

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 electro-dialytic 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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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,

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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 ($\text{Ca}(\text{OH})_2$) 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 $\text{Ca}(\text{OH})_2$ 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 Panasqueira dam (Covilhã, Portugal). The initial and after ED treatment analysis of the sample composition was carried out in an X-Ray

Microdiffractometer (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 NaNO₃ 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.

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

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 $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_{1.8}\text{F}_{0.2}$) 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 electro-dialytic 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/cm³, which corroborates the mass loss observed in the figure. However, other minerals are being formed, since polymorphs such as coesite and stishovite can be produced not only at high temperatures but also

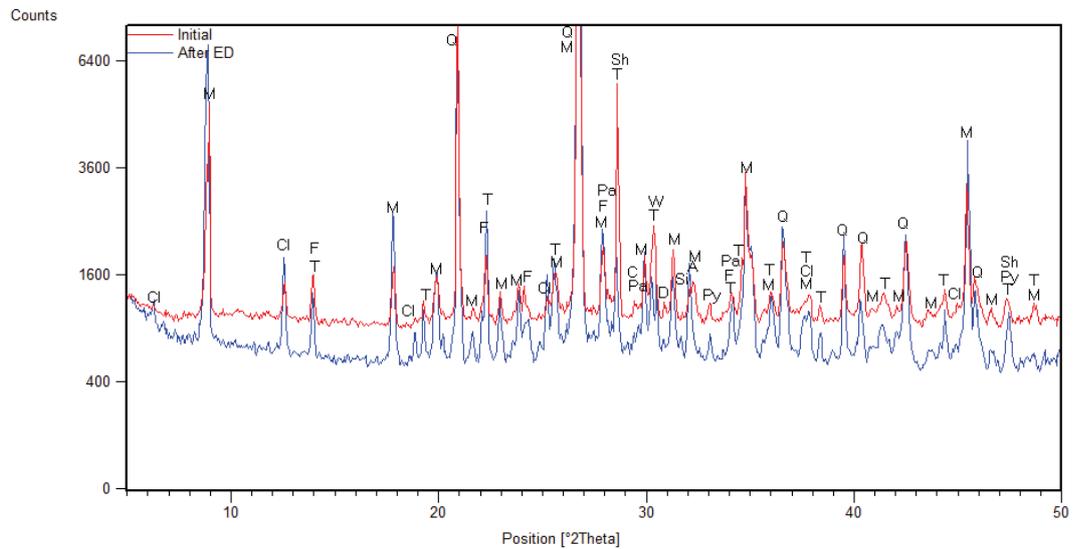


Figure 1: X-Ray Diffraction spectrum of the sample before and after ED treatment.

under high pressures. The density of these minerals is higher, 2.92 and 4.29 g/cm³, 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.

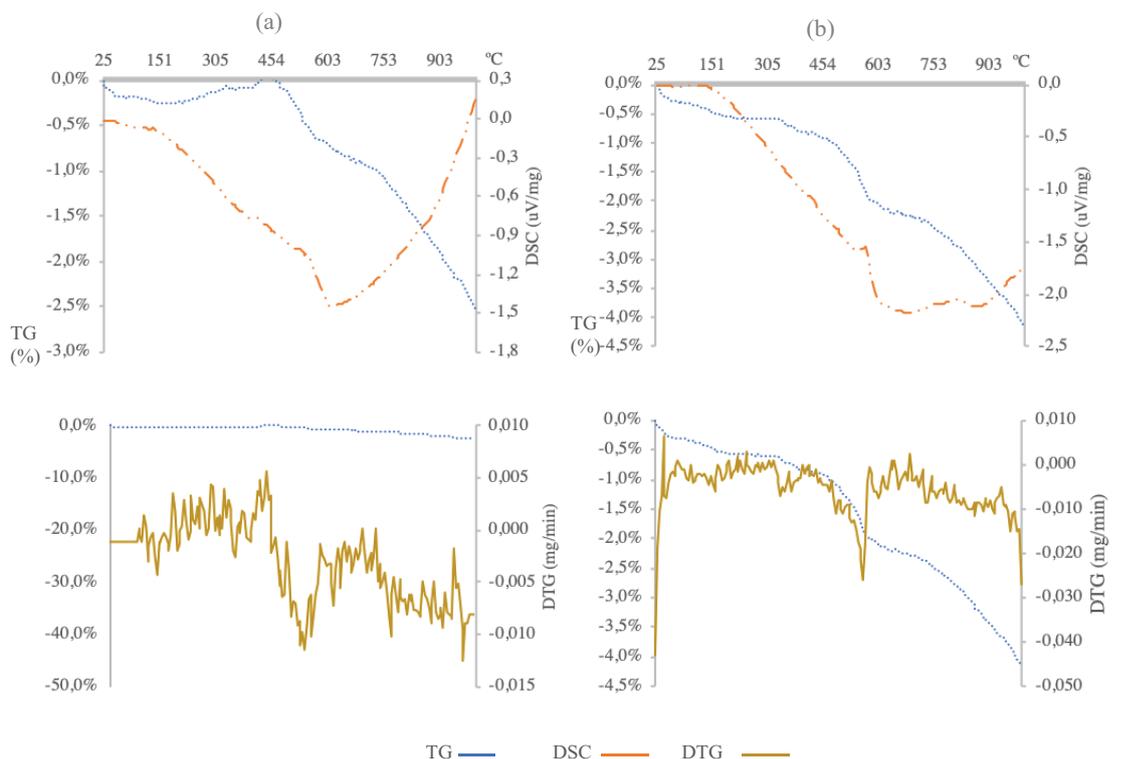


Figure 2: Thermal analysis of the (a) initial sample and the (b) sample after ED treatment.

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

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

Sample	$\text{Ca}(\text{OH})_2$ (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 $\text{Ca}(\text{OH})_2$ fixed from the different samples.

According to NF P 18-513 [14], the minimal consumption of $\text{Ca}(\text{OH})_2$ 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 $\text{Ca}(\text{OH})_2$ 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 $\text{Ca}(\text{OH})_2$ 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 $\text{Ca}(\text{OH})_2$ 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 ($\sim 250\text{--}450$ mg $\text{Ca}(\text{OH})_2$), expanded clay (~ 300 mg $\text{Ca}(\text{OH})_2$), 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 SiO₂ and Al₂O₃ 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.

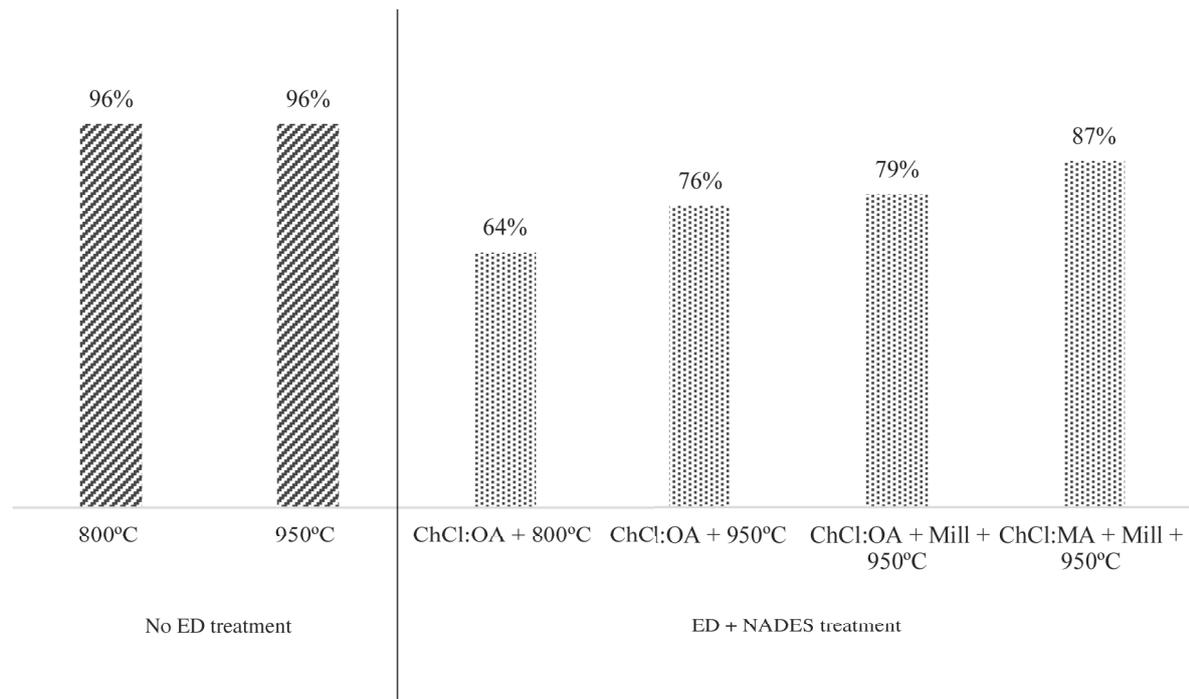


Figure 3: Pozzolanic reactivity increase in relation to the samples with no thermal treatment.

The results showed that it is possible to increase the reactivity of the initial sample, although the values are still 17% under the limit established by the NF P 18-513. Nevertheless, 547.6 mg $\text{Ca}(\text{OH})_2$ 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.

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