 ^{a}
SS50	0.33	0.97	-
SS100	1.02	0.94	32.6 ± 0.5 ^{b}
MR50 *	0.62	0.94	-
MR100 *	1.12	0.97	72.4 ± 0.7 ^{A,B}
MRE50	0.47	0.91	-
MRE100	1.05	0.96	71.3 ± 0.7 ^{A,B,c}
MRSS50	0.50	0.94	-
MRSS100	1.0	0.93	33.6 ± 4.9 ^{A,B,C}

E—Effluent; SS—Sewage sludge, MR—Mining residue; * Data from [17]. Statistical analysis performed through multiple comparisons at $p < 0.05$ (95% confidence interval). Data with capital letters are statistically significantly different from the data with the same lower-case letter.

The gas from the cathode compartment was collected in tedlar sample bags and analyzed. Table 5 shows the hydrogen purity for the experiments performed at 100 mA. Comparing the results from the previous work [17], where the highest hydrogen purity (% *w/w*) was verified during effluent electrodialytic treatment (90.4 ± 0.3%), in the present study sewage sludge reported the lowest hydrogen purity (32.6 ± 0.5%). Effluent hydrogen purity has statistically significant differences ($p < 0.05$) from all the experiments, except from sewage sludge. Moreover, mining residue suspensions with sewage sludge or effluent are statistically significant different between them.

The hydrogen production rate and purity may have been affected due to competing cathode reactions. Comparing effluent and mining residues, sewage sludge is richer in organic matter [31]. Hydrogen production may be affected by methane (CH_4), which is produced by methanogenic organisms commonly present in most of mixed cultures. Hydrogenotrophic organisms may transform CO_2 and H_2 to produce methane gas [32] (Equation (1)). Bacteria may move together through direct current application by electroosmosis and electrophoresis phenomena [33]. Furthermore, some bacteria may adhere to several surfaces or other microorganism [34], promoting also their movement to the cathode compartment. Microorganisms form clusters, due to their natural behavior and may interact with environment in experimental conditions [35].

Hydrolysis and fermentation reactions may also lead to the generation of CH_4 and CO_2 gases in the reactor (Equations (2) and (3)) [36]. Sewage sludge have also nitrogen contents (total nitrogen = 500 mg/L, data provided by the WWTP). This may have contributed for NO_2 gas generation [17] (Equation (4)), decreasing the purity of the hydrogen collected.

$$4H_2 + CO_2 \rightarrow CH_4 + H_2O \tag{1}$$

$$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2 \tag{2}$$

$$4HCOO^- + 4H^+ \rightarrow CH_4 + 3CO_2 + 2H_2O \tag{3}$$

$$NO_2 + H_2O \rightarrow NO_3^- + 2H^+ \tag{4}$$

Considering hydrogen capture conditions at 1 atm and 25 °C and comparing with [17] results at 100 mA, the hydrogen purity collected from each matrix decreased in the following sequence: E100 > MR100 > MRE100 > MRSS100 > SS100 (Table 5).

3.4. Electrical Requirements and Savings

Electrodialytic experiments were carried out at a constant current of 50 and 100 mA. Thus, the electrical energy required during each process, regarding the energy applied by the direct current power source, was determined by Equation (5), where *I* is the current intensity (mA) and $V_{reactor}$ is the voltage inside the electrodialytic reactor (*V*), between the initial (t_0) and final (*t*) operation time (min):

$$E = I\int_{t_0}^{t} V_{reactor}(t)\,dt \quad (5)$$

Electrical energy requirements grow with the increase of electrical current applied, considering the same circulated charge. The experiments performed at 100 mA required 9.5 ± 1.5 kJ of electrical energy and the experiments carried out at 50 mA required 5.50 ± 1.40 kJ.

Considering a H_2 heat of combustion of 141.8 MJ kg^{-1}, and fuel cell energy conversion efficiencies of 40–60% [37,38], between ≈5 to 8% of the electrical energy required in experiment MRE50 (the best case reported) can be saved. This may also translate into economic benefits on the overall electrodialytic treatment.

When the electrodialytic treatment is applied to liquid matrices, the energy requirements for the electrolysis reactions are lower due to associated higher conductivity values. On the other hand, in solid porous matrices, the electrodialytic process reaches higher voltage gradients due to the lower conductivity, requiring longer treatments. Coupling fuel cell technologies may be a key factor in electrodialytic energy savings, through the improvement on operation and energy efficiencies. In addition, self-hydrogen produced in electrodialytic reactors can be stored and used/sold for energy dependent industrial sectors.

In this sense, a proton-exchange membrane fuel cell (PEMFC) was connected directly to the cathode compartment from all the experiments carried out at 100 mA. The PEMFC initial open circuit voltage was between 1.2–1.4 V, showing a pronounced decrease in the first 10 min and remaining stable until the end of the experiments (Figure 4). In all cases, chemical energy was converted to electrical energy, supporting the versatility of PEMFC applicability to a broad range of matrices. Although PEMFC chemical energy transformation into electrical energy is not directly dependent on hydrogen quality, it may have repercussions on future PEMFC performance and long-term stability. Impurities in the gas that flows inside the PEMFC, such as CO, H_2S, NH_3, and CH_4, could cause damage on electrodes, catalyst poisoning and, consequently, fuel cell functioning degradation [39].

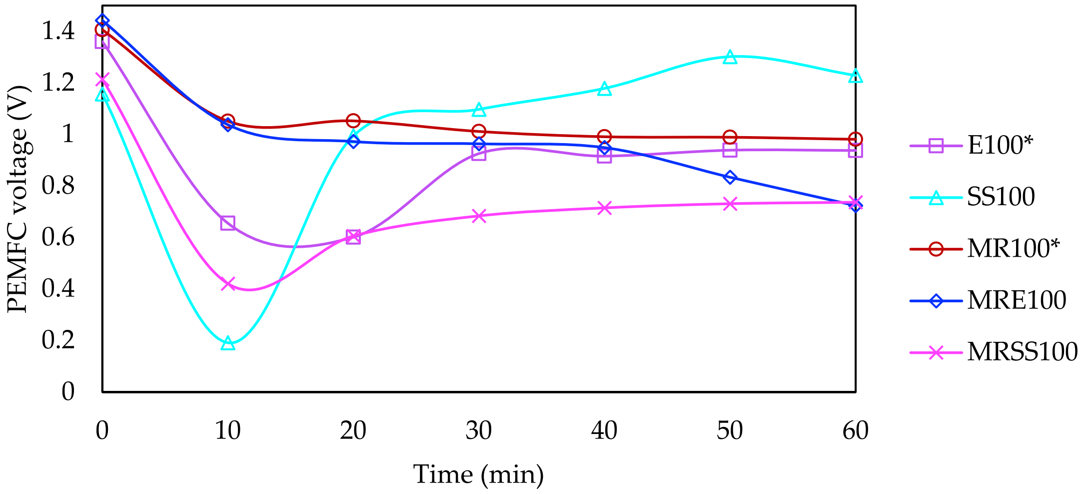


Figure 4. Proton-exchange membrane fuel cell voltage variation. E—Effluent; SS—Sewage sludge, MR—Mining residue. * Data from [17].

4. Conclusions

The present study proved the suitability of wastewater resources, as secondary effluent and sewage sludge, to enhance electrodialytic critical raw materials recovery from mining residues.

Simultaneously, clean energy production was addressed due to the self-hydrogen generated during the electroremediation of the environmental matrices.

The electrodialytic extraction of P (71%) and W (62%) from sewage sludge and mining residues suspensions was more effective when both matrices were combined. This can potentiate circular economy while mitigating environmental negative impacts of waste disposal from both sewage sludge and mining industries.

Regarding the potential of electrodialytic technologies as hydrogen sources, the experiments performed demonstrated that hydrogen was produced in all tested cases, with purities between 33% (sewage sludge) and 71% (mining residues suspension with effluent). Competitive cathode reactions may affected the hydrogen purity, namely in sewage sludge due to its complex composition. Thus, future works should address the composition of other gases to verify competitive cathode reactions. Self-hydrogen produced during electroremediation of the matrices promotes a stable electrical energy generation (1.2–1.4 V) and a way to reuse the previous energy recovered. This was validated through a proton-exchange membrane fuel cell connected to the cathode compartment of the electrodialytic reactor. Hydrogen generated at cathode electrolysis reaction can reduce electrical energy requirements from 5% to 8%, namely in terms of electrodialytic treatments or other remediation strategies concerning electrochemically induced transport.

The critical raw materials recovered and the energy achievements may empower the sustainable growth of electrodialytic technologies, as these technologies can couple economic benefits.

Author Contributions: Conceptualization, J.A. and C.M.; Data curation, J.A. and C.M.; Formal analysis, E.P.M. and A.B.R.; Funding acquisition, A.B.R.; Methodology, J.A.; Project administration, A.B.R.; Resources, E.P.M., and A.B.R.; Supervision, A.B.R.; Validation, E.P.M. and A.B.R.; Writing—original draft, J.A.; Writing—review & editing, J.A., C.M., E.P.M., and A.B.R. All authors have read and agreed to the published version of the manuscript.

Funding: This work received funding from the European Union's Horizon 2020 research and innovation program under Grant Agreement No. 776811, under the Marie Skłodowska-Curie grant agreement No. 778045, and from Portuguese funds from FCT/MCTES through grant UIDB/04085/2020. J. Almeida acknowledges Fundação para a Ciência e a Tecnologia and EcoCoRe Doctoral program for her PhD fellowship PD\BD\135170\2017.

Acknowledgments: The authors acknowledge Carla Rodrigues and Nuno Costa from REQUIMTE for the ICP and GC-TCD analysis, Olga Paredes from SIMARSUL Grupo Águas de Portugal for the sewage sludge samples and characterization, and Manuel Pacheco from Panasqueira mine for providing the mining residues. Authors also thank Adriana Silva for her help with the reactor drawing. This research is anchored by the RESOLUTION LAB, an infrastructure at NOVA School of Science and Technology.

Conflicts of Interest: The authors declare no conflict of interest.

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Scientific journal article

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Published in Applied Energy journal (2019)

This article was published in Applied Energy, Vol 255, C Magro, J Almeida, JM Paz-Garcia, EP Mateus & AB Ribeiro, Exploring hydrogen production for self-energy generation in electroremediation: a proof of concept, 113839, Copyright Elsevier (2019).

Applied Energy 255 (2019) 113839

Contents lists available at ScienceDirect

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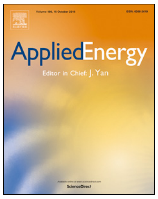

Exploring hydrogen production for self-energy generation in electroremediation: A proof of concept

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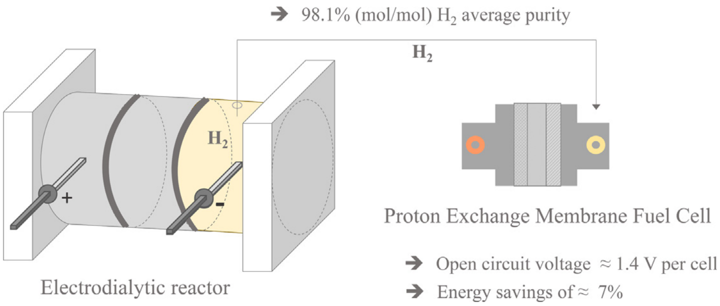
HIGHLIGHTS

- Self-produced H_2 from electrodialytic treatment of environmental matrices collected.
- Collected H_2 average purity (% mol/mol) of ≈98%.
- A fuel cell used to produce electricity from the self-produced H_2 (~1 V).
- Experimental self-generated energy promotes savings on electroremediation (≈7%).

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Electrodialytic treatment
Hydrogen production
Proton-exchange membrane fuel cell
Energy savings

ABSTRACT

Electrodialytic technologies are clean-up processes based on the application of a low-level electrical current to produce electrolysis reactions and the consequent electrochemically-induced transport of contaminants. These treatments inherently produce electrolytic hydrogen, an energy carrier, at the cathode compartment, in addition to other cathode reactions. However, exploring this by-product for self-energy generation in electroremediation has never been researched. In this work we present the study of hydrogen production during the electrodialytic treatment of three different environmental matrices (briny water, effluent and mine tailings), at two current intensities (50 and 100 mA). In all cases, hydrogen gas was produced with purities between 73% and 98%, decreasing the electrical costs of the electrodialytic treatment up to ≈7%. A proton-exchange membrane fuel cell was used to evaluate the possibility to generate electrical energy from the hydrogen production at the cathode, showing a stable output (~1 V) and demonstrating the proof of concept of the process.

1. Introduction

Global energy demands from an increasing human population is a major concern for the planet sustainability. Extensive research and technology development have been focused on renewable energy sources and other strategies to reduce CO_2 emissions [1]. Fuel cell technology, which can efficiently generate electricity using hydrogen as fuel, has attracted widespread attention in recent years [2]. The proton-exchange membrane fuel cells success depends on their ability to obtain optimal fuel to electricity conversion with a high current density, as well as the sustainable and economical production of the fuel [3]. Pure hydrogen gas is scarce in Earth's atmosphere. However, it can be

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https://doi.org/10.1016/j.apenergy.2019.113839
Received 21 March 2019; Received in revised form 11 August 2019; Accepted 1 September 2019

produced from different primary-energy sources. For instance, it can be generated from fossil fuels through steam reforming, partial oxidation or gasification and from renewable sources through biomass gasification and water electrolysis [4,5]. Generation of H_2 via water electrolysis is still limited by the high cost, namely ≈ 3.8 times more expensive than gasification, and ≈ 5 times more expensive than from methane steam reforming [6]. Hence, steam reforming, which combines high-temperature steam with natural gas, currently accounts for the majority of the H_2 produced. Hydrogen production via water electrolysis is currently only applied in combination with renewable energy sources, like solar or wind, and used as an energy storage system.

Electro-based technologies, such as electrokinetic and electrodialytic processes, have been the focus of vast environmental remediation research over the last three decades [7,8], both *in-situ* [9,10], and *ex-situ* [11–13]). Despite such research efforts, the technology readiness level (TRL) for many of those technologies remains very low; although most are considered promising, many are far from being introduced as efficient processes into the market. Important barriers need to be overcome to reach high TRLs [14]. Operational energy costs have to be considered and, are related not only to the electrolysis reactions but mainly with the stirring, the ohmic losses and the energy required for the transport of charge through the porous matrix. In fact, the distance between electrodes (cell size) plays a crucial role in the energy costs of the specific-energy required for the target contaminants removal [7,15]. To the best of our knowledge, there has been minimal research conducted related to the reuse of the elemental gases produced in the electrolysis reactions during electrochemically-induced treatments. The drawbacks found in the current literature are associated to the reactors' design. Most electrokinetic and electrodialytic (ED) setups are designed to allow for the produced gases to flow freely into the atmosphere, while aiming to reduce pressure-related transport mechanisms. Thus, a gas collection strategy during the treatment is not included in the system, causing gas losses to the atmosphere. As a novel feature, the H_2 produced during the treatment at the cathode compartment may be used as fuel in a proton-exchange membrane fuel cells to produce electrical energy and reduce the energy costs of electro-remediation. Additionally, as an energy carrier, H_2 can be used to accumulate energy during the electric power demand valleys, and to generate electric power during the peaks. Therefore, a reservoir can be integrated into the ED system where it can recover and use the H_2 produced for different purposes.

This work evidences the possibility of using the H_2 produced during electrochemically-induced remediation of three different environmental matrices: (1) moderately-salted water – briny water, (2) secondary effluent from a wastewater treatment plant, and (3) mine tailings. Our proof of concept demonstrates that the H_2 captured and reused from these ED treatments is feasible. Herein, a three-compartment ED set-up was used to minimize the interactions of the sample and the contaminants with the electrolysis reactions (Fig. 1).

2. Theory

2.1. Proton-exchange fuel cell

A fuel cell is an electrochemical device that converts the chemical energy from a fuel into electricity through the reaction of the fuel with oxygen or another oxidizing agent. For example, a proton-exchange membrane fuel cell (PEMFC) combines H_2 and O_2 to produce electricity and heat without emitting other products which are different from the water formed in the reaction Eq. (1) [16]:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{1}$$

A fuel cell, unlike a battery, produces electricity as long as fuel is supplied, never losing its charge. The pollution-free production of energy and high power density makes the fuel cell technology a viable approach for future energy industries [2]. Fuel cells show high energy conversion efficiency, up to 60%, higher than traditional internal combustion engines [17]. This efficiency can increase up to 80% with heat-recovery systems [18].

2.2. Electro-based technologies

Electrokinetic and ED strategies are commonly applied to remove organic [19] and/or inorganic contaminants from soils or other porous matrices, such as sewage sludge, fly ash or construction materials [20–22]. The electrochemically-induced transport is based on the application of a low level direct current which promotes electrolysis reactions at the electrodes [20,23,24], involving in most cases water oxidation at the anode, Eq. (2), and water reduction at the cathode, Eq. (3):

$$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l);\quad E^o_{anode}(25\ ^\circ C) = 1.23\ \ V \tag{2}$$

$$H_2(g) + 2OH^- \rightarrow 2H_2O(l) + 2e^-;\quad E^o_{cathode}(25\ ^\circ C) = 0.83\ \ V \tag{3}$$

Competing redox reactions may occur as, for example, the production of chlorine at the anode in systems with high chloride contents [25], Eq. (4):

$$Cl_2(g) + 2e^- \rightarrow 2Cl^-;\quad E^o_{anode}(25\ ^\circ C) = 1.36\ \ V \tag{4}$$

or the deposition of metals (Me) at the cathode, Eq. (5):

$$Me^{2+} + 2e^- \rightarrow Me^o \tag{5}$$

The electrochemical-induced transport of chemical species takes place by three main transport mechanisms: electromigration, electroosmosis, and electrophoresis. Diffusion and advection may also play an important role [20]. In the case of the ED process, electrodialysis also occurs, as ion-exchange membranes are used to separate the matrix from the electrode compartments (aiming to control the pH conditions of the electrolytes and the treated matrix while improving the selectivity on the contaminant removal [20]). Over the years, different electro-based remediation set-ups have been proposed, where the configuration of the sample and the electrode compartments have been modified depending on the nature of the contaminant and matrix [26,27].

3. Materials and methods

3.1. Materials

The briny water solution was prepared with NaCl (PA grade, Merck, Germany) and tap water (Almada, Portugal). Effluent, the liquid fraction that results from wastewater treatments, was collected in the secondary clarifier at a wastewater treatment plant (Lisbon, Portugal). Mine tailings were collected at Panasqueira mine (Covilhã, Portugal, 40°10′11.0604″N, 7°45′23.8752″W). Panasqueira mine produces around 900 t WO_3/year [28] and the pond where the residues are deposited is an open air impoundment that contains rejected ore concentrates with high metal levels [29]. The matrix used for this study is a rejected fraction from the sludge circuit, that is directly pumped to the Panasqueira dam.

3.2. Experimental set-up

The ED cell set-up was a 3 compartment acryl XT cell [30] (RIAS A/S, Roskilde, Denmark), as represented in Fig. 1. The internal diameter was 8 cm and the central and electrolyte compartments length were 5 cm. The two electrode compartments were separated from the central section by an anion exchange membrane, AR204SZRA, MKIII, Blank (Ionics, USA) and a cation exchange membrane, CR67, MKIII, Blank (Ionics, USA). The electrodes were made of Ti/MMO Permaskand wire: $\varnothing = 3$ mm, $L = 50$ mm (Grønvold & Karnov A/S, Denmark). Ti/MMO

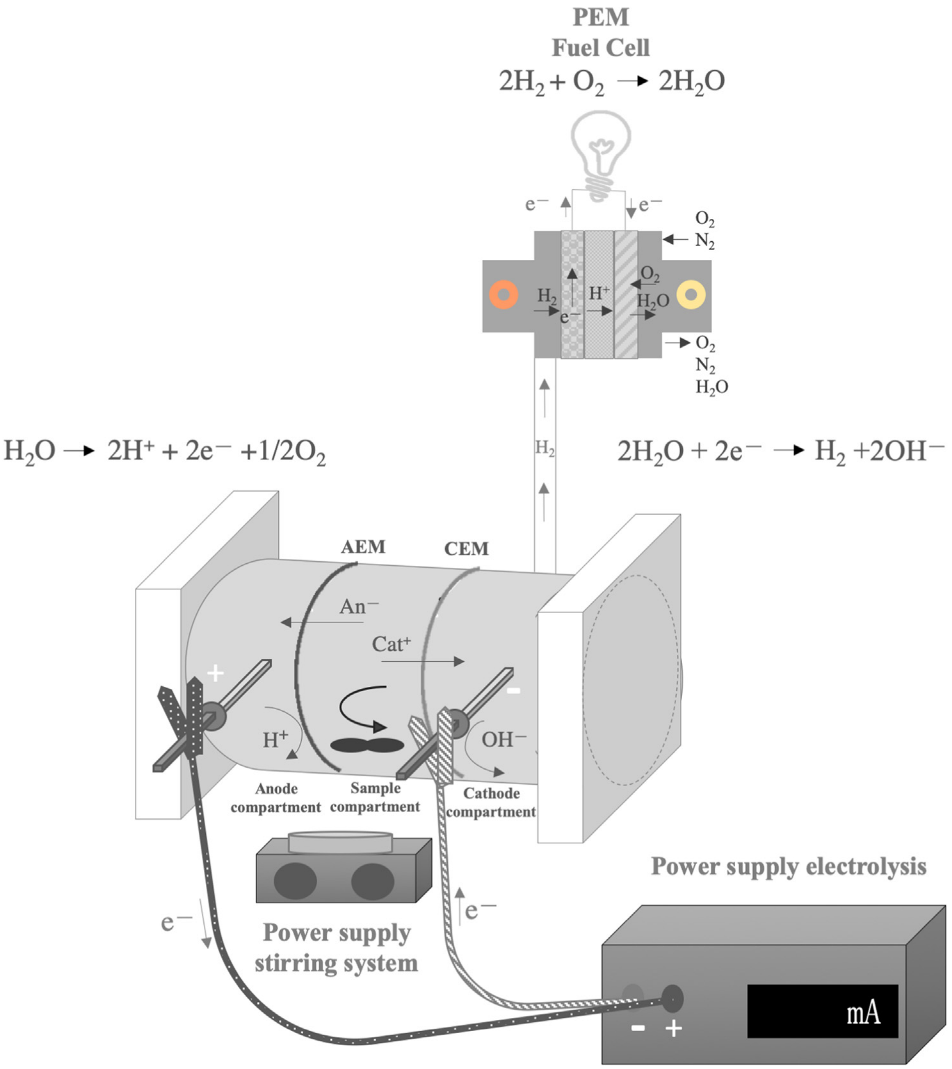

Fig. 1. Electrodialytic cell with 3 compartments [ø = 8 cm, central and electrolyte compartments with L = 5 cm, CEM – cation exchange membrane; AEM – anion exchange membrane, An⁻ – anions, Cat^+ – cations], stirrer (only used for mine tailings suspension) connected to a proton-exchange membrane fuel cell.

anodes are used to degrade organic contaminants in wastewaters, and Ti/MMO is also applied as cathode to reduce chlorinated and nitro compounds in groundwater [31]. A power supply E3612A (Hewlett Packard, Palo Alto, USA) was used to maintain a constant current in the ED cell.

For briny water and effluent experiments, 250 mL of liquid sample was added to the central cell compartment. For the mine tailings experiments, suspensions were prepared at a liquid/solid (L/S) ratio of 9, by mixing 22.2 g of solid mine tailings within 200 mL of briny water. The anolyte and catholyte compartments were set with 250 mL of 0.01 M $NaNO_3$.

Twelve ED experiments were carried out in duplicate according to the conditions presented in Table 1. In experiments 1–6 the gas produced at the cathode, rich in H_2, was collected in a 30 mL storage cylinder (Horizon Fuel Cell Technologies, USA) (experimental scheme at supplementary data B.1), where the volume was verified every 10 min. In experiments 7–9, the cathode compartment exhaust was directly connected to the tedlar sample bag, single polypropylene fitting with 500 mL of capacity (SKC, USA), for purity analysis. In experiments 10–12, the cathode compartment exhaust was directly connected to the PEMFC. In all cases, the ED cell voltage and the fuel cell open circuit voltage were registered every 10 min. The fuel cell open circuit voltage was measured in order to validate the H_2 catchment and conversion into power needs.

Table 1
Electrodialytic experimental conditions.

Experiment ED	Code	Duration (h)	Current intensity (mA)
ED tests with gas capture at the cell cathode compartment (n = 2)			
1	BW 50	2	50
2	EF 50	2	50
3	BW 100	1	100
4	EF 100	1	100
5	MTBW 50	2	50
6	MTBW 100	1	100
ED tests to H_2 purity (n = 2)			
7	BW	6	100
8	EF	6	100
9	MTBW	6	100
ED tests with direct connection to PEMFC (n = 2)			
10	BW	1	100
11	EF	1	100
12	MTBW	1	100

BW-Briny Water; EF-Effluent; MT-Mine Tailings; PEMFC – Proton-Exchange Membrane Fuel Cell.

The single PEMFC (Horizon Fuel Cell Technologies, USA) was used (32 × 32 × 10 mm), with a nominal voltage of ≈ 1 V. The PEMFC has a cathodic plate, designed as a part of the cell's membrane electrode assembly that collects O_2 directly from the air by natural convection. PEMFC voltage and resistance were measured and monitored by a multimeter KT1000H (KIOTTO, Portugal).

3.3. Methods

pH and conductivity were measured at the beginning and at the end of all ED experiments, both in central and electrode compartments. Briny water, effluent and mine tailings pH were measured with a Radiometer pH-electrode EDGE (HANNA, USA), and conductivity was measured in a Radiometer Analytic LAQUA twin (HORIBA Ltd., Japan). The mine tailings pH and conductivity measurements are referred to the liquid phase resulting from the suspension from a liquid component (either deionized H_2O or briny water), with a L/S ratio of 9.

Total concentrations of As, Ca, Cu, K, Mg, Na, P, S, Sn, W, and Zn were determined by Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES) (HORIBA Jobin-Yvon Ultima, Japan), equipped with generator RF (40.68 MHz), monochromator Czerny-Turner with 1.00 m (sequential), automatic sampler AS500 and dispositive CMA-Concomitant Metals Analyser. Cl^- and SO_4^{2-} were analyzed by Ion Chromatography (IC) (DIONEX ICS-3000, USA), equipped with conductivity detector. To quantify the elements in the solid matrix, an acid extraction was carried out mixing 0.5 g of mine tailings, 3 mL of HCl (37%) and 9 mL of HNO3 (65%) and, placed on a shaking table for 48 h at 125 rpm. For the IC analysis of the mine tailings (Cl^- and SO_4^{2-} content), microwave assisted acid extraction was carried out according to EPA method 3051 A: 0.5 g of mine tailings were placed in a vessel with 3 mL of HCl (37%), and 9 mL of HNO3 (65%) and placed in a microwave Ethos (Milestone S.r.l, Bergamo, Italy). At the end, all the samples were diluted in deionized water (1:25), filtered by vacuum using 0.45 µm MFV3 glass microfibre filters (Filter lab, Barcelona, Spain) and analyzed by ICP-OES and IC.

The H_2 purity percentage was determined by Gas Chromatography Thermal Conductivity Detector (GC-TCD) using a Trace GC Ultra (Thermo Electron Corporation, USA), with a Carboxen 1010 plot column (length: 30 m, diameter: 0,32 mm). The analytical run was performed in an isothermal mode at 35 °C for 50 min. A gastight syringe (vici precision sampling, Baton Rouge, Lousiana, USA) was used to inject a volume of 250 µL (injector at 200 °C), detector/transfer line at 120 °C. To calculate the H_2 purity two methods were used: (1) internal linear calibration and response factor (H_2 peak area/response factor), where the standard deviation is related to error of these methods, by comparing with the injection of 100% H_2; (2) molar proportions (mol/mol), were determined assuming air as impurity in the $H_{2.}$ Thus, the H_2 was calculated considering the number of H_2 mol in 100 mol of air (H_2 + air gases).

All sample analysis was carried out in duplicate. The data from the experiments were analyzed by the software Origin Pro 8.5 and the statistical data obtained by the GraphPad Prism version 7.0e. Statistically significant differences among samples for 95% level of significance were calculated through ANOVA tests.

4. Results and discussion

4.1. Matrix characterization

Matrices selection is an important step as the matrices' characteristics will affect H_2 purity and further energy generation. PEMFC, despite the robustness and stability, may be sensitive to contaminants in the fuel [32]. The briny water was chosen as a working system blank, where NaCl was added to emulate the effluent without interferences. Briny water, with sufficient ionic conductivity to maintain the current applied for the remediation period chosen (1 and 2 h), is typically used in systems for the electrolytic production of H_2. The effluent and mine tailings are, individually, matrices with high potential to be reused as raw materials in several sectors. For example, ED treated effluent has recently been tested for cement based construction materials [33]. Mine tailings are an example of solid matrix that can be successfully treated via ED as stirred suspensions mixtures [34]. In these cases, H_2 production and exploitation is highly attractive, since it can allow the decrease of energy costs in an industrial scale application.

Table 2
Initial characterization of briny water, effluent and mine tailings.

	Matrix		
	BW*	EF**	MT*
pH	6.89 ± 0.08	7.67 ± 0.16	4.57 ± 1.74
Conductivity (mS/cm)	1.81 ± 0.11	2.41 ± 2.12	0.84 ± 0.52
ICP-OES analysis	(mg/L)	(mg/L)	(mg/kg)
Ca	29.06 ± 0.02	51.74 ± 18.34	91.11 ± 27.08
K	5.33 ± 0.01	47.80 ± 29.10	–
Mg	10.30 ± 0.38	118.00 ± 137.17	–
Na	602.5 ± 17.68	524.55 ± 532.55	–
P	*0.07* ± 0.10	3.21 ± 0.04	36.57 ± 18.74
S	49.04 ± 26.07^{a}	84.89 ± 65.27	789.59 ± 214.13^{A}
As	*n.d.*	*n.d.*	218.57 ± 132.31
Cu	0.09 ± 0.01	0.04 ± 0.00	76.82 ± 39.30
Sn	*n.d.*^{b}	*n.d.*^{b}	1.95 ± 0.53^{B}
W	*n.d.*^{c}	*n.d.*^{c}	5.34 ± 1.42^{C}
Zn	1.07 ± 0.88	0.07 ± 0.06	–
IC analysis	(mg/L)	(mg/L)	(mg/kg)
Cl^-	499.3 ± 8.1	908.1 ± 1013.7	5.6 ± 2.3
SO_4^{2-}	66.8 ± 1.5^{de}	149.45 ± 127.07^{dE}	240.9 ± 4.6^{D}

BW-Briny Water; EF-Effluent; MT-Mine Tailings.
*collected at 2-09-2018; ** collected at 5-09-2018 and 12-09-2018; nd- not detected.
Statistical analysis: Multiple comparisons were statistically performed at $p < 0.05$ (95% confidence interval); data with lower case letters is statistically significantly different to the ones with the same capital letter.

Table 2 presents the initial characterization of the three studied matrices. The matrices had enough initial conductivity to allow current passage and facilitate the electrolysis reactions to occur at the imposed rate. The initial pH of the studied matrices was in the range 4.6–7.7. Mine tailings were slightly acidic (pH ≈ 4.57), presenting a high concentration of arsenic (218.57 ± 132.31 mg As/kg), and significant amounts of other metals (76.82 ± 39.30 mg Cu/kg, 1.95 ± 0.53 mg Sn/kg and 5.34 ± 1.42 mg W/kg), as well as a high sulfur content (240.9 ± 4.6 mg/kg).

The ED process was applied to briny water, effluent and mine tailings suspension in briny water. In all cases, the pH at the anode compartment decreased to ~2 and the pH at the cathode compartment increased until ~12. The pH at the central compartment also decreased in all cases. This phenomenon was expected as anion exchange membranes are known to have limited perm-selectivity, which means that only protons (H^+) are able to cross this membrane. The acidification of the central compartment was more noticeable in the experiments at 100 mA (Fig. 2). The acidification phenomena proved to be influenced by the current intensity. The smallest variation in the potential applied in the ED cell will increase the H^+ production in the media. Thus, not only the current intensity should be considered to analyze the results, but also the error associated to the power supplier (± 3 mA).

Final concentrations of the major concerned elements in the liquid matrices (Cl^- and SO_4^{2-}) and in the mine tailings suspension (As, Cu, Sn and W) are presented in Tables 3 and 4, respectively.

In general, the target contaminants removal from the matrices was higher in the experiments operated at 100 mA, for the same amount of circulated charge. When ED treatment is performed at higher current intensities, the electromigration transport is predominant over diffusion or other transportation phenomena. The amount of salts amount is extremely heterogeneous in the effluent. The season periods of the sampling procedure affected chemical and physical properties of the

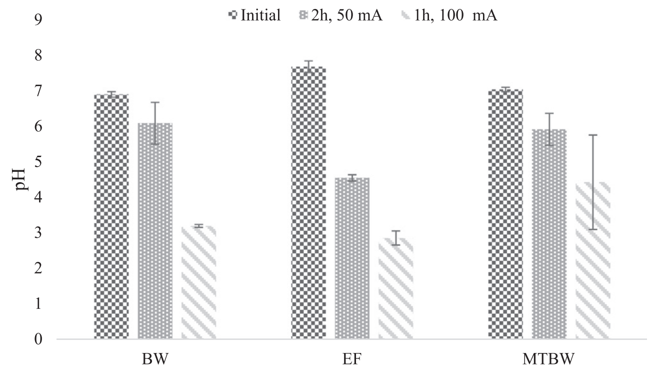

Fig. 2. pH of the liquid phase at the central cell compartment before and after the electrodialytic experiments at 50 mA and 100 mA (error bars related to the standard deviation: n = 2). BW-Briny Water; EF-Effluent; MT-Mine Tailings.

Table 3
Concentration of anions in briny water and effluent, before and after the electrodialytic experiments at 50 mA (2 h) and 100 mA (1 h).

		Initial (mg/L)	50 mA Final (mg/L)	100 mA Final (mg/L)
Cl^-	BW	499.3 ± 8.1	285.5 ± 40.3	15.7 ± 22.2
	EF1	1624.9	*490.5*	129.1
	EF2	191.3	83.0	20.5
SO_4^{2-}	BW	66.8 ± 1.5	16.8 ± 2.3	14.1 ± 5.0
	EF1	239.3	114.4	36.1
	EF2	59.6	30.0	27.9

BW – Briny Water; EF-Effluent.
EF1 – collected at 5-09-2018.
EF2 – collected at 12-09-2018.

Table 4
Concentration of elements in mine tailings before and after the electrodialytic experiments at 50 mA (2 h) and 100 mA (1 h).

	Initial solid phase (mg/kg)	50 mA Final solid phase (mg/kg)	100 mA Final solid phase (mg/kg)
As	218.6 ± 132.3	196.2 ± 50.73	113.9 ± 19.7
Cu	76.8 ± 39.3	38.3 ± 13.9	26.4 ± 3.5
Sn	2.0 ± 0.5	2.2 ± 0.2	1.7 ± 0.4
W	5.3 ± 1.4	5.7 ± 0.4	4.9 ± 1.6

samples collected due to the fluctuations in weather conditions and also the wastewater treatment plant process efficiency.

The slightly extraction of Sn and W from mine tailings may be related to specific chemical limitations, such as desorption or dissolution mechanisms. For example, W complexes are quickly decomposed and stabilized by high concentrations of chloride ions (MT: 5.6 ± 2.3 mg/kg; BW: 499.3 ± 8.1 mg/kg), where the most common product of the decomposition is $[W_2Cl_9]^{3-}$. Alternatively, the adsorption of sulfate ions on metallic W surface results in the electronic structure modification. The O_2 reduction reaction is blocked during the ED process, which is already low in cationic dissolution in electrochemical processes [35].

4.2. Hydrogen generation and use

Fig. 3 shows the volume of collected gas produced at the cathode compartment during experiments 1–6. As the volume of the gas deposit was 30 mL, it was filled before the ED process ended. Experiments at 50 mA showed matrix related differences in the gas flow rate, reaching the 30 mL of H_2 production at different rates. There are no statistically significant differences for the flow rates obtained at 100 mA (Table E at supplementary data). However, the flow rates of H_2 are significantly different ($p < 0.001$) in the experiments at 50 mA.

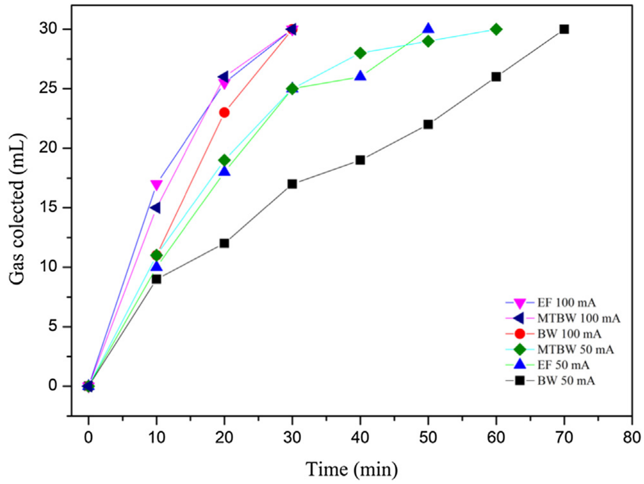

Fig. 3. Gas flow rate generation (mL/min) during the electrodialytic experiments with BW, EF and MTBW, at 50 mA and 100 mA (collected maximum volume 30 mL). BW-Briny Water; EF-Effluent; MT-Mine Tailings.

The gas generated at the cathode compartment, in the experimental setup 3, 4 and 6 during 6 h, was captured and analyzed via GC-TCD, in a tedlar sample bag. Table 5 presents the purity of the captured gas for these experiments carried out at 100 mA.

The average H_2 purity (% w/w) of the produced gas was ≈ 73% (w/w), where the highest value observed was in the ED experiment applied to the effluent, that produced a gas with 90.4 ± 0.3% of H_2. Thus, only the H_2 purity in the effluent experiment has a statistically significant difference ($p < 0.05$) compared to briny water and mine tailings suspension, while briny water and mine tailings suspension does not have a statistically significant difference between each other (Table 5). In order to validate and make a comparison with the purity results obtained in % w/w, another approach to determine the H_2 purity was carried out. Thus, the calculation of the gas was also performed considering the molar fraction of the H_2 in the air gases. Comparing the two methods, the % mol/mol of H_2 of the produced gas was 19% higher, in average, comparing to the % w/w (Table 5). In the % mol/mol analysis, the purity of the H_2 was higher than 97% in all samples, whereas in the % w/w the H_2 purity oscillated between 72% and 90%. The mass and the molar compositions are different, and it is expected a higher molar purity, as long as the other components in the gaseous phase are heavier (e.g. N_2, O_2).

As mentioned before, the flow rate production for H_2 in the ED treatments can be directly related to the current intensity and the matrix. Assuming the H_2 captured at 1 atm and 25 °C, a total of ≈ 45.6 mL of pure dry H_2 would be theoretically obtained, at a rate of 0.76 mL/min in the experiments at 100 mA. The volume of collected gas at the cathode, shown in Fig. 3 (Table B.2 at supplementary data), was clearly higher than the expected during the first few minutes of treatment, with

Table 5
H_2 purity analysis by GC-TCD.

Matrix	H_2 (% w/w)	H_2 (% mol/mol)*
BW	74.19 ± 0.63^A	97.63 ± 0.08^B
EF	90.43 ± 0.25^a	99.26 ± 0.02^b
MTBW	72.39 ± 0.68^A	97.41 ± 0.09^B

*Calculated assuming air as impurity in the H_2; Statistical analysis: Multiple comparisons were statistically performed at $p < 0.05$ (95% confidence interval); data with lower case letters is statistically significantly different to the ones with the same capital letter; BW-Briny Water; EF-Effluent; MT-Mine Tailings.

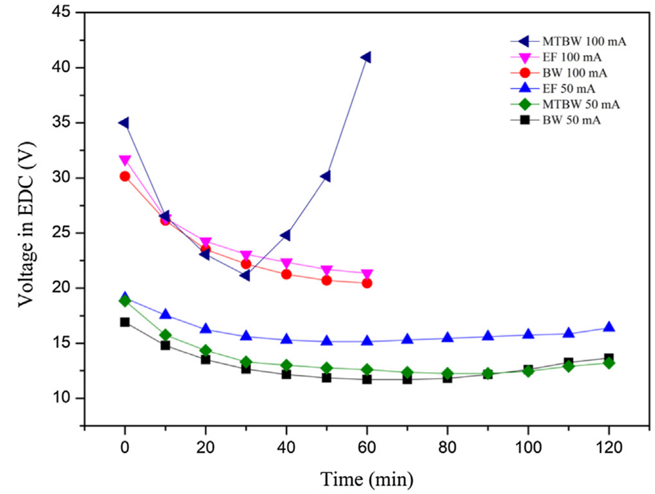

Fig. 4. Cell voltage during the electrodialytic experiments with BW, EF and MTBW, at 50 mA and 100 mA. BW-Briny Water; EF-Effluent; MT-Mine Tailings.

a change in the production rate after the first 10 to 20 min. This may indicate that competing cathode reactions took place. For example, a possible electrode reaction that could have taken place is the formation of NO_2 (g) from the reduction of the nitrates ($E_0 = 0.803$ V), shown in Eq. (6).

$$NO_2(g) + H_2O \rightarrow NO_3^-(aq) + 2H^+ + e^-; \qquad E^o_{cathode}(25\ ^\circ C) = 0.803\ \ V \tag{6}$$

This reaction produces 1 mol of NO_2 (g) per circulated electron, twice as much as the H_2 reaction and would increase the pH of the cathode compartment twice as fast. However, the pH changes at the cathode and the decrease of nitrate concentration in time will promote that the water reduction electrolysis reaction become predominant after the first several minutes of the reaction. NO_2 (g) might be in a solution in the form of N_2O_4 below 21 °C.

4.3. *Electrical energy requirements in the ED experiments*

Among the ED experiments with H_2 capture (experiments 1–6 in Table 1), the ED cell voltage decreased overtime. The rapid decrease of the cell voltage was more evident in the experiments at 100 mA (Fig. 4).

According to the Ohm's law, if the current intensity (I) is constant, the voltage (V) and the resistivity (R, or conductivity) are strongly related, Eq. (7):

$$V = RI(V) \tag{7}$$

where I is the current intensity, V the voltage and, R is the resistance.

The decrease of the ED cell voltage is related to a conductivity increase in the electrode compartments. The initial conductivity of the electrolyte was moderately low, 0.90 ± 0.06 mS/cm, and it increased to values between 3 and 4 mS/cm at the anode, and 2–3 mS/cm at the cathode, at the end of all experiments, which is consistent with the pH changes observed. In the central compartment, the conductivity changed depending on the matrix (Fig. 5). Due to the highly heterogeneous environmental samples under study, high standard deviations in the ED experiments' behavior were observed. Nevertheless, in general, it stayed with values that assure conductivity. However, the experiment MTBW at 100 mA had a voltage increase after half an hour and a decrease on the conductivity at the end of the experiment (Fig. 5). The treatment at 100 mA produced the reduction of ions (related to the H^+ migration through the anion exchange membrane) in the central compartment, and an energy efficiency decrease of the process due to an increase of the ohmic losses. In the experiments at 50 mA, the longer running times allowed diffusion and dissolution/desorption kinetics to replete the ion content in the central cell compartment. Effluent and mine tailings are matrices with high dependency on the sampling and weather conditions (effluent high standard deviations in the salts content, in line with the conductivity values). Mine tailings are a heterogeneous matrix implying different amounts of metals and salts content, with different variations in the charged species during the sampling.

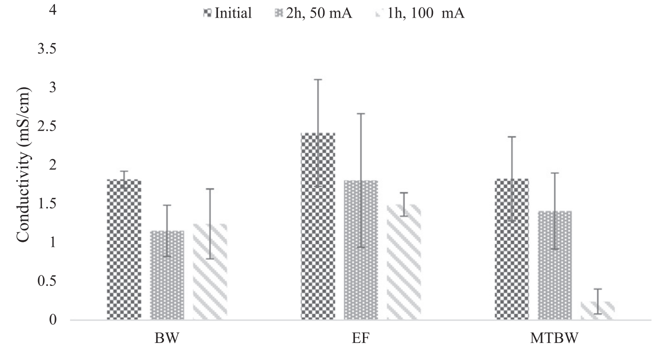

Fig. 5. Conductivity of the liquid phase at the central cell compartment before and after the electrodialytic experiments (error bars related to the standard deviation: n = 2). BW-Briny Water; EF-Effluent; MT-Mine Tailings.

As the ED experiments are carried out at a constant current, the electrical energy required during the process, accounting only for the energy applied by the DC power source, can be calculated from Eq. (8):

$$E = I\int_{t_0}^{t} V_{cell}(t)dt \tag{8}$$

Using a numerical chained-trapezoidal integration, the estimated electrical energy is presented in Fig. 6. As expected, the electrical energy required increases as the electrical current increases, for the same amount of circulated charge. These results are consistent with the conductivity of those matrices. According to the results presented in the Fig. 6, the experiments carried out at 100 mA required ~8.7 ± 0.8 kJ of electrical energy, while the experiments carried out at 50 mA required an average of ~4.8 ± 0.7 kJ.

4.4. *Energy savings*

Considering a faradaic efficiency of 100% and no competition to the water reduction as the cathode electrolysis reaction, ~1.86 mmol of H_2 would be produced in experiments 1–6 at the end of the ED experiment, either at 50 mA in 2 h or at 100 mA in 1 h. Using a fuel cell at low

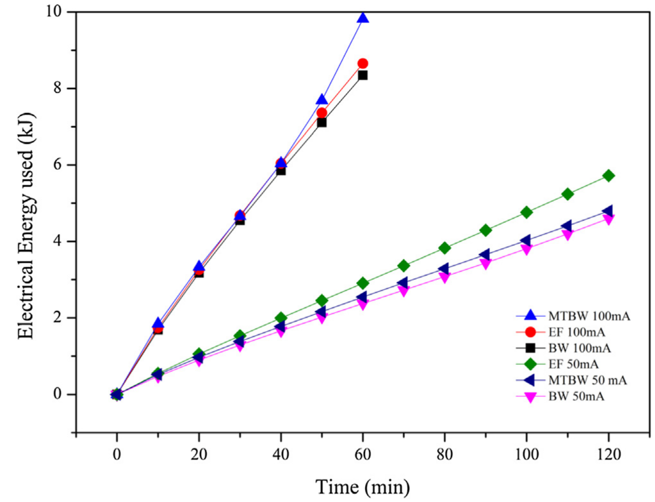

Fig. 6. Estimation of the cumulative electrical energy consumed during the electrodialytic experiments. BW-Briny Water; EF-Effluent; MT-Mine Tailings.

temperatures and considering the higher heat of combustion of H_2 as 141.8 MJ kg^{-1}, a total of 0.53 kJ may have been recovered from the process. The efficiency of the chemical energy conversion to electrical energy at the fuel cell depends on the quality of the H_2 gas produced, where a maximum of 98% (mol/mol) hydrogen average purity was achieved during the ED treatments. Considering that current fuel cell has energy conversion efficiencies of around 60%, a total of 0.32 kJ could have been transformed into electrical energy. This translates to ~3.1% of the electrical energy required in experiment 4 (EF 100 mA, the worst case), and ~6.9% of the electrical energy required in experiment 5 (MTBW 50 mA, the best case). Reducing the electrical energy dependency, mainly due to stirring needs (for solid fine matrices), transport of charge through the porous matrix, and to feed a power supply for the electrode's reactions, may also have impact in the total variable costs of the overall ED process (~7%).

As expected, the higher the current intensity used in the ED treatment, the higher the electrical energy requirements for the same amount of circulated charge. In the experiments presented, those carried out at 50 mA during 2 h required almost half of the electrical energy to produce the electrolysis reactions than those carried out at 100 mA during 1 h. On the other hand, higher applied currents obtain better removal efficiencies, provided that there are no phase-transfer kinetic limitations, such as dissolution or desorption processes.

In general, one of the main advantages of the ED treatment applied to liquid matrices compared to ED treatments applied solid porous matrices is that the energy requirements for the electrolysis reactions are considerably smaller, due to the higher conductivity of the matrices. Thus, in solid porous matrices, the ED treatment would reach higher voltage gradients due to the lower conductivity and will require long-lasting treatments. The ED treatments presented show requirements of electrical power for the electrolysis in the range of 1–5 W. However, ED treatments carried out for the mine tailings suspension required additional energy for the stirring system at the sample central cell compartment. A 10 W stirrer system was used, meaning that the electrical energy required for the stirring system could be up to ten-fold compared to the energy required for the electrolysis reactions. For the purpose of energy optimization in ED treatments applied to suspensions, the reduction of stirring costs is critical. In this sense, PEMFC could be an important factor in ED energy savings by reducing the operation costs by powering a low-energy stirring system.

To evaluate the possibility of reducing energy requirements from the ED treatments by the *in-operando* production of electricity from H_2 gas formed at the cathode, a PEMFC was connected directly to the exhaust pipe of the cathode compartment in experiments 7–9, corresponding to the same matrices under ED treatment at 100 mA during 1 h.

The initial open circuit voltage of the PEMFC was, in all cases, near 1.4 V, and it decreased and stabilized at a value of ~1 V (Fig. 7), as expected for a single PEMFC [32]. To obtain higher voltages, a stack of FCs connected in series could be used. Comparing the voltage generated by PEMFC in the different cases, there are no statistically significant differences ($p < 0.05$) (see Table C at supplementary data). The data supported the statement that the production of electricity by a PEMFC is independent of environmental matrices used in the ED treatments presented, despite the fluctuation observed for the case of effluent.

The data presented in this study indicates that the gas produced at the cathode has a purity between 72.4% and 99.3%. Therefore, in a field scale ED treatment, the produced H_2 could also be stored and sold for transportation or other industrial sectors. The production costs of H_2 via electrolysis vary around 8–11 €/kg, which is higher than that obtained via steam methane reforming using natural gas or biogas [36,37]. The H_2 produced during ED treatments, that until now has been an unexploited byproduct, may be an alternative source of H_2 for transportation or energy storage.

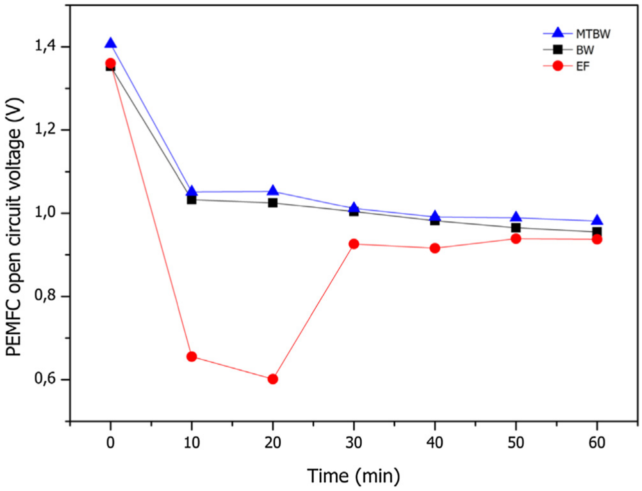

Fig. 7. Proton-exchange membrane fuel cell (PEMFC) generated open circuit voltage during the electrodialytic experiments at 100 mA. BW-Briny Water; EF-Effluent; MT-Mine Tailings.

5. Conclusions

In this study it is proved the possibility to produce H_2 with average purities between 73% and 98% from electrodialytic treatments and used to generate electrical energy with a proton-exchange membrane fuel cell. This estimation was performed according to the H_2 formed at the cathode electrolysis reaction, which can reduce the energy costs associated to the electrodialytic treatments, as well as any other remediation treatment based on electrochemically-induced transport.

The efficiency of chemical to electrical energy conversion at the fuel cell would depend on the quality of the H_2 gas produced. Thus, specific studies on possible competitive cathode reactions are needed depending on the system. However, in the matrices tested in this study, H_2 gas was produced in all cases. This suggests that H_2 purity seems to be more affected by external factors (experimental errors, nitrate reduction to NO_2 or temperature increase) than the matrices composition. Flowing the produced H_2 gas through a single proton-exchange membrane fuel cell, resulted in a stable open circuit voltage (~1 V), that demonstrated the potential to recover energy from the H_2 byproduct, that otherwise would be released to the atmosphere and lost.

This research shows there are new possibilities for energy saving and H_2 production for different purposes in electrodialytic treatment, leading to an increase in the sustainability and applicability of the electro-remediation, decontamination or degradation contaminantś processes.

Acknowledgments

This work has received fundings from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 776811, under the Marie Skłodowska-Curie grant agreement No. 778045, and from Portuguese funds from FCT/MCTES through grants UID/AMB/04085/2019 and PTDC/FIS-NAN/0909/2014. C. Magro and J. Almeida acknowledge Fundação para a Ciência e a Tecnologia for their PhD fellowships SFRH/BD/114674/2016 and PD\BD \135170\2017, respectively. The authors acknowledge Carla Rodrigues and Nuno Costa from REQUIMTE for the ICP and IC analysis, and Ricardo Chagas from LAQV- REQUIMTE.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apenergy.2019.113839.

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Glossary

ED: Electrodialytic
GC-TCD: Gas Chromatography with Thermal Conductivity Detector
IC: Ion Chromatography
ICP-OES: Inductively Coupled Plasma with Optical Emission Spectrometry
PEMFC: Proton-exchange membrane fuel cell

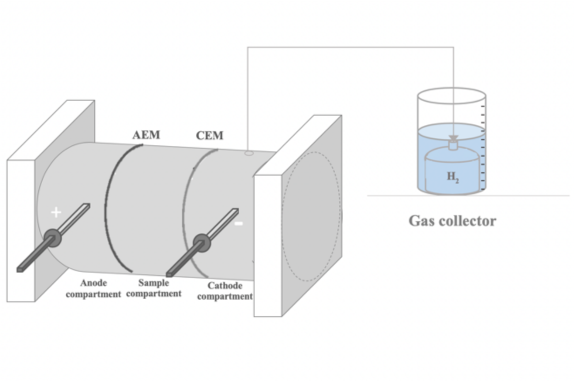
Supplementary Data

A. Cell voltage during electrodialytic treatments: BW, EF and MTBW experiments at 50 mA or 100 mA

Time (min)	BW 50 mA	SD	BW 100 mA	SD	EF 50 mA	SD	EF 100 mA	SD	MTBW 50 mA	SD	MTBW 100 mA	SD
0	16.9	2.4	30.2	0.4	19.1	5.1	31.7	3.8	18.9	0.2	34.8	0.7
10	14.8	2.4	26.2	0.4	17.6	6.0	26.4	5.4	15.8	0.2	26.6	1.3
20	13.5	2.3	23.5	1.0	16.3	5.9	24.3	4.0	14.4	0.1	25.1	1.9
30	12.7	2.1	22.2	0.8	15.6	5.8	23.1	3.3	13.3	0.0	24.4	2.1
40	12.2	2.1	21.3	0.5	15.3	5.9	22.4	2.8	13.0	0.0	24.8	2.3
50	11.9	2.2	20.7	0.0	15.2	6.0	21.7	2.0	12.8	0.1	30.2	2.7
60	11.7	2.3	20.5	0.4	15.2	6.0	21.4	1.8	12.6	0.1	41.0	3.4
70	11.7	2.4			15.3	6.1			12.4	0.4		
80	11.8	2.5			15.5	6.0			12.3	0.5		
90	12.2	2.9			15.6	6.1			12.3	0.9		
100	12.6	3.4			15.8	5.9			12.5	1.3		
110	13.3	3.9			15.9	5.6			12.9	2.3		
120	13.7	4.0			16.4	5.2			13.2	2.8		

BW-Briny Water; EF-Effluent; MT-Mine Tailings; SD – Standard Deviation

B.1 H_2 volume collection during electrodialytic treatments; CEM – cation exchange membrane; AEM – anion exchange membrane



B.2 H_2 generation (mL) in the electrodialytic treatments: BW, EF and MTBW experiments at 50 mA or 100 mA;

Time (min)	BW 50 mA	SD	BW 100 mA	SD	EF 50 mA	SD	EF 100 mA	SD	MTBW 50 mA	SD	MTBW 100 mA	SD
0	3.0	4.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	9.0	1.4	11.0	1.4	10.0	0.0	17.0	1.4	11.0	4.2	15.0	4.2
20	12.0	0.0	23.0	1.4	18.0	2.8	25.5	0.7	19.0	5.7	26.0	0.0
30	17.0	1.4	30.0	0.0	25.0	7.1	30.0	0.0	25.0	5.7	30.0	0.0
40	19.0	1.4			26.0	0.0			28.0	6.4		
50	22.0	2.8			30.0	0.0			29.0	4.2		
60	26.0	2.8							30.0			
70	30.0	0.0										

BW-Briny Water; EF-Effluent; MT-Mine Tailings; SD – Standard Deviation

C. Proton-exchange membrane fuel cell generated open circuit voltage in the electrodialytic treatments: BW, EF and MTBW experiments at 100 mA;

Time	**BW**	**SD**	**EF**	**SD**	**MTBW**	**SD**
0	1.35	0.04	1.36	0.06	1.41	0.00
10	1.03	0.71	0.66	0.67	1.05	0.00
20	1.03	0.70	0.60	0.67	1.05	0.02
30	1.00	0.68	0.93	0.17	1.01	0.04
40	0.98	0.69	0.92	0.15	0.99	0.04
50	0.97	0.63	0.94	0.10	0.99	0.01
60	0.96	0.64	0.94	0.08	0.98	0.00

BW-Briny Water; EF-Effluent; MT-Mine Tailings; SD – Standard Deviation

D. Electrodialytic H_2 flow - ANOVA with 95% of confidence level

y = a + b*x	Matrices					
	BW 50 mA	BW 100 mA	EF 50 mA	EF 100 mA	MTBW 50 mA	MTBW 100 mA
Residual SoS	54.74	6.50	68.18	56.11	173.53	40.36
Pearson's r	0.99	1.00	0.99	0.98	0.98	0.99
Adj. R-Square	0.98	0.99	0.97	0.96	0.94	0.97
Slope (flow)	**0.45^{a}**	**1.05^{b}**	**0.68^{A}**	**1.13^{Bc}**	**0.62^{d}**	**1.12^{Ce}**
Slope standard Error	0.02	0.04	0.05	0.12	0.06	0.10

Statistical analysis: Multiple comparisons were statistically performed at $p<0.05$ (95% confidence interval); data with lower case letters is statistically significantly different to the ones with the same capital letter.

BW-Briny Water; EF-Effluent; MT-Mine Tailings

E. Comparing electrodialytic experiments statistics on H_2 flow - ANOVA with 95% of confidence level

ANOVA summary ED 50mA	
F	13.14
P value	0.0328
P value summary	*
Significant diff. among means *(P < 0.05)?*	**Yes**
R square	0.8975
Combinations Significantly different	
BW 50 mA	EF 50 mA

ANOVA summary ED 100mA	
F	0.4385
P value	0.6807
P value summary	ns
Significant diff. among means *(P < 0.05)?*	**No**
R square	0.2262

F. pH and conductivity data and statistics: ANOVA with 95% of confidence level

	Initial	
	pH	Conductivity (mS/cm)
Electrolyte	6.46 ± 0.55^{a}	0.90 ± 0.06
BW	6.89 ± 0.08	1.81 ± 0.11
EF	7.67 ± 0.16^{A}	2.41 ± 0.69
MTBW	7.03 ± 0.06	1.82 ± 0.54

		ED Final	
		pH	Conductivity (mS/cm)
BW 50 mA	Anolyte	2.02 ± 0.21	4.40 ± 0.28
	Catholyte	12.29 ± 0.14	3.00 ± 0.71
	Central	6.08 ± 0.59	1.15 ± 0.33
BW 100 mA	Anolyte	2.18 ± 0.3	2.95 ± 0.49
	Catholyte	12.13 ± 0.20	1.23 ± 1.65
	Central	3.19 ± 0.04	1.24 ± 0.45
EF 50 mA	Anolyte	2.20 ± 0.02	2.70 ± 0.00
	Catholyte	12.21± 0.01	2.45 ± 0.21
	Central	4.54 ± 2.55	1.80 ± 0.86
EF 100 mA	Anolyte	2.21 ± 0.04	2.85 ± 1.06
	Catholyte	12.11 ± 0.01	1.94 ± 0.23
	Central	2.85 ± 0.20	1.49 ± 0.15
MTBW 50 mA	Anolyte	2.02 ± 0.11	3.25 ± 0.21
	Catholyte	12.30 ± 0.01	2.40 ± 0.14
	Central	5.91 ± 0.45	1.41 ± 0.49
MTBW 100 mA	Anolyte	1.99 ± 0.04	2.55 ± 0.07
	Catholyte	12.21 ± 0.25	2.08 ± 0.46
	Central	4.42 ± 1.33	0.24 ± 0.16

Statistical analysis: Multiple comparisons were statistically performed at $p<0.05$ (95% confidence interval); data with lower case letters is statically significantly different to the ones with the same capital letter.
BW-Briny Water; EF-Effluent; MT-Mine Tailings

International conference article

A7 Assessment on tungsten mining residues potential as partial cement replacement

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Published in KnE Engineering journal (2020)

This article was published in Kne Engineering, RICON19 - REMINE International Conference on Valorization of mining and industrial wastes, J Almeida, A Santos Silva, P Faria & AB Ribeiro, Assessment on tungsten mining residues potential as partial cement replacement, 228–237, Copyright Knowledge E (2020).

Conference Paper

Assessment on tungsten mining residues potential as partial cement replacement

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Abstract

Electroremediation and deep eutectic solvents are well-documented clean-up processes for metals extraction from solid matrices. Depending on the purpose, these treatments may generate a residue free of pollutants and critical raw materials. Several studies were conducted to re-insert treated secondary resources in building materials. However, there is a research gap in the improvement of reactive properties of these secondary resources. In addition, there is a lack of pozzolans that can optimize cementitious materials. This study investigates the pozzolanic reactivity of tungsten mining residues after receiving electrodialytic treatment in the presence of natural deep eutectic solvents. In all cases, thermal treatment after electroremediation potentiated the pozzolanic reactivity of tungsten mining residues, between 64% to 87%. The introduction of these pozzolanic resources in cementitious-based materials may increase their performance, enlarge the range of applications in the construction industry, reduce the environmental impact, and contribute to a circular economy.

Keywords: electro-based technology, tungsten mining waste, construction material, pozzolanicity.

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Received: 20 March 2020
Accepted: 30 April 2020
Published: 13 April 2020

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the RICON19 - REMINE International Conference Conference Committee.

1. Introduction

Currently there is a major concern to find strategies to increase sustainability within the construction sector due to the negative impacts on energy consumption and emissions production [1]. The research into innovative strategies has been empowered by the European Commission standards to accomplish circular economy targets [2]. The result is the study and the development of a wide range of alternatives to safely reuse secondary resources in building materials production and reduce raw materials consumption. Secondary resources from mining industries are particularly attractive since it is possible to obtain different types of supplies. Some examples can be rocks,

How to cite this article: Joana Almeida, António Santos Silva, Paulina Faria, and Alexandra Ribeiro, (2020), “Assessment on tungsten mining residues potential as partial cement replacement” in *RICON19 - REMINE International Conference on Valorization of mining and industrial wastes into construction materials by alkali-activation*, KnE Engineering, pages 228–237. DOI 10.18502/keg.v5i4.6814

gravel, sands or clays, composed mainly by materials such as quartz and muscovite [3].

Although there is an in-depth assessment on techniques and products to include mining residues in building materials, namely through geopolymerization [4] and alkali activation techniques [5], minimal research has been conducted to empower the potential and diverge the applications of the products with secondary resources incorporation.

Pozzolans are natural or artificial fine materials that can partially replace lime or cement in mortars and concrete. They have a high content on amorphous silica and/or alumina, able to react with calcium hydroxide ($Ca(OH)_2$) in presence of water, generating products with cementitious properties [6]. Artificial pozzolans can be used as supplementary cementitious materials with advantages: (1) economic profits obtained by the replacement of cement with cheaper natural pozzolans or industrial by-products; (2) decreasing of the blended cement environmental cost associated with the greenhouse gases emitted during cement production and (3) increased durability of the final product [7].

Electroremediation [8] and natural deep eutectic solvents (NADES) [9] are clean-up strategies deeply addressed for metals removal and critical raw materials recovery from solid matrices. However, electroremediation is now being shaped to address current sustainable priorities [10]. The potential to remove contaminants from secondary resources and eventual enhancement in pozzolanic reactivity of secondary mining resources, through electrochemical phenomena generated inside the reactor, may also contribute to improve the technological maturity and the feasibility for different purposes [11].

The present work aimed to study the pozzolanic reactivity by the total amount of $Ca(OH)_2$ consumed in Chapelle test [12] by tungsten mining residues from Panasqueira mine after being subjected to electroremediation with NADES. The thermal treatment was also coupled with the electrodialytic process (ED) to enhance residues pozzolanicity.

2. Experimental Campaign

2.1. Sample and initial characterisation

Panasqueira mining residues were collected from the rejected fraction of the sludge circuit that is directly pump to the Panasqueia dam (Covilhã, Portugal). The initial and after ED treatment analysis of the sample composition was carried out in an X-Ray

Microdifractometer (BRUKER Discovery, Germany) and a thermal analysis TGA/DSC was performed in a STA449F3 Jupiter (NETZSCH, Germany).

2.2. Electrodialytic and thermal treatment

Panasqueira mining residues were treated in a two-compartment ED acryl XT cell (RIAS A/S, Roskilde, Denmark) with a diameter of 80 mm. The compartment length was 50 mm for the anolyte and 100 mm for the sample. An anion exchange membrane AR204SZRA, MKIII, Blank (Ionics, USA) divided the two compartments. The electrodes were made of Ti/MMO Permaskand wire with a diameter of 3 mm and a length of 50 mm (Grønvold & Karnov A/S, Denmark). To keep a constant current of 50 mA in the cell, a power supply E3612A (Hewlett Packard, Palo Alto, USA) was used and a magnetic stirrer was placed into the sample compartment. A mixture of 39 g of tungsten mining residues with 345 mL of deionized water and 5 mL of NADES (choline chloride/oxalic acid, ChCl:OA and choline chloride/malonic acid, ChCl:MA) was set in the cathode compartment, and in the other compartment 250 mL of 0.01M $NaNO_3$ were added as anolyte. The experiments were performed for 4 days. The aim of the ED treatment was the recovery of critical raw materials and the removal of harmful compounds from secondary mining resources, foreseen a further reuse of the treated matrix in construction materials production [13].

Also, thermal treatment with a temperature of 800°C and 950°C (lower temperature in comparison to cement production, ~1500°C) was applied to the samples with and without ED pre-treatment for 1 hour.

2.3. Pozzolanic reactivity quantification

Before and after the ED process, the pozzolanic reactivity was measured, under different conditions. Modified Chapelle test, referring to the French standard NF P 18-513, Annexe A [14], was carried out to measure the total quantity of fixed $Ca(OH)_2$ by siliceous or aluminosilicates amorphous constituents present in the samples.

Thus, 1 g of tungsten mining residues was mixed with 2 g of CaO and 250 mL of deionized water. The suspension was placed inside a beaker and stirred for 16 h at 85 ± 5 °C. A control test was performed with the same conditions, only with CaO. After, the suspension was cooled down with a water stream until room temperature. Saccharose was added to the suspension (60 g) and 250 mL of deionized water. The suspension was stirred for 15 min to solubilize free $Ca(OH)_2$. Then, 200 mL of the solution were filtrated under vacuum and 25 mL were collected to an Erlenmeyer. A titration with

0.1M HCl was carried out, with phenolphthalein as indicator, until the solution turned to colourless.

The volume of HCl was measured and equation (1) was used to determine the mg of $Ca(OH)_2$ consumed by the sample.

$$Ca(OH\ )_2 \text{ fixed (mg)} = 2 \times ((v_1\text{-}v_2)/v_1) \times 74/56 \times 1000 \qquad (1)$$

In equation (1) v_1 is the control titration volume and v_2 the tested samples titration volume.

3. Results and Discussion

3.1. Samples characterisation

X-Ray Diffraction (XRD) was carried out to the sample before and after ED treatment, as shown in Figure 1. Tungsten mining residues show that quartz (SiO_2) and muscovite (general formula $KAl_3Si_3O_{10}(OH)_{1.8}F_{0.2}$) are the main minerals present in the initial sample composition. SiO_2 and also Al_2O_3 in these minerals can be turned into a pozzolanic reactive material, forming hydrated calcium silicates and hydrated calcium aluminates in presence of $Ca(OH)_2$ and water, increasing materials durability [15]. Herein, a comparison between the principal minerals present in the sample before and after ED treatment is presented. When the ED process was applied to tungsten mining residues, the mineralogy showed slight variations in the minerals' proportions. Thus, regarding the operation time of the treatment, and the variations in pH and conductivity of the media, minerals composition was not strongly affected.

Simultaneous thermal analysis TGA/DSC was carried out (Figure 2). Thermogravimetric analysis (TGA) was performed to verify the mass variation overtime. Thus, samples with and without ED treatment were subjected to a maximum temperature of 1000 °C. Differential scanning calorimetry (DSC) analysis measured the amount of energy absorbed or released by the sample when heated, providing data on endothermic and exothermic processes. Differential thermal analysis (DTG) curve provided data on the transformations that have occurred, such as crystallization, melting and sublimation.

There is a higher mass variation in the sample treated with the electrodialytic process (4.15 %) when compared to the initial sample (2.55%). In both samples, around 600°C the maximum weigh loss occurred. α-quartz can be transformed into β-quartz with temperatures of 573°C and β-tridymite at 870 °C [16]. The density from α-quartz to β-tridymite stage vary between 2.65 - 2.23 g/cm^3, which corroborates the mass loss observed in thefigure. However, other minerals are being formed, since polymorphs such as coesite and stishovite can be produced not only at high temperatures but also

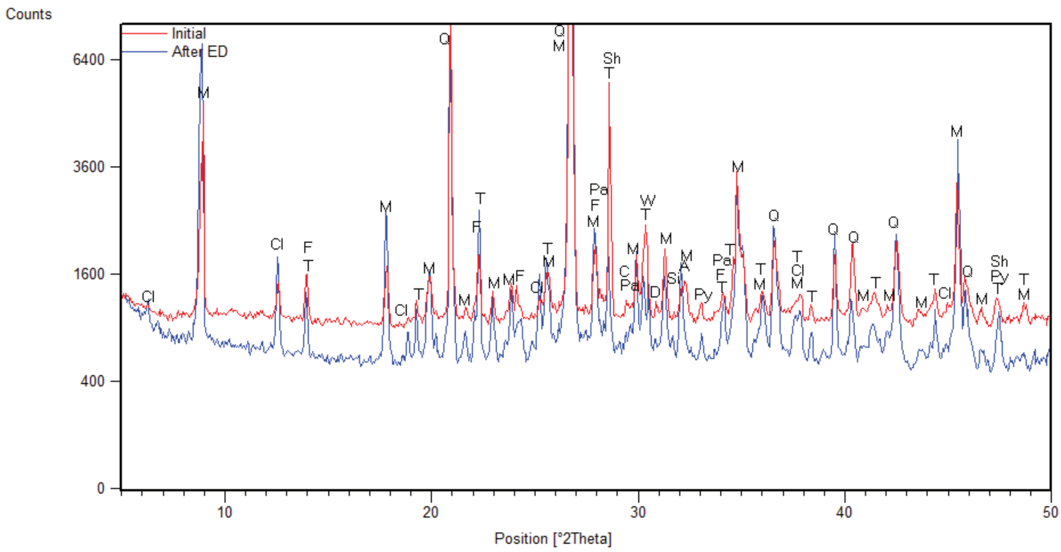

Figure 1: X-Ray Diffraction spectrum of the sample before and after ED treatment.

under high pressures. The density of these minerals is higher, 2.92 and 4.29 g/cm^3, respectively [16], which may explain the mass increase after ~600 °C. Regarding DTG results, when ED was applied, the variation was around ten times lower.

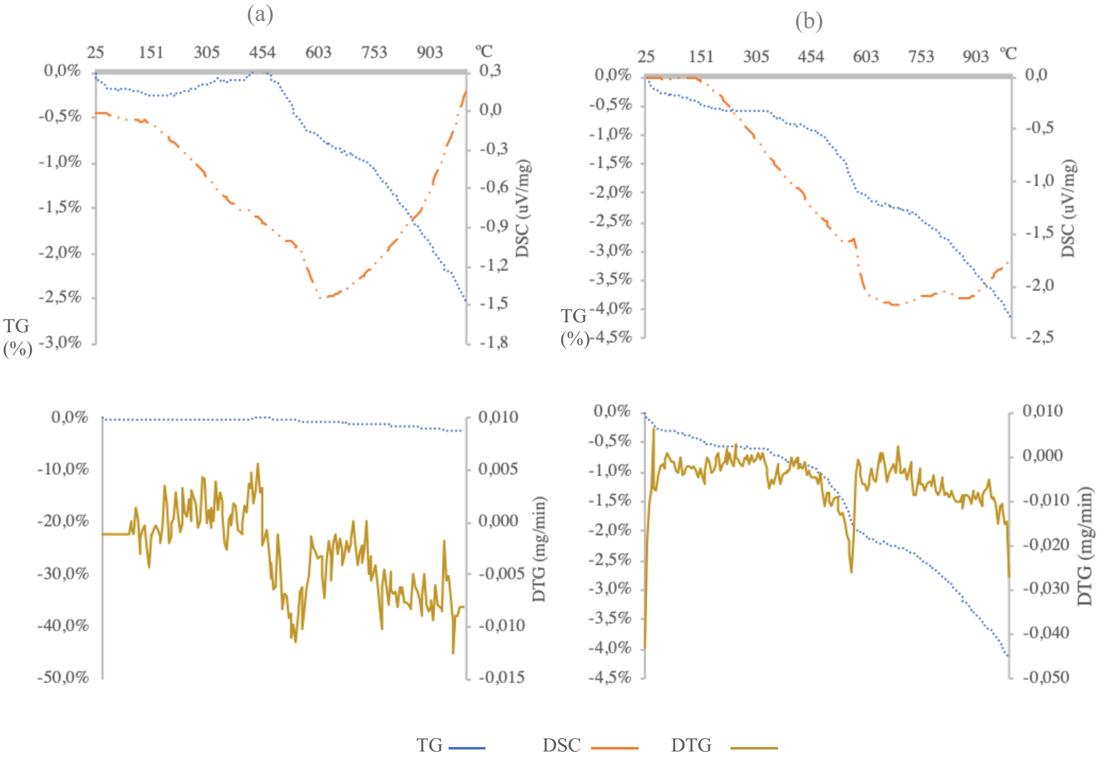

Figure 2: Thermal analysis of the (a) initial sample and the (b) sample after ED treatment.

Although portlandite was not detected on Figure 1, probably due to its vestigial presence, regarding Table 1, the weight losses verified between ~390°C and 500 °C might be also due to $Ca(OH)_2$ dehydration, since CaO can be formed ~500 °C under atmospheric pressure [17]. On Figure 1 is possible to identify calcite in samples composition. Additionally, until ~900 °C, decarboxylation of $CaCO_3$ (calcite) may occur [18]. This may had contributed to the sample mass loss in the range 500 – 900 °C, representing the main percentage contribution on total weight losses observed.

Table 1: Weight losses due to portlandite and calcite phenomena during thermogravimetric analysis.

Sample	$Ca(OH)_2$ (390 - 500 °C)		$CaCO_3$ (500 - 900 °C)		Total weight loss (%)
	Weight loss (%)	H_2O released (mol/mol %)	Weight loss (%)	CO_2 released (mol/mol %)	
Initial	0.16	0.64	1.87	4.24	2.55
After ED treatment	1.13	4.64	3.34	7.60	4.15

3.2. Pozzolanic reactivity quantification

Thermal treatment was applied to tungsten mining residues with and without ED pre-treatment. According to other studies [15], the temperatures selected were 800°C and 950°C to ensure silica and alumina transformation to amorphous forms. Table 2 shows the mg of $Ca(OH)_2$ fixed from the different samples.

According to NF P 18-513 [14], the minimal consumption of $Ca(OH)_2$ for a matrix be considered pozzolanic is 660 mg/1g of pozzolan. When no thermal treatment was applied, no pozzolanic reactivity has been noticed in the samples with no ED pre-treatment (7.9 mg $Ca(OH)_2$ fixed). However, the increment of 800°C and 950°C treatment potentiated in more than 21% the reactivity of the samples. When tungsten mining residues were treated with ED and NADES, the values of $Ca(OH)_2$ fixed were higher, being more effective when 950°C were applied. Also, a mill step before the thermal treatment helped to increase the contact surface area and, consequently, the reactivity of the samples.

ChCl:MA was the NADES tested with higher values, reaching 548 mg of $Ca(OH)_2$ consumed. Although this value is not in compliance with the pozzolanic limit from the NF P18-513 [14], it is promising when compared to other sources, such as metakaolins (~250-450 mg $Ca(OH)_2$), expanded clay (~300 mg $Ca(OH)_2$), biomass ashes (~280 mg

$Ca(OH)_2$), eucalyptus bark ashes (~100 mg $Ca(OH)_2$), coal fly ashes (~500 mg $Ca(OH)_2$) and glass waste powder (~350 mg $Ca(OH)_2$) [6].

TABLE 2: $Ca(OH)_2$ fixed by tungsten mining residues under different conditions.

Conditions	**$Ca(OH)_2$ fixed (mg)**	**$Ca(OH)_2$ fixed/ $Ca(OH)_2$ total (%)**
Tungsten mining residues without ED treatment		
No thermal treatment	7.9	0.8
800°C	214.3	21.3
950°C	214.3	21.2
Tungsten mining residues with ED + NADES treatment		
No thermal treatment	71.4	7.1
ChCl:OA + 800°C	198.4	19.8
ChCl:OA + 950°C	293.7	29.0
ChCl:OA + Mill + 950°C	333.3	32.8
ChCl:MA + Mill + 950°C	547.6	54.2

Figure 3 shows the increase of the $Ca(OH)_2$ fixed (mg) when the thermal treatment was applied, in relation to the samples without no thermal treatment (base line). This increase was more evident in the samples without the ED treatment (up to 96 %). On the other hand, the ED treatment promoted changes in the chemical species due to the electric field generated, making the elements more available in the media due to speciation phenomena and, consequently, more able to react with other species.

4. Conclusions

This study proved the feasibility of using different treatment steps to increase the pozzolanic reactivity of tungsten mining residues. The amount of quartz and muscovite are an evidence of the abundant SiO_2 and Al_2O_3 presence in the sample, which corroborates the potential to diverge the application of tungsten mining residues in the construction sector.

However, with any pre-treatment, these elements are not in the amorphous form and able to react with $Ca(OH)_2$ to increase the reactivity and, consequently, the durability of the products. Thus, ED treatment and NADES were tested to enhance a secondary removal and recovery of elements and, simultaneously, as a pre-treatment to enhance reactivity of residues from Panasqueira mine, coupled with a thermal treatment of 800°C and 950°C.

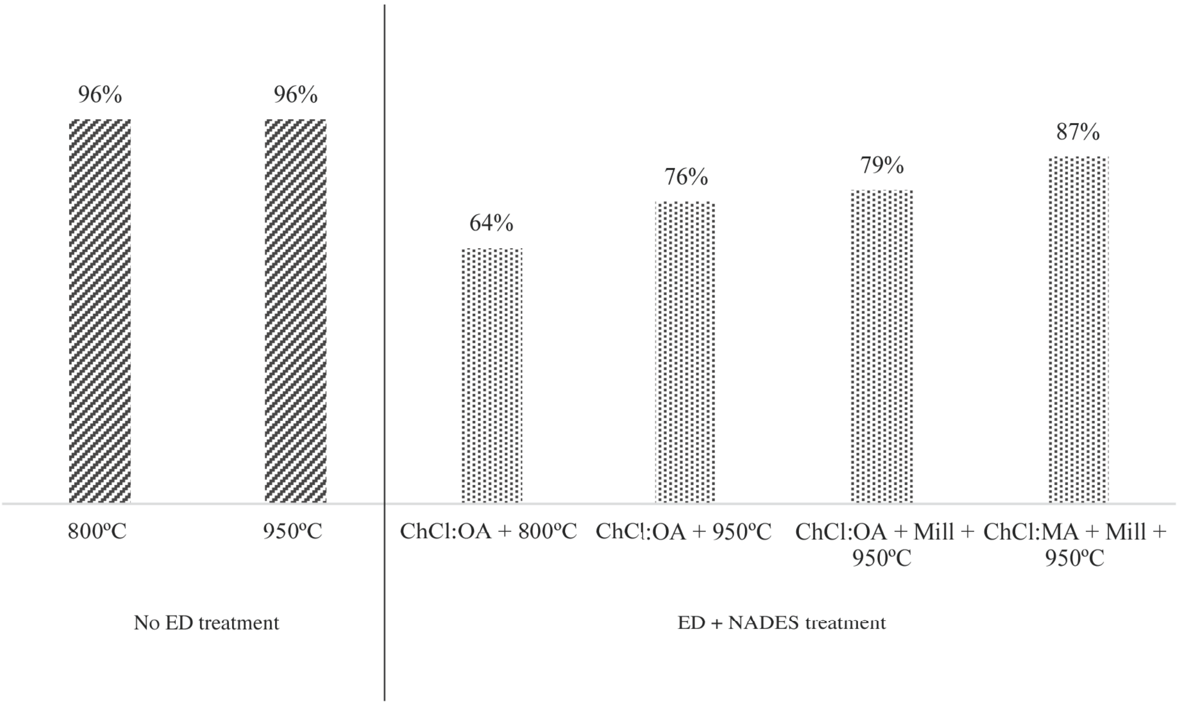

Figure 3: Pozzolanic reactivity increase in relation to the samples with no thermal treatment.

The results showed that is possible to increase the reactivity of the initial sample, although the values are still 17% under the limit stablished by the NF P 18-513. Nevertheless, 547.6 mg $Ca(OH)_2$ were consumed, showing the highest improvement when ED with ChCl:MA, a milling step and a temperature of 950°C were applied to the sample. Comparing with other secondary sources, the values achieved are promising. Moreover, it may open new possibilities for the recovery of secondary mining resources, contributing to circular economy and to increase sustainability in both mining and construction sectors and, eventually, the durability of construction products.

Acknowledgements

This work has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 778045, as well as from Portuguese funds from FCT/MCTES through grant UIDB/04085/2020. J. Almeida acknowledge *Fundação para a Ciência e a Tecnologia* for her PhD fellowship PD\BD\135170\2017. The authors acknowledge Eng. Manuel Pacheco from Panasqueira mine for providing tungsten mining residues samples.

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Scientific journal article

A8 Effect of mining residues treated with an electrodialytic technology on cement-based mortars

J Almeida, P Faria, AB Ribeiro & A Santos Silva

Published in Cleaner Engineering and Technology journal (2020)

This article was published in Cleaner Engineering and Technology, Vol 1, J Almeida, P Faria, AB Ribeiro & A Santos Silva, Effect of mining residues treated with an electrodialytic technology on cement-based mortars, 100001, Copyright Elsevier (2020).

Cleaner Engineering and Technology 1 (2020) 100001

Contents lists available at ScienceDirect

Cleaner Engineering and Technology

journal homepage: www.journals.elsevier.com/cleaner-engineering-and-technology

Effect of mining residues treated with an electrodialytic technology on cement-based mortars

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ARTICLE INFO

Keywords:
Cement composite
Construction product
Electrodialytic process
Mining residue
Masonry mortar

ABSTRACT

Mining residues have been accumulated for centuries due to excavation and mining processes, causing environmental degradation worldwide. Their application in cementitious products is a feasible alternative to waste disposal. Electrodialytic technologies can promote a safer reuse of mining residues in the construction sector, coupling economic advantages due to the possible removal of toxic elements and the recovery of critical raw materials. The application of treated mining residues in construction products, namely their effects on physico-mechanical properties, in comparison to raw residues and cement uses needs to be addressed. This work presents a study of cement-based mortars with the incorporation of mining residues treated with an electrodialytic process in comparison to raw mining residues. The replacement percentages studied were 0, 10, 25 and 50% of the binder in volume. Tests were conducted to evaluate fresh and hardened properties of mortars considering physical, microstructural and mechanical performances. Results show the viability of applying mining residues after the electrodialytic treatment as mortars materials in rendering, plastering, joint repointing, bedding masonry or screed requirements, with improved thermal conductivity and eco-efficiency.

1. Introduction

The sustainable progress of the planet is highly dependent on global population trends. Since the world population is expected to reach 10,900 M by 2100 (from current 7,000 M), urban areas will face serious challenges in its sustainable development (United Nations, 2019).

Concrete is one of the main contributors for greenhouse gas emissions and its manufacture commonly involves Portland cement binders, likewise Portland cement-based mortar production (Arrigoni et al., 2020). Mortars are porous construction composites frequently used for bedding masonry units, plastering, rendering and for screeds (Faria et al., 2015). The performance of mortars depends on the properties of the materials involved, their proportions, production and application procedures and curing conditions (Shi et al., 2020). Typically, masonry bedding mortars require higher compressive strength when compared to plastering and rendering mortars; in turn the latter implies low shrinkage and rigidity, and high workability and flexural resistance (Di Mundo et al., 2020).

Focusing on rendering mortars maintenance, mortar components and application may affect renders' durability, the need for repair interventions and the overall construction sustainability. Cement-based mortars may have higher impacts in the beginning of their life cycle, but these negative impacts generally decrease overtime, mainly due to a reduced need for repair actions in comparison with non-hydraulic mortars (Brás and Faria, 2017). Renders main function is to protect walls where they are applied. Thus, cementitious renders are compatible with concrete monolithic walls, concrete block or fired brick masonry walls (Palomar et al., 2019).

Under circular economy targets, alternative secondary resources are highly encouraged for different purposes (EC, 2020). Thus, research has focused in the development of sustainable cementitious products to minimize the negative impacts associated to ordinary Portland cement (OPC). A partial replacement by alternative secondary resources may bring economic, social and environment benefits, as well as an improvement on durability properties (Li et al., 2020).

During the past decades, mineral exploitation has gained an international demand due to the global economic growth. In Europe, Portugal is one of the main producers of copper and tungsten concentrates at

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https://doi.org/10.1016/j.clet.2020.100001
Received 3 July 2020; Received in revised form 12 August 2020; Accepted 5 September 2020

Abbreviations

Cac	Capillarity absorption coefficient
$Ca(OH)_2$	Calcium hydroxide
CEN	European committee for standardization
Cs	Capillarity saturation value
CStr	Compressive strength
DI	Drying index
DME	Dynamic modulus of elasticity
DR1	Drying rate at phase 1
DR2	Drying rate at phase 2
ED	Electrodlialytic process
FStr	Flexural strength
M	Raw mining residues mortars
ME	Electrodialytic treated mining residues mortars
MIP	Mercury intrusion porosimetry
$NaNO_3$	Sodium nitrate
OPC	Ordinary Portland cement
REF	Reference mortar
RH	Relative humidity
Ti/MMO	Titanium/mixed metal oxide
XRF	X-ray fluorescence
WO_3	Tungsten trioxide

Neves Corvo mine (Capasso et al., 2019) and Panasqueira mine (Almeida et al., 2020b), respectively.

Mining processes are associated to a critical environmental problem worldwide due to their high waste disposal rates. Generally, metal mining generates approximately 15,000 Mt of waste per year, which is 10 times more than global municipal waste (Gankhuyag and Gregoire, 2018). This waste can affect the ecosystems due to their: (1) chemical and mineralogical composition; (2) physical properties; (3) volume and surface occupied and (4) waste disposal method. Mining residues are often disposed in large areas with dumps or in abandoned open pits. The most common management approaches are, thus, terrestrial impoundment, underground backfilling, deep water disposal and recycling. In this sense, the main risks associated are the failure of mining waste disposal dams and the dispersion of waste fines and heap leaching (Lèbre et al., 2017).

Regarding Panasqueira mine (Covilhã, Portugal) several researches focused on tungsten mining residues reuse in construction products. Some examples are alkali activated products (Beghoura and Castro-Gomes, 2019), technical-artistic value added products (Castro-Gomes et al., 2012) and pozzolanic materials (Sousa et al., 2013) that, alone or coupled with other resources, may improve the properties of construction products.

The presence of valuable raw materials and harmful compounds in these secondary resources have pursued the development of new approaches to promote its safe further reuse, namely in the construction sector (Almeida et al., 2020b).

The electrodialytic process (ED) consists on the application of a low-level alternate/direct current density between pairs of electrodes to remove organic and inorganic substances. Ion exchange membranes are used to promote a selective separation of anions and cations in concentrated salty solutions (Ribeiro and Rodríguez-Maroto, 2006). This treatment is commonly applied to liquid [e.g. effluent (Magro et al., 2019)] or solid [e.g. soil (Guedes et al., 2014), sewage sludge (Guedes et al., 2016), fly ash (Magro et al., 2016), timber waste (Ribeiro et al., 2000)] matrices. In particular, ED has shown potential not only to promote the removal of toxic elements or the recovery of critical raw materials but also to enhance properties of tungsten mining residues in the presence of natural adjuvants (Almeida et al., 2020a), namely composites durability (Almeida et al., 2020c). However, to the authors knowledge, the effect of ED treated mining residues in comparison to raw mining residues applications in construction products properties has not yet been studied.

The present work aims to show the feasibility of using secondary mining resources in cement-mortars production as binder replacement, after being treated with an ED process. By the application of the ED pretreatment, this novel procedure contributes to increase critical raw materials recovery (e.g. tungsten), and harmful compounds removal (e.g. arsenic) from mining residues suspensions, promoting a cleaner reuse of this secondary resource in cement composites. Also, this study contributes for a secondary resource reuse approach towards circular economy principles. The present research gives an overview on fresh and hardened properties of the mortars produced with 0, 10, 25 and 50% of cement content replacement (in volume) by raw or treated mining residues in order to access the feasibility of applying the ED technology without materials deterioration when compared to raw residues uses.

2. Experimental campaign

2.1. Materials

Mortars were produced with tungsten mining mud collected directly from the sludge circuit output of Panasqueira mine (Covilhã, Portugal, 40°10′11″N, 7°45′24″W). Samples were dried at 20 °C for 48 h in a fume hood, before starting the experiments. Typically, mud from Panasqueira mine contains fines with particle sizes lower than 2 mm (Castro-Gomes et al., 2011). The annual production of tungsten at Panasqueira mine is estimated in 90,000 t, with concentrated grades of 75% WO_3 (tungsten trioxide) (Franco et al., 2014).

In this work, tungsten mining residues were applied as replacement of CEM II/BL 32.5 N (Secil, Portugal), classified according to EN 197–1 (CEN, 2012). A river siliceous sand was applied as aggregate and tap water was used to hydrate the formulation.

2.2. Methods

2.2.1. Electrodialytic treatment of mining residues

The ED treatment was applied for the recovery of critical raw materials (tungsten), and the removal of harmful compounds (arsenic) from mining residues (Almeida et al., 2020a).

Mining residues were treated in a two-compartment ED acryl XT reactor (RIAS A/S, Roskilde, Denmark), according to Almeida et al. (2020a). The diameter of the reactor was 80 mm, with 50 mm length for the electrolyte compartment and 100 mm for the sample section. An anion exchange membrane AR204SZRA, MKIII, Blank (Ionics, USA) was applied to divide the two compartments. The electrodes selected were made of Ti/MMO with a length of 50 mm and a diameter of 3 mm (Grønvold & Karnov A/S, Denmark). Constant current was maintained inside the reactor (50 mA) with a power supply E3612A (Hewlett Packard, Palo Alto, USA).

Also, a magnetic stirrer was placed into the sample compartment. A suspension of 39 g of mining residues with 345 mL of deionized water and 5 mL of a natural deep eutectic solvent (choline chloride/malonic acid) was set in the cathode compartment. In the anode compartment, 250 mL of 0.01 M $NaNO_3$ were added as anolyte. Twenty experiments were operated during 4 days.

2.2.2. Materials' properties

The particle size distribution of the river siliceous sand was performed by dry sieving following standard EN 1015–1 (CEN, 1998). Loose bulk density of CEM II/BL 32.5 N, river sand, raw mining residues and ED mining residues was determined weighting a recipient with known volume filled with each uncompacted material. The chemical composition of the raw and ED mining residues was determined with a portable X-ray fluorescence equipment (XRF), Tracer 5 from Bruker.

2.2.3. Mortar formulation, samples curing and tests

The production of mortars (type, velocity and time of mixing) was carried out based on EN 196–1 (CEN, 2017). The volumetric proportion of binder, aggregate and water used as reference was 1:3:0.5. The reference mortar was produced with 100% of CEM II/BL 32.5 N as binder. Modified mortars were produced replacing 10, 25 and 50% of the cement volume content by raw (M mortars) and ED (ME mortars) mining residues. The loose bulk density of the materials allowed to determine the exact masses of each component, considering their volumes (Table 1).

Mortars' fresh and hardened state properties were analysed through physical, mechanical and microstructural tests, as summed up in Fig. 1.

Flow consistency tests were performed according to EN 1015–3 (CEN, 2000). A flow table test was used to measure the slump value (average diameter of the specimen measured in different directions). Bulk density of fresh mortars was determined according to EN 1015–6 (CEN, 1999a) by weighting a mould (with known volume) filled with the mortar specimen.

Mortar samples were produced in triplicate in 40 mm × 40 mm x 160 mm metallic moulds. For each mortar formulation, circular samples with 90 mm diameter and 20 mm width were also produced. Mortar samples were kept inside polyethylene closed bags and demoulding was carried out after 48 h. The samples were cured horizontally in a tap water bath for the next 26 consecutive days at 20 °C. The samples were then dried at 60 °C until constant weight.

For thermal conductivity measurements, the circular samples were stabilized in a chamber for 24 h at 20 °C and 75% of relative humidity (RH). Thermal conductivity of all specimens was determined inside the chamber with an Isomet 2104 Heat Transfer Analyzer (Applied Precision, Slovakia), equipped with a contact probe API 210412 of 60 mm diameter and operating range between 0.04 and 0.3 W/(mK).

The dry bulk density of the mortar prisms was determined by the quotient of the mass, with a digital scale (precision of 0.001 g), by the volume, assessed directly with a digital caliper (precision 0.01 mm), based on EN 1015–10/A1 (CEN, 1999b).

The dynamic modulus of elasticity (DME) was determined considering EN 14146 (CEN, 2004), using a Zeus Resonance Meter ZMR 001 equipment. With mass and volume data of each sample, the equipment measured the response to an induced vibration signal along the test samples. For each sample, four nondestructive tests were performed, resulting on twelve tests by mortar.

Flexural and compressive strengths were performed according to EN 1015–11 (CEN, 2019), with a Zwick/Rowell Z050 equipment. For flexural strength tests, three-point bending test was performed with two steel supporting rollers separated by 100 mm. The loading was gradually applied at a constant rate of 50 ± 10 N/s until failure occurred. Compressive strength tests were subsequently performed with one of the half samples disjointed in the previous flexure tests. The loading was progressively applied at a constant ratio of 2,400 ± 200 N/s until mortar failure.

Capillarity absorption test, based on EN 1015–18 (CEN, 2003), and drying test, based on EN 16322 (CEN, 2013), were performed in a conditioned laboratory at temperature of 20 °C and 65% of RH. Tests were conducted on 40 mm cubic samples, cut from halves of previous flexural tests original prisms. The lateral faces were waterproofed by painting with Sikagard 570 W (Sika, Portugal). Samples were placed into a plastic box and the cut surface was maintained in contact with water to a level of 5 mm.

The capillarity absorption curve of mortar samples, in mass increase per area in contact with water by square root of time, was determined by weighing the samples sequentially until an asymptotic value was obtained. The capillarity coefficient was determined using the mass of water absorbed per unit area and square roof of time between 10 and 30 min (initial strait segment of the curves).

Drying ability of the mortars was tested immediately after capillarity tests, moving the cubic samples to a waterproofed surface, inverting (to promote drying only by the surface previously in contact with water) and weighing the samples sequentially until achieving a constant weight (CEN, 2013). From the mortars drying curve (with the mass decrease per drying area) by time, the drying rate of the first drying phase was determined by the negative slope of the initial segment. From the drying curve by square root of time, the second drying phase rate was determined by the negative slope of the intermediate linear segment. The drying index (DI) was also calculated based on equation (1), from EN 16322 (CEN, 2013):

$$DI = \int_{t_i}^{t_f} \frac{M_{t_i} dt}{M_{max} t_f} \tag{1}$$

where t_f is the total duration of the test, M is the water content in time t_i, and M_{max} is the maximum water content. A lower DI corresponds to a higher drying capacity.

A mercury porosimeter Micromeritics Autopore II was used to determine pore size distribution from mortars produced with 0, 10, 25 and 50% of raw mining residues. Specimens with approximately 1.7 cm^3 (total capacity of the bulb from penetrometers) were collected from samples and stabilized in an oven at 40 °C during 24 h.

3. Results and discussion

3.1. Raw materials characterisation

The chemical composition obtained by XRF of raw and ED mining residues is presented in Table 2. The most abundant elements in both samples is silicon, expressed as SiO_2 (up to 65%), followed by aluminium, expressed as Al_2O_3 (raw = 19% and ED = 22%). Harmful metalloids were also detected in mining residues, such as (M = 0.59%), although 64% of the As was successfully removed by the ED treatment, decreasing the potential of leaching.

Table 1

Weight proportion of binder, aggregate and water used in the mortar formulations, materials loose bulk density and water/binder mass ratio.

Code	Binder and mining residues					Aggregate		Water		Mass proportion	
	CEM II/BL 32.5 N (1,000 kg/m^3)		Mining residues			Sand (1,540 kg/m^3)		Tap water (1,000 kg/m^3)		Binder:sand:water	Cement:residue:sand
	%	Weight (g)	Treatment	%	Weight (g)	%	Weight (g)	%	Weight (g)		
REF	100	431.8	–	–	–	100	2,000	100	333.3	1:4.6:0.8	1:0:4.6
M10	90	388.7	No treatment (M)	10	36.6					1:4.7:0.8	1:0.1:5.1
M25	75	323.9	(1,180 kg/m^3)	25	91.4					1:4.8:0.8	1:0.3:6.2
M50	50	215.9		50	182.9					1:5.0:0.8	1:0.9:9.3
ME10	90	388.7	Electrodialytic treated (ME)	10	42.0					1:4.6:0.8	1:0.1:5.1
ME25	75	323.9	(1,003 kg/m^3)	25	105.0					1:4.7:0.8	1:0.3:6.2
ME50	50	215.9		50	209.9					1:4.7:0.8	1:1.0:9.3

Notation: REF - Reference mortar; M - Raw mining residues mortars; ME – Electrodialytic treated mining residues mortars.

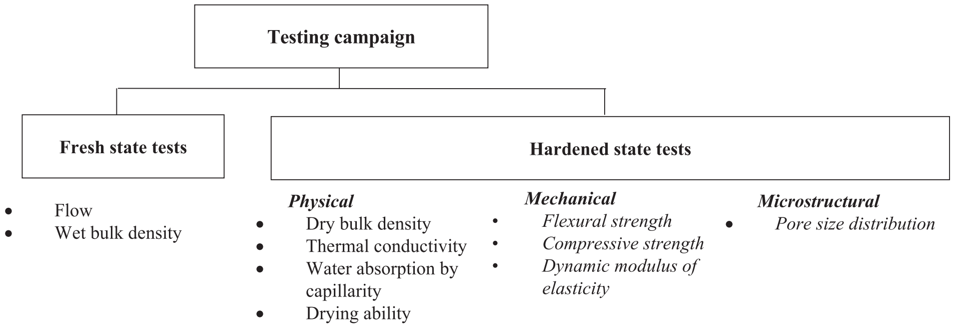

Fig. 1. Tests performed to assess fresh and hardened mortars properties.

Table 2
Semi-quantitative chemical analysis by XRF of raw and ED mining residues (weight %).

Determinations	Raw	ED
Al_2O_3	18.80	21.98
SiO_2	68.35	65.58
P	0.15	0.10
S	0.83	0.74
Cl	N.D.	N.D.
K_2O	3.29	4.31
Ca	0.55	0.40
Ti	0.46	0.55
Mn	0.08	0.07
Fe	5.81	5.37
Cu	0.18	0.10
Zn	0.58	0.29
As	0.59	0.21
Sn	0.07	0.04
W	0.27	0.26

Notation: N.D. – Not detected.

The loose bulk density of the components used for mortar formulation is presented in Table 1. When mining residues were subjected to the ED treatment, their loose bulk density decreased 15% compared to the raw case (1,180 kg/m^3), which might be due to the extraction of inorganic substances during the process (Almeida et al., 2020a). Additionally, after the ED treatment of mining residues, their loose bulk density (1,003 kg/m^3) became similar to CEM II/BL 32.5 N (1,000 kg/m^3). Therefore, the volumetric replacement of the cement binder by ED mining residues almost corresponds to the same weight. On the other hand, the same volumetric replacement by raw mining residues corresponds to a higher weight. Thus, a higher filler effect is expected (Table 1).

The particle size distribution of the river siliceous sand was analysed (Fig. 2). Particles are mainly between 0.5 and 2.0 mm, similarly to the CEN reference sand particle size distribution (CEN, 2017).

Calcium and aluminium silicates in presence of $Ca(OH)_2$ and water may potentiate a pozzolanic reaction. Mining residues from Panasqueira mine were studied by Almeida et al. (2020c) in terms of its pozzolanic reactivity through the modified Chapelle test (AFNOR, 2010). Herein, the total quantity of fixed $Ca(OH)_2$ by siliceous/aluminosilicates amorphous constituents present in raw and ED mining residues was reported as 7.9 mg and 71.4 mg per g of material, respectively (Almeida et al., 2020c), representing low pozzolanic features.

3.2. Fresh state characterisation

The ability to mix and apply a mortar with minimal loss of homogeneity can be assessed by the fresh state characterisation (Chindaprasirt and Cao, 2015). In this study all the mortars were produced with a constant water content (Table 1). Concerning the fresh state characterisation, flow table consistency and wet bulk density were determined (Table 3).

Wet bulk density of M and ME showed higher values when compared to the reference mortar, increasing as the content of mining residues augmented in the formulations. Since the loose bulk density of the raw mining residues is higher than cement (Table 1), it was expected that wet bulk density of M mortars was also higher. However, differences on the

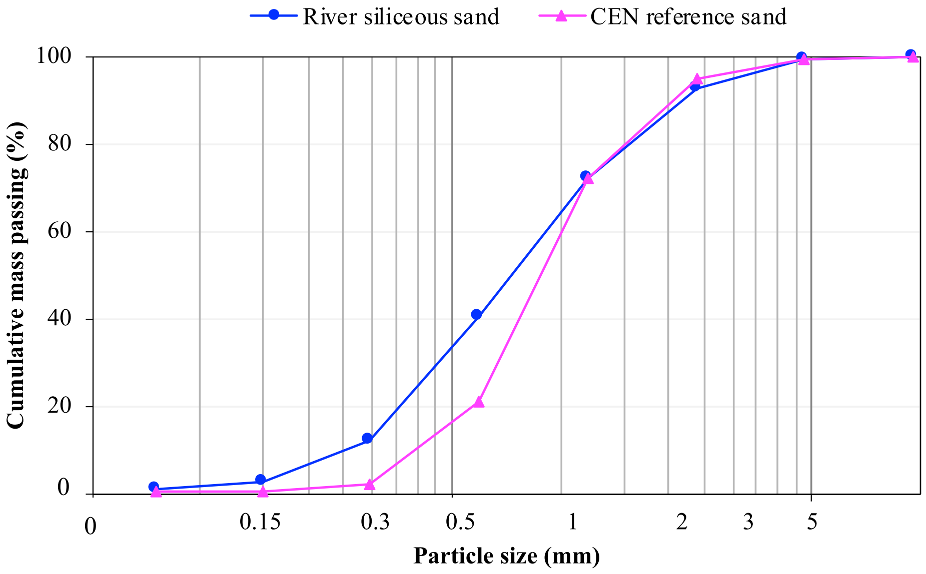

Fig. 2. Dry particle size distribution of river siliceous sand and CEN reference sand.

Table 3
Mortars wet bulk density and flow table consistency.

Mortar	Flow table consistency (mm)	Wet bulk density (kg/m^3)
REF	156.3	1,997.9
M10	154.3	2,018.7
M25	147.8	2,035.2
M50	139.5	2,038.2
ME10	146.5	2,029.2
ME25	132.3	2,038.7
ME50	129.3	2,069.8

Notation: REF - Reference mortar; M - Raw mining residues mortars; ME - Electrodialytic treated mining residues mortars.

mortars with ED mining residues, that have similar loose bulk density to cement, were observed.

Loose bulk density of the particles and filler effect are the main factors affecting mortar wet bulk density (Jesus et al., 2019). Mining residues have a pH in water suspension of approximately 5, but after the ED treatment, the pH of mining residues suspensions dropped to about 4 (Almeida et al., 2020a). This may have also affected the difference on bulk density between M and ME mortars, since chemical species present in the residues may have solubilized at a slightly lower pH. The application of natural deep eutectic solvents during the ED treatment, as well as other extreme conditions that mining residues were subjected during the four days of ED experiment, may also have contributed for the bulk density increase. Furthermore, direct water uptake from both raw and ED mining residues could justify the values observed.

The inverse trend was verified for flow consistency tests. The consistency test was performed to assess the fluidity and workability of fresh mortars based on the constant water content (Table 1). Considering the results in Table 3, and also the observations during manual handling of mortars, the incorporation of both types of mining residues (raw and ED) decreased their workability. This loss of workability with the increase of mining residues content may be related to mining residues particles, which may absorb more water due to their permeability and surface properties. The increase of mining residues incorporation may require more water to achieve the same consistency of the reference mortar, also due to cement hydration reactions. The presence of other chemical substances can interfere with water-binder reactions (Tiwari et al., 2014). The addition of mining residues may hinder chemical bonding between hydration products due to their crystalline phases and inert characteristics (Simonsen et al., 2020).

Mortars were produced with the same volumetric ratio and, consequently, equal binder volume contents but slightly different water/binder mass ratios (Table 1). When mining residues are incorporated in the formulation, the water/binder is affected, which may have also decreased the filler effect, namely in mortars M50 and ME50. The higher incorporation of mining residues reduced the plasticity of the mortars (flow table consistency of 139.5 mm for M50, and 129.3 mm for ME50) compared to the reference (flow table consistency = 156.3 mm). In real conditions, depending on the type of mortar application (e.g. screeds, rendering or plastering), the incorporation of a plasticizer as admixture may be needed to fill water requirements and consistency improvements.

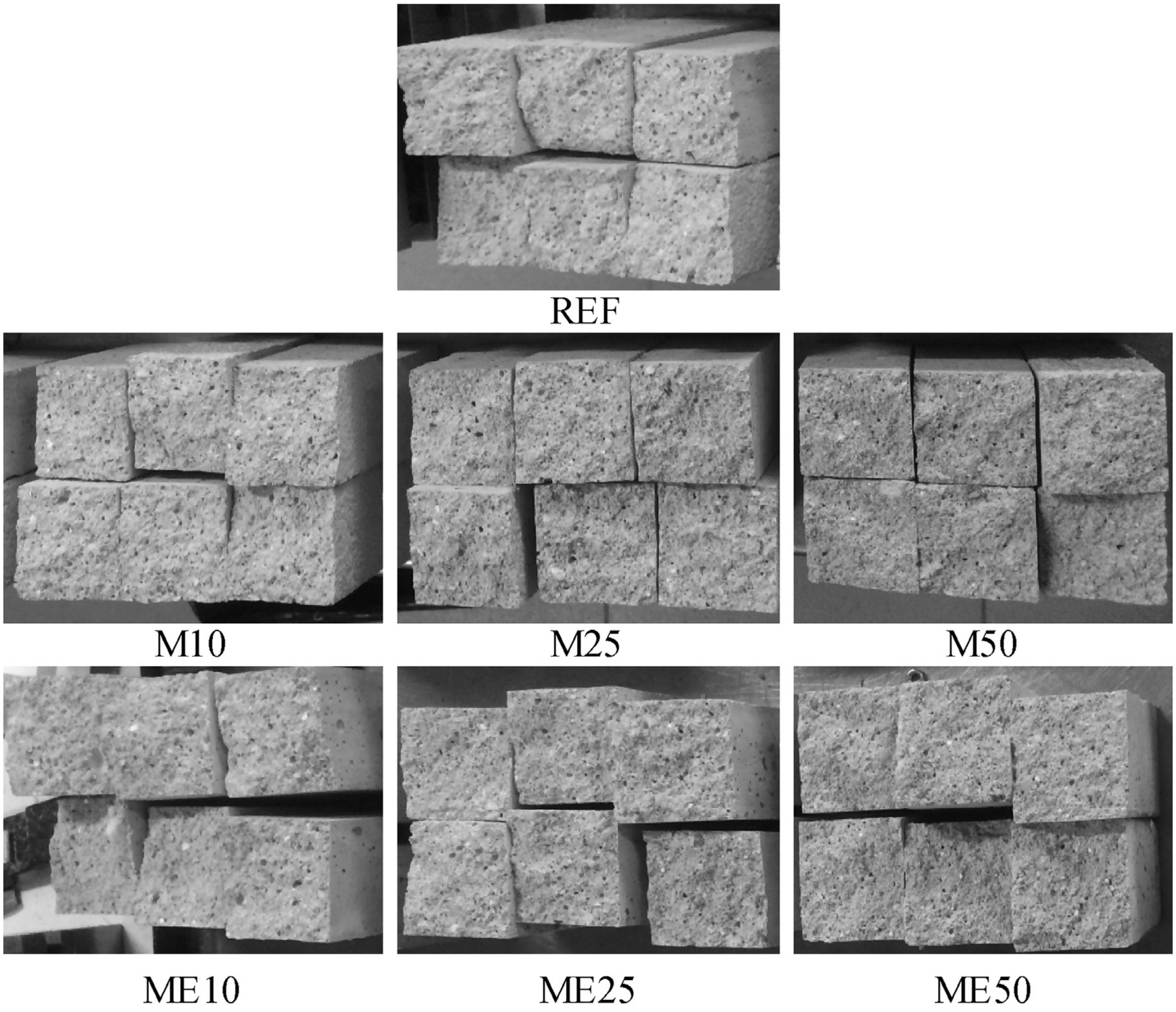
REF
M10
M25
M50
ME10
ME25
ME50

Fig. 3. Mortar samples after 28 curing days (REF - Reference mortar; M - Raw mining residues mortars; ME - Electrodialytic treated mining residues mortars).

3.3. Hardened state characterisation

The mortar samples used to conduct the hardened state characterisation are presented on Fig. 3.

3.3.1. Dry bulk density and thermal conductivity

Hardened mortar results of dry bulk density and thermal conductivity after 28 days of cure are presented in Fig. 4.

The trend verified on wet bulk density, with an increase with the content of both mining residues in comparison to the reference, is not observed for the dry bulk density. When 10% of raw or ED mining residues were introduced in the formulation, dry bulk densities decreased to 1,928.9 ± 27.0 kg/m^3 (M10) and 1,971.8 ± 12.4 kg/m^3 (ME10) when compared to REF (1,975.6 ± 16.8 kg/m^3). However, cement replacement of 25 and 50% for both M and ME increased the dry bulk density of the mortar by 1–2% compared to REF, as verified for wet bulk density. Particularly for raw mining residues, this may be explained by the higher mass proportion (Table 1).

For most building applications, low thermal conductivities contribute for thermal comfort, namely for layering masonry mortars or roof screeds. Additionally, low thermal conductivity is desirable in renders to promote the attenuation of thermal expansion stresses (Van Riessen et al., 2009). The reference mortar presents the highest thermal conductivity, 1.54 W/(mK), suggesting that mining residues incorporation on mortars can improve thermal comfort.

Considering raw mining residues, the trend observed for dry bulk density is maintained: Mortars with higher dry bulk densities were coupled with higher thermal conductivity values. However, the set of mortars with ED mining residues (ME10, ME25 and ME50) did not corroborate the previous trend. ME25 showed the lowest thermal conductivity, 1.15 W/(mK). The ED treatment may have enhanced the microstructure of the mortar, with optimal conditions for thermal conductivity reduction at 25% of mining residues incorporation. Therefore, the ED treatment is feasible in terms of both bulk density and thermal conductivity, considering ED mining residues application on cement mortars.

3.3.2. Mechanical resistance

Fig. 5 presents the results of flexural (FStr) and compressive (CStr) strengths, as well as dynamic modulus elasticity (DME).

As expected, all the mechanical properties decreased when cement was replaced by mining residues, in a proportional way. This is explained by the cement content decrease and its replacement by the residues that are lower strength materials (as shown in Table 1). The non-pozzolanic behaviour of these residues may also justify the decrease observed in mechanical properties. Raw mining residues reported only 8 mg of $Ca(OH)_2$ fixation and ED mining residues 71 mg (Almeida et al., 2020c), being both samples far below the limit (660 mg $Ca(OH)_2$/g) to be considered as pozzolans according to NF P 18–513 (AFNOR, 2010).

When 10% of raw mining residues replaced CEM II/BL 32.5 N, the loss in DME when compared to the reference was 12%. DME translates mortars stiffness, where lower values indicate that mortars are more prone to absorb deformations (Gomes et al., 2018). Therefore, low DME may be beneficial to mortars, without jeopardizing other mechanical properties. Considering rendering and plastering mortars, cracking issues due to loading applications can be alleviated in the presence of low DME mortars (Sandin, 1995).

As expected, DME decrease is consistent with the reduction on flexural and compressive strengths. Generally, the cement replacement by mining residues provided mortars with lower strengths, which in the present circumstance was more evident in the compressive strength case. Apart the declining trend with the increase of mining residues content, that may be explained by the lower proportion of cement, a retarding effect on cement hydration can be caused by amounts of phosphorus (Jiang et al., 2019) and the presence of other chemical impurities on mining residues (Tiwari et al., 2014).

The presence of phosphorus in mining residues, as reported in Table 2 for M (0.15%) and ME mortars (0.10%), may have contributed to decrease mechanical performance. Internal micro-cracking of mortars may also have occurred, although this behaviour is more common in the presence of high cement contents (Gomes et al., 2018).

Comparing to the reference, mechanical strength decreased 11% and 19% in terms of flexural performance in M10 and ME10, respectively. Also, for the same formulations a decrease of 30% on compressive strength occurred. Other studies conducted aiming mortars production with blended cements including mining waste also reported a decrease in compressive and flexural strengths, that becomes more pronounced as the mining waste content increases (Wu et al., 2020).

Additionally, mortars that couple resistance to cracking and deformability can be evaluated by DME/flexural strength ratio, where low values mean increased mechanical performance. Thus, M and ME mortars showed better DME/flexural strength ratio in the following sequence:

M50 > M25 > ME25 > ME10 > ME50 > REF > M10.

3.3.3. Mortars classification and application

Renders and masonry joint repointing mortars, as highly exposed construction elements, need to be repaired and eventually replaced cyclically during buildings life cycle (Sandin, 1995). Considering the classification for rendering (and plastering) mortars from EN 998–1 (CEN, 2016a), mortars with mining residues may be classified according to their compressive strength at 28 days as CS III (M25, ME25, M50 and

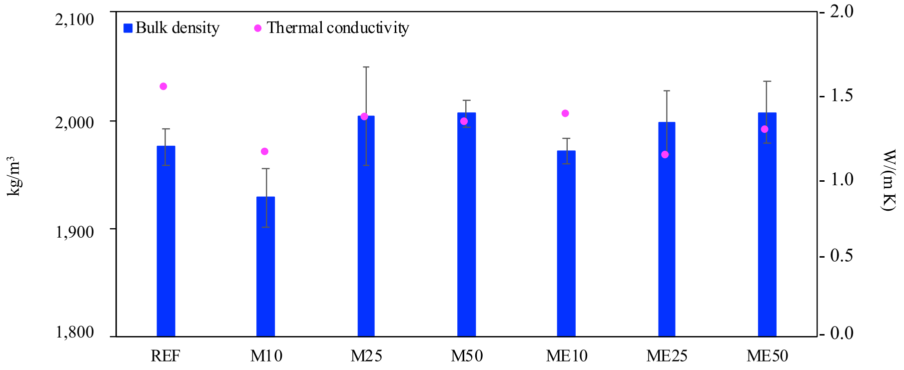

Fig. 4. Dry bulk density and thermal conductivity of mortars (REF - Reference mortar; M - Raw mining residues mortars; ME - Electrodialytic treated mining residues mortars).

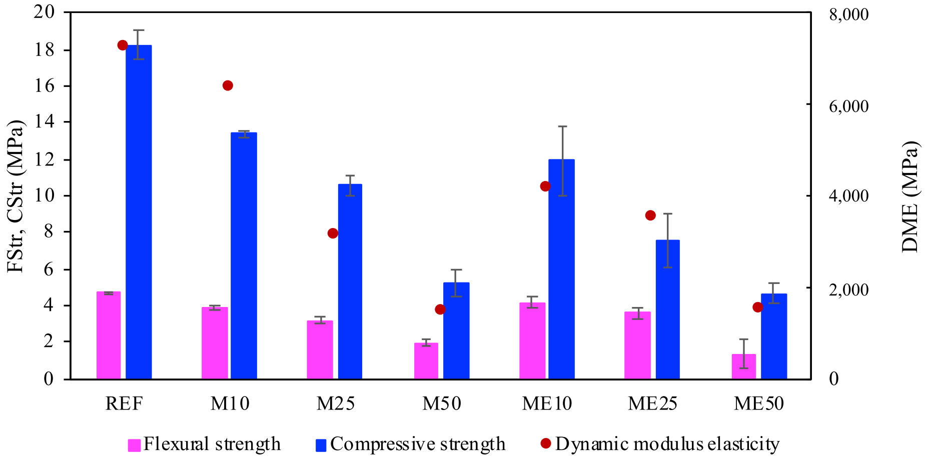

Fig. 5. Flexural and compressive strength and dynamic modulus of elasticity of the mortars (REF - Reference mortar; M - Raw mining residues mortars; ME - Electrodialytic treated mining residues mortars).

ME50) and CS IV (M10 and ME10). These classes are much superior to the limit for CS I mortars (0.4 MPa), corresponding to extremely stiff mortars to some traditional and historical walls. Therefore, even the mortars with 50% of cement replace by mining residues presented mechanical performances compatible with common concrete and contemporary fired brick masonry walls.

On the other hand, regarding EN 998–2 (CEN, 2016b) classification of bedding mortars for masonry units layering, mortars with mining residues can be classified in classes M5 (M50 and ME50) and M10 (M10, ME10, M25 and ME25). Concerning class M1 (maximum of 1 MPa), the mortars produced are not in compliance with some traditional and historical walls low resistance needs. As the previous case, M50 also showed compatibility with traditional concrete and contemporary fired brick masonry walls.

Furthermore, the incorporation of 10 and 50% of mining residues after the ED treatment was not significantly affected, in comparison to the raw mining residues use, considering applications where compressive strength is essential. Contrarily, when flexural strength is the key factor, such as for rendering, plastering and joint repointing, mortars with both 10% and 25% of ED mining residues showed better properties in comparison to the replacement of cement by raw mining residues. In addition, the mechanical performance of ME mortars was not strongly affected when compared to M mortars.

3.3.4. Water absorption by capillarity and drying

The capillarity curves allow to evaluate the initial absorption rate of mortars, by the capillary coefficient, and the total absorbed water, by the asymptotic value. The average capillarity curves of mortars are presented in Fig. 6.

The capillary curves showed that all the mortars with mining residues behaved negatively in comparison to REF in terms of capillary absorption, proportionally to the residue increase. Mortars with 10% of mining residues presented similar values both in terms of initial capillarity absorption rate and asymptotic value. Mortars with 25% of residues, although presented an increase of initial absorption rate, maintained an equivalent total of water absorbed by capillarity. Mortars with 50% residues not only showed an increase on the initial rate but also on the total absorbed water, that may be explained by the mortars pore size distribution. The initial absorption rate is quantified by the capillarity coefficient in Table 4, as well as capillarity saturation values.

From the observation of the capillary curves (Fig. 6 and Table 4), the capillarity coefficient increased with the increase of mining residues incorporation, as well as the capillarity saturation value. Additionally, no significant deterioration on those properties occurred between mortars with raw or ED mining residues, being the ED case more advantageous for the product lifecycle.

Capillarity coefficients of M50 [0.088 ± 0.000 kg/(m^2.$s^{0.5}$)] and ME50 [0.067 ± 0.005 kg/(m^2.$s^{0.5}$)] represented the worst cases, since

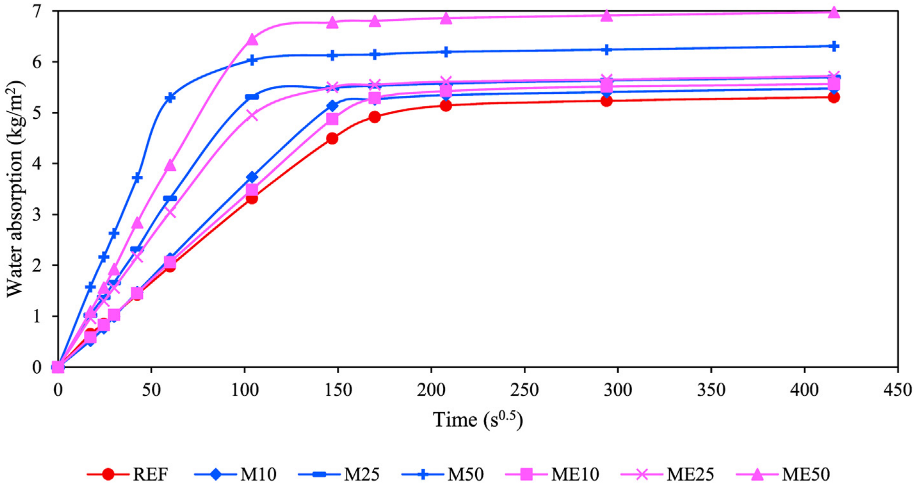

Fig. 6. Capillarity absorption curves of mortars (REF - Reference mortar; M - Raw mining residues mortars; ME - Electrodialytic treated mining residues mortars).

Table 4
Capillarity absorption coefficient, capillarity saturation value, drying rates of phases 1 and 2 and drying index of mortars.

Mortar	Cac [kg/(m^2.s$^{0.5}$)]	Cs (kg/m^2)	DR$_1$ [kg/(m^2.h)]	DR$_2$ [kg/(m^2.h$^{0.5}$)]	Drying index
REF	0.033 ± 0.001	5.305 ± 0.593	0.204 ± 0.003	0.456 ± 0.002	0.216 ± 0.009
M10	0.035 ± 0.000	5.476 ± 0.140	0.195 ± 0.010	0.472 ± 0.007	0.218 ± 0.011
M25	0.055 ± 0.002	5.698 ± 0.685	0.192 ± 0.009	0.501 ± 0.008	0.220 ± 0.001
M50	0.088 ± 0.000	6.309 ± 0.337	0.218 ± 0.011	0.594 ± 0.011	0.197 ± 0.000
ME10	0.034 ± 0.000	5.564 ± 0.041	0.206 ± 0.011	0.444 ± 0.006	0.257 ± 0.000
ME25	0.051 ± 0.000	5.717 ± 0.742	0.200 ± 0.019	0.507 ± 0.016	0.228 ± 0.000
ME50	0.067 ± 0.005	6.976 ± 0.198	0.221 ± 0.007	0.539 ± 0.004	0.284 ± 0.001

Notation: REF - Reference mortar; M - Raw mining residues mortars; ME - Electrodialytic treated mining residues mortars; Cac - Capillarity absorption coefficient; Cs - Capillarity saturation value; DR$_1$ - Drying rate (phase 1); DR$_2$ - Drying rate (phase 2).

these formulations absorbed water faster and in higher quantities (6.309 ± 0.337 kg/m^2 and 6.976 ± 0.198 kg/m^2, respectively). On the other hand, M10 and ME10 presented a behaviour similar to REF [0.03 kg/(m^2.s$^{0.5}$)], probably due to their identical permeability properties. Capillarity saturation values and higher rates of initial water absorption compared to the reference mortar were also observed in cement mortars with copper mine tailings incorporation (Onuaguluchi and Eren, 2012).

Mortars water absorption may also have been affected by the internal cure of mortar samples, since mining residues particles may had retained more water in comparison to cement. Thus, short term cement hydration could have hindered, changing porous structure (Simonsen et al., 2020).

Concerning durability issues, the presence of water accelerates the degradation of mortars, as the entry of harmful agents and salts solubilization is facilitated. High drying rates are a key factor for preventing mortars deterioration, given that the drying difficulty of a saturated material may also potentiate the growth of fungi and algae (Salomão et al., 2018).

Following water absorption by capillarity experiments, drying tests were carried out with the same mortar samples. Fig. 7 shows the drying curves of the mortars as function of time and of square root of time.

The drying rates in both phases 1 and 2 are presented in Table 4. The drying rate for phase 1, DR$_1$, was about 0.2 kg/(m^2.h) for all the tested mortars, although the lowest absolute values were observed for M25 and ME25, and the highest for M50 and ME50.

The drying rate obtained for phase 2, DR$_2$, was also higher for mortars with 50% of mining residues incorporation, confirming that the binder matrix is important for water release through the mortars pores. Mortars with mining residues generally presented an increase in the evaporation rate as a consequence of the improved diffusion and permeability.

The results showed that M10 and ME10 obtained the best performance compared to the other modified mortars. Hence, the incorporation percentage of mining residues can influence mortars' drying capacity. Additionally, during the drying process, the presence of soluble salts may promote its crystallization at the sample surface, giving rise to efflorescence or leaching inert materials into the pores causing staining (Faria et al., 2008). In the studied mortars samples, no salt crystallization was observed during drying. Concerning mortars' drying rates, the use of ED mining residues is promising in comparison to both raw mining residues and reference mortars.

Drying index was determined to understand the overall behaviour of the mortars drying (Table 4). The lower drying index was found for M50 (0.197 ± 0.000), indicating that mortars with raw mining residues can dry easier. M50 absorbed water quickly and achieved a moisture content higher than other formulations. However, these mortars dried easily and, at the end of drying, the content of residual water in the pores was lower than for the other samples.

ME10, ME25 and ME50 showed lower capacity to completely dry (corroborated by their higher drying index). These mortars required exposure to a high-intensity source of moisture for a long period to completely saturate. After saturation, the material dried out more hardly, remaining humid for a longer time and keeping a higher moisture content in pores compared to the other formulations.

The behaviour of the mortars during the drying process can be related to their water absorption, as the drying process includes transport mechanisms of water (Salomão et al., 2018). The higher the absorbed water content, the faster the transport velocity of water to the surface where evaporation occurs in the first drying phase.

3.3.5. Porosity and porosimetry of mortars

Due to capillarity absorption similar results considering mortars with the same content of raw and ED mining residues, mercury intrusion porosimetry (MIP) analysis was only performed to compare REF and M mortars. Through MIP, open porosity of mortars was reported higher in sequence M10 (21.01%) ≤ M25 (21.70%) ≤ REF (22.05%) < M50 (30.76%). M10, M25 and REF showed similar porosities, meaning that cement replacement until 25% did not promote significant changes in open porosity. The pore size distribution of REF and M mortars is presented on Fig. 8.

As presented in Fig. 8, in the range of medium capillaries (large mesopores), M25 has a prevalence. REF is dominant on the low range of large capillary pores (macropores), with peaks at 0.17 μm and 0.40 μm. A higher amount of cement in mortar composition leads to an increase of volume in this porosity range, attributed to the clinker phase (Santos et al., 2020). Other authors reported the same trend (Arizzi and Cultrone, 2013), which may also be justified by a higher water retention by the mortars with mining residues during short term hydration.

Regarding large capillary pores, above 1 μm, there is a pore size diameter gradual increase, as well as its concentration, from mortars with 0% (REF = 1.1 μm/6.8%) to 50% (M50 = 2.8 μm/9.9%) of cement replacement by raw residues. The large capillary pores distribution can be affected by the binder-aggregate interaction. When low cement contents were used, the formation of hydration products that improve hydration and carbonation reactions at early ages could be affected, influencing packing density and consequently pores distribution (Santos et al., 2020). In the range of air voids, there is a prevalence on M10 mortar.

The trend on capillary water absorption may be justified by the increased porosimetry of mortars with increased residue content in the range of 1–6 μm. The highest porosimetry of M50 corroborates the increase of capillary water absorption.

Mortars with mining residues generally presented an increase in the evaporation rate due to their higher capillary and total porosity and pore diameter, in comparison with the reference mortar. Also, low drying index values are associated to a higher large capillary porosity of mortars (Santos et al., 2020).

The low level of mortar compactness, as well as air/liquid losses, may influence strength and durability properties, although it could be advantageous in terms of freeze-thaw and salt decay (Santos et al., 2018). An increase of volume and diameter pore size of the coarse porosity promoted a decrease on mechanical performance, namely in compressive strength (Fig. 5), and an increase of water absorption by capillarity (Fig. 6) and the drying capacity (Fig. 7). This trend was also observed in cement-mortars studies performed by Santos et al. (2020).

4. Conclusions

Resource efficiency regarding the decrease of residues generation and disposal is an important step towards a cleaner production in the construction and mining industries. Cement clinker production requires

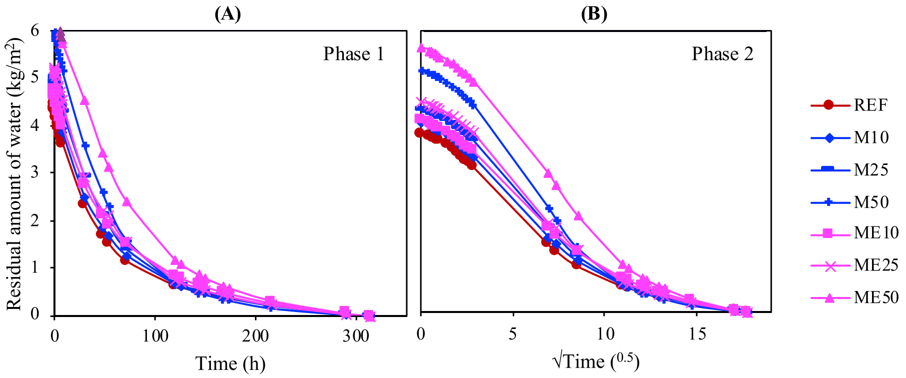

Fig. 7. Drying curves of mortars: (A) by time, showing the initial slope of drying phase 1; (B) by square root of time, showing the intermediate slope of drying phase 2 (REF - Reference mortar; M - Raw mining residues mortars; ME - Electrodialytic treated mining residues mortars).

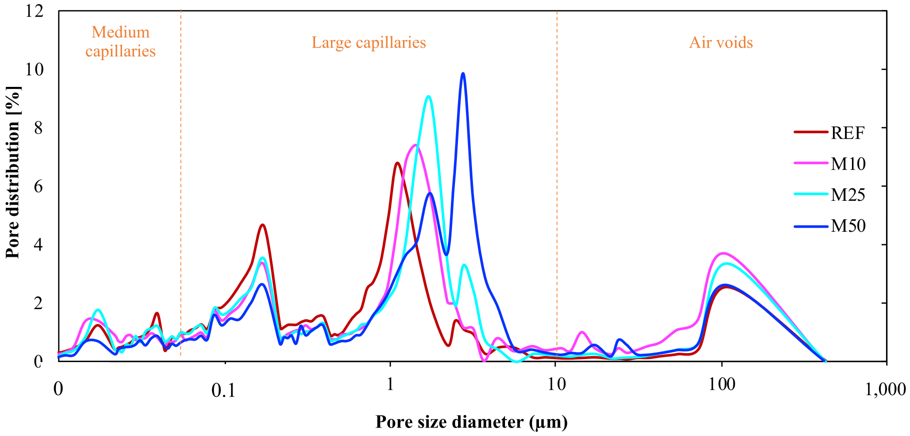

Fig. 8. Pore size distribution of REF and M mortars (REF - Reference mortar; M - Raw mining residues mortars).

firing temperatures above 1,000 °C and energy-consuming milling. When cement is partially replaced by mining residues for mortars production, environmental and economic advantages can be achieved, ensuring economic circularity and increasing the added value of mining secondary resources.

Furthermore, the recovery of critical raw materials and the removal of harmful compounds from those residues is also an important challenge. Therefore, an electrodialytic (ED) process was applied to Panasqueira mining residues to recover tungsten and remove arsenic in a first stage.

The effect of the ED treatment on mortars properties was address through the study of mortars performance, when compared to the same contents of raw mining residues and a reference cement binder mortar. Mortars were produced using 0, 10, 25 and 50% of mining residues replacing cement, maintaining the water/binder ratio (0.5) for 1:3 volumetric proportion of binder:river sand mortars, where the binder was the sum of cement and residues.

Mining residues seemed to have permeability and surface properties that imply the requirement of higher amounts of water to achieve the same consistency, as when using only cement. Thus, further studies should be conducted with different water contents to access the influence on mortars properties versus types of applications. Also, to tackle water scarcity, the reuse of secondary liquid matrices to replace water applications may also be a key factor towards a more sustainable mortar production.

Mechanical performance decreased between 11 and 30%, when 10% of mining residues were incorporated in the formulation. As expected, this decrease was more pronounced with the increasing of mining residues content replacing cement. On the other hand, the increase on mining residues incorporation corresponded to an increase on capillary absorption, justified by mortars porosimetry, and that could be controlled by higher drying rates.

All tested mortars showed mechanical and physical properties suitable for rendering, plastering, joint repointing, bedding masonry or screed uses, with improved thermal conductivity. However, to optimize mortars properties, expand the applications and increase mining residues replacement ratios, under a sustainable perspective, natural additives and admixtures (e.g. re-used oils) could also be tested.

Summing up, results showed that the ED technology could be applied as a pre-treatment for mining residues since physical and mechanical mortars' properties were not deteriorated when compared with mortars formulated with raw mining residues. The ED treatment coupled benefits from a previous removal of harmful compounds and recovery of critical raw materials, providing a more sustainable working material. Mortars produced with treated mining residues are more advantageous in terms of toxicity and, considering the overall product lifecycle, can alleviate the negative impacts associated to their production, when compared to pure cement or cement-raw residues mortars.

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.

Acknowledgments

This work has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No. 778045. The authors acknowledge the Portuguese Foundation for Science and Technology (FCT) for the support given to CENSE through the strategic project UIDB/04085/2020 and for J. Almeida PhD fellowship PD/BD/135170/2017 from the EcoCoRe Doctoral program. The authors thank Eng. Manuel Pacheco from Panasqueira mine for providing mining residues samples and Eng. Vítor Silva for assistance during mortar formulation and mechanical tests.

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Scientific journal article

A9 Cement-based mortars production applying mining residues treated with an electro-based technology and a thermal treatment: technical and economic effects

J Almeida, P Faria, AB Ribeiro & A Santos Silva

Published in Construction and Building Materials journal (2020)

This article was published in Construction and Building Materials, Vol 280, J Almeida, P Faria, AB Ribeiro & A Santos Silva, Cement-based mortars production applying mining residues treated with an electro-based technology and a thermal treatment: Technical and economic effects, 122483, Copyright Elsevier (2021).

Construction and Building Materials 280 (2021) 122483

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Cement-based mortars production applying mining residues treated with an electro-based technology and a thermal treatment: Technical and economic effects

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HIGHLIGHTS

- Mining residues were submitted to an electrodialytic process alone or coupled with a thermal treatment.
- Treated mining resides replaced cement from 10 to 50 wt% in mortars.
- Flexural strength of mortars decreased from 3 to 52%, showing potential for renders.
- Mortars' cost-efficiency with only electrodialytic treatment could be upgraded.

ARTICLE INFO

Article history:
Received 14 October 2020
Received in revised form 19 December 2020
Accepted 19 January 2021

Keywords:
Construction product
Mortar
Mining waste
Electrodialytic process
Thermal treatment
Cost efficiency

ABSTRACT

The combination of treatments may improve the extraction of toxic and critical elements from secondary resources, produce changes in materials' physico-chemical properties and improvements on the sustainability of strategies. Mining residues were treated with an electrodialytic process alone or coupled with a thermal procedure, and reused in cement-based mortars by replacing 10, 25 and 50% of the cement binder content. This study demonstrated the technical and economic feasibility of mortars produced with treated mining residues, namely in applications where flexural strength is key factor. The mechanical properties of the mortars corroborated their compatibility with bedding mortars and fired brick masonry walls.

1. Introduction

Cement industry is facing challenges on supply energy costs, greenhouse gases emissions and alternative pozzolanic materials to thermal plant fly ashes [1]. Cement production is responsible for a majority of the environmental impacts of cementitious products production, namely when compared with the impact of other components, as aggregates and supplementary cementitious materials, and procedures as mixing and transport [2]. Cost/eco-efficient constituents to cement will promote civil engineering practices to become more sustainable and move towards circular economy principles [3].

Research on mining by-products reuse in the construction sector has been conducted during the past decades [4]. Mining industries provide materials to build infrastructures and instruments of daily use [5]. However, mining activities are one of the most disturbing practices for the engaged ecosystems. Their negative impacts are caused by voluminous mining residues disposal and acid mine drainage. Acid mine drainage often results from rock minerals/ore deposits exposure to water and/or oxygen. This facilitate the mobilization of present toxic chemical species and increase their concentrations in water supplies and food chains [6].

The reuse of mining residues in cement composites encourages waste management alternatives to landfill, the balance of mining

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https://doi.org/10.1016/j.conbuildmat.2021.122483

sites and the minimization of primary raw materials needs [7]. Studies have been conducted on mining resources incorporation in cementitious composites (e.g. mortar, concrete), for binder and aggregate partial replacement in building materials. Alkali activated products [8] and pozzolanic materials [9] were successfully produced with tungsten mining residues. The durability of conventional products may be enhanced in terms of resistance to abrasion and acid attack due to a lower water absorption [10].

Mechanical and structural performance of mortars is dependent on the properties of the components involved in the formulation, as well as the need for repair interventions [11]. The effectiveness of mortars maintenance is mainly affected by compressive and flexural strengths, water vapour permeability, water absorption by capillarity action and drying [12].

To enlarge the application of mining residues within the construction sector, several strategies could enhance durability properties of composites produced with mining residues.

The electrodialytic (ED) process is defined as a treatment that promotes the removal of substances from polluted substrates, based on the application of a direct low-level current intensity [13]. This treatment demonstrated potential to improve the removal/recovery of substances from mining residues, namely arsenic (35%) and tungsten (22%) [14]. After the ED treatment, mining residues also proved their viability as cement replacer in mortars [15].

The pozzolanic properties of mining residues, alone or coupled with other treatments could be improved [16]. Amorphous silica (SiO_2) and alumina (Al_2O_3) compounds present in fine graded materials, when combined with $Ca(OH)_2$ and water generate calcium silicates and aluminates hydrates by pozzolanic reaction [17].

The reactivity of materials in cementitious composites is affected by: (1) content of amorphous SiO_2 and Al_2O_3; (2) temperature of the thermal treatment; (3) period at high temperature and cycle of heat treatment; (4) content and type of clays; (5) particle size distribution and specific surface and (6) water and $Ca(OH)_2$ availability for the chemical reactions involved [12].

Heating leads to the loss of water from the structure of the minerals and to the disruption of SiO_2 and Al_2O_3 crystal structure. For most clayish materials, high amounts of residues in the amorphous state are produced during controlled heating intervals, from 600 °C to 900 °C [18]. Particularly, tungsten mine sludge was subject to 950 °C to improve its pozzolanic activity [9].

The application of treatments to mining residues, before its reuse as construction materials, can empower circular economy of elements of interest, as critical raw materials. Also, it may leverage the sustainability of secondary resources, once it allows a prior removal of harmful compounds. This contributes to decrease the disposal of residues in mining sites and a safer reuse of mining residues in several applications (e.g. mortars and concretes). The thermal treatment may also enhance the pozzolanic reactivity of the residues, improving durability properties of construction products, although the curing conditions may influence mortars and concrete performance.

In the present work, mortars were produced by replacing cement binder contents by mining residues from Panasqueira mine, previously treated with the ED process alone or coupled with a thermal procedure. The replacement of cement was 0% for the Control, and 10, 25 and 50% (wt%) for the modified mortars. The characterisation of the mortars fresh and hardened state, after 28 days of cure, was assessed. These properties were also compared with the results from Almeida et al. [15], regarding the economic and technical feasibility of applying a complementary thermal treatment intended to increase pozzolanic reactivity. A cost-efficiency analysis of mortars produced with Panasqueira mining residues was carried out.

2. Experimental

2.1. Materials

Cement-based mortars were prepared with mining waste mud collected from the Panasqueira mine sludge circuit (Covilhã, Portugal, 40°10′11″N, 7°45′24″W). The sample was dried in a fume hood for 48 h, at 20 °C. Panasqueira mine produces 90,000 t of tungsten per year [19] and the mud waste generated is composed by particles below 2 mm [20].

Panasqueira mining residues were tested to replace CEM II/BL 32.5 N (Secil, Portugal), classified based on EN 197-1 [21]. A river siliceous sand was used as aggregate, with particles between 0.5 and 2.0 mm, similar to the CEN reference sand [22] as shown in Table S1 (in appendix A). Tap water was used as mixing water in mortar formulations.

2.2. Electrodialytic and thermal treatment of mining residues

The ED treatment was primary applied for the separation of tungsten and arsenic from Panasqueira mining residues [14]. Mining residues were treated in a two-compartment ED acryl XT reactor (RIAS A/S, Roskilde, Denmark). The diameter of the reactor was 80 mm, with 50 mm length for the electrolyte compartment and 100 mm for the sample section. An anion exchange membrane AR204SZRA, MKIII, Blank (Ionics, USA) divided the two compartments. Two electrodes (Ti/MMO Permaskand wire) with a length of 50 mm and a diameter of 3 mm (Grønvold & Karnov A/S, Denmark) were applied in each compartment. Constant current was maintained inside the reactor (50 mA) with a power supply E3612A (Hewlett Packard, Palo Alto, USA). Also, a magnetic stirrer was placed into the sample compartment. A suspension of 39 g of mining residues with 345 mL of deionized water and 5 mL of choline chloride/malonic acid (CAS 67-48-1; ≥99%, Sigma-Aldrich, Germany) was set in the cathode compartment. In the anode, 250 mL of 0.01 M $NaNO_3$ were added as anolyte. Ten experiments were operated for 4 days.

Following the ED process, a thermal treatment was performed at 950 °C [23]. The oven furnace was set in the selected temperature and the sample was placed inside for 1 h. After, the sample was cooled down for 24 h in a fume hood, at 20 °C.

2.3. Mortar formulation and samples curing

Mortars production was carried out based on EN 196-1 guidelines [22]. The volumetric proportion of binder, aggregate and water used was 1:3:0.5. This proportion ensured an adequate filling of the sand volume by the binder paste. Also, the water content was kept constant in all formulations to guarantee a proper comparison between the conventional production and the use of mining residues and its influence on workability. A Control mortar was produced only with cement. The remain mortars were produced replacing 10, 25 and 50% of the cement weight content by mining residues submitted exclusively to the ED treatment or coupled with the thermal procedure. Table 1 presents the mortars' code, materials loose bulk density, mass proportion and contents of materials. Loose bulk densities of the materials used for mortars formulation were determined by the quotient of the weight of a recipient with known volume, filled with each uncompacted material (volume in kg/m^3).

Mortars were produced in triplicate in 40 mm × 40 mm × 160 mm metallic moulds. For each formulation, circular samples with 90 mm diameter and 20 mm width were also produced. Samples were kept inside polyethylene closed bags at 20 °C and demoulding

Table 1
Materials' loose bulk density, percentual weight and contents of binder, aggregate and water, and mass proportions of mortars formulation.

Mortar code	Binder				Aggregate		Water		Mass proportion	
	CEM II/BL 32.5 N ($1000\ kg/m^3$)		Mining residues – Electrodialytic ($1003\ kg/m^3$) & thermal treatment ($970\ kg/m^3$)		Sand ($1540\ kg/m^3$)		Tap water ($1000\ kg/m^3$)		Binder:sand:water	Cement:residue:sand
	Wt (%)	Wt (g)	Wt (%)	Wt (g)	Wt (%)	Wt (g)	Wt (%)	Wt (g)		
Control	100	432	–	–	100	2000	100	333.3	1:4.63:0.77	1:0:4.63
E10	90	389	10	42					1:4.64:0.77	1:0.11:5.14
E25	75	324	25	105					1:4.66:0.78	1:0.32:6.17
E50	50	216	50	210					1:4.69:0.78	1:0.97:9.27
ET10	90	389	10	44					1:4.62:0.77	1:0.11:5.15
ET25	75	324	25	111					1:4.60:0.77	1:0.34:6.17
ET50	50	216	50	222					1:4.57:0.76	1:1.03:9.26

Notation: Control - Reference mortar; E –mortars with electrodialytic treated mining residues; ET – mortars with electrodialytic and thermal treated mining residues. E10, E25 and E50 mortars are also analysed in [15] in comparison to mortars using the raw mining residue (without any treatment).

was carried out after 48 h (based on EN 196-1 [22]), to guarantee setting before the curing conditions. Mortars were cured horizontally in a tap water bath for the next 26 consecutive days at 20 °C. The samples were then dried at 60 °C until constant weight.

2.4. Mortars' testing campaign

2.4.1. Fresh state

Flow consistency tests (EN 1015-3 [24]) and wet bulk density (EN 1015-6 [25]) were performed. To measure the slump, a flow table test was used while for the bulk density a mould (volume known) was weighted and filled with the mortar specimen.

2.4.2. Thermal conductivity

Circular samples were stabilized in a climatic chamber for 24 h (20 °C, 75% RH). The determinations were carried out inside the chamber with an Isomet 2104 Heat Transfer Analyzer (Applied Precision, Slovakia) equipped with a contact probe API 210412 (Ø = 60 mm) and operation range of 0.04–0.3 W/(m.K).

2.4.3. Dry bulk density and dynamic modulus of elasticity

Based on EN 1015-10/A1 [26], dry bulk density was calculated by the quotient of the mass (digital scale precision = 0.001 g) by the volume (digital caliper precision = 0.01 mm) of the prismatic samples. Using a Zeus Resonance Meter ZMR 001 equipment, the dynamic modulus of elasticity (DME) was determined based on EN 14146 [27]. Considering the mass and volume of each sample, the response to an induced vibration signal along samples was determined. Four nondestructive tests were performed, resulting in twelve tests per sample.

2.4.4. Flexural and compressive strength

A Zwick/Rowell Z050 equipment was used to determine flexural and compressive strengths according to EN 1015-11 [28]. A three-point bending test was carried out with the prismatic samples, with two steel supporting rollers separated in 100 mm regarding flexural strength determination. The loading was progressively applied at a constant rate of 50 ± 10 N/s. Compressive strength tests were performed with one half of each sample resulting from the previous flexure tests. The loading was applied at a constant ratio of 2400 ± 200 N/s.

2.4.5. Capillarity absorption and drying

Capillarity absorption (EN 1015-18 [29]) and drying (EN 16322 [30]) tests were conducted at 20 °C and 65% RH. The assays were performed on cubic specimens (40 mm) cut from one half of each sample resulting from the flexure tests. Cubes lateral faces were waterproofed with Sikagard 570 W (Sika, Portugal). Specimens were placed on a plastic grid, into a plastic box, where the cut surface was maintained in contact with water (5 mm). The capillarity absorption curve was determined by weighing the samples until an asymptotic value was achieved, in mass increase per area in contact with water by square root of time. Both capillarity absorption coefficient and asymptotic values were calculated.

The drying capacity was tested immediately after capillarity tests inverting and moving the cubes to a waterproof surface and weighing the samples until constant weight. From mortars' drying curves (mass decrease per drying area), rates of first (by time) and second (by square root of time) drying phases were calculated by the negative slope of the initial and intermediate linear segment, respectively. The drying index (DI) was determined based on EN 16322 [30].

2.4.6. Mineralogical characterisation

The mineralogical characterisation of mortars was carried out through an X-ray microdiffractometer (BRUKER Discovery, Germany). The global and fine fractions of samples were analysed. Test specimens were prepared from the samples used for compression test. For the global fraction analysis 4 g of mortar were milled and sieved at 0.106 mm, while for the fine fraction analysis 2 g of the binder paste were milled and sieved also at 0.106 mm. The pastes were obtained by previously removing sand particles of each mortar.

Thermogravimetric and differential thermal analysis (TGA/DTA) of global fractions were performed in a Setaram TGA92 equipment in argon atmosphere (3 L/h) and with platinum–rhodium crucible of 50 μL capacity. The heating rate was 10 °C/min, from 20 °C to 1000 °C.

2.4.7. Pore size distribution

For pore size distribution, a mercury porosimeter Micromeritics Autopore II was used. Samples with around 1.7 cm^3 were collected from mortars and stabilized in an oven for 24 h at 40 °C.

2.4.8. Cost-efficiency analysis

The cost-efficiency analysis was performed using a simplified methodology. Cost effectiveness factor (CEF) of mortars was determined applying Eq. (1) [31]:

$$CEF_{f/c} = \frac{F_{f/c}}{C} \times 100 \quad (1)$$

where $CEF_{f/c}$ is the ratio of the flexural (F_f) or compressive strength (F_c) of mortars to the total material cost per m^3 (C). Local prices of construction materials were used to determine cement cost: 0.12 €/

kg CEM II/BL 32.5 N [32]. Sand and water costs were not considered since they are a constant in all mortars. The costs of mining residues resulting from the ED treatment were considered null, once a residue from the mining industry is being reused after a secondary recovery of critical raw materials and removal of harmful elements. When mining residues are submitted to a thermal process, there is an increased cost related to the energy requirements. In this sense, an extra cost of 0.05 €/kg was assumed for ET samples.

3. Results and discussion

3.1. Fresh state

Both flow table consistency and wet bulk density are presented on Fig. 1. Wet bulk density of E mortars showed higher values when compared to the Control, increasing as the content of mining residues increased. On the other hand, ET mortars demonstrated the inverse trend, since as the content of mining residues increased, the wet bulk density decreased.

Loose bulk density of materials and filler properties may affect mortars wet bulk density [33]. The loose bulk density of the uncompacted materials, presented in Table 1, demonstrated that mining residues treated with only ED are slightly denser (1003 kg/m^3) than cement (1000 kg/m^3), corroborating the higher wet bulk density of mortars prepared with ED mining residues. On the other hand, mining residues treated with both ED and thermal treatment showed a lower bulk density (970 kg/m^3) than cement, promoting a decrease trend on mortars wet bulk density when higher contents of treated mining residues were introduced in the formulations.

Both E and ET mortars reduced their workability, proportionally to the residue incorporation increase. Mining residues particles may absorb more water because of their permeability and surface properties. Due to cement hydration reactions, ET mortars may require more water in sequence ET50 > ET25 > ET10 to achieve the same consistency of Control. Mining residues crystalline phases and inert characteristics may potentiate the hindering of chemical bonding between hydration products [34].

Generally, the higher incorporation of mining residues reduced mortars plasticity compared to Control, which can be tackled with the addition of a plasticizer as admixture.

3.2. Mineralogical properties

The mineralogical composition obtained by XRD of mortars is presented in Table 2. Both global - G - and fine - F (binder enriched) - fraction analysis was conducted, and proportions of the main minerals detected were reported.

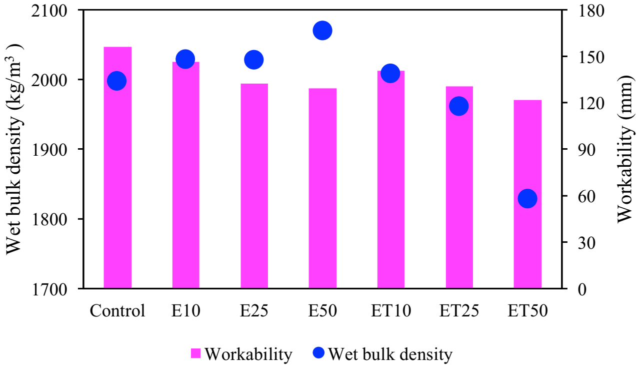

Fig. 1. Wet bulk density and workability of mortars.

The hardened cementitious paste consists in: (1) non-hydrated cement particles, as anhydrous clinker grains; (2) hydrated products (e.g. hydrated calcium silicates and calcium aluminates, hydrated sulfoaluminates and calcium hydroxide); and (3) air voids and capillary pores, that are unfilled spaces between the cement grains [35].

The presence of components as quartz, feldspar, mica (e.g. muscovite) and clay minerals were detected in an average of medium/high proportion. Regarding the effect of mineralogy, higher contents of quartz are effective in adhesive strength features. The silica content of the aggregate is also important on tensile bond strength [36]. Clay minerals are common in aggregates, acting as pore lining rims and pore-filling materials [37].

Calcite was detected in all formulations at similar amounts (low/medium proportion). Calcite comes from the carbonation of calcium hydroxide and from the cement used. In CEM II/BL 32.5 N, the calcite content can vary between 21 and 35 wt% [21]. Calcite has filler properties and affects the distribution of alumina and sulfate phases, changing the mineralogy of hydrated cement pastes [38]. The calcite contents in the samples were sufficient to form hemicarbonate [38], detected in E10, ET10, E25 and ET25 mortars at low/trace amounts.

Amorphous silica and silicates are key factors for pozzolanic reactivity and durability properties of mining residues, in presence of Ca(OH)$_2$ and water. The use of pozzolans may minimize mortars cost and embodied energy. The pozzolanic contribution can be categorized in physical/filler effect attributed by fine particles and in chemical/pozzolanic effect due to the pozzolanic reaction [39].

The pozzolanic reactivity of mining residues treated under different conditions was assessed through modified Chapelle test [40]. The total amount of fixed Ca(OH)$_2$ by siliceous or aluminosilicates amorphous substances from 1 g of raw mining residues was reported as 7.9 mg, from mining residues treated with only ED was 71.4 mg, and coupled with a thermal treatment was 547.6 mg, representing the last high pozzolanic potential [16]. Another study concerning the reuse of solid mining waste in cement-bricks showed that mining waste can achieved good mechanical performance and be considered a pozzolanic material [41].

Furthermore, minor crystalline compounds were identified, as amphibole, monosulfoaluminate (AFm) and ettringite AFt). Amphibole is an inosilicate mineral that may contains iron (Fe) or magnesium (Mg). Fe was detected in Panasqueira mining residues (Table S2 in appendix A), which may justify the amphibole detection in E10, E25, E50, ET10 and ET25 formulations.

AFm and AFt result from the hydration reaction of calcium aluminates from cement clinker with gypsum. AFm is crucial in anion binding in cement, exchanging its original interlayer ions (SO_4^{2-} and OH^-) with chlorides [42]. AFt can slowly dissolve and reform available voids or microcracks and can control stiffening properties. However, AFt may be formed after hardening in the presence of sulfate sources, which may cause materials deterioration due to its expansive behavior. This can lead to cracking of the hardened mortars and concrete, loss of dynamic modulus and, in reinforced concrete, debonding of reinforcing steel bars [43]. AFt was detected in trace proportions/low proportion in all samples, except in the global fraction of the Control mortar. AFm was only detected at small amounts in Control and E10 mortars, which can be justified by the differences in Al_2O_3/SO_3 ratio on these samples.

From TGA/DTA curves (Fig. S1 in appendix A), the mass losses at specific temperature ranges were assessed, as well as Ca(OH)$_2$ and $CaCO_3$ contents (Table 3).

The mass loss registered between 20 and 230 °C occurs due to the loss of adsorbed water and the hydrated compounds decomposition (e.g. ettringite). Regarding the range of 230–390 °C, mass losses are mainly from hydrated calcium silicate and calcium aluminate decomposition. The mass loss at 390–500 °C is due to cal-

Table 2
X-ray diffraction analysis of mortars.

Fraction	Experiment													
	Control		E10		E25		E50		ET10		ET25		ET50	
	G	F	G	F	G	F	G	F	G	F	G	F	G	F
Quartz	+++	+/++	+++	+/++	+++	++	+++	+/++	+++	+	+++	+/++	+++	++
Feldspar	++	+/++	++	+	+/++	+/++	+/++	+	++	+	++	+/++	+/++	+/++
Muscovite	+	tc/+	+	+	+/++	+/++	+/++	++/+++	+	+	+/++	+/++	+	+/++
Chlorite	–	–	?	?	tc	tc/+	tc	tc/+	?	?	?	?	?	?
Amphibole	tc	tc	tc	tc	?	Tc	tc	tc	?/tc	?/tc	tc	?	?	?
Portlandite	+/++	++	++	++/+++	++/+++	+++	+	+	++	++/+++	++	++/+++	+	++
Calcite	+/++	++	+/++	++	+/++	++	+/++	+/++	+/++	++	+/++	++	+/++	+/++
Hydrocalumite	–	–	–	–	–	Tc	tc	tc/+	–	–	–	–	tc	tc/+
Hemicarbonate	–	–	tc	tc	tc/+	+	–	tc	Tc	tc/+	tc	tc/+	–	–
Monosulfoaluminate (AFm)	tc	tc/+	?	tc	–	?	–	–	–	–	–	–	–	–
Ettringite (AFt)	–	tc	tc	tc/+	tc	tc/+	–	tc	Tc	tc/+	tc	tc/+	tc	tc/+
Anhydrous clinker portland silicates	tc	tc/+	tc	tc	tc	Tc	tc	tc	Tc	tc	tc	tc	?/tc	?/tc

Notation: G, Global fraction; F, Fine fraction; +, low proportion; ++, medium proportion; +++, high proportion; tc, traces; ?, doubts on the presence; –, not detected.

Table 3
Mass losses and calcium hydroxide and calcium carbonate contents from TGA/DTA mortars' tests.

		Mass loss per temperature range (%)	Mass loss of ignition (%)			$Ca(OH)_2$ (%)	$CaCO_3$ (%)
Mortar	20–230 °C	230–390 °C	390–500 °C	500–900 °C	20–1000 °C		
Control	2.45	0.84	1.03	5.28	9.67	4.23	12.01
E10	2.58	0.77	0.96	4.56	9.00	3.95	10.37
E25	2.27	0.78	0.93	4.78	8.90	3.82	10.87
E50	1.26	0.47	0.44	4.31	6.63	1.81	9.80
ET10	3.64	0.87	1.03	4.19	9.82	4.22	9.53
ET25	2.66	0.72	0.86	3.49	7.76	3.54	7.94
ET50	1.56	0.43	0.32	3.37	5.71	1.32	7.66

cium hydroxide decomposition. The losses reported in 500–900 °C interval are essentially caused by carbon dioxide decomposition [44]. Regarding all studied mortars, the higher mass loss occurred between 500 and 900 °C, indicating the presence of carbonates ($CaCO_3$) and the calcite detected in XRD analysis (Table 2).

Control showed the higher content of $CaCO_3$ (approximately 12%), and, as mining residues incorporation increased, $CaCO_3$ decreased proportionally in both E and ET cases. The same trend was verified for $Ca(OH)_2$ (Table 3). This may be justified by the pozzolanic reaction between portlandite from mortars with thermal treated and/or ED residues and their pozzolanic content. These mortars have lower portlandite contents due to the lower amount of cement, in comparison to Control. In addition, during the thermal treatment, different hydration levels and, consequentially, carbonatation, may had contributed to slightly reduce the portlandite detected in ET, when compared to E mortars.

The mass losses from 20 to 500 °C were higher for ET10 (5.54%) > Control (4.32%) > E10 (4.31%) > ET25 (4.24%) > E25 (3.98%) > ET50 (2.31%) > E50 (2.17%), which may be caused by the presence of lower contents of hydrated compounds in sequence.

3.3. Physico-mechanical analysis

The loose bulk density of the materials used in mortars is presented in Table 1. Mining residues loose bulk density decreased from 1003 kg/m^3 (ED treatment only) to 970 kg/m^3 (ED and thermal treatment). This may be justified by the extraction of inorganic compounds during the ED process and minerals transformation and/or water losses during the thermal treatment. The replacement of the cement binder (1000 kg/m^3) by treated mining residues (970 kg/m^3) corresponds to almost the same weight. Thus, a similar filler effect is expected.

Hardened mortar results for dry bulk density, thermal conductivity, compressive and flexural strength and dynamic modulus of elasticity after 28 days of cure are presented in Table 4.

When treated mining residues were introduced, dry bulk density slightly decreased on E10 (1971.8 kg/m^3) and ET25 (1949.1 kg/m^3), comparing to Control (1975.6 kg/m^3). This could be justified by the loose bulk density differences between the materials used, namely residues and cement (Table 1).

The lowest thermal conductivity was 1.2 W/(m.K) for E25 and ET50 samples, meaning that treated mining residues incorporation can improve the properties of mortars. The morphology of the matrix could be more relevant for thermal conductivity, comparing with chemical composition of the components. In addition, the pore system promoted by mortars' aggregates can have more impact in thermal conductivity than properties as total porosity and specific gravity [45].

The thermal conductivity of soil–cement bricks using mining waste also demonstrated a direct relation on the construction product density, once the increase in brick density provided a material with lower heat dissipation characteristics [41].

Mortars with low thermal conductivities have advantages in thermal comfort [46], although it depends on the mortar application. For renders and plasters applied with thicknesses of around 2 cm the differences are not significant. Nevertheless, for bedding mortars, namely when joints are thick, these differentiations may cause important changes.

The results obtained for flexural and compressive strengths, as well as dynamic modulus elasticity (DME), are also presented in Table 4. Mechanical properties of mortars decreased proportionally when cement was replaced by mining residues. As expected, besides both ED and thermal treatment, mining residues are still lower strength materials compared to cement.

The DME increased 19% in ET10, when compared to Control. However, when higher contents of mining residues treated with

Table 4
Hardened mortars characterisation: thermal conductivity, bulk density, dynamic modulus of elasticity, compressive and flexural strength.

Experiment	Thermal conductivity [W/(m.K)]	Bulk density (kg/m^3)	Dynamic modulus of elasticity (MPa)	Compressive strength (MPa)	Flexural strength (MPa)
Control	1.5	1975.56 ± 16.78	7208.66 ± 40.72	18.23 ± 0.76	4.68 ± 0.08
E10	1.4	1971.83 ± 12.35	4147.33 ± 78.78	11.91 ± 1.87	4.18 ± 0.34
E25	1.2	1997.86 ± 28.95	3513.00 ± 186.54	7.53 ± 1.46	3.63 ± 0.30
E50	1.3	2007.24 ± 28.33	1508.67 ± 33.50	4.66 ± 0.52	1.34 ± 0.81
ET10	1.7	2003.56 ± 30.82	8948.33 ± 38.50	10.29 ± 1.76	4.52 ± 0.25
ET25	1.7	1949.07 ± 5.19	3495.67 ± 229.24	5.82 ± 1.02	3.94 ± 0.13
ET50	1.2	1866.68 ± 40.90	1260.33 ± 121.72	3.85 ± 0.27	2.25 ± 0.01

both ED and thermal treatment were incorporated in mortars the DME decreased from around 7209 MPa (Control) to 3496 MPa (ET25) and 1260 MPa (ET50). In E mortars, DME decreased sequentially: E10 (4147 MPa) > E25 (3513 MPa) > E50 (1509 MPa). Low DME values mean that mortars are more able to absorb deformations from the substrate, which may decrease vulnerability to crack, particularly important on rendering and plastering mortars [47].

The decrease on flexural and compressive strengths is proportional to the increase of mining residues content (Table 4). This trend, due to the lower proportion of cement, may have promoted a retarding effect on cement hydration for both E and ET formulations.

Comparing to Control, flexural performance decreased 11, 22 and 71% in E10, E25 and E50, respectively. Lower flexural decreases were observed in ET mortars, where 3, 16 and 52% decays were registered for ET10, ET25 and ET50, respectively. Also, for the same formulations, a decrease of 35–74% (E) and 44–79% (ET) on compressive strength was verified, showing that the loss in compression was more accentuated. This decrease can be related to the low pozzolanic activity of mining residues.

Calcined clays were studied as a supplementary cementitious material [48]. The flexural strength could be improved with calcined materials, even at a high cement substitution. However, the decrease in compressive strength was also verified, probably due to the dilution effect. The activity of calcined materials depends on the content and composition of the reactive silica, fineness and calcination. Inadequate grinding may reduce mechanical properties although a progress on anti-cracking properties of plastering mortars could be achieved [48]. The introduction of magnesia, for instance, as an additive in construction products may lead to a greater compressive strength and minimize the chances of micro-crack occurrence due to a delayed hydration [49].

DME, flexural and compressive strengths are correlated in 67% (DME vs. Fstr), 57% (Cstr vs. Fstr) and 55% (DME vs. Cstr). All these properties decreased when cement was replaced by mining residues in the formulations. However, some properties assume more relevance for certain mortars application. For renders and plasters, resistance to crack and capacity of deformability are important characteristics. The DME/flexural strength ratio is an indicator, where lower values mean more appropriate mechanical performance. Thus, mortars showed better behaviors in sequence: ET50 > ET25 > E25 > E10 > E50 > Control > ET10.

Based on EN 998-1 [50] and EN 998-2 [51], E and ET mortars can be classified considering compressive strength data at 28 days and their application (Table S3 in appendix A).

For rendering or plastering, E and ET mortars are classified as CS III or CS IV (the latter as the Control). Regarding masonry bedding mortars, E and ET formulations are categorized as M5 and M10, while the Control classification is M15. Nevertheless, several applications of mortars require relatively low compressive strength, meaning that upper classes are not often needed. Therefore, the mortars studied showed mechanical properties compatible with conventional concrete and contemporary fired brick masonry walls. For traditional vernacular walls applications, E and ET mortars are still exceedingly stiff. Other studies corroborated the suitability of using mining waste to partially replace cement in concrete (up to 10%) and reported the considerable decrease in compressive resistance [52].

3.4. Capillary absorption and drying capacity

The average capillarity curves of mortars are presented in Fig. 2. Through this data is possible to address the initial absorption rate and the total water absorbed from samples by the determination of the capillary coefficient and the asymptotic value, respectively.

Considering capillary absorption of mortars, the capillary curves showed that E10, E25, E50, ET25 and ET50 behaved negatively in comparison to Control. In Table 5 is possible to observe an increase in the initial rate (capillarity coefficient) and in the total absorbed water (capillarity saturation value), in a proportional way to the residue increase. E50 [0.067 kg/(m^2.s$^{0.5}$)] and ET50 [0.059 kg/(m^2.s$^{0.5}$)] represented the worst cases of capillarity coefficient, once these formulations absorbed water at a faster ratio and in higher contents (E50 = 6.976 kg/m^2 and ET50 = 6.626 kg/m^2). ET10 showed an improvement in the initial absorption rate in relation to Control, where a similar asymptotic value (approximately 5.3 kg/m^2) was achieved at a slower rate [Control = 0.033 kg/(m^2.s$^{0.5}$); ET10 = 0.028 kg/(m^2.s$^{0.5}$)]. This behavior may affect abrasion and acid attack resistance and improve mortars durability [10]. The outcomes of another study suggest that molybdenum mine tailings up to 10% can be used to produce cement mortar with improved durability levels [53].

The samples internal cure may have influenced water absorption by mortars, once mining residues particles may had retained more water compared to conventional cement [54]. The short term cement hydration may have been hindered, changing the porous

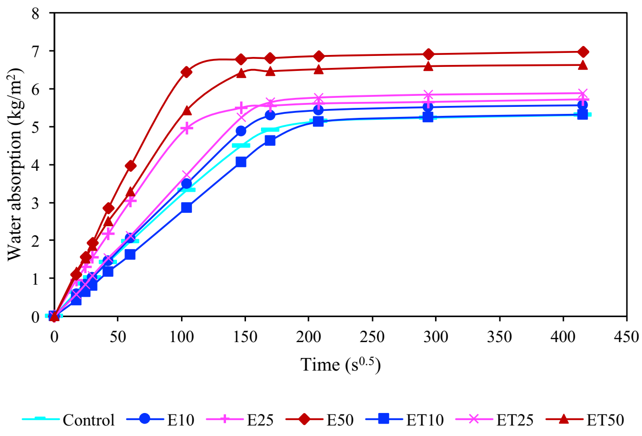

Fig. 2. Capillarity absorption curves of mortars.

Table 5
Capillarity absorption coefficient, capillarity saturation value, drying rates of phases 1 and 2 and drying index after 314 h, of mortars.

Mortar	Cac [kg/(m^2.s$^{0.5}$)]	Cs (kg/m^2)	DR$_1$ [kg/(m^2.h)]	DR$_2$ [kg/(m^2.h$^{0.5}$)]	Drying index
Control	0.033 ± 0.001	5.305 ± 0.593	0.204 ± 0.003	0.456 ± 0.002	0.216 ± 0.009
E10	0.034 ± 0.000	5.564 ± 0.041	0.206 ± 0.011	0.444 ± 0.006	0.257 ± 0.000
E25	0.051 ± 0.000	5.717 ± 0.742	0.200 ± 0.019	0.507 ± 0.016	0.228 ± 0.000
E50	0.067 ± 0.005	6.976 ± 0.198	0.221 ± 0.007	0.539 ± 0.004	0.284 ± 0.001
ET10	0.028 ± 0.006	5.320 ± 0.129	0.200 ± 0.012	0.405 ± 0.005	0.275 ± 0.001
ET25	0.036 ± 0.003	5.882 ± 0.106	0.213 ± 0.010	0.390 ± 0.006	0.323 ± 0.001
ET50	0.059 ± 0.006	6.626 ± 0.271	0.206 ± 0.008	0.474 ± 0.003	0.350 ± 0.011

Notation: Cac – Capillarity absorption coefficient; Cs -Capillarity saturation value; DR$_1$-Drying rate (phase 1); DR$_2$- Drying rate (phase 2).

structure [34]. Both mortars microstructure and strength can be affected by mining residues incorporation because of the lower structuring of a stiff hydrated skeleton that could resist to an internal pressure promoted by capillary stress from self-desiccation [55].

The presence of water can damage mortars due to salts solubilization or harmful substances entry. A high drying capacity improves mortars durability and avoid fungi/algae growth [56]. Through the drying curves of mortars (Fig. 3) as function of time (drying phase 1 by a linear segment) and square root of time (drying phase 2 by a linear segment), drying rates were determined for phases 1 (DR$_1$) and 2 (DR$_2$), as shown in Table 5. The moisture movement during drying is often described by a diffusion process that depends on the moisture content. The moisture diffusivity is related to water in phase 1 and to vapor in phase 2 [57].

The DR$_1$ was approximately 0.2 kg/(m^2.h) for all tested mortars, although the lowest absolute value was observed for E25 and ET10, and the highest for E50. Regarding DR$_{2,}$ the highest rate was observed for mortars with 50% of mining residues incorporation, meaning an increase in the evaporation rate due to improved diffusion and permeability properties.

The presence of soluble salts during the drying process may potentiate their crystallization in the sample surface causing staining [58]. In the samples studied, no salts crystallization was observed during drying. Thus, treated mining residues did not affect mortars drying phases.

The drying index of mortars was also determined (Table 5). The lower drying index was found for Control (0.216), followed by E25 (0.228), E10 (0.257), ET10 (0.275), E50 (0.284), ET25 (0.323) and ET50 (0.350). Mortars with mining residues demonstrated a harder capacity to completely dry, proportionally to the residue content in ET formulations.

During the drying process, the behaviour of mortars can be related to their water absorption, since transport mechanisms of water occur [56]. A faster transport velocity of water promotes a higher water absorption on the evaporation during the first drying phase.

3.5. Pore size distribution

The analysis of the porosimetry was carried out to compare Control, E and ET mortars. The open porosity was lower in sequence E50 (25.3%) > E10 (23.9%) > ET50 (23.7%) > ET25 (23.4%) > E25 (22.2%) > Control (22.0%) > ET10 (20.3%). Nevertheless, the samples revealed similar porosities, meaning that cement replacement by mining residues did not affected expressively the open porosity of mortars. The pore size distribution of Control, E and ET mortars is presented on Fig. 4.

Considering the range of large mesopores (medium capillaries), ET25 and Control mortars are dominant. For pore sizes lower than 0.05 μm, the thermal treatment seems to induce differences in porosimetry, particularly in ET10 and ET25 mortars, that are closer to the Control sample porosimetry. On macropores (large capillary pores), Control has a prevalence until approximately 2 μm. This could be justified by the clinker phase once the Control mortar has the highest content of cement [59]. The water retention by E and ET mortars during short term hydration may have been higher than cement [60].

After 2 μm of pore size diameter, different trends were observed between E and ET formulations. In E mortars, pore size distribution behaved similarly and independently of the proportion of mining residues applied, while in ET mortars the distribution oscillated as function of the mining residues proportion. The peaks observed were: Control = 1.09 μm/6.78%; E10 = 4.47 μm/6.65%; E25 = 4.51 μm/6.62%; E50 = 4.46 μm/6.05%; ET10 = 1.45 μm/3.50%; ET25 = 1.76 μm /6.12% and ET50 = 4.48 μm/6.41%. Hydrated elements formation, associated to hydration and carbonation reactions at early stages, could have been affected by lower cement contents [59].

Regarding the air voids interval, while for E mortars the influence of the cement replacement percentage is insignificant in porosimetry, for ET mortars it differs with the cement replacement ratio. ET50 mortar remains almost unchanged whereas the E25 case showed porosimetry similar to the Control mortar.

The trend observed for capillary water absorption may be related to the mortars porosimetry increase with the residue

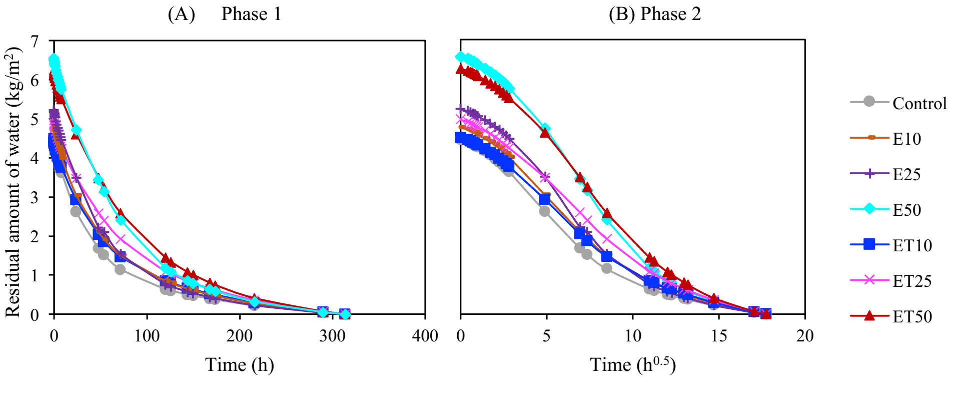

Fig. 3. Drying curves of mortars: (A) by time, showing the initial slope of drying phase 1; (B) by square root of time, showing the intermediate slope of drying phase 2.

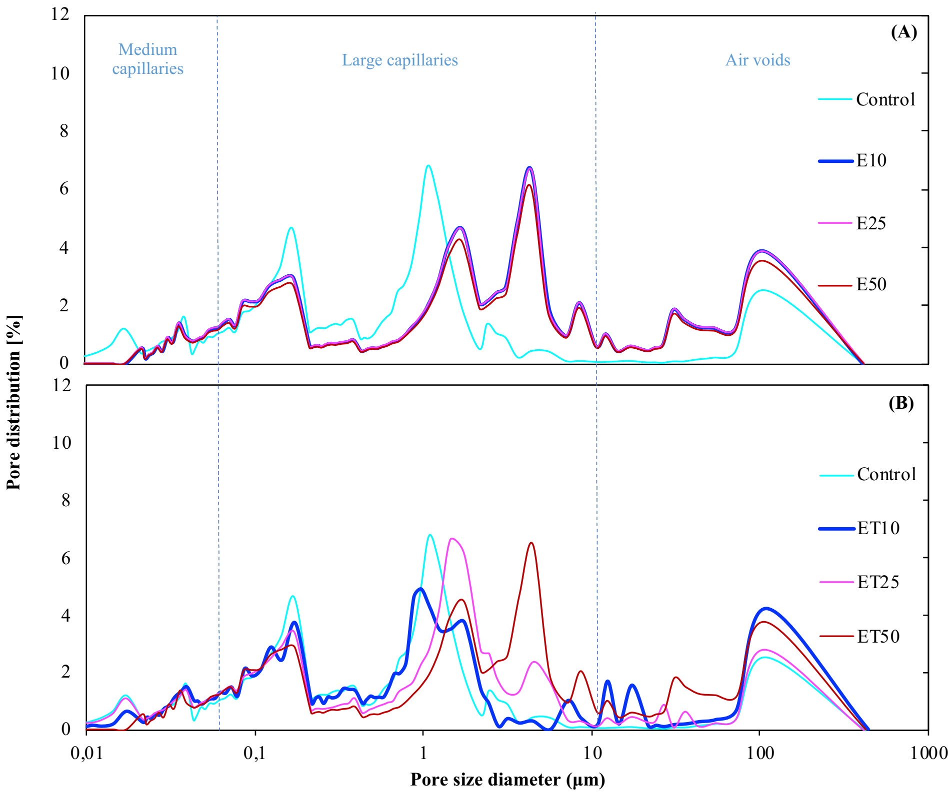

Fig. 4. Pore size distribution of: (A) Control and E mortars; (B) Control and ET mortars.

content increase, considering the interval 1–6 μm. The high porosimetry of E50 and ET50 justified the high capillary water absorption observed.

Samples with mining residues showed a rising trend in the evaporation rate. Their higher capillary, total porosity and pore diameter, in comparison to Control, justify this increase. Additionally, low drying index are related to a high large capillary porosity of samples [59].

Strength and durability may be influenced by samples compactness and air/liquid losses [61]. Generally, the increase in volume and diameter pore size of the coarse porosity promoted a decrease on mechanical performance, more pronounced in compressive strength case (Table 4).

3.6. Cost-efficiency analysis

Fig. 5 presents the cost effectiveness factor (CEF) of the mortars determined based on Eq. (1), considering flexural and compressive strength data (Table 4).

Although including a residue in the formulation, the cost assumed for ET mortars is only lower than Control for ET50 (Fig. 5 notation). That occurred due to the energy cost determined to prepare ET mining residues. The results could differ depending on the efficiency of the thermal treatment, emphasizing the influence that residues treatment may have in the overall analysis.

For compressive strength ratios, the Control mortar presented the highest CEF$_c$ (15.2 ± 0.6). The increase in the replacement level of mining residues resulted in a decrease of the cost effectiveness factor for E and ET mortars. Thus, for applications that need to comply high compressive resistances, e.g. masonry bedding mortars with high strength masonry units, Control is the most feasible option, followed by E10 (11.0 ± 1.7), E25 (8.4 ± 1.6), E50 (7.8 ± 0.9), ET10 (6.7 ± 1.2), ET25 (4.6 ± 0.8) and ET50 (4.5 ± 0.3). However, lower strength products are frequently used for bedding mortars and conventional masonry units.

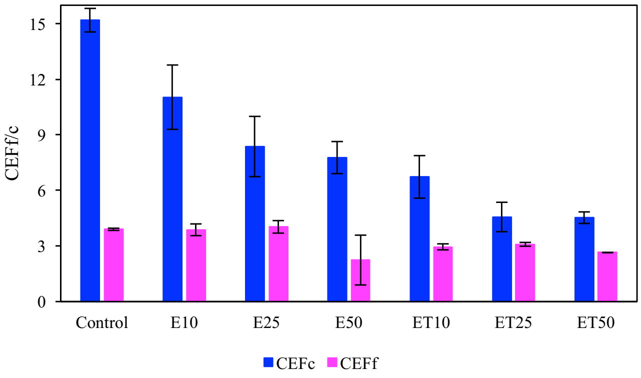

Fig. 5. Cost effectiveness factor (CEF) of cement-based mortars incorporating mining residues as cement replacement. Notation: Cost (€/m^3): Control – 120; E10 – 108; E25 – 90 ; E50 – 60 ; ET10 – 153 ; ET25 – 128 and ET50 – 85. CEFc-Cost effectiveness factor determined with compressive strength data; CEFf-Cost effectiveness factor determined with flexural strength data.

Considering applications where flexural strength assumes more relevance, e.g. plastering and rendering mortars, E25 (4.0 ± 0.4) presented the highest CEF$_f$, in comparison to Control (3.9 ± 0.1). The increase in the replacement level of mining residues resulted in an increase in the cost effectiveness factor of mortars, although the flexural strength decrease verified in E50 (Table 4) did not corroborate this trend. Most probably, an optimal cement replacement percentage between 25 and 50% would optimize flexural strength.

In an environmental perspective, the mechanical performance of ET mortars was not considerably improved when compared to E formulations, except for ET50 case. Although a decrease in compressive strength was registered for ET50 in comparison to E50 mortar (from 4.7 to 3.9 kg/mm^2), a substantial increase on flexural strength was obtained (from 1.3 to 2.2 kg/mm^2). The high dispersion registered by ET50 mortar and the superior energetic needs, that will promote equally higher CO_2 emissions release and cost, may not reward the thermal treatment. Furthers tests should be conducted to determine the technical and environmental feasibility at an industrial scale, for both ED and thermal treatments.

4. Conclusions

The reuse of mining residues in cementitious mortars contributes to reduce impacts in quarries, from where the calcareous marl is extracted, to minimize CO_2 impacts from cement manufacturing and to sustain a balanced ecosystem at mining sites. In this work, mining residues from Panasqueira mine were treated with an electrodialytic (ED) technology, aiming the removal and recovery of elements, alone or followed by a thermal treatment to enhance pozzolanic reactivity and durability. The effect of incorporating treated mining residues on technical characteristics of mortars, by replacing cement in 10, 25 and 50% (wt%), was addressed:

- The mineralogical composition of mortars produced with both thermal and/or ED treated mining residues validated the compatibility of this material with cement mortars and the removal of elements.
- As expected, mining residues mortars are lower strength products compared to cement mortars. The increase in the replacement level of cement by mining residues treated with ED and thermal processes decreased both flexural (3 to 52%) and compressive strength (44 to 79%), comparing to the Control mortar.
- Once ED and thermally treated mining residues have demonstrated pozzolanic reactivity, the water curing optimization may be needed to enhance the pozzolanic reaction in mortars. In future studies, the influence of a humid curing should be addressed.
- Since a large majority of mortars applications require relatively low compressive strength, the studied mortars showed properties compatible with conventional concrete and contemporary fired brick masonry walls, and mining residues feasibility as cement replacement.
- An improvement in the initial absorption rate was only achieved when 10% of mining residues ED and thermally treated were incorporated in mortars, comparing to the reference, once a similar asymptotic value was obtained at a slower rate.
- The cost effectiveness analysis also validated the feasibility of treated mining residues reuse in cementitious mortars, namely considering applications where flexural strength is key factor (e.g. renders and plasters). However, further studies should be conducted to assess the technical and environmental feasibility of using ED mortars at an industrial scale and to quantify the optimized impacts of the thermal treatment.

CRediT authorship contribution statement

J. Almeida: Conceptualization, Methodology, Writing - original draft, Visualization, Writing - review & editing, Software, Investigation. **P. Faria:** Conceptualization, Validation, Supervision, Writing - review & editing, Funding acquisition, Resources. **A.B. Ribeiro:** Validation, Supervision, Writing - review & editing, Funding acquisition, Resources. **A. Santos Silva:** Methodology, Validation, Supervision, Resources, Writing - review & editing.

Declaration of competing interest

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

Acknowledgments

This work has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No. 778045. The authors acknowledge the Portuguese Foundation for Science and Technology (FCT) for the support given to CENSE and CERIS through the strategic projects UIDB/04085/2020 and UIDB/04625/2020, respectively, and for J. Almeida PhD fellowship PD/BD/135170/2017 from the EcoCoRe Doctoral program. The authors thank Ana Paula Menezes from LNEC for the samples TGA/DTA analysis, Professor José Mirão from Hercules laboratory for the XRD assistance, Eng. Manuel Pacheco from Panasqueira mine for providing mining residues samples and Eng. Vítor Silva for the support during mortar formulations and mechanical tests.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.conbuildmat.2021.122483.

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Appendix A. Supplementary data

Table S1. Dry particle size distribution of the river siliceous sand used in comparison to the CEN reference sand.

Particle size (mm)	Cumulative mass passing (%)	
	River siliceous sand	CEN reference sand
0.05	0.0	0.0
0.08	0.7	0.1
0.15	2.7	0.3
0.30	12.0	2.2
0.60	40.6	20.7
1.19	72.1	71.8
2.38	92.9	95.0
4.75	99.3	99.2
9.51	100.0	100.0

Table S2. Chemical analysis by XRF of mining residues treated with ED and with both ED and thermal treatment (wt%).

Determinations	ED	ED & Thermal treatment
Al_2O_3	22.0	21.9
SiO_2	65.6	65.8
P	0.1	0.1
S	0.7	0.5
Cl	nd	nd
K_2O	4.3	4.4
Ca	0.4	0.4
Ti	0.6	0.5
Mn	0.07	0.1
Fe	5.4	5.4
Cu	0.1	0.1
Zn	0.3	0.03
As	0.2	0.4
Sn	0.04	0.1
W	0.3	0.2

Notation: nd. – Not detected.

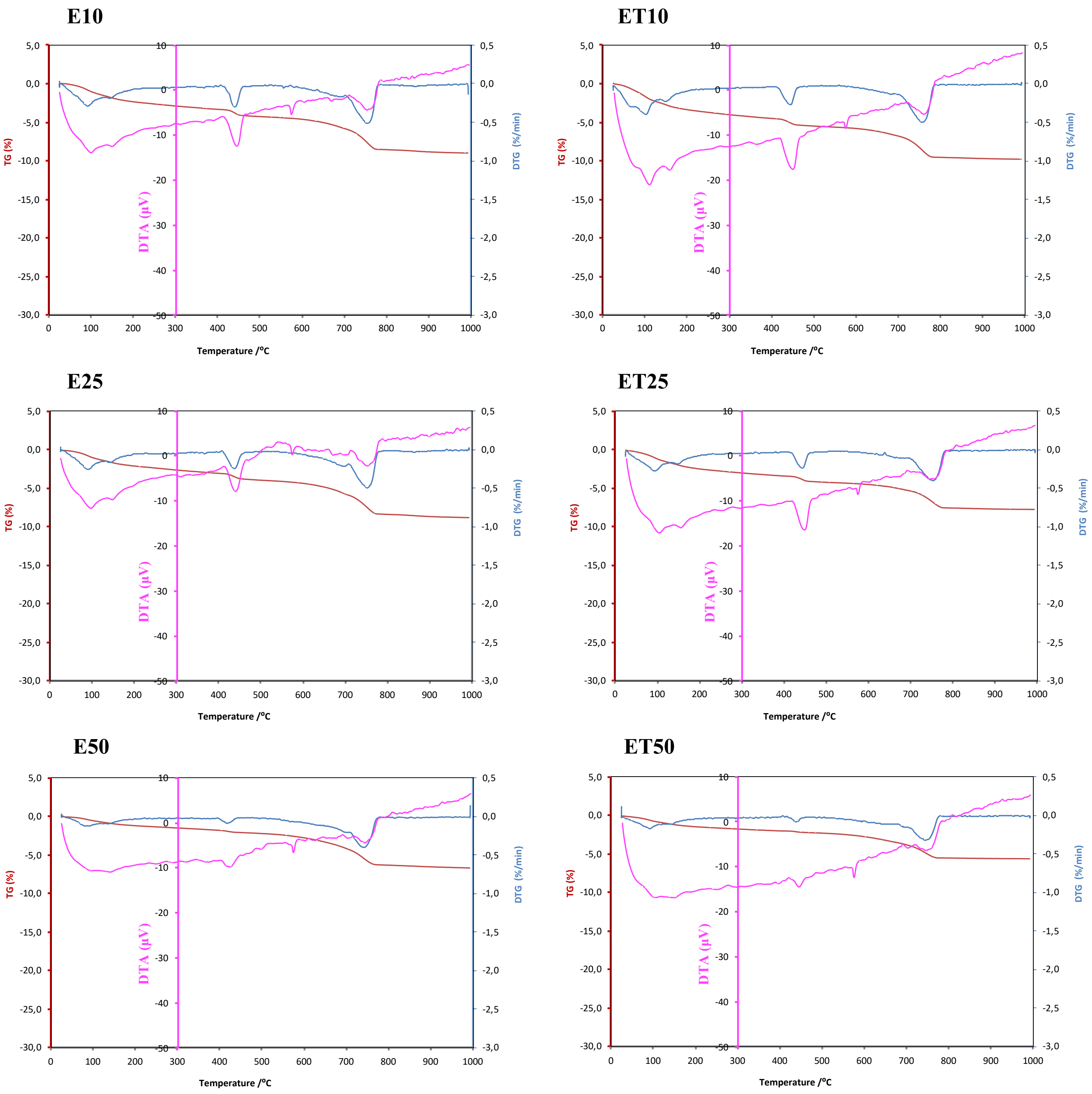

Figure S1. Thermogravimetric (TG), differential thermal analysis (DTA) and thermogravimetric derivate (DTG) curves from thermogravimetric analysis of studied mortars.

Table S3. Classification of mortars with treated mining residues incorporation based on European standards.

Application	Standard	Mortar	Classification
Rendering/plastering	EN 998-1 [50]	Control	CS IV
		E10 / ET10	CS IV
		E25 / ET25	CS III
		E50 / ET50	CS III
Masonry mortar	EN 998-2 [51]	Control	M15
		E10 / ET10	M10
		E25 / ET25	M10 / M5
		E50 / ET50	M5

Scientific journal article

A10 Life cycle assessment of electrodialytic technologies to recover raw materials from mine tailings

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Published in Sustainability journal (2021)

This article was published in Sustainability, Vol 13(7), J Almeida, C Magro, EP Mateus & AB Ribeiro, Life cycle assessment of electrodialytic technologies to recover raw materials from mine tailings, 3915, Copyright MDPI (2021).

sustainability

Article

Life Cycle Assessment of Electrodialytic Technologies to Recover Raw Materials from Mine Tailings

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Abstract: Currently, the development of new sustainable technologies to recover raw materials from secondary resources has shown a lack of available data on the processes and supplies involved, as well as their environmental impacts. The present research has conducted a life cycle assessment of electrodialytic (ED) technologies to improve critical raw materials recovery in the Portuguese mining industry. To critically appraise the activities from the mining sector and gather data on technical and environmental issues, three waste management scenarios were considered: (1) ED treatment with a deep eutectic solvent as an adjuvant; (2) ED treatment with simultaneous H_2 recovery; and (3) ED treatment with sodium chloride as an enhancement. The data presented were based on global databases, technical reports from official sources, and peer-reviewed published experimental outcomes. The estimated results indicated that one of the constraints in applying ED technologies is energy consumption and thus the impacts are highly dependent on energy source choices. On the other hand, as a consequence of the H_2 inherently produced by ED technologies, there is a direct potential for energy recovery. Therefore, considering an upscale approach of the ED reactor based on bench scale experimental results, the H_2 could be reused in the ED facility or stored. Additionally, according to experimental data, 22% of the tungsten from the fine mine tailings could be recovered. Finally, the possibility to remove 63% of arsenic from mine tailings could decrease contamination risks while creating additional marketable co-products.

Keywords: life cycle assessment; secondary mining resources; electrodialytic process; upscale; tungsten; arsenic; hydrogen

Citation: Almeida, J.; Magro, C.; P. Mateus, E.; Ribeiro, A.B. Life Cycle Assessment of Electrodialytic Technologies to Recover Raw Materials from Mine Tailings. *Sustainability* **2021**, *13*, 3915. https://doi.org/10.3390/su13073915

Academic Editor: Alessia Amato

Received: 2 March 2021
Accepted: 29 March 2021
Published: 1 April 2021

1. Introduction

The European Union 2030 climate action targets aim to reduce 55% of the greenhouse gases emissions compared to the values in 1990 [1] and increase the total renewable energy share in energy consumption by up to 32% by 2030 [2]. Moreover, the Sustainable Development Goals include targets for water and energy consumption, waste and biodiversity management, and adaptation of mining operations to climate changing conditions [3].

The European Commission has recently launched the fourth critical raw materials list, where tungsten (W) continues, together with other 29 elements, to be included as a material of high risk of scarcity and economic relevance [4]. Strategies for sustainable reprocessing of mine tailings should be applied to extract valuable raw materials before their disposal or further reuse options.

Tungsten is a valuable transition metal that can be extracted from tungstate minerals [5], such as scheelite ($CaWO_4$) [6] and wolframite ($(Fe,Mn)WO_4$) [7]. Tungsten is applied to produce hard metal and metal carbide powder that can be further treated by powder metallurgical methods for hard metal tools production [8]. If Europe could take full advantage of its own resources, the dependency on other countries to produce hard metal tools could be overcome.

Panasqueira is an underground mine located in Portugal, on the southern edge of the Estrela mountain near the Zezere river, which has operated for more than 130 years. The Panasqueira ores are composed of a series of subhorizontal, stacked, and hydrothermal quartz veins, promoting the mineralization of wolfram-bearing schists and shales. The mineralized area at the Panasqueira mine is 400–2200 m wide, 2500 m long and 500 m deep. During the mining process two types of mine waste are generated: coarse aggregates derived from rock blasting and fine tailings conveyed into dams, both of which have accumulated for more than 100 years [9].

Storage and/or deposition of mine tailings constitute the main threat to the surrounding environment of Panasqueira, particularly via water contamination due to their physical, chemical and mineralogical characteristics and to the volume/area occupied by them. These residues, namely, the most ancient, may leach harmful elements from storage sites, designated by acid mine drainage [10]. These residues are more exposed to oxygen and water, increasing the chance of acids being formed due to sulfide minerals (e.g., pyrite). Other problems that may arise are related to high levels of cyanide and nitrogen compounds in waters at mine sites from heap leaching and blasting. Particulate matter can be released by the wind from mining activities, such as excavations, blasting, transportation of materials and wind erosion. Moreover, exhaust emissions of the vehicles from mining sites increase the levels of particulates [11]. To prevent and control the pollution from several streams, the Panasqueira mine has an environmental license that complies with limits and conditions for the management of the environmental pressures [12].

The current decrease in ore grade has prompted the assessment of existing resources, energy needs and environmental impacts of mine tailings in a life cycle overview, concerning a circular economy perspective. These approaches play not only an important role in supporting cleaner production, resource management and decision-making in the mining industry, but also in identifying new business opportunities. The current demand and metal prices have leveraged the interest in secondary mining resources for critical raw materials, where the recycling of W has lower-energy negative impacts (<6000 kWht^{-1}) compared to virgin production (10,000 kWht^{-1}), depending on the grade and cut-off [13].

The impacts from the processing of raw materials should be considered during the selection of the Best Available Techniques (BATs), which are the up to date technologies for preventing and minimizing emissions and impacts on the environment [14]. Generally, the BATs promote the improvement of the output and energy efficiency of the raw material production process through replacement of the old equipment with new apparatus, which is less energy consuming [15].

One feasible method to alleviate the impacts of rejected fractions from mining activities is the electrodialytic (ED) process, which consists of the application of a direct low-level current density (mA/cm^2) between pairs of electrodes, to remove substances from different environmental substrates. In the ED treatment of mine tailings, anion (AEM) and cation exchange membranes (CEMs) were used to separate the matrix from the electrodes' compartments [16]. This aimed at controlling the pH conditions of the electrolyte and the matrix, improving the selectivity of the removal of contaminants [17]. The membrane surface attracts dissolved ions with the opposite charge (counter-ions) from the pore water of membranes. Thus, the counter-ions are transported through the membrane due to the electrical current while co-ions, that have the same charge of the membrane, are rejected [17].

Research has been performed to assess the feasibility of applying the ED treatment to W mine tailings to (1) recover W contents and other elements of interest [16], (2) remove harmful compounds [18], (3) to recover H_2 that is inherently produced during the treatment [19,20], and (4) to provide a suitable matrix for further reuse in the construction sector as a supplementary cementitious material [21]. Furthermore, the ED process has demonstrated potential to extract W present in fine tailings (approximately 22%) in the presence of biodegradable acid adjuvants—natural deep eutectic solvents (DES) [18].

Life cycle assessment (LCA) is an analysis technique applied to assess potential environmental impacts of a product/service from, e.g., raw material acquisition to waste disposal. LCA provides an estimation of cumulative impacts under environmental categories such as global warming, ozone layer depletion, soil and water acidification, eutrophication, and abiotic depletion of non-fossil and fossil resources [22]. According to ISO 14040 [23] and ISO 14044+A1 [24], the LCA process is systematic and divided into four phases: (1) goal and scope definition; (2) inventory analysis; (3) impact assessment; and (4) interpretation [25]. LCA requires a detailed inventory analysis to ensure a representative assessment of all the inputs and outputs of mass and energy across the whole phases of the product life cycle, designated by life cycle inventory (LCI) [26].

The upgrades on technical processes should, therefore, consider the environmental, social, and economic consequences of managing mine tailings throughout the value chain. For instance, orebody characterization, mine planning, processing, disposal, reprocessing, recycling, and reuse should be integrated. From an economic point of view, decreasing mine tailings is a top priority, followed by reuse, recycling, recovery treatment and disposal. Circular business models supported by public policies could have strategic importance, where economic benefits/incentives could be essential to optimize the recycling management system while increasing recycling rates [27].

The trade-off between raw material extraction from secondary mining resources and the environmental harmfulness of mine tailings after the ED process, as well as the need to critically understand the information that LCA studies can offer, were the base of the present work. Thus, this research shows the potential environmental impacts that should be considered in an LCA when the ED technology is applied to Panasqueira fine tailings. In addition, an upscale hypothetical approach of the ED reactor, based on laboratory experimental results, was developed. The impacts estimated and determined in several scopes are presented in terms of mine tailing management scenarios (direct disposal vs. ED remediation prior to discharge/further reuse options). In this context, three different operational ED conditions were considered: (1) ED treatment with a deep eutectic solvent as an adjuvant; (2) ED treatment with simultaneous H_2 recovery; and (3) ED treatment with sodium chloride as an enhancement.

2. Materials and Methods

2.1. Case Description and Production System

The Panasqueira mine, located in the Centro region of Portugal (Figure 1) and described as the largest Sn–W deposit in Western Europe, has changed its layout over the years due to the W market downturns. In this way, the optimization of mechanical processes and the exploration of alternative ores were considered. The Panasqueira mine process is summarized in Figure 2. The mine has a production plan extending to 30 years in the future [9].

Wolframite, cassiterite and chalcopyrite are the minerals extracted and used to produce W, copper (Cu) and tin (Sn) concentrates, respectively. The extraction process consists of a room and pillar method, considering geo-mechanical and geological properties of the rock mass. The first stage for the production of W is crushing and milling of the ore, promoting the release of the W mineral from the material. Then, a heavy media separation (HMS) between fine and coarse fractions is performed. This stage promotes the removal of 80% of the ore that does not contain W. Then, the W preconcentrated fraction is subjected to a conventional gravity concentration technique, followed by magnetic flotation in the presence of sulfide and dry magnetic separation [29]. The process is mostly gravitational due to the relative density of the concentrated products in relation to the sterile material [30].

Additionally, there is a wastewater treatment facility, the Mine Water Treatment Station (MWTS), located in *Salgueira*. The MWTS was projected to treat a maximum of 500 m^3/h, where the wastewater comes from the mine, wash activities and heaps [30].

Figure 1. The Panasqueira mine geografic location—Covilhã, Portugal, 40°10′11.0604″ N, 7°45′23.8752″ W (source: Google maps).

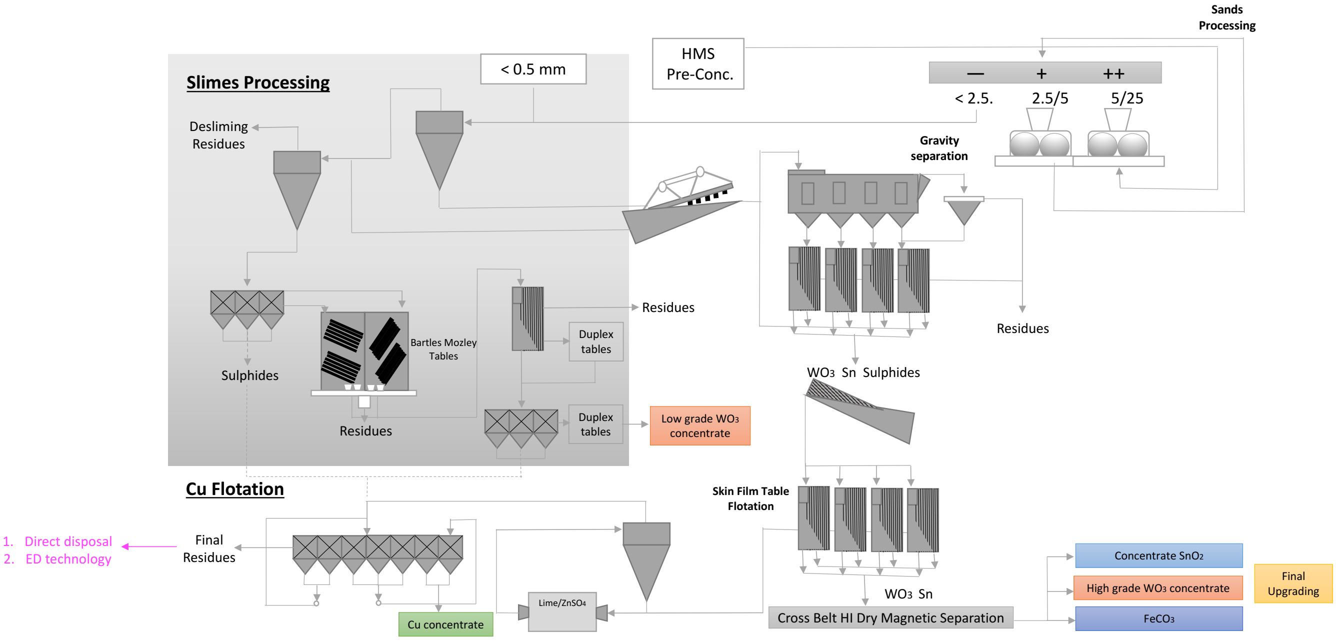


Figure 2. The Panasqueira mine process and scenarios considered for the management of mine tailings generated (based on [28]). HMS—Heavy media separation.

2.2. System Boundaries and LCA Road Map

Figure 3 shows the steps considered for the present LCA study. The analysis starts on the exploration of the ore for the W concentrate production. Then, for the rejected fraction of the mining process, three waste management scenarios were considered: (1) ED treatment with DES as an adjuvant; (2) ED treatment with simultaneous H_2 recovery; and (3) ED treatment with sodium chloride (NaCl) as an enhancement. Based on the analysis of the ED scenarios, an ED upscaling study was carried out that also coupled financial projections.

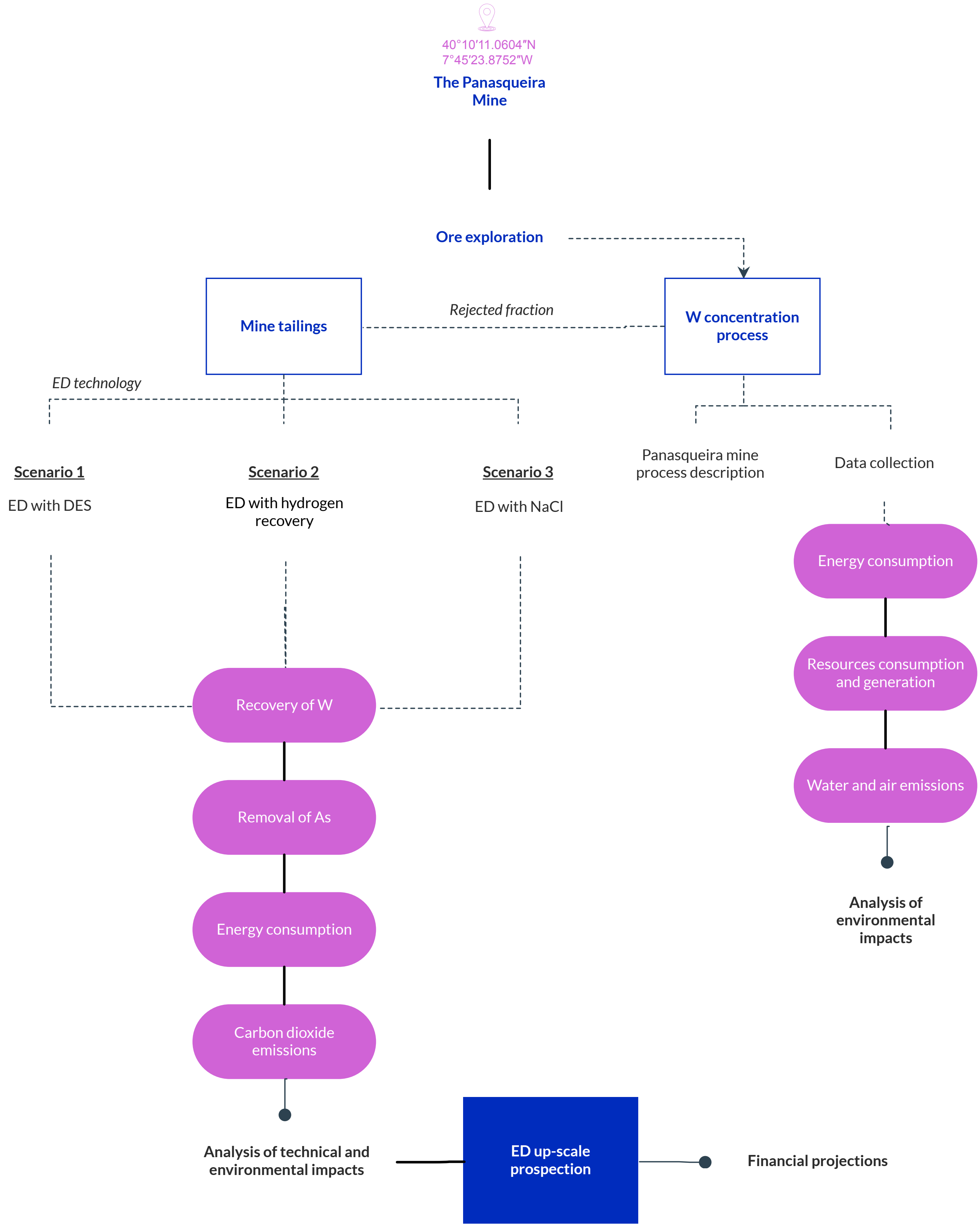


Figure 3. Flowchart of the life cycle analysis performed for the production of W concentrate and the electrodialytic treatment of mine tailings.

2.3. Data Collection

The data used to build the LCA were selected from three main sources: Ecoinvent database version 3.7.1, technical reports published from the European Commission and results from laboratory works published in international scientific journals (Table 1).

Table 1. Main sources used for the Life cycle assessment (LCA) data collection.

Source	Topic	Documents Consulted
Ecoinvent version 3.7.1	Tungsten concentrate production	- Tungsten mine operation and beneficiation [31]
European Commission technical reports	Mining industry operation	- Integrated Pollution Prevention and Control (IPPC) reference document on best available techniques in the nonferrous metals industries [8]
Research works published in international scientific journals	Electrodialytic process	- Exploring hydrogen production for self-energy generation in electroremediation: A proof of concept [20] - Electrodialytic hydrogen production and critical raw materials recovery from secondary resources [19] - Hydrogen recovery in electrodialytic-based technologies applied to environmental contaminated matrices [32] - Electrodialytic removal of tungsten and arsenic from secondary mine resources—deep eutectic solvent enhancement [18]

2.4. Mine Tailings Characterization

Considering the Panasqueira mine plant (Figure 2), the processing of 1000 kg of ore (from excavation activities) was considered as the functional unit for the LCA study. Table 2 presents estimations regarding W concentrate production and mine tailings generation from the processing of 1000 kg of ore. The calculations were based on scientific data available on Panasqueira resource compositions, as referenced in Table 2.

Table 2. Resources consumed and generated during the production of tungsten concentrate at the Panasqueira mine.

Item	Value per Functional Unit	Units	References
Panasqueira mine resources–ore	1000 (functional unit)	kg	-
W content in Panasqueira mine resources	3.0	kg/t ore	0.3% WO_3 [33]
W concentrate after the concentration process	2.3	kg/t ore	75% WO_3 [29]
Mine tailings generation	997.4	kg/t ore	-
W in mine tailings	0.8	kg/t ore	[29,33]
As in mine tailings	3.7	kg/t ore	[16]
W price	25,500	EUR/t	[34]
H_2 price	2.7–6.5	EUR/kg	[35]

Thus, concerning Table 2, from the processing of 1000 kg of ore, only 2.3 kg of W concentrate is produced, with grades of 75% of WO_3. This means that around 997 kg of fine tailings are generated from the processing of 1000 kg of ore. From the mine tailings it is possible to recover 0.8 kg of W/t of ore. The W price (25,500 EUR/t) makes the W recovery attractive from an economic perspective.

2.5. Water and Air Emissions and Resources Consumed

The processing of 1000 kg of ore was selected as the functional unit for the LCA. Water and air emissions during W concentrate production were determined based on Ecoinvent database [31]. In the Ecoinvent platform, the information is presented considering 1 t of W concentrate production. Thus, an extrapolation based on the W concentrate production at the Panasqueira mine was used to estimate its environmental impacts.

The resources consumed and generated during the production of tungsten concentrate at the Panasqueira mine were determined, considering the amount of fine tailings that results from the processing of 1000 kg of ore. In this sense, the amount produced from fine tailings generation was determined by subtracting the initial fraction (1000 kg ore) of the quantities of W, Cu and Sn concentrates produced. The W contents in mine tailings per functional unit were determined based on the concentrate grade of W trioxide (WO_3) produced in the plant—75% [29].

The plant also produces Cu and Sn concentrates. However, the amounts of Cu and Sn were only considered to estimate the fine tailings generation, and production impacts were not considered for this study.

2.6. Energy Consumption and CO_2 Release

To estimate the energy consumed by the ED system, Equation (1) was applied:

$$E\ (kWh) = \frac{V_i \times A \times t}{1000} \tag{1}$$

where V_i is the average voltage (Volts) in time i, A is the current intensity (Amperes) and t is the duration (hours) of the experiment. To convert the energy consumed into the quantity of CO_2 released for the environment, a conversion factor of 0.23314 kg CO_2 per kWh was considered [36].

3. Results and Discussion

3.1. Tungsten Concentrate Production at the Panasqueira Mine: Environmental Impacts

3.1.1. Energy Consumption

During the W concentrate production at the mining site, there are several high energy consuming phases. The overview presented in Figure 4 is based on data from technical reports. Herein, an average of the energy consumption of each processing step per ton of processed ore during the W production is shown.

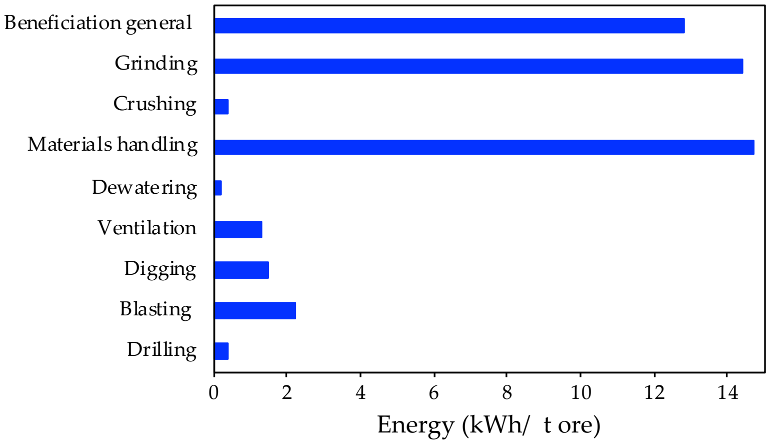


Figure 4. Energy consumption of mining processing activities (adapted from [37]).

The high energy consuming stages are materials handling (more than 14 kWh/t ore) and grinding (14 kWh/t ore). On the other hand, crushing, dewatering and drilling activities present lower energy consumptions (below 1 kWh/t ore). In addition, the environmental categories which are more affected by those processing steps are global warming potential (12.6 kg CO_2 eq/t ore), cumulative energy demand (133 MJ eq/kg), terrestrial acidification (0.29 kg SO_2 eq/t ore) and human toxicity (3.4 × 10^{-5} CTUh/t ore) [37].

3.1.2. Air and Water Emissions

During the processing of 1000 kg of ore, air and water emissions are generated, causing the main environmental pressures. Table 3 presents the emissions that were determined for Panasqueira mine processing based on Ecoinvent data from W concentrate production impacts.

Table 3. Emissions to the environment during the tungsten concentrate production (determined based on Ecoinvent data for tungsten concentrate production [31]).

Emissions	Value per Functional Unit	Units
Air		
Carbon dioxide, nonfossil	0.35	kg/t ore
Carbon disulfide	7.74×10^{-6}	kg/t ore
Particulates < 2.5 µm	0.01	kg/t ore
Particulates > 10 µm	0.13	kg/t ore
Particulates > 2.5 µm and < 10 µm	0.11	kg/t ore
Water		
Aluminum	9.26×10^{-6}	kg/t ore
Biological oxygen demand (BOD_5)	2.08×10^{-3}	kg/t ore
Chemical oxygen demand (COD)	4.15×10^{-3}	kg/t ore
Dissolved organic carbon (DOC)	1.54×10^{-3}	kg/t ore
Hydrocarbons	1.29×10^{-5}	kg/t ore
Iron	3.66×10^{-5}	kg/t ore
Nitrite	1.29×10^{-5}	kg/t ore
Phosphorus	1.29×10^{-5}	kg/t ore
Total organic carbon (TOC)	1.54×10^{-3}	kg/t ore
Tungsten	1.29×10^{-5}	kg/t ore
Water	0.26	m^3/t ore

Carbon dioxide is the major substance released to air (0.35 kg/t ore) and as observed in Figure 4, the materials handling and grinding are the main operations contributing to its release, in addition to the emission of particles. Regarding water load emissions per ton of ore, the chemical parameters that have higher impacts on aquatic systems are chemical oxygen demand (COD) (4.15 × 10^{-3} kg), biochemical oxygen demand (BOD_5) (2.08 × 10^{-3} kg) and total organic carbon (TOC) (1.54 × 10^{-3} kg).

COD is generally used to indirectly determine the amount of organic compounds in aquatic systems and is useful as an indicator of the degree of organic pollution in surface waters [38]. The COD is the most affected parameter by mining activities (4.15 × 10^{-3} kg/t ore), indicating that not all forms of organic matter (biodegradable and nonbiodegradable) are available.

The BOD_5 presents the second highest impacts (2.08 × 10^{-3} kg/t ore), meaning a decrease in the amount of oxygen consumed, by aerobic biological organisms, to decompose the organic matter in 5 days. An excessive microbial activity causes a reduction in the quantity of oxygen in the water, which may foment the growth of anaerobic organisms and decay the development of other existing communities [39].

The dissolved organic carbon (DOC), which is a potential source of carbon and energy for ecosystem metabolism, plays a central role in many limnological processes, since it is largely derived from terrestrial vegetation, deposited from lake catchments either by streams or by overland flow [40]. The mining impacts in terms of DOC are less pronounced (1.54 × 10^{-3} kg/t ore), although changes in DOC cycling can result in air–water exchange of CO_2 alterations [41].

Mining processes demonstrated the lowest impacts on the total organic carbon (TOC) (1.54×10^{-3} kg/t ore), mainly in the form of DOC. The TOC measures the amount of carbon found in an organic compound. A high organic content means a higher oxygen consumption and, consequently, an increase in the growth of microorganisms that deplete oxygen supplies [42].

The chemical water contamination is reflected in composition changes, while physical contamination results from the presence of fine material, affecting both surface water and aquifers. In the case of metallic ores, chemical contamination can be relevant due to the oxidation of pyrite producing sulfides that may leach heavy metals. In addition, yellowish to red $Fe(OH)_3$ precipitates are formed when acidic water meets neutral water in river basins. These precipitates affect the growth of aquatic plants [30]. Physical contamination by fines occurs when there is a discharge of treatment effluents in water courses. Contamination by suspended solids seriously affects fish communities [30]. In the case of the Panasqueira mine, the Zezere river is the main concern of water pollution.

Mining at levels below the water table will subsequently promote risks of evaporation of aquifers, water degradation by eutrophication and chemical contamination [43]. Acid mining drainage is characterized by a pH below 5 and is related to the sulfides (S^{2-} and $S_2{}^{2-}$), sulfur (S) or thiosulfate ($S_2O_3{}^{2-}$) being in contact with water and the atmospheric oxygen (oxidizing conditions). Acid water results from the oxidation of pyrite (FeS_2), usually catalyzed by bacteria. Other sulfides such as blends (ZnS), galena (PbS), chalcopyrite ($CuFeS_2$), pyrrhotite (Fe_7S_8) and arsenopyrite (FeAsS) can contribute to acidifying water resources. Generally, acidic effluents present high concentrations of Fe, manganese (Mn) and aluminum (Al) [30].

To decrease water resources contamination in the area, the Panasqueira mine has an in-house Mine Water Treatment Station (MWTS). The wastewater comes from the surface through infiltration and from the production process, since a significant amount of water is used during drilling and irrigation of the work fronts. The wastewater treatment facility has a volume capacity of 7000 m^3. The outlet and the receiving tank were designed to convert relatively soluble ions, such as Fe^{2+} and Mn^{2+}, into the respective less soluble oxidized forms (Fe^{3+} and Mn^{4+}). The treatment plant is composed of four tanks with mechanical agitation in which the addition of flocculant and lime is carried out. Lime is added to increase the pH of acidic water and prevent a possible drop in pH when ions such as Fe^{3+} and Mn^{4+} precipitate in the form of hydroxides. The solid hydroxides formed and in suspension are deposited at the bottom of the tank, being pumped into the mud dam [30].

3.2. Mine Tailings Management

3.2.1. Electrodialytic Scenarios

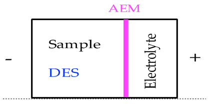
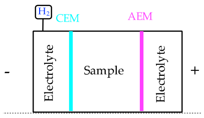
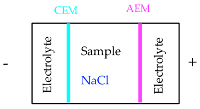
Following the assessment of air and water emissions during W concentrate production, the environmental pressures of mine tailings were studied in particular in terms of ED process efficiency for elements extraction and recovery, energy consumption and CO_2 emissions. This assessment was based on experimental data from previous works. In fact, the major impacts from waste disposal at mine sites can be divided into two categories [37]:

(1) the loss of productive land following its conversion to a waste storage area;

(2) the introduction of sediment, acidity, and other contaminates into surrounding surface water and groundwater from water running over exposed problematic or chemically reactive wastes, and the consequent soil contamination.

In this sense, alternative ways to direct disposal of mine tailings are desired. Table 4 presents three different scenarios where the ED technology was studied as an alternative to direct disposal. The systems defined have diverse extraction ratios of elements and other features, being important to compare the ED scenarios in terms of achievements and environmental impacts.

Table 4. Data from the electrodialytic treatment of mine tailings.

				Extraction (%/kg t ore)		
Scenario	**ED Scheme**	**Duration (h)**	**Current Intensity (A)**	**W**	**As**	**H_2 Purity/ Recovery (%)**
1. ED treatment with DES [1]		96	0.05	22/0.2	16/0.6	n.a.
2. ED treatment with H_2 recovery [2]		1	0.1	7.5/0.06	48/1.8	74/50
3. ED treatment with NaCl [3]		120	0.1	13/0.1	63/2.4	n.a.

[1] According to [18]; [2] according to [20,32]; [3] according to [19]; AEM—Anion Exchange Membrane; CEM—Cation Exchange Membrane; DES—Deep Eutectic Solvent; Electrolyte ($NaNO_3$ 0.01 M); NaCl—sodium chloride; n.a.—not applicable.

Scenario 1 involves the use of a DES in the sample compartment during the ED treatment. DES present advantages in terms of yield, costs and toxicity when compared to conventional ionic liquids [44], which are composed of strong acids and bases [45]. In this way, a two-compartment reactor was operated for 4 days at 0.05 A. The electrolyte and sample sections were separated by an anion exchange membrane [18]. The main outcome of this reactor configuration was the quantity of W extracted from the matrix. The use of choline chloride/oxalic acid (1:1) promoted a higher solubilization of the W and, together with the current applied, a synergetic effect on the recovery of this critical element was observed.

Scenario 2 includes a three-compartment ED reactor and the simultaneous collection of self-produced H_2 in an eco-friendlier manner. This configuration presented the lower W recovery, where only 7.5% of W was extracted. However, it should be noted that this system operated only for 1 hour at 0.1 A. Applying this current intensity was possible to access the production of H_2, an energy carrier, with 74% H_2 purity. Electrokinetics have been coupled with electrodialytic technology for H_2 production during the removal of pollutants [20], where the energy requirements for this system are considerably smaller owing to the higher conductivity of the matrix [46]. Additionally, regarding the As removal, a better performance was achieved (48%) in comparison with scenario 1 (16%). Considering the functional unit defined for this study, hypothetically, this system could avoid 1.8 kg of As contamination (Table 4).

Finally, in scenario 3, a three-compartment ED reactor was tested at 0.1 A for 5 days using NaCl to improve the current passage [19]. The main achievement of this system was a 63% As removal from a total of 3.7 kg As/t ore (Table 2), meaning less than 2.4 kg of As contamination per t of ore (Table 4).

Regarding different market segments and environmental concerns, the scenarios considered may show different potentials. In this way, the trade-off for the three scenarios was studied to understand the impacts on resources consumption and its economic feasibility. Table 5 presents an energy assessment for the three bench scale ED treatment scenarios. These tests were performed to treat 39 [18] and 22 g [16,20] of fine tailings in a two- and/or three-compartment ED reactor, respectively. The energy was determined according to Equation (1).

Table 5. Estimation of the energy consumed and CO_2 released during the electrodialytic laboratory treatment of mine tailings.

Scenario 1. ED Treatment with DES

Measure	Voltage (V)	Current intensity (A)	Energy consumed (kWh)	kWh/g W extracted	kWh/g As extracted	g CO_2
Day 0	32.30	0.05	2.0×10^{-3}	1.0×10^{-2}	4.2×10^{-5}	0.38
Day 1	13.20		1.0×10^{-3}	5.0×10^{-3}	2.1×10^{-5}	0.15
Day 2	11.10		1.0×10^{-3}	5.0×10^{-3}	2.1×10^{-5}	0.13
Day 3	10.80		1.0×10^{-3}	5.0×10^{-3}	2.1×10^{-5}	0.13
Day 4	11.80		1.0×10^{-3}	5.0×10^{-3}	2.1×10^{-5}	0.14
		Average	1.0×10^{-3}	6.0×10^{-3}	2.5×10^{-5}	0.18

Scenario 2. ED treatment with H_2 recovery

Measure	Voltage (V)	Current intensity (A)	Energy consumed (kWh)	kWh/g W extracted	kWh/g As extracted	g CO_2
0 min	35.00	0.1	4.0×10^{-3}	6.7×10^{-2}	2.8×10^{-5}	0.82
10 min	27.50		3.0×10^{-3}	5.0×10^{-2}	2.1×10^{-5}	0.64
20 min	25.80		3.0×10^{-3}	5.0×10^{-2}	2.1×10^{-5}	0.60
30 min	26.10		3.0×10^{-3}	5.0×10^{-2}	2.1×10^{-5}	0.61
40 min	28.00		3.0×10^{-3}	5.0×10^{-2}	2.1×10^{-5}	0.65
50 min	38.80		4.0×10^{-3}	6.7×10^{-2}	2.8×10^{-5}	0.90
60 min	59.50		6.0×10^{-3}	1.0×10^{-1}	4.2×10^{-5}	1.39
		Average	3.0×10^{-3}	6.2×10^{-2}	2.6×10^{-5}	0.80

Scenario 3. ED treatment with NaCl

Measure	Voltage (V)	Current intensity (A)	Energy consumed (kWh)	kWh/g W extracted	kWh/g As extracted	g CO_2
Day 0	98.40	0.1	1.0×10^{-2}	1.0×10^{-1}	5.3×10^{-5}	2.29
Day 1	77.25		8.0×10^{-3}	8.0×10^{-2}	4.2×10^{-5}	1.80
Day 2	46.80		5.0×10^{-3}	5.0×10^{-2}	2.7×10^{-5}	1.09
Day 3	41.65		4.0×10^{-3}	4.0×10^{-2}	2.1×10^{-5}	0.97
Day 4	27.85		3.0×10^{-3}	3.0×10^{-2}	1.6×10^{-5}	0.65
Day 5	14.70		1.0×10^{-3}	1.0×10^{-2}	5.3×10^{-6}	0.34
		Average	5.0×10^{-3}	5.2×10^{-2}	2.7×10^{-5}	1.19

The highest energy consumption occurred in scenario 3, where a three-compartment reactor and NaCl were used. An average of 5.0×10^{-3} kWh was consumed, with a release of 1.2 g CO_2. In fact, this system was operated at a higher current intensity (0.1 A) and thus, it was expected to have a higher energy consumption, and consequently, higher amount of CO_2 release. However, the addition of NaCl promoted the control of the power consumption once it led to an increase in media conductivity and therefore lower resistance [47].

On the other hand, scenario 1, performed with natural extractants (DES), demonstrated a decrease in the energy consumption of more than 80%. In this set-up, a current intensity of 0.05 A was applied, which was the main contributor to the energy consumption decrease (1.0×10^{-3} kWh) when compared to the other two scenarios. This means approximately 0.9 g of CO_2 emissions to the environment. In fact, this scenario presented the lowest energy consumption per mass of elements extracted (6.0×10^{-3} kWh/g W and 2.5 E $\times 10^{-5}$ kWh/g As).

Scenario 2, which includes H_2 recovery, demonstrated an intermediate energy consumption. In scenario 2, as in scenario 3, a current intensity of 0.1 A was applied. However, due to the use of a totally sealed reactor (to ensure no leakage of gases), a decrease in the voltage occurred and thus a decrease in the resistivity inside the reactor was observed. Based on Ohm's law, if the current intensity is constant, the voltage and the resistivity (or conductivity) are strongly related. The decrease in the ED cell voltage is linked to a conductivity increase in the electrodes' compartments [20].

This may explain the lower energy consumed (3.0×10^{-3} kWh) compared to scenario 3 (ED with NaCl). Additionally, the possibility to recover the self-hydrogen produced by the ED treatment and reuse to feed the reactor in terms of energetic requirements could provide energy savings of up to 50% [32].

Regarding the water needs for sample suspensions and electrolyte preparation with sodium nitrate ($NaNO_3$), ED configurations that have three compartments require 700 mL (32 times the sample weight) and the two-compartment systems require 600 mL (15 times the sample weight). However, the reuse of secondary water resources during the ED treatment (e.g., secondary effluent) have shown promising results [16] that may contribute to alleviate tap water needs.

Summing up, the laboratory experiments could follow structural designs, such as a central factorial design. However, it is pivotal to properly assess the industrial interest. In a scale-up perspective, the experiments should be carried out sequentially, followed by a process analysis and economic evaluation. Even in the first steps of the research, which can affect the experimental domain of interest, the quality of the information provided could be improved and be key factor for a pilot unit.

3.2.2. Electrodialytic Treatment Upscale Prospection

In order to increase the understanding of the scenarios studied, a perspective of a full scalable ED reactor model to support commercial roll-out was carried out. The implementation of the theoretical ED pilot reactor would result in a full running removal and recovery of the target compounds from the fine mine tailings, hypothetically aiming zero liquid or solid discharges. A full closed-loop of residues would change the perspective of mine tailings, which would become a valuable resource instead of a costly waste stream.

The ED plant, which can be either vertical or horizontal, is presented in Figure 5, showing a simplified flow sheet of a loop reactor. It is important to point out that the design of the reactor does not need to be similar to the laboratory scheme. However, it has to be designed to achieve the best data, both in terms of fluid dynamics and transport properties. In Figure 5, the design of the reactor is used as an example of the concept, and merges the best parts of both scenarios 1 and 2:

(1) two-compartment reactor design, which is easier to operate;
(2) DES as enhancements, alleviating the consumption of strong acids and bases while incrementing the W recovery;
(3) cation-exchange membrane, which allows H_2 recovery for depreciation of implementation and maintenance costs, as well as flexibility in different market segments.

A balance between the ED treatment plant and downstream units needs to be ensured in order to decrease environmental pressures from the disposal of mine tailings. The final product (after the ED treatment) needs to have such a quality that consecutive ED phases will work optimally at minimal operational costs. Since the Panasqueira mine has available land, the installation of solar panels in the south direction with 144 cells at 400 W (2025 × 996 × 40 cm) [48] will promote the use of renewable energy and overcome the environmental pressures and costs regarding ED technology. The use of solar panels decreases the investment cost by avoiding the use of batteries, solar inverters, and power supplies and the maintenance cost since there is no battery waste to manage [49].

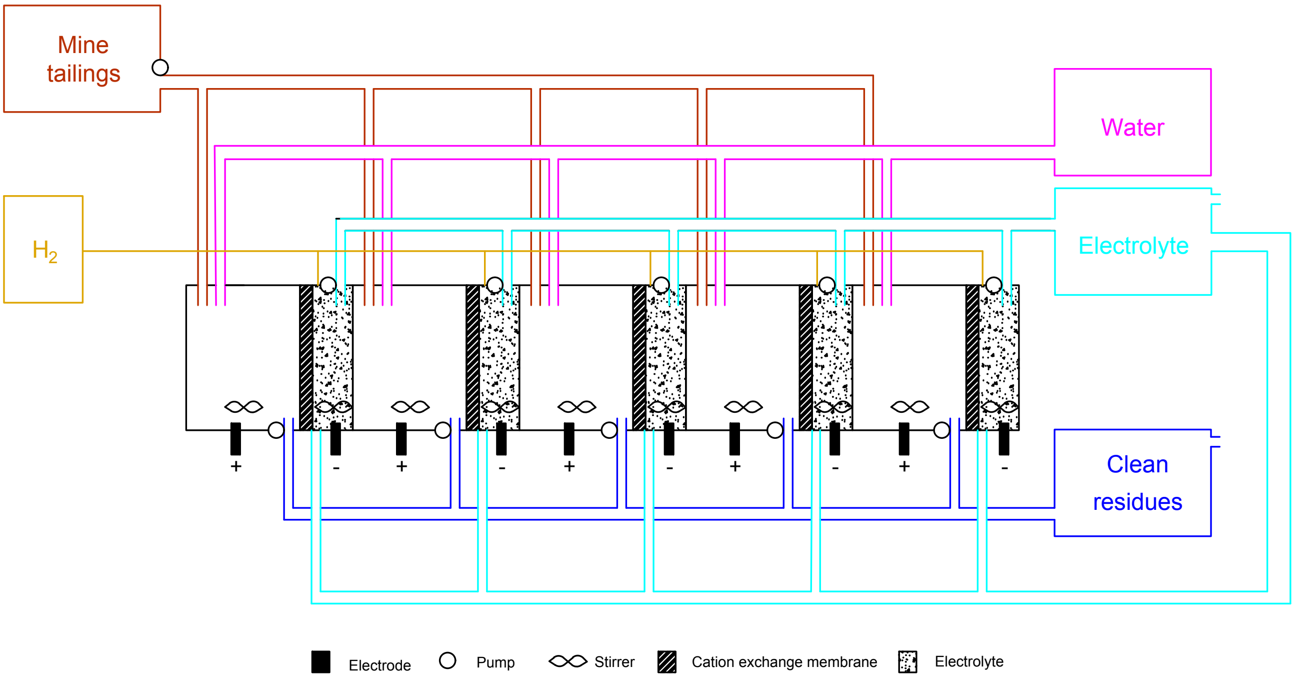


Figure 5. Theoretical electrodialytic plant facility based on bench scale experiments.

Additionally, the scaled-up reactor was dimensioned addressing issues related to a seamless operation with minimal needs for cleaning. The material selected for the reactor was polyethylene due to its chemical and impact resistance, electrical properties and low coefficient of friction. In addition, polyethylene is lightweight, easily processed and offers near-zero moisture absorption [50]. The reactor was dimensioned to treat 10 m^3 per day (8 h running time, based on average labor schedules in Portugal) in five conjugate sequential units. The capacity of each block is 2 m^3, as reported by other pilot studies [51]. These dimensions promote the treatment of the volume of mine tailings produced per day (0.4 m^3), considering: (1) mud's density of 3031 kg/m^3 [52]; (2) 997 kg volume of mine tailings; (3) water needs both for the electrolyte ($NaNO_3$ 0.01 M) and sample suspensions. The ED facility was projected to be fully distributed by individual blocks. Each section includes pumps (when gravity transport is not possible), membranes, and sample and electrolyte compartments. Additionally, it includes reservoirs for ED treated and nontreated mine tailings (before the ED process), water, electrolyte and H_2, to either reuse or storage. This simplifies the maintenance of the reactor and, consequently, reduces the problems during the treatment.

Scaling in ED occurs due to inorganic species, e.g., PO_4^{3-}, NH_4^+, Mg^{2+}, Ca^{2+} and CO_3^{2-}, forming low-solubility minerals. The more effective the process is at removing these elements, the less scale will be formed and therefore the maintenance costs for the ED unit will be lower [53].

A constraint of the ED facility is the goal of achieving total reuse of water, since there is a need to treat and/or crystallize the salt from the brine stream ($NaNO_3$) and the effluent suspension produced. There are several technological options for waste brine crystallization. The projection of the ED facility intends to concentrate and crystallize the salts in the brine solution. Crystallization plays an important role in many industries where water recycling is implemented. If it is not possible to perform the purification of brine solutions, the Panasqueira MWTS (capacity = 500 m^3/h) [30] could also include the treatment of both brine solution and effluent suspension. In addition, treated water resources from the Panasqueira MWTS could be used to prepare the mine tailings suspensions, aiming for circularity of by-products. This step would promote savings in water consumption by the generation of suitable mixtures to reuse in the ED system.

Moreover, the proposed ED unit combines a reservoir for the collection of the self-produced H_2, increasing the value proposition of the ED pilot. Lead-acid batteries are the most useable storage systems, as well as rechargeable batteries, supercapacitors, and redox flow batteries. The most promising systems for renewable energy storage are the lithium-ion batteries and redox flow batteries [49]. Coupling a unit for H_2 recovery at the mine can direct the site towards a clean energy transition [54]. In fact, the implementation of H_2 as a flexible energy carrier in future energy systems is a top priority in the new EU Green Deal. The smart integration across sectors is encouraged and promotes investments on cutting-edge research and innovation for clean energies [1]. Together with W recovery and As removal, the H_2 transfer to be used in the mine ED facility could have socio-economic impacts both on recovery of raw materials and clean energy transition, since it addresses applicable solutions to industries. This stimulates the fostering of synergies in industrial sectors, the creation of new services and the transition and adaptation to eco-innovated systems. The ED treated fine tailings can be further used in construction materials with compatible applications with conventional concrete and fired brick masonry walls [21]. On the other hand, the As can be used in purification processes of zinc leach solutions [55], and residues containing As could be recovered by glass industries, since arsenates can be turned into silicoarsenates during vitrification [56].

Further roll-out may be hampered by the lack on financial commitment to implementation in a declining industry, where investments in utilities are not seen as strategic to the core business. However, low investment solutions with limited capital expenditures (CAPEX) and operating expenditures (OPEX) costs are required. Table 6 presents the financial projections of the ED plant for the initial investment, as well as the first and the fifth years of ED operation.

Table 6. Financial projections of the expenditures of implementing the theoretical electrodialytic plant facility presented in Figure 5.

Item	Quantity	Cost/Uni (EUR)	Initial Investment (EUR)	1 Year of ED (EUR)	5 Years of ED (EUR)
Stirring	10	1986.00	19,860.00		
Reactor in polyethylene (diameter = 1.6 m; length = 1 m)	5	650.00	3250.00		
Block compartments (diameter = 1.6 m; length = 1 m)	20	149.00	2980.00		
Electrodes Ti/MMO (0.5 × 0.1 m; width = 3 mm)	10	100.00	1000.00		
Membranes CEM–CR67, MKIII, Blank (diameter = 0.8 m)	5	499.00	2495.00		
$NaNO_3$ * (1 kg per unit)	29	151.90	4405.10	1,101,275.0	5,506,375.0
Natural deep eutectic solvents (choline chloride. 1 kg per unit + oxalic acid. 25 kg per unit) *	6	143.00	858.00	214,500.00	1,072,500.00
Pumps	11	489.00	5379.00		
Tubes	36	1.89	68.04		
Power boxes	10	383.81	3838.10		
Crocodiles + wires	20	0.99	19.70		
Solar Panels (2025 × 996 × 40 cm)	5	476.00	2380.00		
Implementation	10% of the total reactor price		4653.29		
Maintenance	5% of the initial investment (every 3 months)			10,237.25	51,186.23
Cleaning of Membranes	15 EUR/m^2 (twice per month for 2 m^2 of membranes area)			3600.00	18,000.00
Replace of Membranes	Every 4 years				2495.00
Cleaning of Reactor	2% of the initial investment (once per year)			1023.72	5118.62
Total investment			51,186.23	1,330,635.97	6,655,674.86

* Number of packaging to buy. Costs were based on: stirring—[57]; reactor—[50]; compartment block—[58]; electrodes—[59]; membranes—[60]; $NaNO_3$—[61]; Adjuvants—[62,63]; pumps—[64]; tubes—[65]; power box—[66]; crocodiles + wire—[67]; solar panels—[48]; implementation—[68]; maintenance; cleaning of reactor and membranes; changing membranes lifetime—[69,70]. Ti/MMO—titanium/mixed metal oxide.

It should be noted that Table 6 shows a simplified economic approach of the ED concept, considering only its physical implementation. Through this assessment it is possible to understand the impact of these figures on the broad uptake potential in the mine industry. This section does not cover the fully CAPEX or OPEX estimating procedures. Nevertheless, it provides concepts that can be used in the project evaluation to help the understanding of its application in a full implementation mode. Moreover, Table 6 also details the costs of the components needed for the ED facility. The materials for the ED plant construction (e.g., electrodes, membranes, pumps, tubes) and the reagents needed for the electrolyte and sample suspensions ($NaNO_3$ and DES) are the main contributors of the costs reported in the first- and fifth-year projections. Together with the costs for the manufacturing, and, therefore, the total investment in the first year, a set of other expenses to guarantee the success of the ED process during its lifetime is also foreseen. The total investment before developing the ED facility in a full run mode is approximately 51,000 euros, increasing from around 1 to 7 millions of euros in the first and fifth years, mainly due to $NaNO_3$ and DES consumption.

The investments can be considered high, although further optimization of the processes and research could decrease the values presented. Additionally, the up-scaling theoretical approach should be further optimized, based on a pilot study, to decrease inputs related to energy and resources in a more positive way. This strategy may promote minimization of the negative pressures in the environment and the adaptation of industrial sectors to eco-innovative markets. In particular, the ED plant presented could leverage new market possibilities, the requalification of mining areas after close and the development of new technologies with regard to achieving the Sustainable Development Goals [3].

4. Conclusions

Mining industries have been stimulated to operate in a more sustainable way, reducing their environmental burdens and improving resource management. In this way, eco-efficient processes and alternative scenarios to direct waste disposal of rejected fractions are desired.

This research work evaluated the impacts on the environment that may come from mining processes and three potential scenarios that involve the ED treatment of fine tailings from the Panasqueira mine.

Regarding the impacts of mining processes, materials handling and grinding presented the highest energy consumption and, consequently, CO_2 release (0.35 kg/functional unit). A carbon footprint of 12.6 kg CO_2 eq/t ore is associated with mining activities. On the other hand, the chemical parameters that have the highest impacts on aquatic systems are COD (4.15×10^{-3} kg), BOD_5 (2.08×10^{-3} kg) and TOC (1.54×10^{-3} kg).

The analysis of previous ED data at the bench scale was a key factor to estimate the potential environmental burdens involved in an ED plant conception. In particular, energy consumption is a major concern at an industrial scale. Herein, the ED technology could have a central role in the recovery of metals below 45 microns, a main challenge for the mine. In addition, the mine has a project spanning more than 30 years, which means that new market segments could be explored to keep the development and the requalification of the Panasqueira area after its closure. In this context, aligned with the removal of As contents, the recovery of W and H_2 seems to be attractive for the development of the Centro region of Portugal, considering a circular economy perspective, both in terms of raw materials recovery and sustainable energy production. These aspects might decrease the risk associated with mining activities and leverage new business opportunities in the mining sector in the upcoming years.

Thus, concerning the three scenarios studied, different advantages were pointed out. Scenario 1, which involves the use of DES, exhibited a better performance in terms of the quantity of W extracted from the matrix (22%). Scenario 2 considers self-produced H_2 recovery during the ED treatment with 74% H_2 purity. Scenario 3 presents an approach with conventional reagents and the main achievement of this system was the As removal (63%).

Based on the best features of the scenarios analyzed, a sequential theoretical ED facility was presented. The dimensioning of the reactor was based on the quantity of mine tailings that need to be treated and laboratory data. An investment of approximately 51,000 euros was estimated, increasing from 1 to 7 millions euros in the first and fifth years due to maintenance and operational costs. Nevertheless, the upscaling effect may reduce the inputs—namely, those regarding operational costs and energy consumption. In future works, a pilot study of the ED treatment should be performed to assess the scaling-up influence on technical aspects and to determine the economy of scale's percentage.

This study provides new insights for the life cycle of mine tailings and a basis for environmental decision-support in the application and roll-out of ED technologies.

Author Contributions: Conceptualization, J.A. and C.M.; Data curation, J.A. and C.M.; Formal analysis, E.P.M. and A.B.R.; Funding acquisition, A.B.R.; Methodology, J.A.; Project administration, A.B.R.; Resources, E.P.M., and A.B.R.; Supervision, A.B.R.; Validation, E.P.M. and A.B.R.; Writing—original draft, J.A.; Writing—review and editing, J.A., C.M., E.P.M., and A.B.R. All authors have read and agreed to the published version of the manuscript.

Funding: This work has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No. 778045. The authors acknowledge the Portuguese Foundation for Science and Technology (FCT) for the support given to CENSE through the strategic project UIDB/04085/2020 and for J. Almeida PhD fellowship PD/BD/135170/2017 from the EcoCoRe Doctoral program.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The authors acknowledge Eng. Manuel Pacheco from Panasqueira mine for providing the sample and Eng. António Galvão for the support in LCA development. This research is anchored by the RESOLUTION LAB, an infrastructure at NOVA School of Science and Technology.

Conflicts of Interest: The authors declare no conflict of interest.

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International conference article

A11 Environmental benefits and mechanical performance of cement mortars with tungsten mining residues incorporation

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Published in the conference proceedings of the 2nd International Conference on Sustainable, Environmentally Friendly Construction Materials, Szczecin, Poland (2021)

ICSEFCM 2021

Proceedings of the 2nd International Conference on Sustainable, Environmentally
Friendly Construction Materials (2021) 27–32
Edited by: E. Horszczaruk, P. Brzozowski

Environmental benefits and mechanical performance of cement mortars with tungsten mining residues incorporation

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CONFERENCE PAPER

Abstract

Secondary mining resources have been largely applied for the development of alternative building products. Additionally, its reuse versatility increases the potential on the future circular economy generation. Herein, mining residues from Panasqueira mine were applied in the formulation of cement-based mortars, according to EN 196-1 standard. Mechanical performance of mortars was analysed after the replacement of the conventional binder (cement) by mining residues in 10, 25 and 50 % (v/v). As expected, compressive and flexural strength decrease when compared to the reference mortar (100 % cement) in all cases. This decrease was more significant in terms of compressive strength (between 27 % and 71 %), when compared to flexural strength results (between 18 % and 56 %). Furthermore, an environmental approach of secondary mining resources incorporation on mortars, regarding Portugal and Poland data, was carried out. The savings in terms of primary resources may promote to minimise energy impacts. When mining residues replace cement in 10 % is possible to save 0.3 or 1.9 Mt of cement production and 0.14 or 0.89 CO_2 Mt emissions, in Portugal and Poland, respectively.

Keywords: Secondary mining resource, Building product, Flexural strength, Compressive strength, Sustainability

1. Introduction

The improvement on building energy performance for saving energy and enhancing sustainability within the construction sector is now on the top list. The growth of urban areas is considered a severe problem as 50 % of the global population lives in metropolitan zones and is foreseen to achieve up to 70 % until 2050. This radical growth will mean the need of additional infrastructure resources to serve the population [1].

A large percentage of current construction products are cement-based (e.g. concrete and some mortars), where concrete has been reported as the second most consumed substance on the world, immediately after water [2]. According to worldwide cement production data, it was estimated that 4.1 billion t of cement were produced in 2018, where clinker production reached ~77.7 million t [3]. Concrete exploration is one of the main contributors of greenhouse gas emissions [4]. Approximately 10 % of the global CO_2 emissions are due to provision of construction materials, where cement accounts for ~85 % [5]. Cement CO_2 emissions mainly come from raw materials mining, firing and product milling processes, which involves energy/fuels and electricity. Shipping also increases CO_2 emissions depending on distances, although it can be considered a stream common to other products [6].

To revert the negative impacts that came up from global emissions, European Commission has set a greenhouse gases reduction up to 40 % (regarding 1990 levels) until 2030, coupled with an energy efficiency improvement of processes above 32.5 % [7]. In addition, the reuse of potential secondary resources towards circular economy targets should be pursued [8].

Mining industries produce high rates of mining wastes once, to access the ore, waste rock needs to be removed and other residues are generated from ores' extraction processes. The accumulation of these residues, namely in open pits, generate critical landscape and other environmental problems. One example is Panasqueira mine, one of the largest tin (Sn) – tungsten (W), that is located in Covilhã, Portugal. Panasqueira mine has been active for more than one century. There are almost 8,500,000 t of tungsten mining wastes in Panasqueira mine area, and ~100 t per day are still being generated due to mining processes [9,10].

Tungsten mining residues have shown feasible reuses in innovative construction products, as part of alkali activated products [11,12] or as pozzolanic material [13], promoting the decrease of mining waste disposal and primary raw materials needs in the construction sector. Thus, it is imperative to pursue new solutions to empower the sustainability of both industrial sectors.

In the present work, cement-based mortars were produced by partially replacing conventional cement content by tungsten mining residues in 10, 25 and 50 %. To increase the add-value of tungsten mining secondary resources, residues from Panasqueira mine (collected directly from the tube output, after the extraction of the mined ores) were applied in cement-based mortars formulation. The mechanical performance of the mortar was studied through compressive and flexural strength tests. Additionally, an environmental approach of mining residues incorporation on mortars production was assessed, regarding Portugal and Poland cement production available data.

2. Materials and methods

2.1 Materials

For mortars formulation, tungsten mining residues were collected from Panasqueira mine sludge circuit (Covilhã, Portugal, 40°10′11″N, 7°45′24″W) and were used as binder together with Portland limestone cement CEM II/BL 32.5 N (Secil, Portugal). Washed siliceous sand (Portugal), with particle sizes mainly between 0.5 and 2.0 mm, was applied as aggregate (Figure 1). Tap water was used to hydrate the formulation.

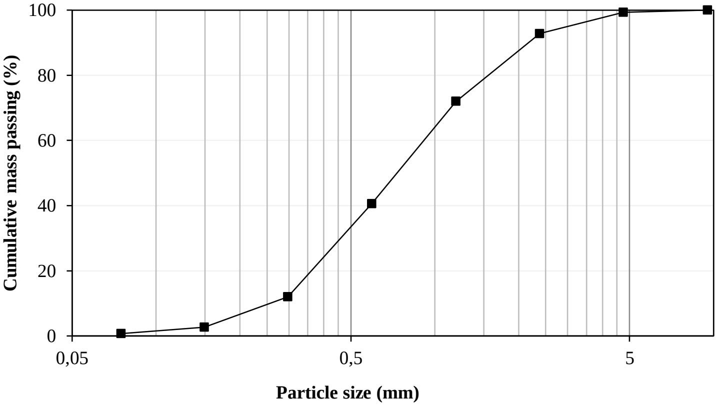


Figure 1. Dry particle size distribution of the sand used in mortar formulation.

2.2 Methods

Mortars were produced based on EN 196-1 [14], considering a volumetric proportion of cement, washed siliceous sand and water of 1:3:0.5 as reference. The reference mortar was produced with 100 % of cement as binder. Mortars were also produced replacing 10, 25 and 50 % of the cement volume content by tungsten mining residues (Table 1). The materials loose bulk density (Cement = 1.00 g/cm^3; Mining residues = 1.18 g/cm^3; Washed siliceous sand = 1.54 g/cm^3) were used to determine the volumes of the components as exact masses. Samples were produced in 40 mm x 40 mm x 160 mm metallic moulds.

Table 1. Quantity of binder, aggregate and water used to formulate the mortars according to the volumetric proportion of 1:3:0.5.

	Binder (1)				**Aggregate (3)**		**Water (0.5)**	
	Cement		*Mining residues*		*Washed siliceous sand*		*Tap water*	
Code	%	g	%	g	%	g	%	g
REF	100	666.7	-	-	100	2000	100	333.3
MR10	90	600.0	10	66.7		2000		333.3
MR25	75	500.0	25	166.7		2000		333.3
MR50	50	333.3	50	333.3		2000		333.3

Following the formulation, the samples were demoulded after 48 hours and left in a water curing for 26 days, at ~20 ºC. Then, the samples were dried at 60 ºC, until achieved a constant weight. The mechanical performance of the specimens was carried out according EN 196-1 [14], considering the analysis of the flexural and compressive strength in a Zwick/Rowell Z050 equipment.

For flexural strength tests, three-point bending test was performed. The loading cell applied was gradually lowered at a constant rate of 50 ± 10 N/s until failure occurred. Flexural resistance (F_r) was determined in MPa, according to equation (1), where F_f is the maximum force (N), l is the distance between the supports length (100 mm) and b the width of the sample (40 mm).

$$F_r = \frac{1.5 \times F_f \times l}{b^3} \tag{1}$$

Compressive strength tests were performed with the half samples disjointed in the previous flexure tests. The loading cell was progressively lowered at a constant ratio of 2400 ± 200 N/s until the mortar failure occurred. Compressive resistance (C_r) was determined in MPa by the quotient of Fc - the critical compressive force (N) - and the cross-sectional area subjected to compression (1600 mm^2).

All sample analysis was carried out in triplicate. Statistical analysis of data was performed with the software GraphPad Prism, version 7.0e. The statistically significant differences between samples for 95 % level of significance were evaluated by ANOVA tests.

3. Results and discussion

3.1 Mechanical tests

Figure 2 shows the flexural and compressive behaviour of all the formulated mortars. Both studied strengths showed a resistance decrease with the increase of the amount of tungsten mining residues incorporation. When 10 % of tungsten mining residues was incorporated in mortars production, it was possible to achieve a mechanical behaviour more similar to the reference mortar (100 % cement binder). However, both compressive and flexural strengths decrease 27 % and 18 %, respectively, in comparison to the REF mortar. Particularly, the flexural decrease may had occurred due to the stress concentrations induced by the filler particles [15], since tungsten mining residues have dissimilar properties when compared to cement. The ratio between cement and washed siliceous sand decrease, promoting the failure to occur sooner, when the load was applied.

Additionally, regarding compressive strength results, mining residues composition include chloride and sulphate contents [16], which may also had affected MR50>MR25>MR10 performance in sequence. Lower amounts of chloride will promote lower potential of corrosion (considering steel reinforced concrete applications), and reduced quantities of sulphates will reduce the formation of expansive complexes, and consequently, cracking issues [17]. Comparing to the REF, MR10 would be the most reliable alternative, regarding coating applications, instead of structural uses, once flexural strength decreases less significantly than compressive strength.

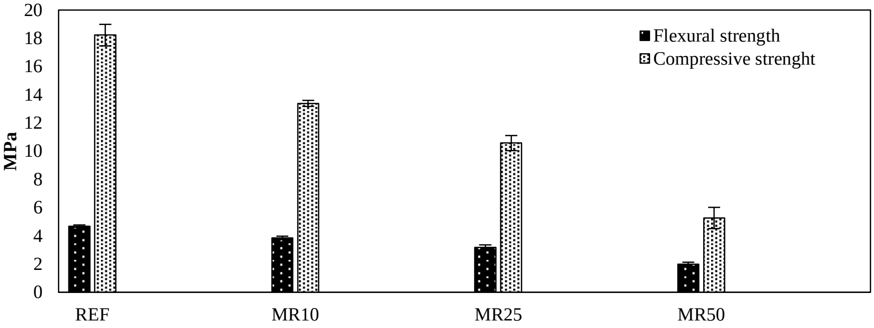


Figure 2. Flexural and compressive strength of the formulated mortars.

All tested mortars flexural and compressive strength results are statically significant different ($p < 0.0001$), corroborating the influence of mining residues incorporation and replacement percentage on the mechanical properties studied. Also, strengths decrease almost linearly with an increase of tungsten mining residues incorporation (Figure 3). The decrease was deeper in the compressive strength case (-1.34 MPa/ mining residues %) when compared to the flexural strength (-1.11 MPa/ mining residues %). The linear tendency was validated by the R^2 determined for flexural (~0.99) and compressive (~0.96) strength.

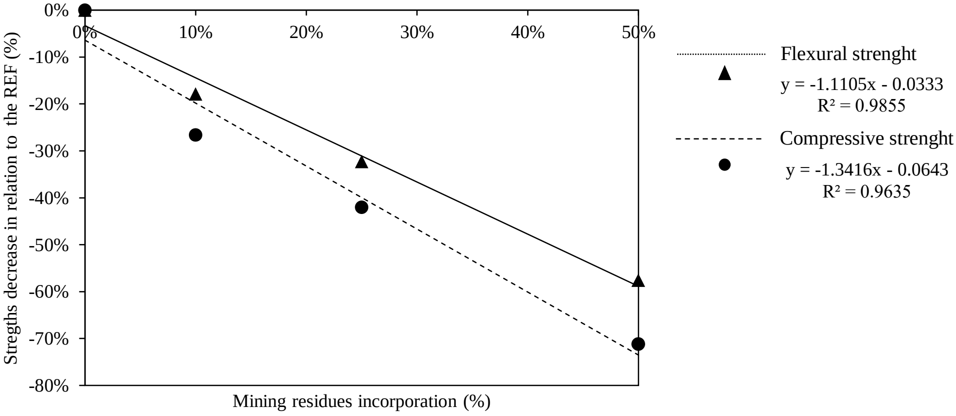


Figure 3. Flexural and compressive strength and mining residues percentage of incorporation in mortars linear tendency.

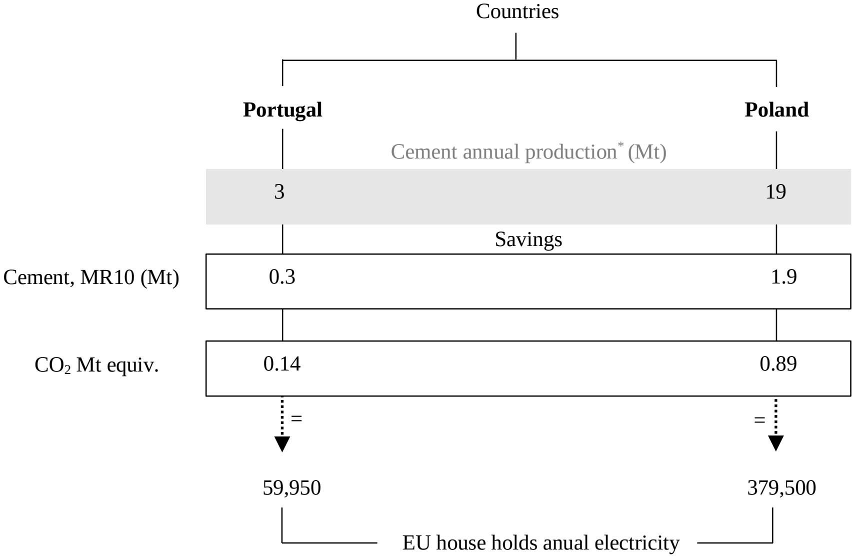
Mining residues properties can be enhanced through different techniques [18]. Electroremediation may decrease salts contents [17] and also other harmful compounds present in the sample [16], while thermal treatment may improve pozzolanic reactivity [19] of mining residues, promoting a larger application of the products within the construction industry.

3.2 Environmental assessment

The incorporation of alternative secondary resources in mortar production may be key factor for waste disposal and energy savings. Figure 4 illustrates how the replacement of 10 % of cement by secondary mining resources may minimize Portugal and Poland cement production issues.

The annual production of cement reported in 2019 for Poland was ~19 Mt [20] and for Portugal around 3 Mt [21]. Considering the formulations tested in the present work with properties more similar to the reference mortar, an approach of cement production savings was determined regarding MR10 case. Thus, having in mind a minimization in 10 % of cement production, Portugal may have savings ~0.3 Mt, while in Poland this value may reach almost 2 Mt, due to its higher production. Also, it will be possible to minimize the same amount of mining waste disposal, respectively.

In terms of carbon footprint, it is reported that the manufacture of 1 ton of cement yields ~0.471 t CO_2 [22]. Assuming this emission impacts, a 10 % lower cement production will promote to decrease an amount of 0.14 CO_2 Mt in Portugal, which is equivalent to ~59,950 EU house holds annual electricity needs (considering that 1 EU house has a carbon footprint equivalent to an average of ~2.35 [23]). On the other hand, in Poland CO_2 emissions may be avoided in ~0.89 Mt, translating in ~379,500 EU house holds annual electricity.



*data from 2019 annual reports

Figure 4. Portugal and Poland approach for cement production and CO_2 equivalents savings considering a cement replacement of 10 % (MR10).

4. Conclusions

Secondary mining resources have high disposal rates and features in terms of raw material, making them particularly attractive for enhancing building products. In the present work, different replacement percentages of tungsten mining residues in the binder content of cement-based mortars were tested to assess its influence on mechanical properties. Coupling cement and tungsten mining residues may also potentiate the decrease of primary resources need, while decreasing associated costs due to its exploitation, namely in industrial scale perspectives.

Higher ratios of tungsten mining waste incorporation in mortars formulation showed influence on mechanical properties in sequence 50 %>25 %>10 %, comparing with a mortar formulated under the conventional method with only cement as binder. In all cases, compressive strength (between 27 % and 71 %) was more affected than flexural strength (between 18 % and 56 %) in the final products, being the formulation with 10 % of cement replacement by tungsten mining residues more similar to the reference (flexural strength = 3.8 MPa; Compressive strength = 13.4 MPa), as expected.

Secondary resources incorporation on cementitious-based mortars may empower the sustainable growth of the involved sectors due to the minimization of waste disposal and CO_2 emissions. Considering an approach in Portugal and Poland, a CO_2 reduction of 0.14 and 0.89 Mt, respectively, was estimated, considering a minimization in cement production of 10 %.

Acknowledgements

This work has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 778045, and European Research Council under grant agreement No. ERC-2016-CoG 725034, as well as from Portuguese funds from FCT/MCTES through grant UID/AMB/04085/2020. J. Almeida acknowledges *Fundação para a Ciência e a Tecnologia* for the PhD fellowship PD\BD\135170\2017. The authors acknowledge Eng. Manuel Pacheco from Panasqueira mine for providing mining residues samples and Eng. Vitor Silva for the help during mortars formulation and analysis.

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Scientific journal article

A12 Life cycle assessment of mortars: a review on technical potential and drawbacks

T Santos, J Almeida, JD Silvestre & P Faria

Published in Construction and Building Materials journal (2020)

This article was published in Construction and Building Materials, Vol 288, T Santos, J Almeida, JD Silvestre & P Faria, Life cycle assessment of mortars: a review on technical potential and drawbacks, 123069, Copyright Elsevier (2021).

Construction and Building Materials 288 (2021) 123069

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Review

Life cycle assessment of mortars: A review on technical potential and drawbacks

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HIGHLIGHTS

- Mortars sustainability was reviewed through a life cycle assessment (LCA) approach.
- Results normalization improved the feasibility to compare diverse LCA studies.
- Global warming potential category is strongly affected during mortars production.
- Conventional binders' replacement by secondary resources alleviates mortars impacts.

ARTICLE INFO

Article history:
Received 19 October 2020
Received in revised form 11 February 2021
Accepted 12 March 2021

Keywords:
Environmental impacts
Life cycle assessment
Masonry mortar
Plaster
Render

ABSTRACT

The in-depth research on efficient processes and alternative constituents for mortars production has a lack on the quantification of their environmental impacts. This work presents a critical review of life cycle assessment (LCA) studies performed in the construction sector, namely related to mortars. The gaps and barriers of these methods and final results are discussed through an overview of the main achievements on mortars' environmental life cycle studies in Europe. Despite the future trends, LCA studies are more focused on cement-mortars and few researches on air lime, gypsum or earth mortar binders are reported in the literature.

Contents

Abbreviations: ADP-E, Abiotic resource depletion potential for elements; ADP-F, Abiotic resource depletion potential of fossil fuels; AP, Acidification potential of land and water; $Ca(OH)_2$, Calcium hydroxide; CC, Climate change; CEN, European committee for standardization; CO_2, Carbon dioxide; EIAM, Environmental impact assessment method; EC, European Commission; EP, Eutrophication potential; EPD, Environmental product declaration; FD, Fossil fuels depletion; GWP, Global warming potential; ILCD, International life cycle data system; ISO, International organization for standardization; LCA, Life cycle assessment; LCI, Life cycle inventory; LCIA, Life cycle impact assessment; PEF, Product environmental footprint; POCP, Formation potential of tropospheric ozone photochemical oxidants; ODP, Ozone depletion potential; OEF, Organizational environmental footprint guidelines.

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https://doi.org/10.1016/j.conbuildmat.2021.123069
0950-0618/

1. Introduction

During the past decades, concerns on environmental deterioration, energy consumption and materials scarcity have pushed the development of life cycle approaches aiming the environmental profiling of products [1] and the shift towards circular economy principles [2].

In the European context, around 50% of processed raw materials are applied in construction and approximately 30% of waste is generated during construction and demolition activities [3]. Also, the construction industry is on the top of the list of greenhouse gas contributors and is responsible for up to 40% of the global primary energy demand [4].

The focus on sustainable construction is now relevant in terms of buildings operational phase, energy demand, resources, emissions, waste generation, maintenance and the end-of-life stages. Thus, research on the assessment of the environmental impacts of building products over their entire life cycle have been intensified [3]. To evaluate and compare the advantages and drawbacks of emerging construction materials and products in an economic, social and environmental perspective, coupled with the chemical, mechanical and physical performance of the final products, with or without eco-friendly substitutes, methods should be optimized in order to provide reliable tools for the users.

Moreover, it is increasingly necessary for professionals, as architects, engineers, builders, decision-makers and investors, to analyze the impacts related to the entire life cycle of a building by means of empirical and comparable data, based on well-stablished indicators of building performance [5].

Life cycle assessment (LCA), an approach that evaluates the environmental impacts of products/services from raw material acquisition to waste disposal [6], has been providing new insights and led to changes in policy [1]. There is, therefore, a growing need to understand, critically appraise and apply the information that LCA studies provide, particularly in the construction sector regarding mortars' sustainability. Other tools may also be used for the sustainability assessment of buildings, regarding environmental, social and economic pillars. Nevertheless, the environmental dimension is the most used and standardized method worldwide [5].

The present work aims at reviewing the existing literature on mortar studies performed using LCA. Herein, the methodologies applied for different mortar types and goals are discussed, presenting their advantages and drawbacks, as well as mortars sustainability evolution overtime.

2. Mortars characteristics

Common mortars are porous materials produced with at least one mineral binder (agglomerate) and one aggregate (natural or artificial sand), which are knead with water. There are records of the use of earth as a building material since the prehistoric period [7] and of lime mortars before Christ [8]. From the middle of the 19th century, there was a gradual replacement of earth and lime by cement-based mortars [8].

Generally, sand is the mortar component incorporated in a higher ratio (in volume and/or weight). The binder and filler paste should be present in a suitable proportion to fill the voids promoted by the sand grains [9]. Nowadays secondary materials are being reused as artificial sand to increase mortars' circularity [10].

Numerous binders can be applied in mortars formulation as clayish earth, gypsum, lime (air, hydraulic, natural or formulated) or cement, generating composites with diverse technical properties and embodied energy [11]. The energy involved on mortar binder production depends on raw material extraction, milling processes, thermal treatment and the transportation involved. The production of cement and limes with hydraulic properties requires calcination temperatures of around 1,500 °C and 1,100 °C, respectively. Air lime requires lower temperatures for its production (about 900 °C), but still higher than the temperature required to produce current gypsum (about 120–180 °C) [12]. The clayish earth, as a mortar binder, does not require calcination, avoiding thermal energy consumption. Currently, cement is the second most used material worldwide (after water) and, to produce 1 ton of cement, approximately 900 kg of CO_2 are released into the atmosphere [13].

The replacement of traditional (with high environmental impacts) by alternative binders, which require less energy for production and transportation, would be advantageous in a technical and social way. Simultaneously, the use of recycled aggregates in mortars instead of natural sand can also bring benefits [14]. This would lead to a reduction in the extraction of raw material, in the energy consumption for thermal treatment and in a lower volume of waste for landfilling.

Additions and admixtures can enhance mortars' fresh or hardened properties, even at extremely low contents. The additions can be fibers, fillers – fine non-reactive aggregates, such as stone dust – or pozzolans – fine compounds rich in silica and/or alumina in a non-crystallized state that, in the presence of moisture, react with $Ca(OH)_2$, promoting its hardening even without contact with CO_2 [15]. The addition of natural/artificial fibers may contribute to reduce shrinkage and cracking. The natural fibers may have a broad origin [16]. Some examples are: (1) agricultural wastes, such as wheat, barley, oat straw [17] or rice husk; (2) textile industry waste, as cotton [18] or linen; (3) wood processing residues (e.g. wood chips, sawdust); (4) plant stems, as typha [19], hemp [20], flax or jute; (5) stem and ears of aquatic plants (e.g. reeds, planks or algae) [21] and (6) leaves and fruits of plants (e.g. olive [22], sisal, palms or coconut).

Mortars are frequently used as bedding mortars, to layer masonry units, to re-point masonry joints [23], to coat outdoor and indoor walls and ceilings (renders and plasters, respectively)

[24] or as screeds in floor. The selection of appropriate components, and of their proportion, to achieve adequate workability, strength and durability requirements, are key challenges for mortars production in a cost-effective way [25].

After decades where cement was the most common binder used for mortars, the study of raw earth and other clayish resources as construction materials is moving mortars development towards a cleaner production. There is a growing interest in earth as a building material, a resource composed by clay (binder), silt (filler), sand (aggregate) and coarser aggregates, including on earth mortars. For mortars that growing interest have been stimulated by their advantages: (1) based on a natural raw material; (2) available and with no shipping needs (local earth can be used); (3) low cost material; (4) reusable (considering no chemical stabilization); (5) non-toxic; (6) low CO_2 emissions associated to its manufacturing and application [26]. Although earth mortars have generally low mechanical resistances when compared to gypsum or cement mortars, they report high capacities to adsorb/desorb water vapor. Therefore, earth plasters can be key factor on relative humidity control, improving indoor air quality and energy performance in buildings [17].

Advances in solid waste management resulted in alternative materials to replace or add to conventional raw materials on construction materials production. These materials can be applied directly (e.g. as pozzolans, fillers and coarser aggregates with mortar sand size) or used after particle size and/or thermal treatments [27]. Thus, a wide range of secondary resources are being tested on mortars as feasible substitutes, namely to overcome cement carbon footprint, such as mining residues [28], construction and demolition wastes [29], sewage sludge [30], recycled plastic waste fibers [31] and ceramic wastes [32].

In the past, ceramic waste was used to partially replace aggregates and binders in air lime mortars due to pozzolanic characteristics of ceramic dust and for fragments reuse as aggregates in lime mortars [33]. This may potentiate the pozzolanic reaction between $Ca(OH)_2$ and the amorphous silica and alumina of the dust, resulting in an improved performance of the mortars [33], as well as a filler effect [34].

Mining residues have been applied in mortars with aggregate or binder functions. For instance, the introduction of mining residues were studied for bedding and coating mortars, where iron ore tailings replaced natural aggregates or lime [35], and where gold-mine tailings replaced Portland cement contents [36]. Base-metal tailings where also applied on rendering and masonry mortars, as aggregates, with minor risks of metals release [37]. These approaches provided mortars with improved mechanical properties when compared to the conventional production [35] and CO_2 -emissions minimization due to cement manufacture [36].

Table 1
Life cycle assessment standards.

Standard	Goal	Reference
ISO 14040:2006	Principles and framework	[38]
ISO 14044:2006 + A1:2017	Requirements and guidelines	[6]
ISO 14006:2020; ISO 14062:2002	Technical guidance reports on LCA applications	[39,40]
ISO 14020:2000; ISO 14063:2020	Communication of environmental performance	[41,42]
ISO 14025:2006; ISO 21930:2017; EN 15804:2012 + A2:2019	Requirements of the Environmental Product Declaration (EPD)	[43–45]
ISO 14064–1:2018; ISO 14064–2:2019; ISO 14064–3:2019	Greenhouse gas reporting and reduction	[46–48]
EN 15643–1:2010; EN 15643–2:2011; EN 15643–3:2012; EN 15643–4:2012	Guidelines on environmental, social and economic performance assessment on buildings	[49–52]
EN 15978:2011	Calculation method	[53]

3. Life cycle assessment requirements

3.1. Standards and guidelines

In the European context, standards were published regarding the evaluation of construction performance under sustainability pillars, as shown in Table 1. The adoption and development of LCA resulted from the release of ISO 14040 series standards. In 2006, and complemented later in 2008, the ISO 14044 [6] combined all the previous standards detailing LCA requirements and guidelines. Other standards aiming technical guidance for LCA studies were addressed in ISO 14000 series.

Furthermore, the European Commission developed an international life cycle data system (ILCD) including a life cycle inventory database and methodological guidelines [54]. Afterwards, the European Commission launched the Product Environmental Footprint (PEF) and Organizational Environmental Footprint (OEF) Guidelines as abbreviated versions of the ILCD. Herein, different categories of products/services are presented particularly for companies/organizations reporting on their environmental performance [55].

The impact categories considered for LCA studies of construction products are defined in EN 15804+A2 [45]. The EN 15643-2 [50] shows the principles and requirements for the environmental performance assessment of buildings considering technical and functional characteristics. Based on LCA and quantified environmental data related to buildings' environmental performance, EN 15978 [53] describes the calculation method and its interpretation for reporting and communicating the outcomes of an assessment.

3.2. LCA methodology

The LCA enables the estimation of cumulative potential environmental impacts under categories as global warming, ozone layer depletion, soil and water acidification, eutrophication, abiotic depletion for non-fossil resources and for fossil resources [45]. These cumulative environmental impacts, that result from all stages of a product life cycle, can also be used to determine the embodied energy. This method includes impacts not considered in traditional analyses, where mainly raw material extraction, material transportation and product disposal are considered.

Typically, the LCA process is systematic and divided into four phases, according to ISO 14040 [38] and ISO 14044+A1 [6] as seen in Fig. 1: (1) Goal and scope definition; (2) Inventory analysis; (3) Impact assessment; (4) Interpretation.

First, the product/process/activity system boundaries and the declared unit are defined and described. Then, the life cycle inventory (LCI) is developed aiming a detailed description of the product production process and the quantification of inputs and outputs from all unit processes included in the product life cycle (energy, water and materials use and environmental releases). The life cycle impact assessment (LCIA) phase provides the LCA results and additional information to complete and support the environmental importance of LCI results. Finally, the interpretation of the results is carried out, based on LCI and LCIA.

The LCIA stage evaluate the magnitude and significance of the potential environmental impacts of a product and should include [5]:

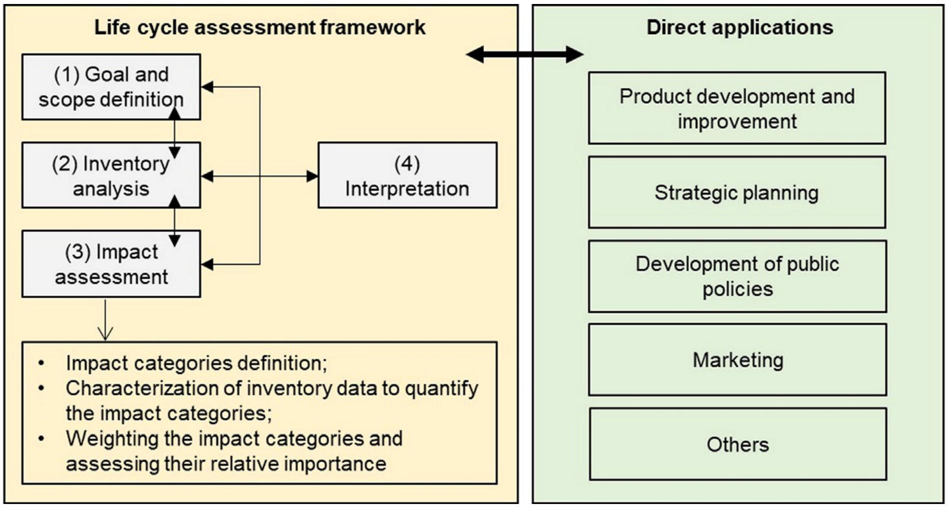


Fig 1. LCA phases (adapted from ISO 14040 [38]).

(1) Selection of the impact categories, category indicators and characterization models.
(2) Classification: each elementary flow of the inventory is assigned to the impact categories selected according to the material's contribution to the different environmental problems.
(3) Characterization: calculation of the results for each category indicator, where in each impact category several materials contribute with specific magnitudes.

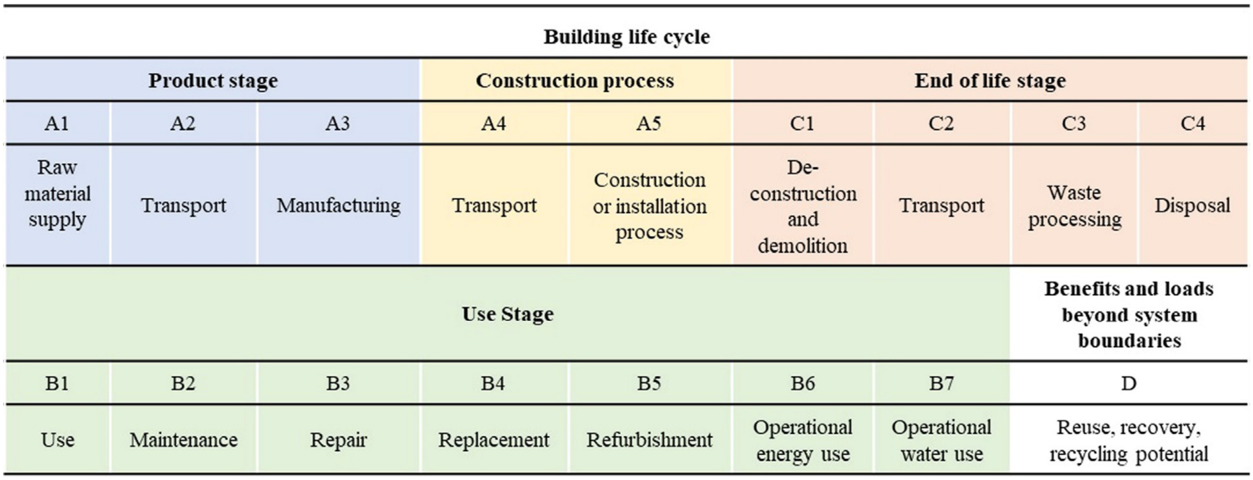
After the conclusion of the LCIA, it is necessary to carry out an analysis of the quality of the data presented, and this may require additional techniques and information to better understand the significance, uncertainty and sensitivity of the LCIA results. The latter can be necessary because LCA practice often justifies modelling choices and omissions.

The occurrence of uncertainties of different types and sources in LCA results is a fact. However, if managed, they allow the quantification and the improvement of the precision and robustness of studies. LCA practice often justifies modelling choices and omissions. The terms variability and uncertainty are often not distinguished or overarching one another, where variability is often included as one aspect of uncertainty [1].

This analysis helps to distinguish whether or not significant differences are present, to identify insignificant LCI results or to guide the iterative process of LCIA [6]. The specific techniques to analyze the quality of LCIA data are [6]:

(1) Gravity analysis: statistical procedure that identifies those data having the greatest contribution to indicator result (e.g. Pareto analysis). So, this data can be investigated with a higher priority to ensure that the right decisions are made.
(2) Uncertainty analysis: procedure to determine how the uncertainties from the data and assumptions calculated may affect the reliability of the LCIA. The uncertainty of the results can be characterized by ranges and/or probability distributions.
(3) Sensitivity analysis: procedure to determine how changes in data and methodological choices affect the results.

These techniques can be applied alone or combined, depending on the accuracy and level of detail necessary to fulfil the goal and scope defined for the LCA. Since LCA is an iterative process, the result of the analysis of the quality of LCIA data can lead to a revision of the LCI [6].



Building life cycle								
Product stage			Construction process		End of life stage			
A1	A2	A3	A4	A5	C1	C2	C3	C4
Raw material supply	Transport	Manufacturing	Transport	Construction or installation process	De-construction and demolition	Transport	Waste processing	Disposal
Use Stage							Benefits and loads beyond system boundaries	
B1	B2	B3	B4	B5	B6	B7	D	
Use	Maintenance	Repair	Replacement	Refurbishment	Operational energy use	Operational water use	Reuse, recovery, recycling potential	

Fig. 2. Different stages of the LCA of construction materials (adapted from EN 15978 [53]).

Site-specific data shall be used, as much as possible, instead of generic data, since the latter may not be sufficiently (geographically, temporally and/or technologically) representative of the product under analysis. For this reason, the gravity, uncertainty and sensitivity analysis are very important to determine the way forward and what data should be used or excluded from the LCA analysis.

Additionally, to convert the impacts of all categories in a common equivalent unit (normalization), equivalence or weighting factors can be applied during this step. The EN 15978 [53] defines the unit process for products and processes. In the construction sector, LCA generally includes production, use, construction and end of life stages. The benefits and loads beyond the system boundaries may be considered, as demonstrated in Fig. 2.

LCA requires system boundaries definition to limit the unitary processes. These boundaries can be defined as [45]:

(1) Cradle to gate: includes the supply of raw materials, transport, production and associated processes.
(2) Cradle to grave: includes the steps mentioned above, plus transport and installation in the building, use and maintenance, replacements, demolition and final disposal.
(3) Cradle to cradle: in addition to the previous stages, includes reuse, recovery and/or recycling.

Commonly, the analysis of the phases subsequent to the manufacture and application of product (B-C phases, Fig. 2) is based on scenarios, constructed and evaluated mainly based on generic data, which should be realistic and representative. This generic data can bring uncertainty to the results. So, these scenarios lack an uncertainly and sensitivity analysis.

The environmental product declaration (EPD) is a voluntary basis with quantified environmental data about individual products' life cycle, such as a dry pre-mixed mortar. EPD allows the comparisons between products that fulfil the same function [43] and is based on data related to a material/product LCA. The results for each impact categories are engaged in EPD that are verified by an independent scientific body or other related organizations. In the European context, there are several EPD programs for the construction sector, being INIES (France) and IBU (Germany) the most widely known. In Portugal, EPD are managed by DAPHabitat [56].

Both LCA and EPD must define the product declared or functional unit to guarantee the comparability of the LCA results between different studies. These units describe what is being analyzed since it provides a reference to which the inputs and outputs are related [38]. Regarding mortar studies, declared or functional units are commonly defined as 1 ton of dry mortar [57], 1 m^3 of pre-mixed mortar [58] and 1 kg of mortar or 1 m^2 of wall [59].

Allocation is also an important topic and, according to EN 14040 [38], consists of "*partitioning the input or output flows of a process or a product system between the product system under study and one or more other product systems*". The allocation should be used when the system involves several products – due to the need to split the environmental impacts of multiple industrial processes – and in industrial processes with recycling systems – when recycled or rejected intermediate products are used as raw materials (e.g. sub-products). Allocation procedures should be considered for comparisons between studies and systems. The differences on these aspects, between studies, must be clearly identified and reported, as it may influence the results.

The sum of allocated inputs and outputs of a unit process should be equal before and after the allocation. When several allocation procedures are possible to be used, a sensitivity analysis shall be carried out to illustrate the consequences of not using the selected practice [6].

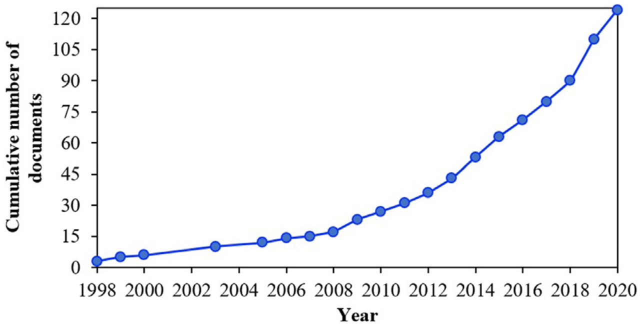


Fig. 3. Documents on LCA of mortars – evolution between 1994 and 2020 in the SCOPUS database, accessed in 01.10.2020.

EN 14044 [6] defines that, wherever possible, allocation should be avoided by: diving unit process to be allocated into two or more sub-processes, and collecting the input and output data related to these sub-processes; or expanding the product system to include the additional functions related to the co-products, taking into account the requirements of system boundaries. Also defines that when reuse and recycling activities are considered, it is crucial to consider that inputs and outputs associated to unit processes for extraction and processing of raw materials, and final disposal of products, are to be shared by more than one product system; reuse and recycling may change the inherent properties of materials in subsequent use; and specific care should be taken when defining system boundary with regard to recovery processes. If feasible, allocation should be applied preferentially in sequence: physical properties (e.g. mass); economic value (e.g. market value of recycled material in relation to primary material); and the number of subsequent uses of the recycled materials.

ReCiPe is an environmental impact assessment method (EIAM) commonly applied for the LCIA [60]. The group of authors include the developers of the CML 2001 method, where results are grouped in midpoint categories according to common mechanisms/accepted groupings, and of Ecoindicator 99, a top-down model that identifies environmental damage endpoints and shows the final result in a single score [61]. The CML 2001 and Ecoindicator 99 methods are LCIA methods that can play an important role in the results of LCA, depending on the type of analysis intended, due to their different approaches.

Studies have been conducted to assess and overcome mortars impacts. LCA allows to identify opportunities to improve the production of materials/products while reducing their environmental impacts. This approach provides a baseline to compare the performance of conventional or alternative raw materials, final products, processes, applications and end-of-life scenarios.

4. Environmental sustainability evaluation of mortars

4.1. Methodology

The scientific research status on LCA studies of mortars was performed using Scopus database (October 2020). With the search words "life cycle assessment", "mortar", "plaster" and "render", a total of 124 scientific papers were obtained from 1994 to 2020 across Europe, with a more pronounced increasing trend in the scientific community during the last few years (Fig. 3). The dominant research areas are engineering (30.7%), environmental science (21.2%) and energy (11.3%), being Germany, Spain and Italy the top 3 countries. The documents published are mainly in article format (57.3%). This work is based on the referred sample of scientific literature.

Table 2
Scope and purposes of reported LCA studies of mortars.

Scope	Purpose	Reference
Supplementary/ Symbiotic cementitious materials	• Comparison of mortars with different replacement ratios of secondary resources - recycled concrete • Alternative secondary resources vs conventional production - ash recycling in Portland cement production as clinker substitution, earth vs industrial plasters • Alternative resources incorporation - woody biomass types, sewage sludge, recycled fine aggregates from construction and demolition waste, sanitary ware, glass fiber reinforced polymer, forest biomass, textile fibers, LCD scrap	[10,26,57,58,64–74]
Energy performance	• Comparison of alternative fuels with fossil fuels used on binder's production • Thermal insulating – alternative lightweight materials (e.g. cork waste) vs reference mortars • Comparison of alternative mortars and paints - aerogel-based thermal renders for external walls of buildings	[69,75–77]
Type of construction	• Mitigation potential of specific mortar materials/resources when employed at real scale (e.g. urban houses) in specific regions of the world - limestone, lime, fired brick, solid cement blocks and earth blocks	[59,78,79]
Material applications	• Compare the same material for different purposes - biomass fly ash for cement replacement vs alkaline material • Compare the same material for different structural options - local replacement of damaged masonry, mortar injection, steel chain installation, grid-reinforced • Alternative concrete mixtures comparison with ordinary reference mixtures - steel slags on industrial pavement and pervious paving blocks, heavy-weight concrete, shotcrete and ready-mixed repair mortar	[80–83]
Leaching	• Comparison between mortars with different binders to predict the longevity of the rendering (e.g. cement vs lime)	[84]

4.2. LCA studies

The most common software applied on LCA studies are SimaPro, Gabi, Umberto and OpenLCA [62]. Umberto software is useful to evaluate the carbon footprint of a product, building or service according to ISO 14040 [38] and ISO 14044 + A1 [6], although with minor applications on construction materials analysis [63]. The OpenLCA platform, which is a free open source, can provide fast and reliable determinations on sustainability assessment and/or LCA [62]. Additionally, companies have developed their own software, making the standardization of these approaches difficult for comparison with other works [1].

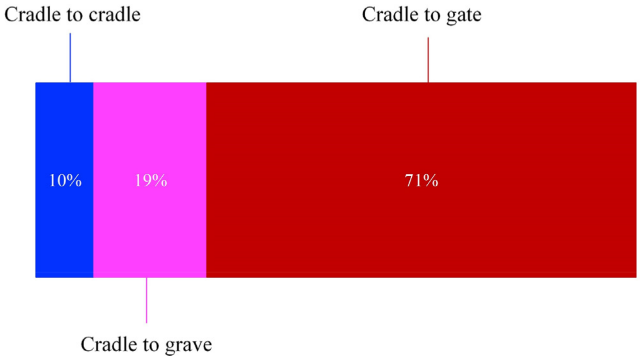


Fig. 4. System boundaries distribution of 21 mortars' LCA studies, from 1994 to 2020, found in literature.

Table 2 presents some examples of scope and purposes for mortar studies reported in literature, emphasizing the wide range of LCA studies.

Additionally, the boundaries defined in the literature for mortar systems are presented in Fig. 4. Considering that only 21 of the 124 scientific documents analyzed in this work reported the boundaries of the system processes, the most common approach was cradle-to-gate (71%). Although the need to deep reuse/recycling strategies for materials being on the top of the list, few studies consider a cradle-to-cradle approach, probably due to unavailable data and other difficulties on determining the benefits involved in the scenarios from gate to grave.

4.3. Life cycle inventory

LCA requires an inventory analysis to ensure a representative assessment of all inputs and outputs of mass and energy across the whole phases of the product life cycle, notated by LCI [57]. The LCI should include site-specific data for the product analyzed by measurements, calculations or estimations, which can be complemented by LCI database and EPD [1].

The Ecoinvent database contains datasets as an average for a region [85]. The data selection for modelling each process is a major issue since it varies greatly between regions and production plants. The compilation of a credible LCI is essential since LCA relies heavily on the availability and completeness of LCI data. The development of the inventory should be detailed to be reproductible by an independent practitioner [57].

Considering each unit process that is included within the system boundary, quantified data about the raw materials, energy and fuels needed for the processes involved, and of transportation and emissions across the production chain shall be collected from available and reliable sources [86].

System inputs may include resources (e.g. stone, water), services (e.g. transportation) or energy supply, and the use of maintenance materials (e.g. lubricants for equipment). The outputs can include products, co-products/waste and releases to air, water and soil [6].

The requirements on data quality must be specified through references and details about the data collection process (e.g. time when data was collected/analyzed). Data from specific sites or representative averages should be used for the unit processes that contribute to the major mass and energy flows of the system processes. If possible, data from sites should be used for unit processes that are considered to have environmentally relevant inputs/outputs [6]. In LCIA, the operational steps outlined in Fig. 5 should be performed.

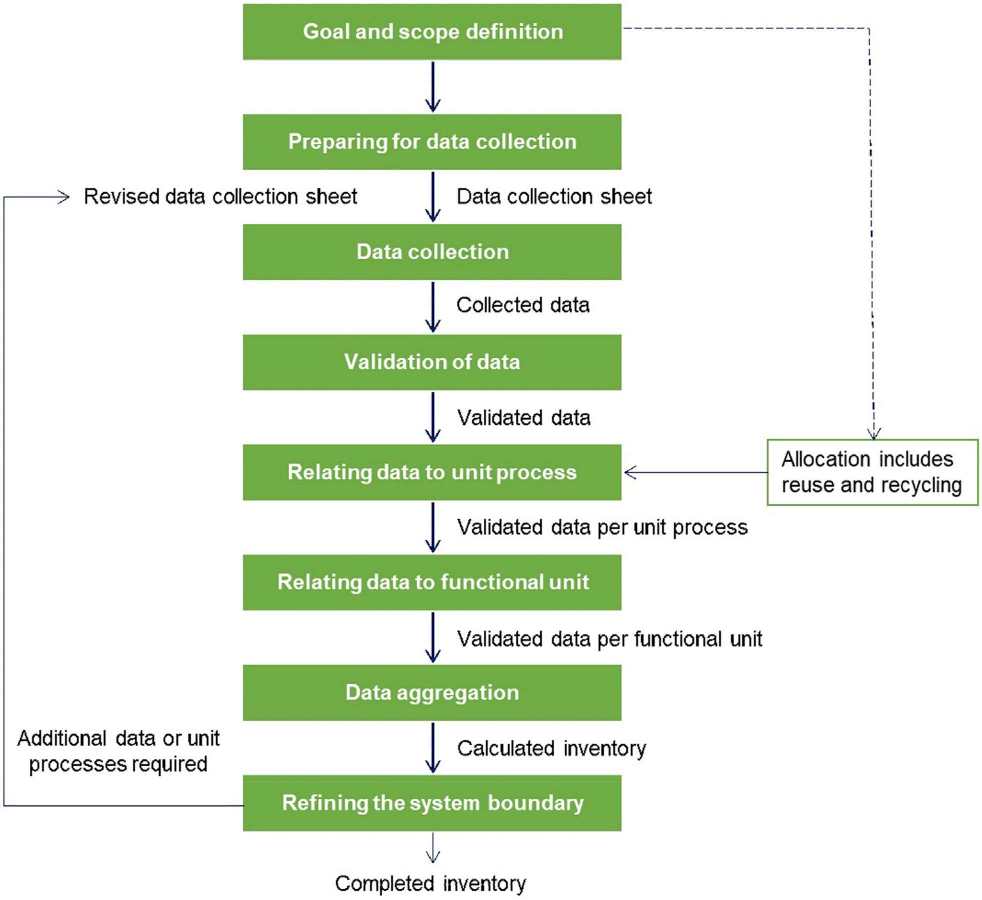


Fig. 5. LCA steps (based on EN ISO 14044 [6]).

4.4. Impact assessment and results interpretation

Cement-based mortars are the most common construction products reported by LCA studies. After analyzing several studies, those with comparable declared units and impact categories and with quantitative results were selected. Examples of studies found in literature aiming the introduction of alternative materials to replace cement in mortars and their impacts in the considered categories are presented in Table 3. Fig. 6 and Fig. 7 show a comparison of the results from the mortars studies presented in Table 3, according to the declared unit used. Only GWP and ADP-F were considered since both categories have often been included in the works developed in this field, demonstrating to be the most relevant environmental categories.

The works analyzed differ in terms of declared or functional unit, databases considered, allocation methods, impact categories, normalized data and regional differences. Even tough, the use of a similar declared unit for the results provides a way to compares the figures from all these LCA studies. But it is crucial to have in mind the methodology applied (e.g. database selected, software used), in order to explain the variability found in the results, as presented in the next paragraphs. The variability from a group of LCA studies can be considered to improve the accuracy of the LCI data used and to present a more accurate analysis of the results. In this case, variability indicators (e.g., average and standard deviation) are not presented in Fig. 6 and Fig. 7 because of the significant difference between the results of the studies.

Moreover, the estimations of each approach have intrinsic uncertainties, but these are more difficult to identify without more detailed information about each study. Nevertheless, the uncertainty related to parameters, models and choices, and also the spatial, temporal and objects/sources variability, should be taken into account during the LCA interpretation phase of each case study.

Moreno-Juez *et al.* [69] performed an analysis from a cradle to gate perspective using the OpenLCA software and considering the CML impact assessment method to calculate the environmental impacts of several mortar mixing solutions with ultrafine recycled concrete. For the same LCA purpose, Moropoulou *et al.* [58] used the Eco-indicator 95 method. In the case of Farinha *et al.* [10] and Teixeira *et al.* [82], the impacts' assessment was carried out through an cradle to gate analysis using SimaPro software. Therefore, different methods and software can be used to analyze environmental impacts for the same purpose.

Farinha *et al.* [10] and Teixeira *et al.* [82] analyzed a vast number of mortars. Table 3 shows the impacts of each category for the reference mortar (REF) and the minimum and maximum value obtained for the remaining ones (modified mortars). Herein is observed that REF mortars presented the highest environmental impact in all categories. The exception occurred in GWP, EP and ADP-E impacts, where mortars with sanitary ware presented impacts equal (1.66×10^2 kg. $CO_{2\text{-eq}}$ for GWP, 5.40×10^{-2} kg. $(PO_4)^{3-}_{\text{-eq}}$ for EP and 2.82×10^{-4} kg.$Sb_{\text{-eq}}$ for ADP-E) to the reference mortar in Farinha *et al.* [10]. In ADP-F category, the impact of modified mortars was higher than the reference mortar: mortar with forest biomass ash from Farinha *et al.* [10] and with 50% of biomass fly ash from Teixeira *et al.* [82]. In Moreno-Juez *et al.* [69] it is also observed a decrease in the environmental impacts of modified mortars with ultrafine recycled siliceous or limestone concrete (2.14×10^{-5} kg.CFC-11$_{\text{-eq}}$ for ODP, 1.37×10^{0} kg.$SO_{2\text{-eq}}$ for AP, 3.8×10^{-1} kg.$(PO_4)^{3-}_{\text{-eq}}$ for EP, 5.22×10^{-2}–5.19×10^{-2} kg.Ethene$_{\text{-eq}}$ for POPC, 2.88×10^{-4}–2.87×10^{-4} kg.

Table 3
Examples of LCA applied to cement-based pre-mixed mortars production with secondary resources.

Mortar composition	Impact category							Declared units
	GWP ($kg.CO_{2\text{-}eq}$)	ODP ($kg.CFC\text{-}11_{\text{-}eq}$)	AP ($kg.SO_{2\text{-}eq}$)	EP ($kg.(PO_4)^{3-}_{\text{-}eq}$)	POCP ($kg.Ethene_{\text{-}eq} \times 10^{-2}$)	ADP-E ($kg.Sb_{\text{-}eq}$)	ADP-F (MJ)	
Mortars with addition of ultrafine recycled siliceous or limestone concrete (obtained by diesel or biomass fuel*) to replace 5% of cement [69]	7.72×10^2 (REF, diesel and biomass)	2.25×10^{-5} (REF) 2.14×10^{-5} (diesel and biomass)	1.44×10^0 (REF) 1.37×10^0 (diesel and biomass)	4.0×10^{-1} (REF) 3.8×10^{-1} (diesel and biomass)	5.45 (REF) 5.22 (diesel) 5.19 (biomass)	3.02×10^{-4} (REF) 2.88×10^{-4} (diesel) 2.87×10^{-4} (biomass)	2.88×10^3 (REF) 2.80×10^3 (diesel) 2.74×10^3 (biomass)	1 ton of mortar
Mortars with different types of binders and with or without metakaolin (mix 1: hydrated air lime and sand; mix 2: hydrated air lime, metakaolin and sand; mix 3: cement and sand) [58]	Mix 1 ≈ 1.7×10^{-1} Mix 2 ≈ 1.6×10^{-1} Mix 3 ≈ 2.3×10^{-1}	-	Mix 1 ≈ 2.3×10^{-4} Mix 2 ≈ 1.6×10^{-4} Mix 3 ≈ 6.6×10^{-4}	Mix 1 ≈ 2.4×10^{-5} Mix 2 ≈ 2.0×10^{-5} Mix 3 ≈ 1.22×10^{-4}	-	-	-	1 ton of mortar
Mortars with industrial wastes (sanitary ware, glass fiber reinforced polymer, forest biomass ashes, and textile fibers) replacing sand and/or cement [10]	1.66×10^2 (REF) 1.31×10^2 – 1.66×10^2 (modified mortars)	8.45×10^{-7} (REF) 2.51×10^{-7} –8.41×10^{-7} (modified mortars)	3.40×10^{-1} (REF) 2.53×10^{-1} –3.35×10^{-1} (modified mortars)	5.40×10^{-2} (REF) 4.06×10^{-2} –5.40×10^{-2} (modified mortars)	2.99 (REF) 2.30–2.96 (modified mortars)	2.82×10^{-4} (REF) 2.39×10^{-4} –2.82×10^{-4} (modified mortars)	3.19×10^2 (REF) 2.22×10^2– 3.25×10^2 (modified mortars)	1 m^3 of mortar
Mortars with addition of superplasticizer, replacement of cement or hydrated air lime by coal fly ash and biomass fly ash [82]	5.66×10^2 (REF) 3.31×10^2 – 3.66×10^2 (modified mortars)	2.70×10^{-5} (REF) 1.87×10^{-5} –2.11×10^{-5} (modified mortars)	1.29 (REF) 8.1×10^{-1} – 9.6×10^{-1} (modified mortars)	3.26×10^{-1} (REF) 2.19×10^{-1} –2.39×10^{-1} (modified mortars)	5.20 (REF) 3.34–4.23 (modified mortars)	-	3.06×10^3 (REF) 2.02×10^3 – 4.23×10^3 (modified mortars)	1 m^3 of mortar

Notation: GWP - Global warming potential; ODP – Ozone depletion potential; AP – Acidification potential of land and water; EP – Eutrophication potential; POCP – Formation potential of tropospheric ozone photochemical oxidants; ADP-E – Abiotic resource depletion potential for elements; ADP-F – Abiotic resource depletion potential of fossil fuels; REF – reference mortar; *ultrafine recycled siliceous or limestone concrete were produced using different energy sources (diesel and biomass fuel) in order to assess their impacts on the final product.

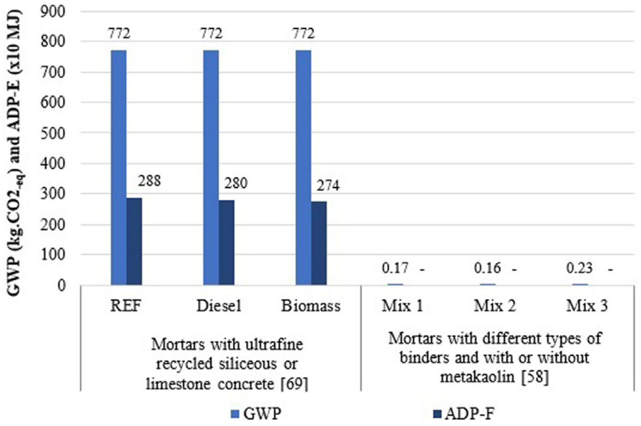


Fig. 6. Comparison of the results from studies with declared unit of 1 ton of mortar (adapted from [58,69]).

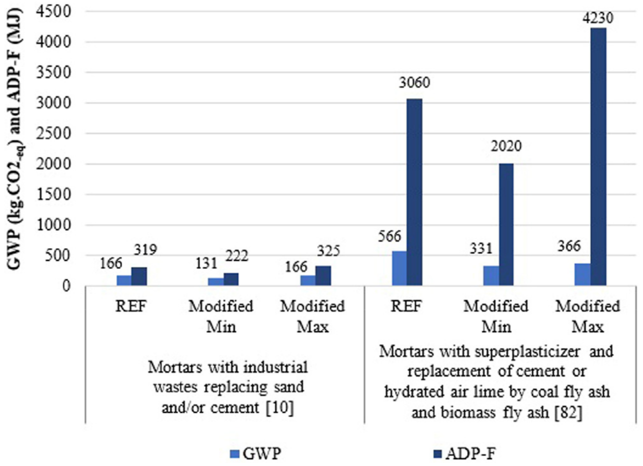


Fig. 7. Comparison of the results from studies with declared unit of 1 m^3 of mortar (adapted from [10,82]).

$Sb_{\text{-}eq}$ for APD-E, 2.80×10^3–2.74×10^3 MJ for ADP-F) compared to REF (2.25×10^{-5} $kg.CFC\text{-}11_{\text{-}eq}$ for ODP, 1.44×10^0 $kg.SO_{2\text{-}eq}$ for AP, 4.0×10^{-1} $kg.(PO_4)^{3-}_{\text{-}eq}$ for EP, 5.45×10^{-2} $kg.Ethene_{\text{-}eq}$ for POPC, 3.02×10^{-4} $kg.Sb_{\text{-}eq}$ for APD-E, 2.88×10^3 MJ for ADP-F).

The studies reported have different declared units (1 ton and 1 m^3 of mortar). Since mortars have different densities, generally not defined by the authors, the results should be analyzed individually. From Table 3, ultrafine recycled siliceous or limestone concrete obtained by diesel or biomass fuel additions to replace 5% of cement promoted the highest GWP (772 $kg.CO_{2\text{-}eq}$) observed. On the other hand, mortars with alternative binders and with or without metakaolin achieved approximately 0.2 $kg.CO_{2\text{-}eq}$ on the GWP category. Both studies were conducted considering the same declared unit (1 ton of mortar). The use of ultrafine recycled siliceous or limestone concrete obtained by diesel or biomass fuel did not promote any change in the GWP. The use of distinct energy sources (diesel or biomass fuel) only impacted negatively POCP, ADP-E and ADP-F categories. Mortars with hydrated lime and cement as binder, and with or without metakaolin, presented low acidification (≈2–7×10^{-4} $kg.SO_{4\text{-}eq}$) and eutrophication potential (≈0.2×10^{-4}–1.2×10^{-4} $kg.(PO_4)^{3-}_{\text{-}eq}$). The incorporation of industrial wastes, such as sanitary ware, glass fiber reinforced polymer, forest biomass ashes and textile fibers, to replace sand and/or cement promoted lower impacts in the categories analyzed [10], in comparison to mortars with superplasticizer additions and cement or hydrated lime replacement by coal fly ash and biomass fly ash for 1 m^3 of mortar [82]. The categories that show the major differences on the results presented were: GWP (131–166 and 331–556 $kg.CO_{2\text{-eq}}$, respectively), ODP (0.0251–0.0845 and 1.87–2.70 $\times 10^{-5}$kg.CFC-$11_{\text{-eq}}$, respectively), EP (4.06–5.40 and 21.6–32.6 $\times 10^{-2}$ $kg.(PO_4)^{3-}_{\text{-eq}}$, respectively), and ADP-F (222–325 MJ and 2020–4230 MJ, respectively).

Moropoulou *et al.* [58] analyzed a traditional hydrated air lime mortar with and without metakaolin. Traditional mortars were reported as more sustainable options compared to cement-based mortar, since the latter had higher impacts on GWP, AP and EP categories. For all impact categories, the hydrated lime mortar with metakaolin (mix 2) had the lowest impacts, while the cement mortar (mix 3) had the highest ones. This is explained by the fact that cement production is a more energy intensive process, with temperatures of approximately 1,300 °C and, consequently, with larger CO_2 emissions, in comparison to air lime, that is obtained at a lower firing temperature and with CO_2 capture when drying. The use of about 5% of metakaolin, obtained by firing kaolin at ≈700–800 °C [58], to replace hydrated air lime promoted a lower environmental impact when compared to the same mortar without metakaolin. This impact decrease can also be justified by the energy required to produce hydrated lime, since air lime is obtained at 900 °C.

The ultrafine recycled siliceous/limestone concrete replacing cement [69] promoted mortars with higher impacts on GWP, AD and EP, when comparing with mortars with different binders and with or without metakaolin [58], with the same declared unit of 1 ton of mortar. This can be justified by the way LCA results are presented, since Moreno-Juez *et al.* [69] and Moropoulou *et al.* [58] applied different impact assessment methods (CML and Eco-indicator 95 method, respectively).

The industrial wastes replacing sand and/or cement [10], the replacement of cement or hydrated lime by coal fly ash and biomass fly ash and the addition of superplasticizer [82] showed similar impacts (declared unit of 1 m^3 of mortar). The replacement of cement or hydrated lime by coal and biomass fly ash and the addition of superplasticizer presented the highest impact in all categories considered, namely regarding ADP-F. The need of thermal processes to convert the raw material into ash involves the highest energy impacts of the process.

Other LCA studies aiming to compare mortars produced with different binders are reported. Environmental impacts of earthen and conventional industrial mortars (cement and hydraulic lime) were compared in terms of energy demand, CO_2 emissions and ReCiPe impact categories [26]. Table 4 shows an overview of the major impacts from these three approaches. Herein it is possible to confirm that cement and hydraulic lime mortar production implies a higher energy demand and, consequently, higher CO_2 emissions are associated. Both binders are considered more harmful to climate change issues. Contrarily, an earth mortar showed lower energy demand and CO_2 emissions, with major impacts on fossil fuels depletion.

Table 4
Comparison of energy demand, CO_2 emissions and impact categories more affected by the use of cement, hydraulic lime and earth as mortar binders (adapted from [26]).

Mortar binder	Energy demand	CO_2 emissions	Categories more impacted
Cement	++	++/+++	CC > FD
Hydraulic lime	+++	+++	CC > FD
Earth (ochre/yellow)	+	+	FD > CC

Notation: +++: high proportion; ++: medium proportion; +: low proportion; CC: Climate change; FD: Fossil fuels depletion.

5. Discussion and research perspectives

During the past decades, the minimization of environmental impacts in the construction sector is receiving increased attention by researchers, policymakers and companies. The main focus is on energy consumption and alternative materials use, while the application of the concept of life cycle thinking is growing [87].

The LCA application in the construction sector, as a strategy to reduce its environmental impacts, is often identified as complicated and time-consuming [5]. Most of the EIAM commonly result in a set of categories that are not easily understood or interpretable. LCA requires an intensive use of data to estimate the potential impacts of the entire life cycle of a product, from resource extraction, through production, use and recycling. Despite these limitations, LCA is a tool that allows the identification of "critical points" and opportunities to improve the product environmental performance in the various stages of its life cycle.

LCA also provides a platform to support professionals from the construction industry and decision markers, in the search for sustainable strategies of consumption and production, by designing or redefining products. Thus, relevant environmental performance indicators should be selected for marketing activities and EPD development [5,38].

As a decision supporting tool, LCA results should be presented in a clear and simple way. In the present study, the presentation of the results is very broad, due to the wide-ranging methods available, limiting the comparison of mortars from different studies found in the literature. The main drawback identified in current practices of LCA is the generation of significantly different results by the application of different methods to identical cases, such as carbon footprint study vs studies with a set of more differentiated impact indicators [87]. In fact, different methods can allocate dissimilar relevance to properties/impacts, resulting in diverse results, namely regarding the actions to reduce the environmental burdens.

The definition of the declared unit of the study is not always reported in the publications, as well as the system boundaries, also limiting the comparisons between LCA approaches. The selection of different declared units in the studies reviewed also turned difficult to compare results between them. In addition, several authors presented drawbacks in boundary scoping, methodology framework, data inventory and practices, which compromise LCA as a decision making support tool for sustainable building design [88].

Another constraint is the presentation of LCA results in non-absolute values by some publications. These studies do not express the impacts of a product/service but might be useful to compare them.

The comparison of LCA studies is only feasible when mortars fulfil exactly the same function in accordance with their goal and scope definitions (e.g. mortars applied as plasters). Additionally, the quantification of local impacts should be improved through risk assessment-based tools, as generally environmental damage is calculated on global scale. However, common trends and specification of some aspects, namely regarding impact categories and declared units, could be clearly identified, turning the comparisons between studies feasible in a general way.

The combination of data from production and unit processes allows the development of production inventories in terms of materials and, in greater detail, the inventories of mortars, namely regarding the equipment used for the production processes. This should result in a clear LCI that match the reality of the process, promoting the reproducibility and the identification and quantification of the inputs/outputs related to the mortars' life cycle.

Summing-up, LCA can be evaluated under three premises: (1) comprehensiveness; (2) "best estimate" principle; (3) better scenario [1]. All these evidences can present strengths and limitations on mortars' LCA studies, as presented in Table 5.

The bibliometric analysis of LCA research applied to mortars showed that cement-based mortars studies predominated, with or without additions and/or substitutions. Only few studies were related to other types of binders, such as clayish earth. Currently, and in IBU [89] and DAPHabitat [56] programs, only approximately 13 EPD on mortars/plasters were identified. The lack of EDP constrains the availability of data for inventories and the comparison of results.

In addition to the environmental impacts of products and/or construction solutions, the cost of these strategies is also important. Monetization expresses the relative importance of an environmental impact category in a monetary value and can be determined based on the associated costs (e.g. damage costs using market prices) or the cost that people are willing to pay to avoid a particular environmental impact [5]. Although a solution has positive effects on environmental impacts, it may introduce extremely high costs to the system, making the application unfeasible. Thus, a balance between the assessment of the environmental and economic impact of a product should be obtained.

Durão *et al.* [5] presented a summary of the monetization approaches and methods/weighting sets that were developed to weight the environmental impacts resulting from LCA studies (e.g. Eco-costs, Ecotax 2002, Ecovalue 08).

Considering standard buildings, the use phase (when heating and/or cooling are needed) contributes to above 90% of the total environmental burdens. New buildings built considering present requirements for comfort are more energy efficient, turning other phases of the life cycle more relevant, such as the selection of materials, construction, end-of-life and water use [87]. Thus, an in-depth research on these topics should be conducted, coupled with economic issues, the improvement of data quality and statistical analysis.

Table 5
Strengths and limitations of LCA mortars studies.

Premise	Strengths	Limitations
Comprehensiveness	Life cycle perspective and coverage of environmental issues (through impact categories definition) allows the comparison of environmental impacts of mortars systems that are made up of several processes, resource uses and emissions.	Simplifications in the activities/processes, and generalizations from standards or available data in world's leading databases, are needed for modelling the mortar system and to quantify the environmental impacts. Uncertainties in mapping of resource uses/ emissions and on modelling their corresponding impacts (calculated by impacts aggregation over time and space).
"Best estimate" principle	In the context of comparative assessments, unbiased comparisons since the same level of precaution is applied throughout the impact assessment modelling.	LCA mortars' production models are based on the average performance of the processes and do not support the consideration of rare risks.
Better scenario	LCA is suitable for answering which mortar is better for the environment.	LCA cannot corroborate if a mortar product/process is environmentally sustainable, in absolute terms, only because of having lower environmental impacts than another mortar.

The impacts from off-site generation of electricity or processing of raw materials must be considered when selecting the Best Available Techniques (BAT) for plant facilities [90]. The measures recommended by BAT are related to the improvement of the output and energy efficiency of raw materials production process through replacement of the old equipment with new one, less energy-consuming, in order to minimize CO_2 and other greenhouse gases emissions [91]. Thus, BAT can contribute to decrease energy consumption and CO_2 emissions in the European Union's construction industry, where the environmental benefits of BAT implementation can also be quantified using LCA.

The use of different impact categories, depending on the methodology applied in a study, often difficult the comparison between studies and products. Defining the impact categories/subcategories that must be analyzed for a single or group of mortars could be advantageous. The standardization on outcomes presentation leads to a better understanding and comparison of the results.

In addition to the mortar life cycle analysis data, Moreno-Juez *et al.* [69] also presented a normalization of the results based on European data. The normalization factor used was the European emission considering a citizen emission unit in the year 2000, which was proposed by CML. These results showed that GWP is the most affected category from the production of cement-based mortars in all individual systems. Despite presenting less expression when compared to GWP, AP and ADP-F categories are also affected by the production of cement mortars. Additionally, the ODP was the category with lower impacts associated. On the other hand, the reference mortar presented high impacts in all categories. Similar results were obtained by Moropoulou *et al.* [58], considering the contribution analysis of each impact category (GWP, AP and EP) on the total environmental score. Herein, GWP was the most affected category followed by AP. The inverse trend was observed in the cement mortar (mix 3), where AP showed the highest impacts.

Currently, it is imperative to rethink the use of cement as major binder and the possibility of integrating by-products into mortars, at least for some types of applications. Farinha *et al.* [10] performed the LCA of cement mortars with incorporation of industrial wastes. The binder was the component that showed the highest impacts on GWP: cement contributed more than 85% and natural sand only 8%. When natural sand and/or cement were replaced by industrial wastes, there was generally a decrease in the GWP compared to the reference mortar. On the other hand, sand and admixtures from these mortars contribute significantly to increase ADP-F impacts: sand was responsible for 40–60% and admixtures for about 30% of the total emissions. The waste also pursued the impacts increase on ADP-F due to the transport involved, since transport is the main factor related to the fossil fuels component [10]. In general, 16 of the 19 mortars analyzed by these researchers showed, in all impact categories, a performance equal to or better than the reference cement mortar. Also, the transportation of industrial waste influenced the LCA results of some mortars. Thus, local waste should be considered as a first option to alleviate shipping impacts. The availability of resources and the pressure on their exploitation is also an important indicator that should be deeply addressed in future LCA practices.

Construction materials may be able to reabsorb CO_2 during their lifetime, decreasing the impacts of the overall life cycle. This is also the case of mortars, but none of the studies analyzed focused this aspect. This should be addressed by further LCA studies by quantifying the benefits that may came and the potential to achieve a carbon neutral construction product, for instance.

6. Conclusions

LCA is an approach with few decades of development and application, although over the years this methodology and applications have matured in a scientific perspective. LCA is crucial for mortars optimization since these are buildings products with many applications in modern construction and throughout the service life of buildings. Hence, mortars with less environmental impacts can significantly reduce the embodied energy in buildings.

In the present work, the LCA general methodology was synthetized and LCA studies of mortars were discussed in terms of goals, specific methodologies, results, limitations and strengths, as well as their contribution to support decision making.

SimaPro, Gabi, Umberto and OpenLCA are common software used for LCA studies. They offer many options in terms of methodologies and quantification of impacts. The main focus of mortars' LCA has been cement-based composites, although, currently, there are still few studies regarding mortars.

Typically, GWP is an impact category considered in most of the studies reviewed. Nonetheless, impact categories such as ODP, EP and ADP are also often analyzed in LCA studies.

The use of alternative materials, as a replacement or addition to conventional raw materials in the mortars manufacture may represent an environmental benefit that can be quantified by LCA. This may empower materials' circular economy and provide mortars with increased performance properties, namely due to eventual pozzolanic characteristics and filler effect. The reduced need of treatments and transport of materials, that are the most energy consuming steps of materials processing, turns the use of clayish earth advantageous in a social, economic and environmental way, compared to other types of mortars. Nonetheless, earth mortars may not be as efficient as other mortars to all kind of applications.

LCA presents drawbacks, namely the use of subjective criteria, limitations on scientific knowledge about impacts, lack of a consolidated method, data access and analysis difficulties. This could be overcome by a clear and uniform LCA report with the data needed to reproduce the study. The development of specific databases for mortars with real data could be key factor to improve LCA studies. A complementary economic analysis could show if the best solution in environmental terms is also cost-efficient.

CRediT authorship contribution statement

T. Santos: Conceptualization, Methodology, Data curation, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. **J. Almeida:** Conceptualization, Methodology, Data curation, Formal analysis, Visualization, Writing - original draft, Writing - review & editing. **J.D. Silvestre:** Writing - review & editing, Visualization, Supervision. **P. Faria:** Conceptualization, Writing - review & editing, Visualization, Supervision.

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.

Acknowledgements

The authors acknowledge the Portuguese Foundation for Science and Technology (FCT) for the support given to CERIS and CENSE, through the strategic projects UIDB/04625/2020 and UIDB/04085/2020, respectively. T. Santos and J. Almeida also thank FCT for their PhD fellowships SFRH/BD/147428/2019 and PD/BD/135170/2017 (the second from the EcoCoRe Doctoral program), respectively.

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Scientific journal article

A13 Life cycle assessment of mortars produced partially replacing cement by treated mining residues

J Almeida, P Faria, A Santos Silva & AB Ribeiro

Published in Applied Sciences (2021)

This article was published in Applied Sciences, Vol 11, J Almeida, P Faria, AB Ribeiro & A Santos Silva, Life cycle assessment of mortars produced partially replacing cement by treated mining residues, 7947, Copyright MDPI (2021).

applied sciences

MDPI

Article

Life Cycle Assessment of Mortars Produced Partially Replacing Cement by Treated Mining Residues

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Abstract: The use of secondary mining resources to replace conventional constituents in mortars production has proved the effectiveness to preserve the quality of mechanical, physical, and chemical properties. However, minimal research has been performed to quantify the environmental impacts of mortars with mining residues. In the present work, a life cycle assessment of 10 mortars was carried out. A reference mortar (100% of cement binder) and mortars with cement substitutions in 10%, 25%, and 50% by raw, electrodialytic treated, and electrodialytic plus thermal treated mining residues were analysed. The impacts were studied in six environmental categories: (1) abiotic depletion; (2) global warming; (3) ozone depletion; (4) photochemical ozone creation; (5) acidification; and (6) eutrophication potentials. The results demonstrated that mortars formulated with raw mining residues may decrease the environmental impacts, namely in global warming potential (55.1 kg CO_2 eq./t modified mortar). Considering the treatments applied to mining residues, the major mitigations were reported in photochemical ozone creation (−99%), ozone depletion (−76 to −98%), and acidification potential (−90 to −94%), mainly due to the disposal impacts avoided in comparison to the reference mortar. Analysing all mortars' constituents and their management options, products with electrodialytic treated mining residues showed higher influence in ozone depletion (18 to 52%). Coupling a thermal procedure, mining residues contributed for 99% of the abiotic depletion potential of mortars.

Keywords: life cycle assessment; environmental impact; mortar; secondary mining resources; electrodialytic technology; thermal treatment

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Citation: Almeida, J.; Faria, P.; Ribeiro, A.B.; Santos Silva, A. Life Cycle Assessment of Mortars Produced Partially Replacing Cement by Treated Mining Residues. *Appl. Sci.* **2021**, *11*, 7947. https://doi.org/10.3390/app11177947

Academic Editor: María Ángeles Martín-Lara

Received: 3 August 2021
Accepted: 26 August 2021
Published: 27 August 2021

1. Introduction

In 2020, the release of greenhouse gases from building operations achieved 10 Gt CO_2, being the highest level ever reported. Together with manufacturing, transportation and construction materials' uses, this represents 38% of global energy-related CO_2 emissions [1].

Climate change and rapid urbanisation with growing population have prompted an emerging interest on construction industries to include more sustainable practices. To accomplish a net-zero carbon building stock in 2050 [2], direct and indirect building CO_2 release needs to be reduced by an average of 55% [3].

Furthermore, the emissions from the production of construction materials, and the construction itself, are mainly driven by cement and steel manufacturing. Their growth in use is the main contributor to buildings embodied carbon emissions. Around 50% of the cement demand comes from the construction sector, being imperative to reduce its use and replace cement by materials with lower embodied carbon [1].

The growing conscientiousness of mining residues impacts have empowered the study of feasible reuse options to reduce waste disposal, concerning a circular economy perspective and the Sustainable Development Goals [4]. Mining activities have reported high amounts of rejected fractions for hundreds of years, as a result of concentrate production. The accumulation of mining residues overtime, in open air impoundments, have led to an intense environmental degradation [5]. The contamination risks for the involved communities are a consequence of the emissions from chemical processes during concentrate production. Nitrogen and cyanide substances may reach aquatic systems, contributing to eutrophication and loss of biodiversity in water streams [6]. Sulfide minerals may contain harmful metals and metalloids, that could promote the formation of acids when in contact with water and oxygen, intensifying acidification phenomena [7]. On the other hand, fines and other particles may be released by the wind, increasing the cross contamination in the region [8].

To tackle climate change issues, the reuse of mining residues in construction products have been studied [9]. Mining resources were applied in geopolymers [10], innovative alkali-based materials for road pavement applications [11], red clay bricks [12], and lightweight construction products [13], with eco-efficient gains in mechanical strength, thermal stability, chemical and fire resistance, and costs [14]. In particular, the use of mining residues in mortars may improve their chemical and structural stability, although some research works reported low replacement cement percentages (e.g., 5%) as effective for materials' requirements [15].

In this sense, the continuous optimization of secondary resources reuse to achieve a higher replacing rate of the virgin material in construction products manufacture, is also important.

The electrodialtytic (ED) process is a long-proven technology to remove substances of environmental concern from matrices, as well as to overcome raw materials' shortage and to contribute towards clean energy transition [16]. The ED process is based on the use of a direct low-level current intensity, in pairs of inert electrodes, that promotes the transport of contaminants by electromigration, electroosmosis, and electrophoresis mechanisms [17].

In comparison to metakaolin production and effect [18], the thermal treatment is also regarded as a strategy to take advantage of amorphous silica and/or alumina from fine secondary materials, conferring them pozzolanic properties whilst increasing the durability proprieties of final products [19].

Both ED and thermal treatments were applied to mining residues, and the treated material was used to replace cement in mortars production. The mortars produced with treated mining residues demonstrated positive achievements, and comprised the requirements needed for rendering, plastering, joint repointing, bedding masonry, or screed uses [20]. However, minimal research has been conducted to environmentally support the reuse of secondary resources in the roll out of sustainable cementitious construction products [21].

The life cycle assessment (LCA) has emerged as an important decision-making support tool in the construction industry [22]. This analysis technique provides an overview on the potential environmental impacts during a product/service life cycle. The LCA methodology is defined in ISO 14040 [23] and ISO 14044+A1 [24], and should be structured as follows: (1) goal definition and scope; (2) inventory appraisal; (3) impacts evaluation; and (4) interpretation [21]. The LCA provides an estimation of cumulative impacts that can also be used to quantify the embodied energy of products, considering environmental categories defined in EN 15804+A2 [25]. The inventory is the core of the LCA and, for this reason, reliable data from environmental product declarations (EPD), peer-reviewed scientific research works, in-site quantifications, and international databases should be preferentially used [26].

The built environment involves significant pressures on global resources. In this sense, the need to develop LCA methods, that critically appraise data on products environmental burdens to leverage new business opportunities, are a top priority. The present work aims at determining the environmental impacts that result from the incorporation of non-treated and treated mining residues, in different proportions, for cement-based mortar production. Those mortars were previously tested [20,27], presenting suitable properties for several current applications. The environmental impacts estimated and determined, based on six environmental categories, were analysed in terms of: (1) mitigation potential from mining residues uses, comparing to traditional mortar production with cement, (2) contribution of mining residues management scenarios (direct disposal, ED process and ED plus thermal treatment) in mortar manufacture, and (3) contribution of all the mortar components and respective management scenarios for the mortar lifecycle.

2. Materials and Methods

2.1. Materials

The mortars analysed in the present work were produced with mining residues from the Panasqueira mine (located in Covilhã, Portugal) and a Portuguese cement CEM II/B-L 32.5 classified according EN 197-1 [28]. A river siliceous sand was applied as aggregate, with similar proprieties to the CEN reference sand [29], and tap water was used to hydrate the formulation.

Mortar samples were produced in triplicate replacing 10%, 25%, and 50% (wt %) of the original cement content by mining residues under different conditions: raw, ED treated [27], and ED plus thermal treated [20]. A reference (REF) mortar was also included to compare the environmental impacts of the mortars with mining residues. The mortars analysed and their compositions are summarized in Table 1.

Table 1. Composition of the cement-based mortars analysed (adapted from [20,27]).

		Weight Proportion		
Mortar Code	**Binder Composition**	**Binder (Cement + Mining Residues)**	**Sand**	**Water**
REF	100% cement	1	4.6	0.8
M10	10% raw mining residues + 90% cement		4.7	
M25	25% raw mining residues + 75% cement		4.8	
M50	50% raw mining residues + 50% cement		5.0	
ME10	10% ED mining residues + 90% cement		4.6	
ME25	25% ED mining residues + 75% cement		4.7	
ME50	50% ED mining residues + 50% cement		4.7	
MET10	10% ED + TT mining residues + 90% cement		4.6	
MET25	25% ED + TT mining residues + 75% cement		4.6	
MET50	50% ED + TT mining residues + 50% cement		4.6	

ED–Electrodialytic treatment; TT–Thermal treatment. Density of the constituents: Cement = 1000 kg/m$^{3;}$ Mining residues: Raw = 1180 kg/m^3, ED = 1003 kg/m^3 and TT = 970 kg/m^3; Sand =1540 kg/m^3.

2.2. Scope Definition and LCA Boundaries

The LCA of mortars was performed based on ISO 14040 [23] and ISO 14044+A1 [24]. Herein, the environmental sustainability of mortars was quantified at the product stage. Thus, the impacts of raw materials extraction and processing, and the mining residues management scenarios were analysed as presented in Figure 1. The declared unit defined for the present study was 1 t of mortars.

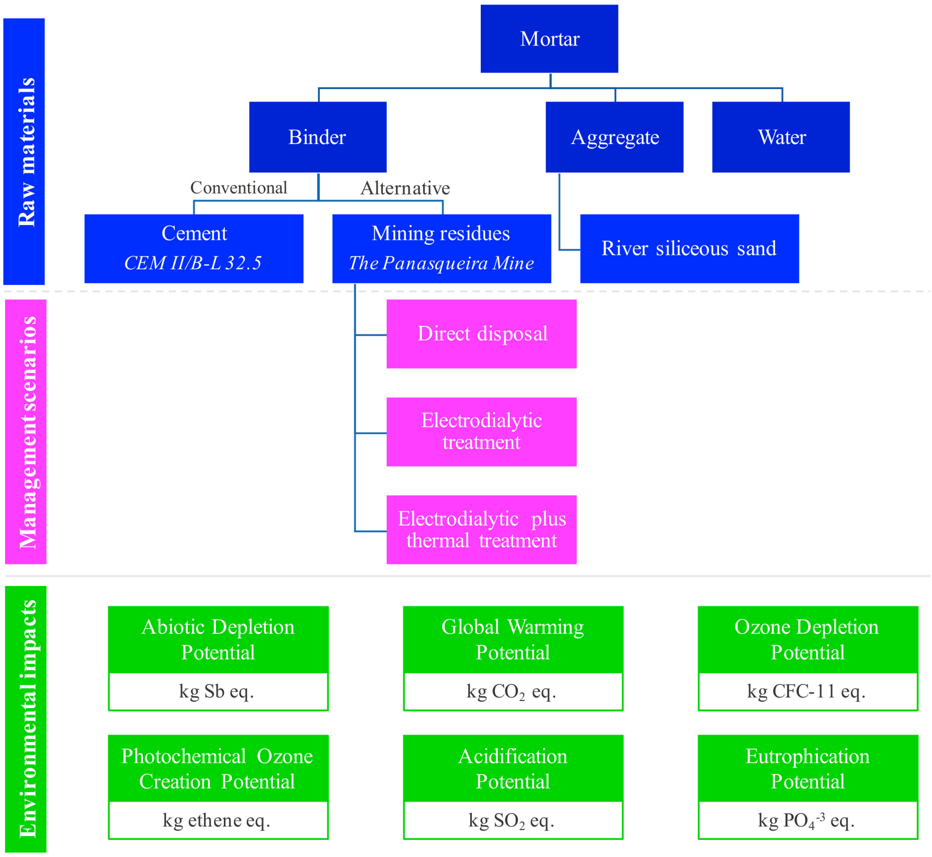

Figure 1. Flowchart of the elements included in the LCA of mortars, and the environmental impact categories analysed.

The environmental burdens were assessed through the analysis of six impact categories, based on EN 15804+A2 [25]: Abiotic depletion potential (ADP), global warming potential (GWP), ozone depletion potential (ODP), photochemical ozone creation potential (POCP), acidification potential (AP), and eutrophication potential (EP). The analysis was performed based on the CML (*Centrum voor Milieukunde Leiden*) methodology, developed by the Institute of Environmental Sciences from Leiden University, the Netherlands [30].

2.3. Data Collection

The data used to shape the LCA of the raw materials involved was collected from peer-reviewed scientific research works [7,26,31–34]. To determine the impact of the mortars with mining residues in the environmental categories studied, the composition of the mortars produced in previous works was considered (Table 1). The environmental impacts of 1 kg of cement, sand, water and mining residues, in the categories considered, are presented in Table 2, as well as the respective sources.

Regarding the management scenarios considered for mining residues, before their application in mortars, the data was equally collected from peer-reviewed scientific research works [18,35]. The environmental impacts considered from the disposal of 1 kg of mining residues, and also from the ED treatment of the same amount, are presented in Table 3. The impacts from the thermal treatment of mining residues were considered the same as the calcination of metakaolin, once both could be considered artificial pozzolans when subjected to identical thermal procedures [36].

Table 2. Environmental impacts of 1 kg of cement, sand, water, and mining residues.

Mortar Constituent	**Environmental Impact Category**						**Reference**
	ADP	**GWP**	**ODP**	**POCP**	**AP**	**EP**	
	kg Sb eq.	**kg CO_2 eq.**	**kg CFC-11 eq.**	**kg ethene eq.**	**kg SO_2 eq.**	**kg $PO_4{}^{3-}$ eq.**	
Cement (CEM II/B-L 32.5)	1.10×10^{-6}	7.38×10^{-1}	1.10×10^{-10}	1.17×10^{-4}	1.21×10^{-3}	1.74×10^{-4}	[26]
Sand	7.31×10^{-11}	2.46×10^{-3}	3.83×10^{-10}	1.08×10^{-6}	1.90×10^{-5}	2.03×10^{-6}	[26]
Water	1.57×10^{-11}	1.33×10^{-4}	5.93×10^{-12}	3.87×10^{-8}	9.70×10^{-7}	4.99×10^{-8}	[31]
Mining residues [a]	1.02×10^{-5}	4.75×10^{-3}	7.54×10^{-10}	4.24×10^{-5}	2.26×10^{-5}	1.06×10^{-4}	[7,32–34]

ADP—Abiotic Depletion Potential; GWP—Global Warming Potential; ODP—Ozone depletion Potential; POCP—Photochemical Ozone Creation Potential; AP—Acidification Potential; and EP—Eutrophication Potential. [a] Mining residues impacts were determined based on the production of 1 kg of concentrate at the mine. The impacts reported for ADP [32], and for the remaining impact categories analysed [33] were estimated per kg of mining residues produced, assuming that 1 kg of concentrate generates 442 kg of mining residues (ore grade = 0.3% WO_3 [7] and concentrate grade = 75% WO_3 [34]).

Table 3. Environmental impacts of the direct disposal, the electrodialytic treatment, and the thermal treatment of 1 kg of mining residues.

Mining Residues Management	**Environmental Impact Category**						**Reference**
	ADP	**GWP**	**ODP**	**POCP**	**AP**	**EP**	
	kg Sb eq.	**kg CO_2 eq.**	**kg CFC-11 eq.**	**kg ethene eq.**	**kg SO_2 eq.**	**kg $PO_4{}^{3-}$ eq.**	
Direct disposal	3.35×10^{-9} [a]	6.90×10^{-1}	9.80×10^{-8}	1.60×10^{-2}	1.20×10^{-2}	1.10×10^{-4}	[35]
Electrodialytic treatment	2.92×10^{-10} [a]	7.00×10^{-2}	4.10×10^{-9}	1.50×10^{-4}	2.80×10^{-4}	1.40×10^{-5}	[35]
Thermal treatment [b]	3.39×10^{-3}	4.21×10^{-1}	3.98×10^{-8}	5.20×10^{-5}	1.03×10^{-3}	6.47×10^{-5}	[18]

ADP—Abiotic Depletion Potential; GWP—Global Warming Potential; ODP—Ozone depletion Potential; POCP—Photochemical Ozone Creation Potential; AP—Acidification Potential; and EP—Eutrophication Potential. [a] ADP data was converted from kg Fe eq. [35] to kg Sb eq. based on reference [37] data. A conversion factor of 1.17×10^7 was applied. [b] The impacts reported from the thermal treatment of metakaolin were assumed as the same of mining residues due to the process similarities (e.g., considering thermal treatment up to 750 °C).

3. Results and Discussion

3.1. Impacts of Raw Materials in Mortar Manufacture

During mortar production, there are several high energy consuming phases in regard to raw materials acquisition. In this context, the environmental impacts of using conventional materials, as cement, or raw mining residues in mortar manufacture was determined for 1 t of mortars. The environmental pressures based on the typology of the binder used (cement and residue) as function of their content, in each category, are presented in Table 4.

Table 4. Environmental impacts from the production of 1 t of mortars with cement and raw mining residues as binder constituents.

Mortar	**Weight of Cement Replaced (%)**	**Environmental Impact Category**					
		ADP	**GWP**	**ODP**	**POCP**	**AP**	**EP**
		kg Sb eq.	**kg CO_2 eq.**	**kg CFC-11 eq.**	**kg ethene eq.**	**kg SO_2 eq.**	**kg $PO_4{}^{3-}$ eq.**
REF	0	1.58×10^{-4}	1.08×10^{2}	2.72×10^{-7}	1.76×10^{-2}	1.87×10^{-1}	2.64×10^{-2}
M10	10	2.67×10^{-4}	9.73×10^{1}	2.79×10^{-7}	1.64×10^{-2}	1.70×10^{-1}	2.52×10^{-2}
M25	25	4.30×10^{-4}	8.15×10^{1}	2.91×10^{-7}	1.46×10^{-2}	1.44×10^{-1}	2.34×10^{-2}
M50	50	7.03×10^{-4}	5.51×10^{1}	3.10×10^{-7}	1.17×10^{-2}	1.01×10^{-1}	2.03×10^{-2}

ADP—Abiotic Depletion Potential; GWP—Global Warming Potential; ODP—Ozone depletion Potential; POCP—Photochemical Ozone Creation Potential; AP—Acidification Potential; and EP—Eutrophication Potential.

The major impacts that come from raw materials exploration and uses are reported in the GWP category. The GWP is based on the quantity of greenhouse gases released to the atmosphere, namely CO_2 (that is dominant), methane (CH_4) and nitrous oxide (N_2O). Thus, GWP means the total climate change impact of all the greenhouse gases caused by an item as function of the amount of CO_2 that would have the same impact over a 100-year period [38].

From the production of 1 t of mortars, 1.08×10^2 kg CO_2 eq. are released by the REF, followed by M10, M25, and M50. The highest the mining residues incorporation as binder, the lowest the GWP. When 50% of cement was replaced by secondary mining resources (M50), a decrease of 49% in GWP was achieved (55.1 kg CO_2 eq.)

Zajac et al. [39] reported the same trend, where CO_2 emissions depend on the cement composition, and also on the level of fineness of the components. Since the emissions associated to the cement clinker are significantly higher than for other materials, the modification of the binder composition results in a significant reduction of the GWP [39].

The EP, POCP, and AP were lower than the REF, in sequence, when mining residues were used to replace cement at 50% (less 23%, 34%, and 46%, respectively).

The EP gives an overview on nutritional elements presence in aquatic systems, namely nitrogen and phosphorus. The excessive concentration of these compounds decreases the oxygen available in water bodies and, consequently, water quality. This results in increased primary productivity and phytoplankton proliferation, where some species may present toxic risks [40].

Mines are often reported as a source of nutrients, namely regarding nitrogen that is used in the concentrate process for pH regulating, acid washing, or lixiviant agent [41]. In this way, significant decrease in EP is not expected, as it is foreseen in other environmental categories. The M50 mortar presented the lowest EP (2.03×10^{-2} kg PO_4^{3-} eq.). On the other hand, the various gases occurring by the hydration process of cement may release NH_4^+ (ammonium) to the environment [42], contributing to the impacts observed in the EP for the REF (2.64×10^{-2} kg PO_4^{3-} eq.). Although EP is quantified in phosphates (PO_4^{3-}) equivalents, it is also possible to convert them in ammonia (NH_3) equivalents, considering that 1 kg of NH_3 has the same EP of 0.35 kg PO_4^{3-} [43].

The POCP is a secondary air pollution, also known as smog. This effect is mainly caused by the reactions between sunlight and emissions from fossil fuel combustion, promoting the formation of other chemicals in the troposphere, as ozone and peroxides. This leads to an increase of the ground-level ozone concentration [44]. The POCP is mainly related to the technology involved in raw materials production. In particular, grinding contributes to approximately 50% of the energy consumed from cement production [39]. This may contribute to the higher emissions from REF (1.76×10^{-2} kg ethene eq.) that affect POCP, in comparison to M10, M25, and M50 mortars (an average of 1.42×10^{-2} kg ethene eq.)

The AP is also affected by the combustion of fossil fuels, from industrial equipment, such as nitrous and sulfide oxides. In the presence of water and oxygen, these substances may leach and present risks for the surrounding ecosystems [45]. The presence of sulfide minerals in mining residues composition [5] may contribute to the AP detected at higher incorporation ratios of mining residues in mortars (M50 = 1.01×10^{-1} kg SO_2 eq.). However, the AP of using mining residues still have lower proportions than REF (1.87×10^{-1} kg SO_2 eq.). The emissions from the combustion processes of the kilns in a cement industry may release HCl and HF [46], with repercussions in the AP.

Contrarily, mining residues demonstrated to have higher ODP (up to 2.5%) and, more significant, ADP (above 41%), in comparison to cement. The ODP is related to the ozone density decrease through the thinning of the stratospheric ozone layer, as a consequence of anthropogenic pollutants (e.g., halocarbons) [47]. Once more, the source of pollution associated to ODP is predominantly associated to the equipment involved in mining activities and cement production, being the differences between the two types of binders marginal (an average of approximately 3.0×10^{-7} kg CFC-11 eq. for all the mortars).

The natural resources needed for raw materials production can be considered renewable (e.g., groundwater and wood) and nonrenewable (e.g., minerals and fossil fuels). The ADP refers to the exhaustion of nonrenewable resources and the resultant environmental impacts, being mainly affected by the rate of resources extraction [47]. In fact, the exploration of mine ores involves extremely high quantities of mining residues generation, due the low ore grades in comparison to the past [48]. Comparing to REF (1.58×10^{-4} kg Sb eq.), there are more wastage when the initial source is being explored, which explains the higher impacts observed in ADP for M10, M25, and M50 mortars (between 2.67×10^{-4} and 7.03×10^{-4} kg Sb eq.).

3.2. *Impacts of Mining Residues Management Scenarios in Mortar Production*

Bearing in mind the potential of mining residues as a secondary source of raw materials with high economic potential and in risk of scarcity [49], the ED process was applied to mining residues as a way to contribute for circular economy targets [50]. Furthermore, the thermal treatment prospective for enhancing mining residues pozzolanic reactivity and improve durability properties, could enlarge the applicability of this material in construction products [19]. In this sense, mortars were produced with mining residues treated with the ED technology [27] and with ED plus thermal treatment [20]. To complement the technical analysis of the properties of the mortars produced with treated mining residues, the environmental impacts were determined and compared to the REF (Table 5). Three management scenarios were considered for the mining residues: direct disposal; ED treatment; ED plus thermal treatment. Once REF did not include mining residues, it is assumed that the amount of cement used is the same quantity of mining residues that are directly disposed at the mining site.

Table 5. Environmental impacts from the production of 1 t of mortars with cement and treated mining residues as binder constituents.

Mortar	Weight of Cement Replaced (%)	Management of Mining Residues	Environmental Impact Category					
			ADP	**GWP**	**ODP**	**POCP**	**AP**	**EP**
			kg Sb eq.	**kg CO_2 eq.**	**kg CFC-11 eq.**	**kg ethene eq.**	**kg SO_2 eq.**	**kg PO_4^{3-} eq.**
REF	0	Disposal	1.59×10^{-4}	2.07×10^{2}	1.44×10^{-5}	2.32	1.91	4.22×10^{-2}
ME10	10	ED	1.43×10^{-4}	9.83×10^{1}	3.28×10^{-7}	1.80×10^{-2}	1.73×10^{-1}	2.41×10^{-2}
ME25	25	ED	1.19×10^{-4}	8.38×10^{1}	4.11×10^{-7}	1.86×10^{-2}	1.53×10^{-1}	2.06×10^{-2}
ME50	50	ED	7.92×10^{-5}	5.97×10^{1}	5.51×10^{-7}	1.96×10^{-2}	1.19×10^{-1}	1.49×10^{-2}
MET10	10	ED + TT	4.99×10^{-2}	1.05×10^{2}	9.14×10^{-7}	1.89×10^{-2}	1.89×10^{-1}	2.51×10^{-2}
MET25	25	ED + TT	1.26×10^{-1}	9.95×10^{1}	1.89×10^{-6}	2.08×10^{-2}	1.92×10^{-1}	2.31×10^{-2}
MET50	50	ED + TT	2.51×10^{-1}	9.11×10^{1}	3.51×10^{-6}	2.41×10^{-2}	1.97×10^{-1}	1.97×10^{-2}

ED—Electrodialytic treatment; TT—Thermal treatment; ADP—Abiotic Depletion Potential; GWP—Global Warming Potential; ODP—Ozone depletion Potential; POCP—Photochemical Ozone Creation Potential; AP—Acidification Potential; and EP—Eutrophication Potential.

Based on Table 5 data, the REF presented the higher impacts per t of mortars in GWP (2.07×10^{2} kg CO_2 eq.), ODP (1.44×10^{-5} kg CFC-11 eq.), POCP (2.32 kg ethene eq.), and AP (1.91 kg SO_2 eq.). Furthermore, the management scenario selected for mining residues in the REF case (direct disposal), demonstrated higher GWP, ODP, POCP, and AP than the other options (Table 3). This augmented the overall environmental pressures from REF production.

The application of the ED technology showed positive achievements, once the lowest impacts were observed in all the categories analysed. In particular, ADP (7.92×10^{-5} kg Sb eq.), GWP (59.7 kg CO_2 eq.), AP (1.19×10^{-1} kg SO_2 eq.), and EP (1.49×10^{-2} kg PO_4^{3-} eq.) were strongly alleviated when 50% of ED mining residues were incorporated in mortars. The reuse of a rejected fraction that is commonly disposed as waste and the removal of harmful compounds, that have severe risks for the environmental, coupled with a secondary recovery of raw materials, are the main benefits of using the ED technology. In addition, the land occupied by mining residues discharges is also reduced. These aspects overlap the energy consumed during the ED process.

The ODP and POCP were also lower than REF, albeit the impacts increased with ED mining residues incorporation increase in mortars. An impact intensification of 40% and 8% was observed for ODP and POCP, respectively, from ME10 (ODP = 3.28×10^{-7} kg CFC-11 eq. and POCP =1.80×10^{-2} kg ethene eq.) to ME50 (ODP = 5.51×10^{-7} kg CFC-11 eq. and POCP = 1.96×10^{-2} kg ethene eq.). During the ED treatment, the gases that could be formed due to the electrode reactions are commonly released to the atmosphere. The gases generated during the ED process depend on the matrix composition. For instance, chlorine gas could be generated at the anode in systems with high chloride contents [51]. This may have contributed to the impacts increase verified with more replacing content of cement by ED mining residues.

When mining residues were submitted to ED plus thermal treatment, an increase in the impacts was observed in comparison to ED mining residues. In fact, the energy consumed to heat the sample is the major contributor to the impact's intensification, as well as other VOC (volatile organic compounds) emitted from the calcination process [36]. For this reason, the impacts of MET10, MET25, and MET50 in ADP (from 4.99×10^{-2} to 1.26×10^{-1} kg Sb eq.) and GWP (from 91.1 to 105 kg CO_2 eq.) were higher than ME10, ME25, and ME50. The need of more fossil fuels and, consequently, the higher CO_2 released during the calcination affected both categories. Figure 2 presents the mitigation of the environmental burdens achieved when mortars were produced with treated mining residues, in relation to the REF baseline.

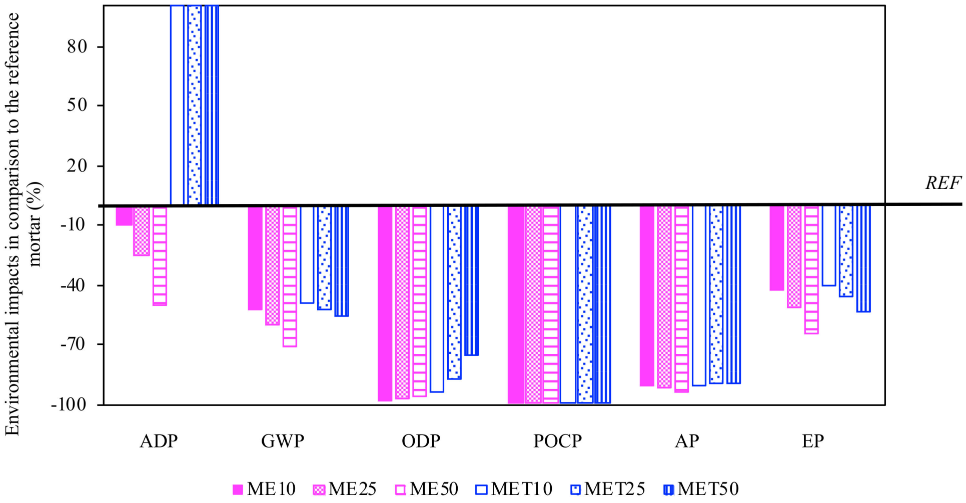

Figure 2. Environmental impacts mitigation of mortars produced with treated mining residues, compared to the reference mortar baseline. ADP—Abiotic Depletion Potential; GWP—Global Warming Potential; ODP—Ozone depletion Potential; POCP—Photochemical Ozone Creation Potential; AP—Acidification Potential; and EP—Eutrophication Potential.

Almost all the environmental pressures of mortars with treated mining residues reduced, namely in POCP (−99%), ODP (−76 to −98%), and AP (−90 to −94%). This occurred due to the lower cement amount, that requires less energy and related emissions from cement production. Also, the disposal impacts of mining residues that are avoided, in comparison to the REF, promoted the decrease of environmental deterioration. High CH_4 emissions are associated to waste disposal, that are 28 times more potent than CO_2 [38].

Nevertheless, the ADP of MET10, MET25, and MET50 (from 4.99×10^{-2} to 1.26×10^{-1} kg Sb eq.) were higher than REF (1.59×10^{-4} kg Sb eq.). Apart from the cement production and mining residues generation burdens, the fossil fuels needed for the thermal treatment augmented the exploration of more resources, highly impacting this category.

3.3. Impacts of Constituents and Management Scenarios in Mortars' Lifecycle

Mortars are commonly composed by mineral binders, aggregates, and water [52]. In this study, only the binder was modified during mortar production, comparing with conventional manufacture. However, the impacts of mortars should gather all the involved elements in its assembly. In this sense, Figure 3 summed up the weight that mortars' components and their respective management scenarios, may have in the environmental categories analysed (based on data from Tables A1–A6, in Appendix A).

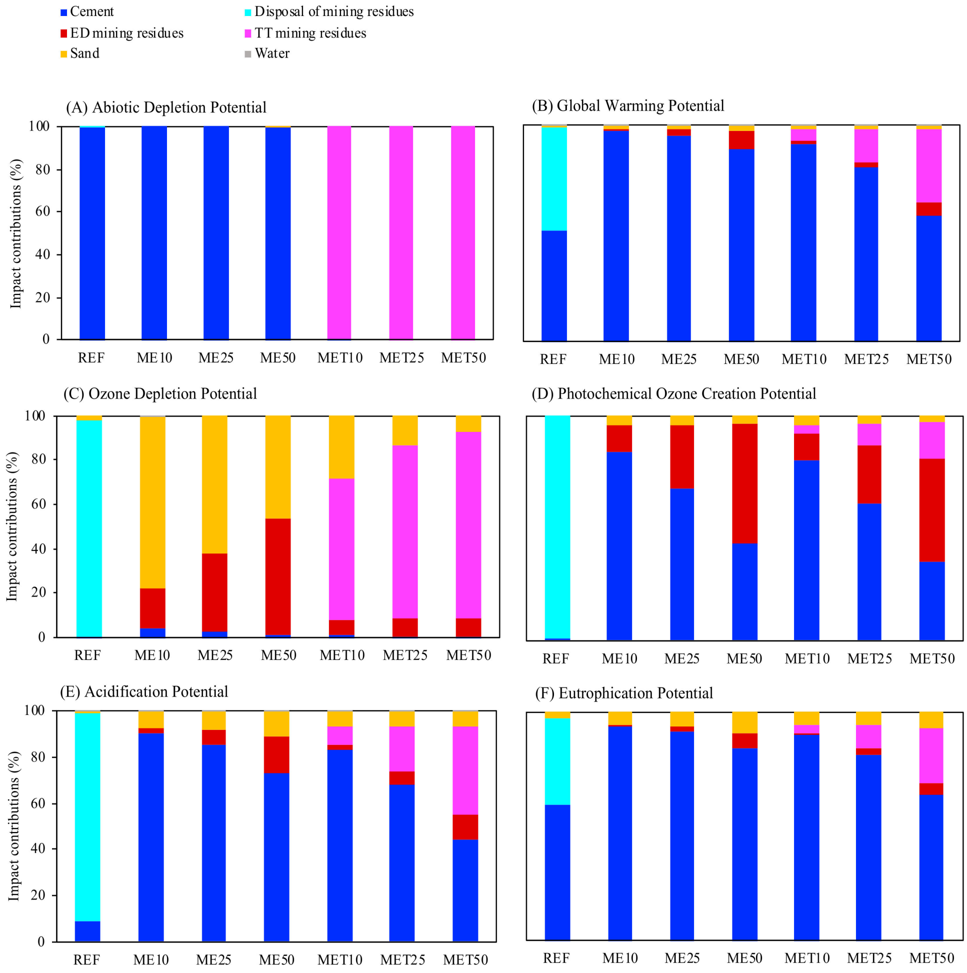

Figure 3. Contribution of mortars' constituents for the environmental impacts in the categories analysed: (**A**) Abiotic Depletion Potential; (**B**) Global Warming Potential; (**C**) Ozone depletion Potential; (**D**) Photochemical Ozone Creation Potential; (**E**) Acidification Potential; and (**F**) Eutrophication Potential.

The water used in mortar manufacture has no significant expression in the environmental categories analysed, when compared with the other components. However, it is important to notice that water is the most consumed substance on the planet. The rapid economic and population growth have increased water demand and limited water supplies, and better management measures to alleviate water scarcity are desired [53].

The aggregate fraction (sand) demonstrated higher weight in ODP, particularly in ME10 (78%), ME25 (62%), and ME50 (46%). From the production of 1 t of mortars, a total of 2.55×10^{-7} kg CFC-11 eq. are released from sand exploration. (Table A3, in Appendix A). The extraction of alluvial material from river beds and sections present degradation risks, increasing the need to develop new strategies for the extraction quarries [54]. Raw silica sand could also be excavated from deposits in open-pit mines. However, sand shortage is also an important issue, constituting one of the greatest sustainability challenges of this century [55]. The exploitation of silica sand for industrial application implies the removal of gangue minerals from excavated topsoil, commonly carried out in a processing plant [56]. The equipment involved on sand exploitation justify the higher ODP, when compared to the other constituents processing methods.

The typology of the binder applied in mortars manufacture demonstrated different behaviors in mortars' overall impacts. The ED mining residues showed higher percentual representativity in POCP (53%) and ODP (52%), for ME50. Coupling the thermal treatment to mining residues contributed to 64–84% of the ODP in MET10, MET25, and MET50, and for almost 100% of the ADP. The disposal of mining residues, as a result of the reuse absence in REF, contributed to the majority of the ODP (98%), POCP (99%), and AP (90%).

Concerning the conventional option, cement has a significant expression in ADP (almost 100% for REF, ME10, ME25, and ME50), GWP (from REF = 51% to ME10 = 97%), AP (from MET50 = 44% to ME10 = 90%), and EP (from REF = 59% to ME10 = 94%). Even when cement was replaced at 50% ratios, the impacts of mortars with treated mining residues incorporation were mainly due to the cement presence. Only the mining residues subjected to ED plus thermal treatment exceeded the cement impacts in the ADP.

4. Conclusions

The decarbonisation of the power sector and the implementation of materials' strategies will be important drivers towards a net zero carbon emissions in the construction industry. In particular, the incorporation of innovative circular materials and products, that can be recovered in closed-loop systems, could contribute to decrease the environmental burdens from cement uses in mortars. Although technological and commercial viable solutions exist, stronger policies and collaborations to accelerate scale up are crucial.

Aiming to provide a decision-making tool for future developments, while keeping up with the technological progress, this work presents a LCA methodology to quantify the sustainability of mortars produced with secondary mining resources partially replacing cement. Considering six environmental categories, 1 t of 10 different mortars were analysed: a reference mortar (100% of CEM II/B-L 32.5 as binder) and mortars with cement substitutions in 10%, 25%, and 50% by raw, electrodialytic treated and electrodialytic plus thermal treated mining residues.

- Generally, mortars produced with mining residues presented an eco-friendlier behavior than the reference mortar. The use of mining residues as binder can avoid almost 50% of the GWP, meaning the release of 55.1 kg CO_2 eq./t modified mortar. The lower the cement content, the lower the energy involved in mortar production, namely due to the clinker formation that requires temperatures above 1000 °C and energy consuming milling.
- The adoption of mining residues management scenarios, before their reuse in mortars' manufacture, was assessed considering direct disposal, ED treatment and ED treatment coupled with a thermal procedure. Herein, the impacts of mortars were strongly alleviated in POCP (−99%), ODP (−76 to −98%) and AP (−90 to −94%), comparing to the reference. The avoided mining residues discharges were key factor for these decreases, together with lower cement incorporation.
- The overall mortar lifecycle was performed considering all the mortar components and respective management scenarios. The aggregate fraction demonstrated higher impact weight in ODP (between 46 and 78%), while the typology of the binder applied showed different environmental performances. ED mining residues showed higher representativity in POCP (53%) and ODP (52%), whereas ED plus thermal treated mining residues contributed to 64–84% of the POCP, and to almost 100% of the ADP.
- Cement has a significant expression in ADP (almost 100%) and GWP (51–97%). The impacts of mortars with treated mining residues are mainly caused by cement contents, even at higher replacement ratios. Nevertheless, fossil fuels needed for the thermal treatment of mining residues increased the resources required, promoting a higher ADP than cement.

Furthermore, other stages not considered in the present work may influence the embodied energy of mortars, namely construction, use and end-of-life phases. The energy spend on grinding activities can differ from material to material, and according to industrial methods. Scaling up approaches and the increase of renewable energy in the grid will be important steps to decrease the impacts of fossil fuels consumption during the involved processes. The cost analysis of the mortars produced by partial replacement of cement with treated mining residues could also complement the life-cycle assessment. This step is relevant to evaluate the economic feasibility of the mortars in the current market and correlate data with the environmental benefits observed.

Author Contributions: Conceptualization, J.A.; Data curation, J.A.; Formal analysis, P.F., A.B.R. and A.S.S.; Funding acquisition, P.F. and A.B.R.; Methodology, J.A.; Project administration, P.F. and A.B.R.; Resources, P.F. and A.B.R.; Supervision, P.F., A.B.R., and A.S.S.; Validation, P.F., A.B.R., and A.S.S.; Writing—original draft, J.A.; Writing—review and editing, J.A., P.F., A.B.R., and A.S.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No. 778045. The authors acknowledge the Portuguese Foundation for Science and Technology (FCT) for the support given to CENSE and CERIS through the strategic projects UIDB/04085/2020 and UIDB/04625/2020, respectively, and for J. Almeida fellowship PD/BD/135170/2017 from the EcoCoRe (Eco-Construction and Rehabilitation) Doctoral program.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A. (Supplementary Data)

Table A1. Environmental impacts in the Abiotic Depletion Potential category, from the production of 1 t of mortars with cement and treated mining residues as binder constituents.

Mortar	ADP (kg Sb eq.)						
	Cement	Disposal of Mining Residues	ED Mining Residues	TT Mining Residues	Sand	Water	Total
REF	1.58×10^{-4}	4.82×10^{-7}	n.a.	n.a.	4.87×10^{-8}	1.74×10^{-9}	1.59×10^{-4}
ME10	1.43×10^{-4}	n.a.	4.08×10^{-9}	n.a.			1.43×10^{-4}
ME25	1.19×10^{-4}	n.a.	1.02×10^{-8}	n.a.			1.19×10^{-4}
ME50	7.92×10^{-5}	n.a.	2.04×10^{-8}	n.a.			7.92×10^{-5}
MET10	1.43×10^{-4}	n.a.	4.28×10^{-9}	4.97×10^{-2}			4.99×10^{-2}
MET25	1.19×10^{-4}	n.a.	1.08×10^{-8}	1.25×10^{-1}			1.26×10^{-1}
MET50	7.92×10^{-5}	n.a.	2.16×10^{-8}	2.51×10^{-1}			2.51×10^{-1}

ED—Electrodialytic Treatment; TT—Thermal Treatment; ADP—Abiotic Depletion Potential; and n.a.—not applicable.

Table A2. Environmental impacts in the Global Warming Potential category, from the production of 1 t of mortars with cement and treated mining residues as binder constituents.

Mortar	GWP (kg CO_2 eq.)						
	Cement	Disposal of Mining Residues	ED Mining Residues	TT Mining Residues	Sand	Water	Total
REF	1.06×10^{2}	9.93×10^{1}	n.a.	n.a.	1.64	1.48×10^{-2}	2.07×10^{2}
ME10	9.56×10^{1}	n.a.	9.80×10^{-1}	n.a.			9.83×10^{1}
ME25	7.97×10^{1}	n.a.	2.45	n.a.			8.38×10^{1}
ME50	5.31×10^{1}	n.a.	4.90	n.a.			5.97×10^{1}
MET10	9.57×10^{1}	n.a.	1.03	6.17			1.05×10^{2}
MET25	7.97×10^{1}	n.a.	2.59	1.56×10^{1}			9.95×10^{1}
MET50	5.31×10^{1}	n.a.	5.18	3.12×10^{1}			9.11×10^{1}

ED—Electrodialytic Treatment; TT—Thermal Treatment; GWP—Global Warming Potential; and n.a.—not applicable.

Table A3. Environmental impacts in the Ozone Depletion Potential category, from the production of 1 t of mortars with cement and treated mining residues as binder constituents.

Mortar	**ODP (kg CFC-11 eq.)**						
	Cement	**Disposal of Mining Residues**	**ED Mining Residues**	**TT Mining Residues**	**Sand**	**Water**	**Total**
REF	1.58×10^{-8}	1.41×10^{-5}	n.a.	n.a.	2.55×10^{-7}	6.59×10^{-10}	1.44×10^{-5}
ME10	1.43×10^{-8}	n.a.	5.74×10^{-8}	n.a.			3.28×10^{-7}
ME25	1.19×10^{-8}	n.a.	1.44×10^{-7}	n.a.			4.11×10^{-7}
ME50	7.92×10^{-9}	n.a.	2.87×10^{-7}	n.a.			5.51×10^{-7}
MET10	1.43×10^{-8}	n.a.	6.01×10^{-8}	5.84×10^{-7}			9.14×10^{-7}
MET25	1.19×10^{-8}	n.a.	1.52×10^{-7}	1.47×10^{-6}			1.89×10^{-6}
MET50	7.92×10^{-9}	n.a.	3.03×10^{-7}	2.95×10^{-6}			3.51×10^{-6}

ED—Electrodialytic Treatment; TT—Thermal Treatment; ODP—Ozone depletion Potential; and n.a.—not applicable.

Table A4. Environmental impacts in the Photochemical Ozone Creation Potential category, from the production of 1 t of mortars with cement and treated mining residues as binder constituents.

Mortar	**POCP (kg Ethene eq.)**						
	Cement	**Disposal of Mining Residues**	**ED Mining Residues**	**TT Mining Residues**	**Sand**	**Water**	**Total**
REF	1.68×10^{-2}	2.30	n.a.	n.a.	7.20×10^{-4}	4.30×10^{-6}	2.32
ME10	1.52×10^{-2}	n.a.	2.10×10^{-3}	n.a.			1.80×10^{-2}
ME25	1.26×10^{-2}	n.a.	5.25×10^{-3}	n.a.			1.86×10^{-2}
ME50	8.42×10^{-3}	n.a.	1.05×10^{-2}	n.a.			1.96×10^{-2}
MET10	1.52×10^{-2}	n.a.	2.20×10^{-3}	7.63×10^{-4}			1.89×10^{-2}
MET25	1.26×10^{-2}	n.a.	5.55×10^{-3}	1.92×10^{-3}			2.08×10^{-2}
MET50	8.42×10^{-3}	n.a.	1.11×10^{-2}	3.85×10^{-3}			2.41×10^{-2}

ED—Electrodialytic Treatment; TT—Thermal Treatment; POCP—Photochemical Ozone Creation Potential; and n.a—not applicable.

Table A5. Environmental impacts in the Acidification Potential category, from the production of 1 t of mortars with cement and treated mining residues as binder constituents.

Mortar	**AP (kg SO_2 eq.)**						
	Cement	**Disposal of Mining Residues**	**ED Mining Residues**	**TT Mining Residues**	**Sand**	**Water**	**Total**
REF	1.74×10^{-1}	1.73	n.a.	n.a.	1.27×10^{-2}	1.08×10^{-4}	1.91
ME10	1.57×10^{-1}	n.a.	3.92×10^{-3}	n.a.			1.73×10^{-1}
ME25	1.31×10^{-1}	n.a.	9.80×10^{-3}	n.a.			1.53×10^{-1}
ME50	8.71×10^{-2}	n.a.	1.96×10^{-2}	n.a.			1.19×10^{-1}
MET10	1.57×10^{-1}	n.a.	4.11×10^{-3}	1.51×10^{-2}			1.89×10^{-1}
MET25	1.31×10^{-1}	n.a.	1.04×10^{-2}	3.81×10^{-2}			1.92×10^{-1}
MET50	8.71×10^{-2}	n.a.	2.07×10^{-2}	7.62×10^{-2}			1.97×10^{-1}

ED—Electrodialytic Treatment; TT—Thermal Treatment; AP—Acidification Potential; and n.a.—not applicable.

Table A6. Environmental impacts in the Eutrophication Potential category, from the production of 1 t of mortars with cement and treated mining residues as binder constituents.

Mortar	**EP (kg PO_4^{3-} eq.)**						
	Cement	**Disposal of Mining Residues**	**ED Mining Residues**	**TT Mining Residues**	**Sand**	**Water**	**Total**
REF	2.50×10^{-2}	1.58×10^{-2}	n.a.	n.a.	1.35×10^{-3}	5.54×10^{-6}	4.22×10^{-2}
ME10	2.25×10^{-2}	n.a.	1.96×10^{-4}	n.a.			2.41×10^{-2}
ME25	1.88×10^{-2}	n.a.	4.90×10^{-4}	n.a.			2.06×10^{-2}
ME50	1.25×10^{-2}	n.a.	9.80×10^{-4}	n.a.			1.49×10^{-2}
MET10	2.26×10^{-2}	n.a.	2.05×10^{-4}	9.49×10^{-4}			2.51×10^{-2}
MET25	1.88×10^{-2}	n.a.	5.18×10^{-4}	2.39×10^{-3}			2.31×10^{-2}
MET50	1.25×10^{-2}	n.a.	1.04×10^{-3}	4.79×10^{-3}			1.97×10^{-2}

ED—Electrodialytic treatment; TT—Thermal treatment; EP—Eutrophication Potential; and n.a.—not applicable.

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RECOVERY OF MINING RESIDUES FOR ECO-EFFICIENT MORTAR PRODUCTION

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2021