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Ultrasound-assisted electrodialytic separation of cobalt from tungsten carbide scrap powder

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ABSTRACT

Recycling of tungsten carbide-cobalt (WC-Co) will considerably grow in the future. Thus, efficient and greener methods for the recovery of the critical raw materials, Co and W, will be necessary. In this work, we evaluate the separation of Co from WC using an electrodialytic (ED) process alone and coupled with ultrasound-assisted extraction (UAE). The WC-Co powder was suspended in different leaching agents, and the effects of UAE amplitude (probe system), pulse periods, and treatment time were evaluated. The Co extraction was mainly dependent on the leaching agent when only UAE was applied, being more efficient under acidic pH. The ED process, alone and coupled to UAE, was then applied using a reactor with two compartments separated by a cation exchange membrane with nitric acid as anolyte; and the effect of DC intensity was tested for Co separation from WC. Between 24 % and 58 % of Co were solubilized when ED was applied alone, but these values increased up to 96 % through the combination with UAE. The ED process was also applied without the use of nitric acid, taking advantage of the acid generated through water electrolysis, aiming for a more environmentally friendly process. The best Co selective recovery was achieved when ED-UAE was used, reaching 99 % of Co solubilization and 90 % of the total Co electromigration to the cathode compartment, leaving behind the WC residue at the anode. The ED-UAE process presents as a greener process for Co separation from WC residues, with further tests needed to include W recovery.

1. Introduction

Cobalt and tungsten are important nonferrous metals used in high-temperature alloys, cemented carbides, and magnetic alloys (Mishra et al., 2017). Both metals are important non-renewable resources, with cobalt presenting toxicity effects (Leysens et al., 2017). Considering tungsten and cobalt's high economic importance and the fact that their supply is at risk, both metals have been listed as critical raw materials (CRMs) in Europe (European Commission, 2023) and the United States (U.S. Geological Survey, 2022). According to a U.S. Geological Survey (2020), nearly 60 % of the tungsten consumed in the United States is utilized in cemented carbides, whereas 46 % of cobalt was used in superalloys, mainly in aircraft and gas turbines. Cemented carbides are composite materials consisting of hard carbide particles in a more ductile binder phase, with the most common being composed of WC grains in a Co binder (WC-Co) (Heinrichs et al., 2021). Tungsten-based scrap is expected to become an increasingly important source of raw mater-

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ial for the worldwide tungsten industry (Shemi et al., 2018). Thus, there is a need to find efficient and green methods for cemented scrap recovery.

The main cemented carbide recycling methods are zinc melting, acid leaching, oxidation-reduction, and mechanical crushing based methods (Shemi et al., 2018). Most of the conventional methods fail to provide an effective separation of tungsten, cobalt, and carbon. The electrometallurgy methods (electrochemical, electrodisolution or anodic dissolution or anodic-leaching or electro-leaching techniques or electrowinning) are an alternative to the conventional methods (Katiyar and Randhawa, 2020). These methods usually involve a single step process and require less energy depending on the type of electrolytes used (Katiyar et al., 2014). Although these processes provide very pure products (Hairunnisha et al., 2007; Katiyar and Randhawa, 2020), there are some limitations to their efficiency (Edtmaier et al., 2005). For example, it has been reported that the passivation of the anode (loss of chemical reactivity) during anodic dissolution decreases the effectiveness of the process and limits the electrodisolution efficiency (Edtmaier et al., 2005; Katiyar and Randhawa, 2020; Lin et al., 1996).

An alternative is the use of electro-dialytic (ED) processes in which the separation of ions is promoted through the application of an electric field. An ED cell can be divided into 2 or more compartments with the electrodes being placed in opposite sites. To separate the compartments anion (AEM) and/or cation (CEM) exchange membranes are used, which only allow the passage of anions or cations, respectively. Usually, the compounds of interest are removed from the matrix towards the electrode's compartments (through electromigration), promoting their effective separation and potential recovery. The ED processes have been widely applied for the recovery of elements of interest or contaminants removal from several matrices (Couto et al., 2020; Guedes et al., 2014, 2015; Oliveira et al., 2019; Zhan and Kirkelund, 2021), including for tungsten recovery from mine tailings (Almeida et al., 2020). As far as we could ascertain, the ED process was never applied to the recovery of cobalt and tungsten from cemented carbide scraps.

Ultrasound waves are high frequency sound waves (> 20 kHz) that surpass the human hearing threshold. The basic principle of UAE is acoustic cavitation and micro-streaming. When high power ultrasound waves propagate through a medium, a sequence of compressions and rarefactions is induced in the molecules of the medium causing pressure alteration. The developed negative pressure during the rarefaction phase advances above tensile strength of the fluid causing the formation of cavitation bubbles from the gas nuclei of the medium. These bubbles grow over several cycles until they become unstable and, finally, violently collapse/implode - acoustic cavitation phenomenon (Kumari et al., 2018; Tiwari, 2015). This implosion generates high temperature and pressure, which in turn, results in high sheer energy waves and turbulence causing a combination of mechanical effects on the material (Kumari et al., 2018; Soria and Villamiel, 2010). It also develops strong micro-streaming currents that may alter the characteristics of the medium. Thus, UAE can improve performance by increasing the extraction yield at lower temperatures (avoiding the use of heating devices), and simultaneously decreasing extraction time. The factors influencing the efficiency of ultrasonic treatments can be divided into three categories: (1) process factors such as frequency, amplitude, power, and treatment time; (2) media factors such as pressure, temperature, viscosity, and polarity of the solvent and (3) product factors such as moisture content, particle size and compound of interest (Kumari et al., 2018).

This work aims to assess the potential of the ED process alone and coupled to UAE for the selective separation of cobalt from tungsten carbide scrap powder. The ED process was coupled to ultrasound-assisted extraction (UAE) to assess whether it would increase the extraction yield (at room temperature) and thus result in a more efficient process. For this, the WC-Co powder was suspended in different leaching agents, and the UAE amplitude, pulse periods, and treatment time were initially tested. After, ED was applied alone and coupled to UAE, and the DC intensity was tested for Co separation from WC, with and without the use of a leaching agent (mineral acid) aiming at the development of a greener process. To the best of our knowledge, this is the first work reporting the use of UAE to enhance the ED recovery of cobalt from tungsten carbide scrap powder.

2. Materials and methods

2.1. Chemicals and solvents

All chemicals used were of trace metal grade purity and used without further purification; the deionized water used had a resistivity of 18.3 M Ω cm. Trace metal grade nitric acid (67–69 %; CAS Number 7697-37-2) and reagents sodium hydroxide (pellets, 98 %; CAS Number 1310-73-2) and sodium sulphate (anhydrous, 99 %; CAS Number 7757-82-6) were purchased from Fisher Scientific.

2.2. Characterization of tungsten carbide scrap powder and extraction procedures

WC-Co powder was provided by ReCarb (Boston, USA). Characterization of the WC-Co waste and sample digestion was carried out with oven dried samples (105 °C). The concentrations of different elements in the WC-Co residue (Table 1) were measured by Inductively coupled plasma optical emission spectrometry (ICP-OES) according to the ISO 11885:2007, after pre-treatment of the W-Co waste with hydrofluoric acid (HF), at *Laboratório Central de Análises, Universidade de Aveiro* (Aveiro, Portugal). Microstructural analyses of the WC-Co powder were performed by scanning electron microscope at *Instituto Técnico de Lisboa* (Lisbon, Portugal) and the XRF analysis at *CENIMAT - FCT NOVA* (Caparica, Portugal).

2.3. UAE extraction

For the UAE experiments, a sonifier (20 KHz Branson Ultrasonics Co.) with a 7.7 cm titanium horn was placed in the reactor. The UAE tests were carried out in duplicate according to the following workflow (Figure S1 available in the supporting information): (i) the ultrasonication amplitudes (%) of 10, 30, and 50 were tested, using a fixed ON/OFF pulse period of 6/54 s/s, at pH values of 1, 7 and 13 (using HNO₃, Na₂SO₄, and NaOH as leaching agents, respectively); and (ii) different ON/OFF pulse periods (3/57, 6/54 and

Table 1

Normalized percentage of elements (total identified 88.4 %) determined by XRF for the WC-Co scrap powder.

Element	Normalized concentration (%)	Element	Normalized concentration (%)
W	89.2	Cu	0.161
Co	6.76	Si	0.147
Ti	0.931	V	0.136
Ta	0.827	Ni	0.104
Nb	0.640	Ca	0.0857
Fe	0.320	Zn	0.0765
Cr	0.313	S	0.0746
Mg	0.179	K	0.0550

12/48), consequently total treatment times (400, 200, 100 min, respectively), were tested. The best approach was selected and used in the ED experiments.

Significant differences among the samples (95 % confidence interval, $p < 0.05$) were evaluated through one-Way ANOVA Tukey's multiple comparisons test, using GraphPad Prism software (version 8).

2.4. Electrolytic experiments

2.4.1. Reactor design

An ED 2-compartment reactor (Ottosen et al., 2015) was used to assess the current effect on Co extraction and separation from WC, with and without coupling to UAE (Fig. 1). The reactor was made of plexiglass with an internal diameter of 11 cm, with a suspension compartment length of 11 cm (anode compartment), and a cathode compartment of 6.5 cm. The cathode compartment was separated from the suspension compartment by a CEM (CR67 MKIII blank, GE Water & Process Technologies). Ti/MMO (mixed metal oxide) mesh was used as electrodes (4.8 × 9.8 cm). The anolyte was stirred at 100 rpm using a stirrer manufactured in-house (North-eastern University). A power supply (Hewlett Packard E3612A) was used to maintain a constant DC current. In the ED coupled to UAE, the sonifier probe was placed in the anode compartment.

2.4.2. Electrolytic experiments

A total of 6 ED experiments were performed, 3 for ED alone and 3 for ED coupled to UAE, plus 2 controls (0 mA). A set of experiments was performed in which the WC-Co waste was suspended in the anode compartment using 850 mL of (1) HNO₃ 0.19 M, and (2) Na₂SO₄ (0.1 M) as leaching agents, in both cases the ratio was 1:10 (mass:volume, g:mL). The catholyte was 680 mL of Na₂SO₄ (0.1 M), with pH adjusted to below 4 with HNO₃ (50 % in water). Different currents were tested: 100 mA, 150 mA, and 200 mA (2.13 mA/cm², 3.19 mA/cm², 4.25 mA/cm², respectively). The experimental codes are ED-(applied current) and ED-UAE-(applied current).

All experiments were performed for 24 h. In the ED-UAE tests, the experiments were started at time zero with the simultaneous application of current and ultrasonication; ultrasonication was applied for 200 min (3 h 20 min) and switched off, and the DC application continued to be applied till the total treatment time of 24 h. The UAE conditions were selected based on the preliminary UAE results: 50 % ultrasonication amplitude and a pulse period of 6/54 s/s.

Current intensity, voltage, pH (Thermo Scientific), conductivity (Thermo Orion 5 Star meter), and temperature were monitored at the beginning, during, and at the end of the treatments. At the end of the experiments, membranes and electrodes were soaked in HNO₃ (1 M and 5 M, respectively) for 24 h and the suspended WC-Co waste was filtered by vacuum using 0.45 μm glass fiber filter. The liquid phases (anolyte, catholyte, CEM, and electrodes soaking solution) were filtered through a 0.45 μm glass microfiber filter.

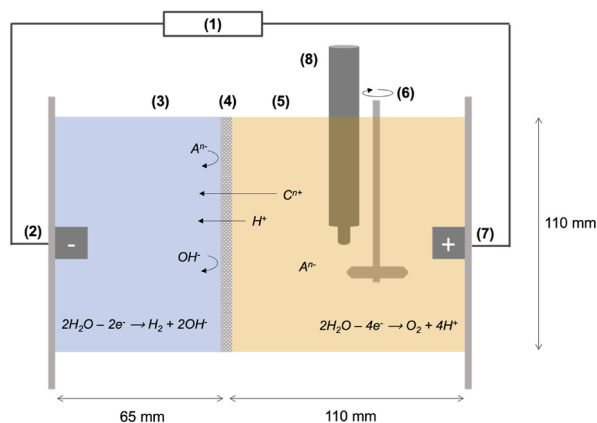


Fig. 1. Electrolytic reactor schematic representation: (1) power supply (2) cathode, (3) cathode compartment, (4) cation exchange membrane, (5) anode compartment (WC-Co liquid suspension), (6) stirrer and (7) anode, and (8) ultrasonic probe in the case of ED coupled to UAE.

The anolyte, catholyte, membranes, and electrode suspensions were analysed for W and Co by ICP-OES. The WC-Co residue was dried (105 °C) till constant weight and analysed according to the procedure described in section 2.2.

The Energy Consumption was calculated to the experiment presenting the best CRM recovery according to Eq. (1).

$$\text{Energy consumption (kWh)} = \frac{V \times A \times h}{1000} \quad (\text{Eq. 1})$$

where V is the cell voltage average in Volts, A is the applied current in Ampere, and h is the time of treatment in hours.

3. Results and discussion

3.1. WC-Co characterization

The chemical composition of the initial sample consists of 845.0 ± 7.1 g/kg of W and 54.5 ± 0.9 g/kg of Co. EDS scanning of the WC-Co powder (Fig. 2) show that particles generally had an irregular shape and that W, C, and Co are the major components (~70 % of W, ~20 % of C and ~5 % of Co), with Ti and Fe also detected in the smaller grinded particles (~3 % of Ti and ~2 % of Fe). These results are in accordance with the values obtained by XRF (Table 1), with ~89 and ~7 % for W and Co. The values for W and Co, are in accordance with the literature for tungsten carbide used in tools that require high hardness, used for metal cutting, mining, and wood-working (Katiyar and Randhawa, 2020). Other elements were present in the sample but with percentages below 1 % (Table 1).

3.2. Ultrasound assisted extraction of Co and W

3.2.1. pH and ultrasonication amplitude

Initially, experiments were performed to assess pH and ultrasonication amplitude effect on the UAE extraction of cobalt and tungsten from de solid phase. No temperature change was observed in the control experiments. When UAE was applied, the temperature increased between 1.5 °C to 9.0 °C and the increase is directly proportional to the sonication amplitude (R^2 between 0.978 and 0.991) being independent of the leaching agent. Amplitudes higher than 50 %, resulting in a temperature increase above 9 °C, were not considered aiming to avoid the deterioration in ultrasonic treatment performance that occurs with increasing temperature in the system, due to the lower cavitation efficiency that is obtained as the density of the liquid decreases with increasing temperature caused by ultrasonication (Tiwari, 2015). The pH values remained constant along the treatments (RSD ≤ 2 %). The tungsten carbide mass loss was between 1-5 % for pH 7, 9-12 % for pH 1, and 7-10 % for pH 13. Initial conductivity was 2.3 ± 0.0 mS/cm for pH 7, 97.5 ± 1.2 mS/cm for pH 13, and 185.1 ± 3.3 mS/cm for pH 1. Conductivity decreased along the treatment for pH 1 and 13 (minus 17-22 % and 8-10 %, respectively), which is attributed to the reactions with the leaching agent, with no relation to the ultrasonication amplitude.

As acidic pH favors Co solubilization, between 57 % and 65 % of Co was detected in the liquid phase, with no correlation to the ultrasonication amplitude (Fig. 3a). Tungsten solubilization was below 13 % (Fig. 3b). In acidic media, using HNO_3 , the element cobalt is mainly solubilized (to Co^{2+} ; inferred from the Pourbaix diagram) and WC remains mainly undissolved. Still, a positive effect of the

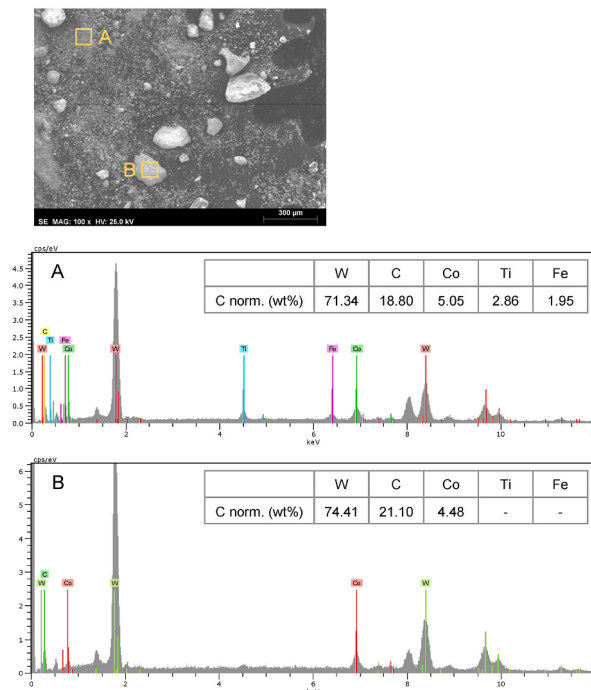


Fig. 2. SEM-EDS micrographs of WC-Co scrap powder.

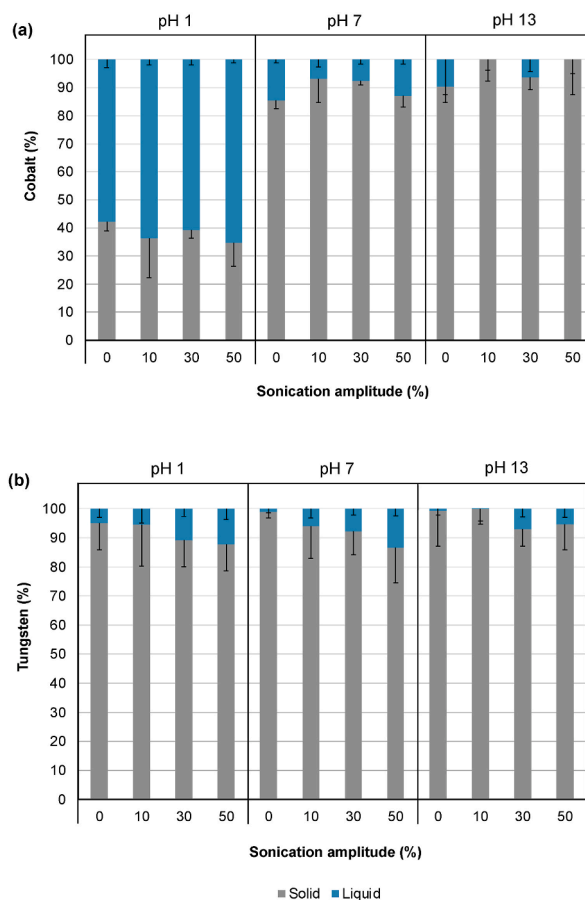


Fig. 3. Percentage of (a) cobalt and (b) tungsten in the liquid and solid phases after ultrasound-assisted extraction.

ultrasonication amplitude is observed for W, as its solubilization at pH 1 is directly proportional to the ultrasonication amplitude ($R^2 = 0.934$), and to the consequent temperature increase that may have contributed to the extraction. Considering the results, the pH 1 and a 50 % of ultrasonication amplitude were chosen for the following tests.

3.2.2. Pulse periods

Pulse periods (ON/OFF in s/s) of 12/48, 6/54, and 3/57 were tested, at pH 1 and 50 % ultrasonication amplitude. The observed temperature increase was proportional to the increasing ON time (ΔT of 4.6 °C for 3/57 ON/OFF, 6.4 °C for 6/54 ON/OFF, and 9.5 °C for 12/48 ON/OFF). No significant pH changes were observed (RSD < 3.5 %) in the sample suspension but the conductivity decreased between 20 % and 25 % in all treatments.

In terms of Co solubilization, the pulse period had a positive effect compared to the control only when a 12/48 pulse period was used (more 10 %, $p < 0.05$; Fig. 4a). Thus, in this study, Co solubilization is more dependent on the treatment time, i.e. time spent in contact with the nitric acid (leaching agent). For W, only the application of the 6/54 pulse period had a positive effect on W solubilization compared to the control ($p < 0.05$; Fig. 4b). Still, in all controls W extraction is low (between 5 % and 8 %), corroborating the low extraction efficiency of W in acidic media. Comparing pulse periods, significant differences were only observed between 12/48 and 3/57 pulse periods in terms of Co solubilization ($p < 0.05$), with more ~8 % of Co being solubilized when the 3/57 pulse period was applied.

Since the difference between the highest and the lowest amount of CRM solubilized during the pulse periods tests was only ~8 % for Co, and ~3 % for W (Fig. 4), the selection of the best pulse period was carried out considering that the ultrasonic probe wears is dependent on (i) the media conditions, (ii) the intensity (which is proportional to the ultrasonication amplitude), and (iii) the use time. Thus, the pulse period of 6/54 (200 min of total treatment time) was selected for the ED experiments.

3.3. Electrodialytic treatment alone and coupled with UAE

The ED experiments were performed, considering the UAE results, using HNO_3 as anolyte. The HNO_3 was chosen as a mineral acid as it is widely used in the recovery of heavy metals using the ED process. The concentration was chosen based on experience and published data on the recovery of other heavy metals from different residues as, e.g., sewage sludge ashes (Guedes et al., 2014, 2016) and municipal solid waste incineration fly ash (Kirkelund et al., 2015), among others. As the water electrolysis at the anode generates H^+

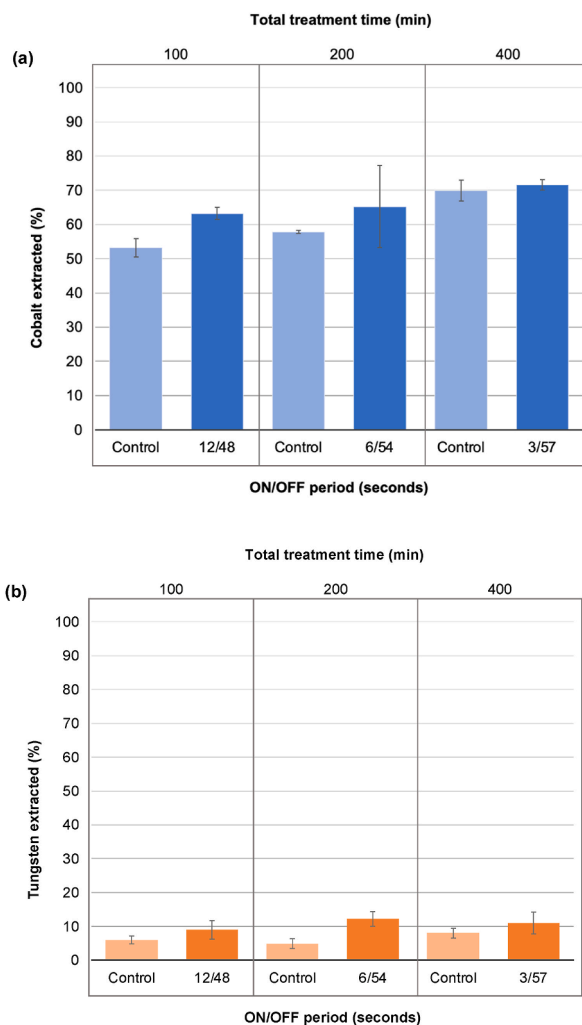


Fig. 4. Percentage of (a) cobalt and (b) tungsten in the liquid phase (extracted) after ultrasound-assisted extraction according to the ON/OFF pulse periods, using nitric acid as leaching agent (pH 1).

which acidifies the medium, the ED experiments were also performed using Na_2SO_4 as anolyte to test if the use of the mineral acid could be avoided, making the process more environmentally friendly.

3.3.1. Variation of pH, conductivity, temperature, and voltage drop

When nitric acid was used as anolyte, the voltage drop varied between 3.0 mV and 5.8 mV at the beginning of the experiment and between 5.3 mV and 5.9 mV at the end, with the higher initial voltages corresponding to the higher current applied (Table 2). The pH in the cathode was kept below 4 by adding HNO_3 (1:1), and at the anode the pH was between 1.2 and 1.3 in all experiments. Conductivity decreased in the anode due to cations migration to the cathode side. This migration together with the catholyte acidification through the addition of HNO_3 (1:1), increased the catholyte conductivity (up to 30.7 mS/cm). The temperature increased from 22.7 ± 0.2 °C to 25.3 ± 0.5 °C during the UAE application (200 min) in the ED-UAE experiments. At the end of the experiments (24 h), the temperature varied between 21.6 °C to 23.2 °C in all experiments (Table 2).

When sodium sulphate was used as anolyte, the voltage drop varied between 7.0 mV and 14.9 mV at the beginning of the experiment and from 4.4 mV to 6.5 mV at the end (Table 2). The pH in the cathode was kept below 4 by adding HNO_3 (1:1). At the anode, pH varied between 7.4 and 7.5 at the beginning, decreasing to values between 2.0 and 2.5 when DC was applied due to the generation of H^+ at the anode. Conductivity increased at the anode due to the ions being released from WC-Co due to the medium acidification and to the ions generated through water electrolysis. Conductivity increased in the cathode to values up to 34.3 mS/cm, due to the acidification through the addition of HNO_3 (1:1). The temperature increased from 22.5 ± 0.2 °C to 26.7 ± 0.5 °C during the UAE application (200 min) in the ED-UAE experiments. At the end of the experiments (24 h), the temperature varied between 21.7 °C to 23.4 °C in all experiments (Table 2).

Comparing both set-ups, the initial voltage was higher when sodium sulphate was used as anolyte (e.g., when 200 mA was used, the voltage drop was 8.2 mV higher when sodium sulphate was used compared to the use of nitric acid). This is attributed to the

Table 2

Initial and Final voltage drop, pH, conductivity, and temperature for the ED experiments, with and without UAE, using nitric acid (pH 1) or sodium sulphate (pH 7) anolyte.

Anolyte	Experiment	Voltage drop (mV)		Anode						Cathode					
		initial	final	pH		Cond. (mS/cm)		T (°C)		pH		Cond. (mS/cm)		T (°C)	
				initial	final	initial	final	initial	final	initial	final	initial	final	initial	final
HNO ₃	ED-0	–	–	1.2	1.2	51.3	35.5	22.2	21.6	5.5	2.0	2.2	5.3	22.5	21.7
	ED-100	3.0	5.3	1.3	1.3	58.8	43.4	22.2	22.6	5.5	2.3	2.3	9.5	22.2	22.6
	ED-150	5.6	5.7	1.2	1.3	61.3	34.5	22.1	23.1	5.4	2.5	2.2	10.1	22.1	22.8
	ED-200	5.8	6.0	1.2	1.3	59.5	40.6	22.5	22.0	5.5	2.4	2.2	12.3	22.5	22.5
	ED-UAE-0	–	–	1.2	1.3	60.1	30.3	21.8	22.9	5.5	2.0	2.3	5.4	21.6	22.7
	ED-UAE-100	3.2	5.9	1.2	1.3	58.5	34.4	22.7	22.6	5.4	2.7	2.2	10.1	22.6	22.8
	ED-UAE-150	4.8	5.3	1.2	1.3	59.1	38.8	22.5	23.1	5.4	2.8	2.1	11.3	22.5	22.8
	ED-UAE-200	5.2	5.9	1.2	1.3	48.3	35.8	22.5	23.2	5.5	2.3	2.2	30.7	22.7	22.9
Na ₂ SO ₄	ED-0	–	–	7.4	7.6	2.2	2.4	22.5	22.3	5.3	2.2	2.2	2.3	22.5	22.5
	ED-100	8.0	4.4	7.5	2.5	2.2	2.9	22.8	23.4	5.2	2.0	2.2	15.2	22.6	21.7
	ED-150	10.4	5.8	7.5	2.1	2.3	3.5	22.7	23.4	5.4	2.1	2.2	29.9	22.8	23.3
	ED-200	14.4	6.5	7.4	2.0	2.2	4.2	22.7	23.0	5.4	2.1	2.2	30.4	22.6	23.0
	ED-UAE-0	–	–	7.5	7.1	2.4	2.3	22.2	23.3	5.2	1.9	2.2	5.2	22.2	22.2
	ED-UAE-100	7.4	4.7	7.4	2.1	2.2	3.7	22.2	23.4	5.5	2.3	2.2	10.1	22.2	22.8
	ED-UAE-150	10.3	5.8	7.4	2.0	2.2	4.0	22.8	22.2	5.5	2.1	2.1	11.2	22.6	22.5
	ED-UAE-200	14.9	6.0	7.5	2.0	2.3	4.3	22.6	22.9	5.4	2.3	2.2	34.3	22.5	22.9

higher initial leaching of Co when HNO₃ is used, as well as other elements, which results in a higher initial conductivity in the anolyte (Table 2) which, consequently, decreases the initial voltage compared to the use of Na₂SO₄. This results in higher electrical energy and higher electrical costs associated with the use of Na₂SO₄. The temperature increase during the UAE application was observed in both set-ups, without statistical differences ($p > 0.05$), being this independent from the ED current application.

3.3.2. Electrodialytic separation of Co and WC

The mass balance is defined as the sum of masses of a chemical element in all the different parts of the reactor at the end of the experiment relative to the initial mass of the same chemical element in the WC-Co residue (based on the average initial concentration, $n = 3$). In this study, the mass balances for the ED samples varied between 94 and 103 %.

3.3.2.1. Nitric acid as a chemical adjuvant. After 24 h, ~13 % and ~8 % of Co were detected in the catholyte of the control experiments with and without the UAE application (ED-UAE-0 and ED-0) when nitric acid was used as leaching agent, with 1 % remaining in the anolyte of ED-0 (Fig. 5). When ED was applied alone, between 24 % and 58 % of Co were solubilized, with approx. 22 %, 32 %, and 51 % electromigrating to the cathode side when 100 mA, 150 mA, and 200 mA were applied, respectively. Cobalt retention by the CEM was below 3 % in all ED tests. The combination of ED to UAE resulted in 43 %–96 % of Co being solubilized with 42 % for ED-UAE-100, 43 % for ED-UAE-150, and 88 % for ED-UAE-200 being detected in the cathode side. The retention by the membrane was below 0.5 % in all ED-UAE experiments. As expected for acidic pHs, W solubilizations were below 7 % in all ED tests independently of its combination with UAE.

The application of a DC resulted in increased Co solubilization (ED alone), with a strong positive relation with the applied current ($R^2 = 0.937$). This strong positive relation was not observed when ED was coupled with UAE ($R^2 = 0.857$), as the amount of Co solubilized at 100 mA was the same as in 150 mA (43 % vs 44 %, respectively). In this case, the fluctuation (increase) in current intensity did not impact the element's recovery. Similar findings have been reported in other studies on the element recovery (Couto et al., 2020), indicating that the reaction kinetics are not solely governed by an increase in current. The best results were obtained for ED-UAE-200 with ~96 % of Co solubilization, from which ~91 % electromigrated to the cathode end (corresponding to 88 % of the total Co). In comparison to the application of ED alone, the combination with UAE resulted in more 38 % of Co solubilization and more 37 % of Co recovered in the catholyte. This means that in 24 h, approx. 48 g of Co per kg of WC-Co residue was recovered in the catholyte.

Co is highly dissolved in acidic medium (Katiyar and Randhawa, 2020; Shemi et al., 2018), whereas the solubility of W is very high in alkaline as compared to the acidic medium (Katiyar and Randhawa, 2020; Shemi et al., 2018). The setting for tungsten species comprises a more complex system than cobalt, but following the Pourbaix diagram which discloses a simplified hydrometallurgical setting for this investigation, in acidic media tungsten tends to form insoluble tungsten oxides, and complexed isopolytungstate ions depending on pH and time. In this study, and considering that W remained in the anode compartment, W was most likely present as WC residue and some amount as tungsten oxides. At the moment, the knowledge of occurring W species remains limited, especially concerning their thermodynamic data. This data is currently being pursued. Contrary to W, Co is mainly dissolved in the anode compartment due to the acidic pH, and, considering the Pourbaix diagram, we can infer that there is a predominance of soluble Co²⁺ and Co³⁺ ions. These Co ions, through the application of the DC current, electromigrate towards the cathode, being potentially present as the pink hexaaquacobalt(II) ion ([Co(H₂O)₆]²⁺; acidic pH), leaving in the anode the undissolved WC residue (Fig. 5).

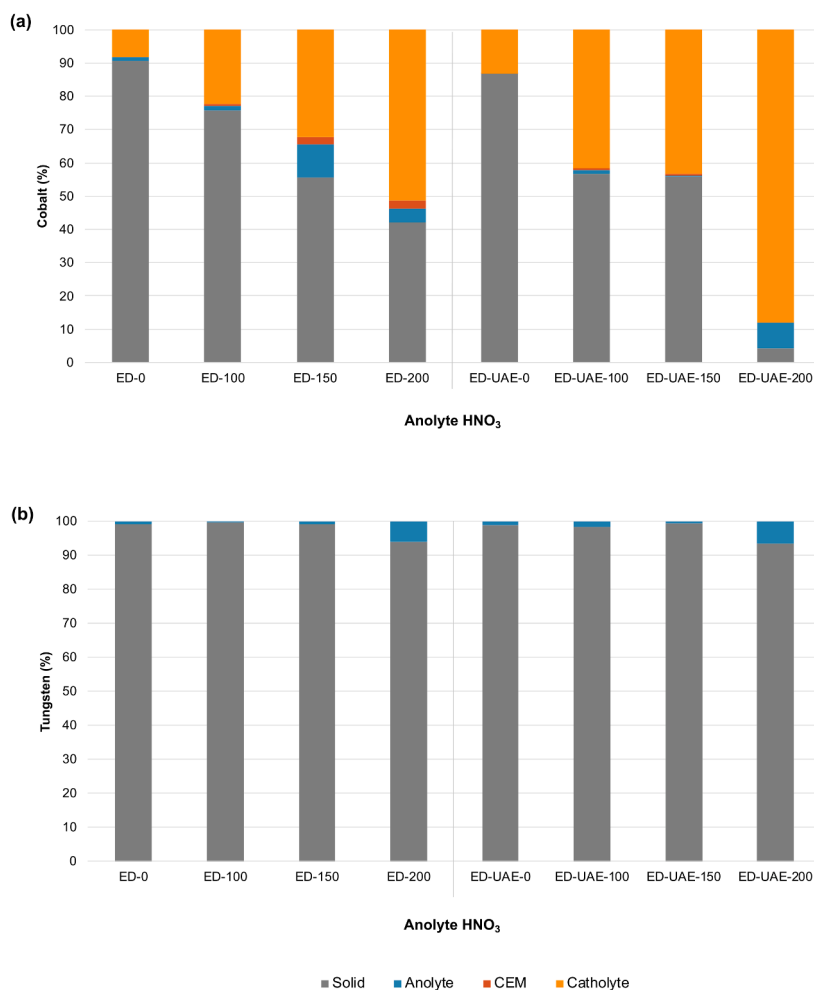


Fig. 5. Percentage of (a) cobalt and (b) tungsten, after ED application alone and coupled to UAE using nitric acid as anolyte, in the solid, anolyte (liquid phase), cation exchange membrane (CEM) and catholyte (W and Co were not detected in the electrodes).

3.3.2.2. Avoiding the use of acids for Co separation. As shown, acidic conditions are the best for Co solubilization (Fig. 3). During the electrochemical processes, the oxidation of the water generates protons (H^+) that acidify the medium, which then promote the leaching of metals (Guedes et al., 2016; Ottosen et al., 2015). Thus, aiming to avoid the use of nitric acid, the matrix was placed in the anode compartment and sodium sulphate was used as the anolyte. This avoided the need to use a mineral acid as leaching agent, making the process more environmentally friendly. After 24 h, in the control experiments, Co was detected in the catholyte at amounts below 0.5 %, with and without the UAE application (ED-UAE-0 and ED-0) when sodium sulphate was used as anolyte, with ~3 % and ~8 % being solubilized and detected in the anolyte (Fig. 6). When ED was applied alone, between 48 % and 77 % of Co were solubilized, with approx. 40 %, 53 %, and 68 % electromigrating to the anode side when 100, 150, and 200 mA were applied, respectively. The Co retention by the CEM was below 1.5 % in all ED tests. The combination of ED and UAE resulted in 55–99 % of Co solubilization with 48 % for ED-UAE-100, 71 % for ED-UAE-150, and 90 % for ED-UAE-200 detected in the cathode side. Co was not retained by the membrane (not detected) in all ED-UAE experiments. W solubilizations were below 3 % in all ED tests independently of their combination with UAE.

In all ED experiments in which sodium sulphate was used as anolyte, Co leaching rate was strongly dependent on current density, R^2 of 0.989 and 0.998 for ED and ED-UAE, respectively. This relation was also observed when nitric acid was used as anolyte (Fig. 5; please see section 3.4.1), although a stronger correlation was observed for the sodium sulphate as anolyte. Similar results were observed in terms of Co solubilization with and without the use of acid in the best conditions, ED-UAE-200, with 96 % vs 99 % of Co solubilized when nitric acid was used vs the use of sodium sulphate, respectively. In terms of recovery, 90 % of Co was detected in the catholyte when no acid was used, and 88 % when nitric acid was used. Thus, in the conditions here tested, the use of nitric acid as leaching agent for Co solubilization can be avoided, and it can be replaced successfully by sodium sulphate. Still, the use of acid is needed for the catholyte pH adjustment. If the pH in the cathode is not controlled thus becoming alkaline due to OH^- generation through electrolysis, Co will deposit on the cathode surface and on the CEM (due to the pH gradient across the membrane), which increases system resistance, and the catholyte conductivity will also decrease (example on supporting information Figure S2; results not

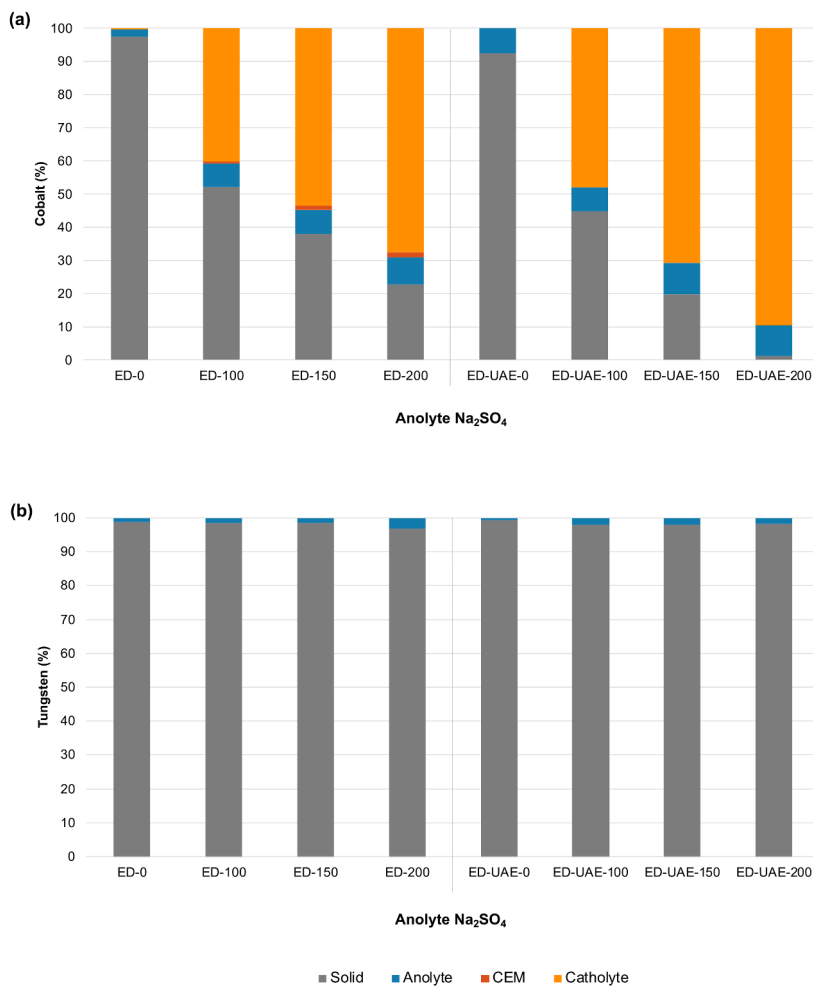


Fig. 6. Percentage of (a) cobalt and (b) tungsten, after ED application alone and coupled to UAE using sodium sulphate as anolyte, in the solid, anolyte (liquid phase), cation exchange membrane (CEM) and catholyte (W and Co were not detected in the electrodes).

shown). This results in the voltage drop increase (in accordance with Ohm's law) which increases the electrical costs. Thus, in this case, the catholyte pH needs to be kept acidic to prevent Co deposition in the cathode and CEM and improve catholyte conductivity thus preventing a steep increase of the voltage drop. Still, due to ions migration from the anolyte to the catholyte which results in the decreased conductivity in the anolyte, a slight voltage increase was observed in all ED experiments with nitric acid (Table 2).

3.3.3. Associated costs and further research

Considering the obtained results, the ED-UAE offers a new possibility for Co selective recovery from WC-Co powder residues, by taking advantage of water electrolysis and the Co electromigration to the cathode compartment.

Considering the energetic costs, the energy consumption was estimated to be 0.05 kWh for the ED process (calculated according to Eq. (1)), 1 kWh for the UAE (rounding 3 h 20 min working time to 4 h), and 2.88 kWh for the overhead stirrer (assuming 120 W). This means that the energy consumption is estimated to be 0.08 kWh per g of Co. Still, the ED-UAE process needs further optimization aiming to decrease the time needed to recover the Co, which in turn would decrease the energy costs.

Considering the material, the main costs are associated with the eventual substitution of the membranes (approx. 17 €/m² in 2022) and electrodes (6 €/m in 2022) due to their wear. It should be also pointed out that under the current intensity applied in this work, the electrodes here tested did not show any signs of corrosion. The sodium sulphate has an associated cost of approx. 7 €/kg (~0.001€ per g of Co).

The existing methodologies for tungsten carbide recycling are classified as direct, indirect and semi-direct and there are a few reviews that overview the processes, advantages, and disadvantages (e.g. Katiyar and Randhawa, 2020; Shemi et al., 2018). Zinc recycling process (direct recycling) is considered the most cost-efficient and environmentally friendly method (Shemi et al., 2018). The zinc melting allows to achieve W recovery yields as high as 95 %, and requires an energy consumption of between 4000 and 6000 kWh/t of W. The chemical processes of W recovery consume around 2000 kWh/t of W (Leal-Ayala et al., 2015; Shemi et al., 2018). The main disadvantage is that most of the tungsten carbide recycling processes focus on the recovery of W, and the other constituents

(like Co) recovery are secondary. The semi-direct processes may allow the recovery of both WC as the binder but require high reagent consumption and have low process kinetics (Katiyar and Randhawa, 2020; Shemi et al., 2018). The electrochemical processes have shown advantages in terms of lower energy consumption, high efficiency, lower costs, and few industrial requirements (Katiyar and Randhawa, 2020). Considering this, the use of ED processes alone or coupled with other processes can present the advantage of promoting multicomponent recovery. The process here studied requires further optimization to be competitive with the processes already in the market. Thus, and considering the results here obtained, future research should address:

- Optimizing the ED(-UAE) process for multicomponent recovery (both Co and W);
- Scale-up studies to assess the process feasibility considering the engineering point of view;
- Costs of the process considering the amount of CRMs recovered and their market value;
- Life cycle assessment to assess the environmental impacts of the process.

3.3.3.1. CRMs recovery under the sustainable development goals framework. The recovery of the critical raw materials, in this case Co and W through the recycling of tungsten carbide scrap (WC-Co) promotes efficient resource use, reduces waste generation, and supports the circular economy, ensuring sustainable consumption and production patterns (SDG 12: Responsible Consumption and Production). Promoting the recovery of CRMs from secondary resources also has the potential to reduce the need for resource-intensive extraction processes, thus promoting the decrease of the carbon footprint associated with raw material production (SDG 13: Climate Action). It also supports proper management of industrial waste, promotes responsible resource extraction, minimizes land degradation and environmental pollution, and prevents the discharge of industrial wastes into water (SDG 14: Life Below Water and SDG 15: Life on Land).

This work assessed the potential of the ED process alone and coupled to UAE for the selective recovery of Co and W and they could be classified as innovative processes for critical resource extraction from waste streams, contributing to leverage a sustainable industrial practice (SDG 9: Industry, Innovation, and Infrastructure). The combined process, ED-UAE may be regarded as a sustainable recovery practice that has the potential to reduce the energy demand associated with the extraction of primary raw materials as it operates at lower temperatures and with a low-level direct current (SDG 7: Affordable and Clean Energy).

In general, the development of new technologies and industrial activities related to critical raw material recovery may contribute to job creation and economic growth (SDG 8: Decent Work and Economic Growth).

4. Conclusions

The ED-UAE offers a new possibility for Co separation from WC-Co powder residues, by taking advantage of water electrolysis and the Co electromigration to the cathode compartment. Acidic conditions are best for Co solubilization from the tungsten carbide waste, with 60–65 % of Co being solubilized without significant influence of the UAE treatment. Thus, Co solubilization is mainly dependent on the leaching agent used when UAE is applied alone. When combined with ED, the UAE together with the application of 200 mA using nitric acid as leaching agent, resulted in 38 % more Co solubilization than ED without UAE. However, the use of nitric acid for leaching Co from the tungsten carbide scrap powder can be avoided by taking advantage of the acidification by water electrolysis. In this case, 99 % of Co leached when 200 mA was applied in combination with UAE, using sodium sulphate as anolyte, with 90 % of the total Co being recovered in the catholyte. In 24 h, approx. 49 g of Co per kg of WC-Co residue are recovered in the catholyte under the conditions tested, without the use of acid for the leaching. Considering the potential of the ED-UAE process to selectively recover Co from the WC-Co, the process involves 4 main steps: (1) anolyte acidification via water electrolysis, (2) Co is solubilized as ions, and WC remains solid; (3) electromigration of Co as ion (Co^{2+} , Co^{3+}) through the CEM to the cathode compartment, and WC remains in the anode compartment; (4) Co is recovered in the catholyte as pink hexaaquacobalt(II) ion.

The ED-UAE process proved to be an efficient method for Co extraction and separation from WC-Co residues, but further tests are needed to optimize W recovery and decrease the process time.

CRedit authorship contribution statement

Paula Guedes: Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Eduardo P. Mateus:** Methodology, Resources, Validation, Writing – review & editing. **Akram N. Alshwabkeh:** Funding acquisition, Methodology, Resources, Supervision, Writing – review & editing. **Alexandra B. Ribeiro:** Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scp.2024.101471>.

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