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Application of the electrodialytic process for tungsten recovery and arsenic removal from mine tailings

Dissertação para obtenção do Grau de Mestre em Engenharia do Ambiente, Perfil de Engenharia de Sistemas Ambientais

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Resumo

A deposição de resíduos de minas em barragens a céu aberto pode causar problemas ambientais. Por outro lado, estes resíduos podem constituir uma fonte secundária de matérias-primas críticas. A presente dissertação consiste no primeiro estudo da eficiência do processo electrodialítico (ED) para recuperar tungsténio (W) e remover arsénio (As) de resíduos da mina da Panasqueira (Covilhã, Portugal).

Realizaram-se nove experiências, algumas em duplicado, com recurso a células com dois (2C) e três (3C) compartimentos, na presença de membranas de troca catiónica (CAT) e aniónica (AN), com intensidades de corrente entre 0 e 100 mA e durações entre 7 e 14 dias. A amostra de resíduos de minas foi colocada no compartimento central na célula 3C e diretamente no compartimento do ânodo ou do cátodo nas células 2C.

Os resultados mostram que a configuração da célula com 2C e uma AN apresentou a maior recuperação de W (0.15 %) e remoção de As (23.51 ± 21.33 %). Nos casos de aplicação de uma CAT na mesma configuração, não se verificou migração de W e As para o compartimento do electrólito pelo que não ocorreu recuperação e remoção dos elementos. Posteriormente realizaram-se testes preliminares com a adição de três adjuvantes à amostra. Utilizou-se uma configuração de célula 2C e uma CAT dado que a célula 2C AN mostrou-se instável. Com a adição do adjuvante B, conseguiu-se uma recuperação de W de 0.64 % e uma remoção de As de 9.48 %.

Quanto maior a intensidade de corrente aplicada, melhor os resultados obtidos na recuperação de W e remoção de As. No entanto, a recuperação de W foi menor que a remoção de As, tal deve-se à presença de sulfatos na amostra que promovem a formação de complexos com o W. Futuramente devem ser realizados trabalhos experimentais para otimizar as condições da célula ED, não obtidas na presente dissertação.

Termos chave: Processo electrodialítico, mina da Panasqueira, tungsténio, arsénio, matérias-primas críticas, remediação

Abstract

Mining tailings (MT) deposited in open dams can cause environmental problems. On the other hand, these residues can be seen as a secondary source of critical raw materials. The present dissertation is the first attempt to study the efficiency of the application of the electrodialytic process (ED) for tungsten (W) recovery and arsenic (As) removal from Panasqueria mine residues (Covilhã, Portugal).

Nine experiments were performed, some in duplicate, using cells with two (2C) and three (3C) compartments, in the presence of cation (CAT) and anion (AN) exchange membranes, with current intensities between 0 and 100 mA and durations between 7 and 14 days. The MT sample was placed in the central cell compartment in the 3C setup and directly in the anode or cathode compartment in a 2C cell.

The results show that the 2C cell setup with an AN presented the highest W recovery (0.15 %) and As removal (23.51 ± 21.33 %). When a CAT was applied to the same cell configuration, W and As migration from the sample to the electrolyte compartment was not verified, and no elements recovery or removal occurred. Further preliminary tests were carried out adding three adjuvants to the sample. The 2C cell setup with a CAT was applied since the 2C AN cell showed to be instable. When the adjuvant B was added, the recovery of W achieved 0.64 % and the removal of As 9.48 %.

The higher the current intensity applied the better the W recovery and the As removal obtained. However, W recovery was lower than the As due to the presence of sulfates in the sample that promote the formation of W complexes. Future experimental work should be carried out to optimize the ED conditions, not obtained in the present dissertation.

Keywords: Electrodialytic process, Panasqueira mine, tungsten, arsenic, critical raw materials, remediation

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Abbreviations and symbols

[Fe/Mn]WO_4 - Wolframite

2C - Two compartment cell

3C -Three compartment cell

AN - Anion exchange membrane

AsO_3 -Trioxide arsenic

CAT - Cation exchange membrane

$CaWO_4$ - Scheelite

CCA - Chromium copper arsenide

CR - Collection rate

CRM - Critical raw materials

DC - Direct current

ED - Electrodialytic

EK - Electrokinetic

EOL-RR - End of life- recycling rate

EPA - Environmental Protection Agency

$FeWO_4$ -Ferberite

GaAs - Gallium arsenide

H_3AsO_3 - Arsenite

H_3AsO_4 - Arsenate

ICP-AES - Inductively Coupled Plasma-Atomic Emission Spectrometry

$MnWO_4$ - Hübnerite

MT - Mine tailings

MTS - Mine tailings solution

MTU -Maximum Transmission Unit

Mw - Microwave

OSR - Old scrap recycling

RSD - Relative standard derivation

STD - Submarine mine tailings disposal

Ti - Titanium

WC -Tungsten carbide

WO_3 - Tungsten trioxide

Wt - Weigh

1 Introduction

Mining activities are essential contributors to human wellbeing. As resource consumption increases, this industry becomes more important in the economy (Ma *et al.*, 2017). However, mining processes generate huge amounts of waste that are placed in open dams causing negative environmental impacts. According to Lottermoser (2010), mining industries annually produce approx. 20 to 25 billion t of solid mine residues, from which 5 to 7 billion t are mine tailings (MT). This production tends to increase up to 14 billion t/year due to the future low ore grades (Mudd & Boger, 2013). MT are fine particles rejected from the grinding, screening, or processing of the raw material. It can be regarded as a secondary source, since these residues still have contents of the explored ores (Cuesta-Lopez *et al.*, 2016).

Tungsten (W), for instance, is a stable transition metal with industrial and economic importance worldwide. Currently, there are several W applications, such as tools of steel, high-speed steels and creep-resistant steels (Lefebvre*et al.*, 2016; Pacheco, 2017). However, W is part of the European Union list of 27 critical raw materials (2017), with high economic importance and high risk of supply interruption. According to Peng *et al.* (2014), to produce 1 t of W concentrate 9 t of W tailings are generated in low grade W minerals.

In Portugal, Panasqueira mine (Covilhã) has been active for more than 100 years and is one of the largest tin (Sn) - W deposits in Europe, with 9.7 Mt of ore resources (Candeias *et al.*, 2014). In this sense, the study of technologies able to recovery W from MT are nowadays gaining importance, as well as the development of strategies that provides a way to channel by-products back into the value chain, contributing for a circular economy in Europe and in Portugal, in particular.

Arsenic (As) can also be found in these residues. It is a toxic metalloid to organisms at concentrations over 50 µg As/g in water, with a long term exposure (WHO, 2001a; Mandal, 2017) with harmful effects in public health, namely in cardiac and gastric systems (Jain et al., 2000; Chakraborti et al., 2002; Ng et al., 2003). According to Portuguese legislation (DL 152/17) As concentration in water for public consumption must be below 10 µg As/L. Therefore, efficient technologies to remove As from polluted matrices, such as MT, is essential for a safe storage and reuse of this source (WHO, 2001b).

The electrodialytic process (ED) consists on the application of a low level current density, either direct current or alternate current of a few mA/cm and a low potential gradient of V/cm, between suitably located electrodes (Acar & Alshawabkeh, 1993) in a contaminated matrix. The contaminants concentrate close to an electrode from where they are removed (Ribeiro & Rodríguez-Maroto, 2006). ED is applied to remove contaminants from porous matrices and it has been proved to be efficient for heavy metals removal from solid matrices, with removal rates over 80 % and low energy consumption (< 0.05 kWh/kg) (Velizarova *et al.*, 2001; Hansen *et al.*, 2004; Pedersen *et al.,* 2017).

The present work aimed to develop an electro-based technology to recover W and remove As from Panasqueria MT, never studied before. Several ED laboratory cell setups and experimental conditions

were tested to reach preliminary results of this treatment strategy.

Study objectives and research

This work carried out is the first attempt to develop an electro-based technology that is able to recover W and remove As from MT. The present dissertation proposes to answer the following questions:

1) Can the ED process be applied for W recovery from MT?
2) Is the ED process efficient for As removal from MT?
3) What are the material costs and the energy consumption of the targeted ED process?

To find answers to questions 1) and 2), laboratory experiments were carried out at RESOLUTION Lab using a MT sample from Panasqueira mine (rejected fraction from the sludge circuit that is directly pumped to the dam). The sample was submitted to the ED process in order to assess the W recovery and the As removal rates. Nine experiments were performed, some in duplicate, under different conditions, such as number of cell compartments, running time, current intensity, sample placement, type of ion exchange membranes and use of adjuvants. It should be stated that the adjuvants used in this dissertation are referred as A, B and C and not explicit due to intellectual property issues that still to be solved.

Finally, to answer question 3), the total energy consumption of the ED process was determinate by the consumption measurement of the pump, the stirrer and the power supply present in the ED scheme. An economic analysis of the process was completed, including material costs. The experiments feasibility was assessed considering the costs and the effectiveness of the process in W recovery and As removal.

Dissertation structure

The present work is organized in eight chapters:

1. Introduction - work scope and relevance, main objectives and structure;
2. Literature review - description of the central theme, relevant terminology and previous work developed;
3. Materials and methods - description of materials used, characterization analysis, identification and data treatment methods;
4. Results and discussion - presentation of results, hypotheses formulation and their discussion;
5. Conclusions – main outcomes;
6. Future developments;
7. References;
8. Appendix.

2 Literarure review

2.1 Mining industry

Resources consumption increases every year, becoming the mining industries one of the most important economic sectors worldwide. Hard rocks are worked to obtain ores with commercial value and, as a result of exploration, mining and processing of mine ores, MT are generated (Ma *et al.*, 2017), as schematized in Figure 2.1. This by-product is removed from mineral ores and it is generally disposed in open-air tailings impoundments without any treatment (Cuesta-Lopez *et al.*, 2016).

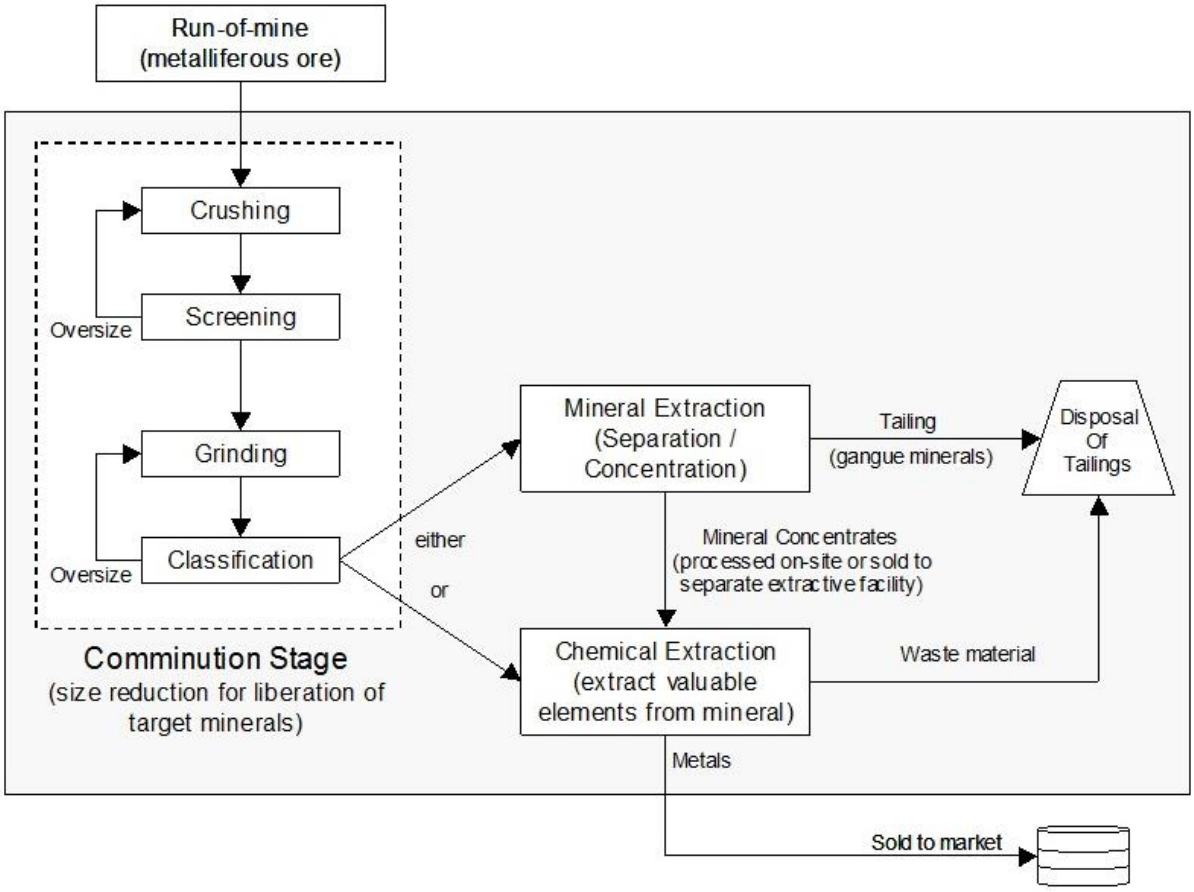


Figure 2.1- Mine processing scheme (Grewal, 2018)

MT predominantly consists of extremely fine particles rejected from the grinding, screening, or processing of raw material. Typically, this material ranges from sand to silt-clay in particle size (Cuesta-Lopez *et al.*, 2016) and usually contains water, heavy metals (Wang *et al.*, 2017) as well as other elements present in the exploited ore.

Mining residues may be inert and pose no danger to the environment. On the other hand, hazardous metals can be found in MT, being a potential risk for the involved ecosystem. Metals leaching may occur, although this process is dependent on the average pH (Guo *et al.*, 2012). Low ranges of pH may lead to an increase of metals solubility and a higher uptake from plants. The solubility of metals in MT is also affected by the temperature, where higher temperatures lead to upper leaching concentrations (Guo *et*

al., 2012). In addition, river beds can collapse or smothering, compromising ecosystem functions. According to the European Commission (2018), waste disposal from mining industries is massive.

Non-ferrous metals in mining industry may contain large quantities of hazardous substances. Metals and metal compounds tend to become chemically more available resulting in acid or alkaline drainage generation. This activity involves chemical residual processing and high concentration levels of metals, damaging the environment (European Commission, 2018).

Social, economic and further environmental considerations

Since 1950, atmosphere and the oceans global warming has been observed, affecting ice poles and sea level. The main reason is due to an increase of greenhouse gas emissions, mainly carbon dioxide (CO_2) (Smith *et al.,* 2017).

Figure 2.2 shows a correlation between global temperature (ºC) and CO_2 concentration (ppm). The continuous CO_2 intensification is followed by an increase of the global temperature (Angel, 2017).

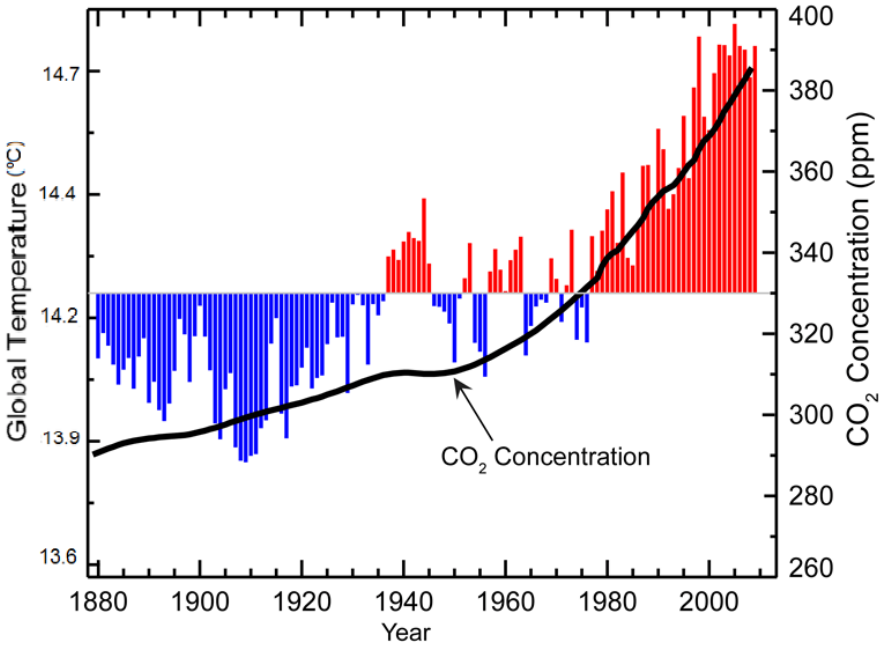


Figure 2.2 – Variation of global temperature vs CO_2 concentration (Adapted from Angel, 2017)

Studies have proved that human health is sensitive to changes in the climate system and it is expected an exacerbation of existing health problems and an appearance of new diseases (Smith et al. 2017). The mining industry is an economic activity with a major impact on the environment with adverse effects such as loss of biodiversity, erosion, contamination of surface water, ground water, soil and air quality, affecting population health (Worldatlas, 2017). Mining is integrated in the industry sector and, as shown in Figure 2.3, in 2010 produced more than 4.47 MGg of CO_2 equivalents, of a total of more than 40 MGg of CO2 equivalents, making this sector one of biggest contributors to climate change.

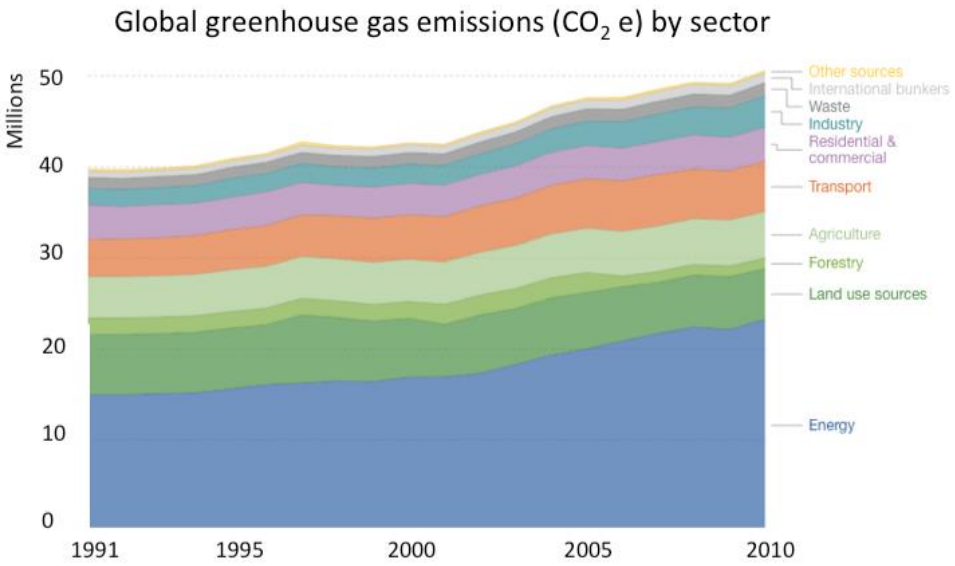


Figure 2.3 – Global greenhouse gas emission by sector (Ritchie & Roser, 2018)

There are different types of mines: underground and surface mines. According to Holmberg *et al.* (2017), rock braking, crushing, grinding, loading, hauling and transportation are the activities where larger amounts of energy are dispended. Holmberg *et al.*, 2017 estimated that mining and mineral industries worldwide use 4-7 % of the total global energy output. Considering Figure 2.4, there are three main operational categories in mining exploration. The highest energy consumption category is materials handling (42 %), followed by processing with 39 % and extraction with 19 % of representatively (Holmberg *et al.*, 2017).

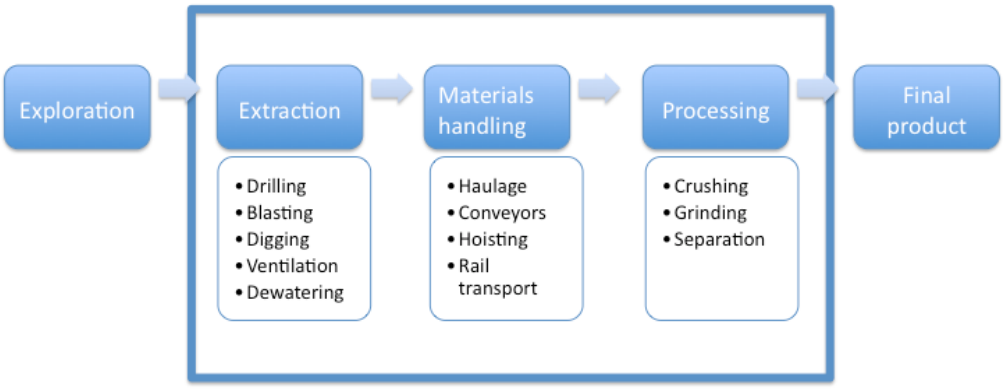


Figure 2.4 - Main operational categories in mining exploration (Adapted from Holmberg et al., 2017)

Regarding the huge amount of CO_2 emissions and the MT disposal ecosystem impact, it is important to carry out cost-benefit analysis to optimize the energy consumption of the process. Figure 2.7 presents a general methodology to do this analysis, commonly applied to support medium and long-term decisions in architectural, engineering and construction interventions (LNEC 2015).

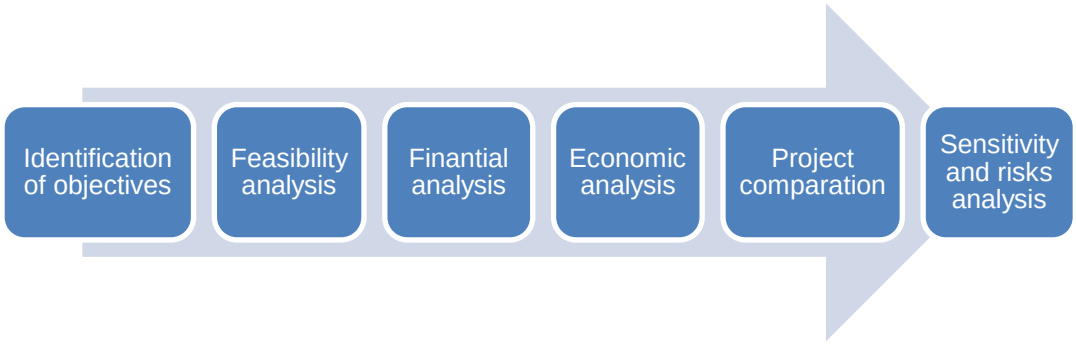


Figure 2.5 – Cost benefit analyses metodologie (Adapted from LNEC, 2015)

W mines in Europe

In Europe there are several mines with W reserves (tungsten trioxide, WO_3) and economic interest (Table 2.1). Portugal has three of those reserves but only Panasqueira mine is active (Yang *et al.*, 2016).

Table 2.1 - Synthesis of tungsten reserves in Europe (Yang et al., 2016;Ormonde, 2018; WResources, 2018)

Location	***Reserves (t) & % WO_3***	***Status***
England- Plymouth	35.7 Mt[1] - 0.18 % WO_3	Production estimated at 350,000 t/year of a tungsten concentrate with a grade of 65% WO3.
Spain- Los Santos	3.6 Mt[1] –0.23 % WO_3	Originally opened in 2008 and produces W concentrate.
Spain- Barruecopardo	27.4 Mt[1] – 0.26 % WO_3	Production rate of 1,100,000 t per year, to produce 260,000 t of WO_3 per year.
Spain- La Parilla	49 Mt[1] - 0.10 % WO_3	Production rate of 1 200 to 1 300 t/year and a grade of 66 % WO_3.
Spain- Valtreixal	2.5 Mt[1] – 0.34 % WO_3	In exploration
Portugal- Panasqueira	4.91 Mt[1] - 0.22 % WO_3	Active since 1890
Portugal- Borralha	18,500 t - 0.29 % WO_3	Closed since 1986
Portugal- Tabuaço	2.75 Mt[1] - 0.57 % WO_3	Closed
Austria- Salzburg	291,140 t - 0.65 %WO_3 (1978)	The deposit was discovered in 1967. Mining activities began in 1975, the ore dressing plant started operations in 1976.

[1]1 Mt = 1,000,000 t

Panasqueira mine

Panasqueira mine is an underground mine and one of the main Sn-W deposits in Europe. It is located in the center of Portugal, Covilhã, district of Castelo Branco (Figure 2.6). The surrounding area topography ranges between 250 to 1080 m in altitude with a deep valley (Candeias *et al.*, 2014).

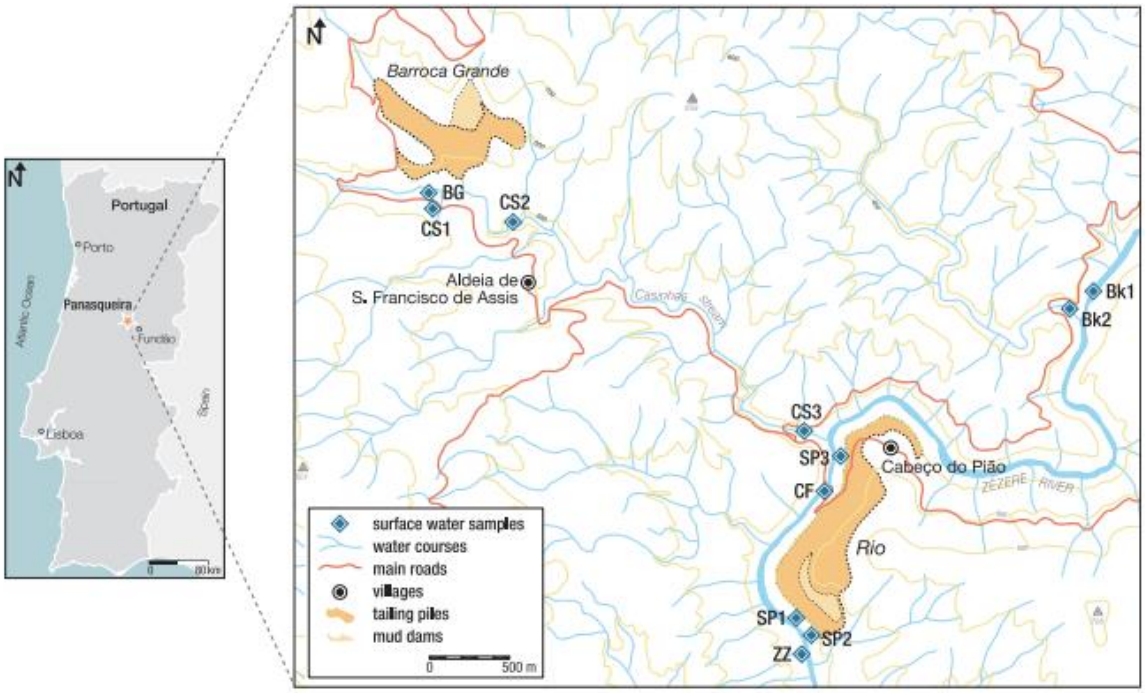


Figure 2.6 - Location of Panasqueira mine (Candeias et al., 2014)

Panasqueira mine have a secondary production of copper (Cu) and arsenopyrite (the main sulfide). These secondary products are discarded to the dams, which contain around 30 % of arsenic (As). This mine is active since 1896 and, between 1947 and 2001, 27 million t of rock were mined, corresponding to 92,800 t of W. The mineralogy of the surrounding area is characterized by wolframite, cassiterite, arsenopyrite, topaz, muscovite and tourmaline (Yang *et al.*, 2016). This is an area with national interest once is where the W active mining is located and there are MT piles and mud dams nearby small villages and the Zêzere river also crosses this area (Candeias *et al.*, 2014).

Figure 2.7 shows the processes that take place during mining exploration in Panasqueira, including the several stages of MT generation and the final ponds disposal.

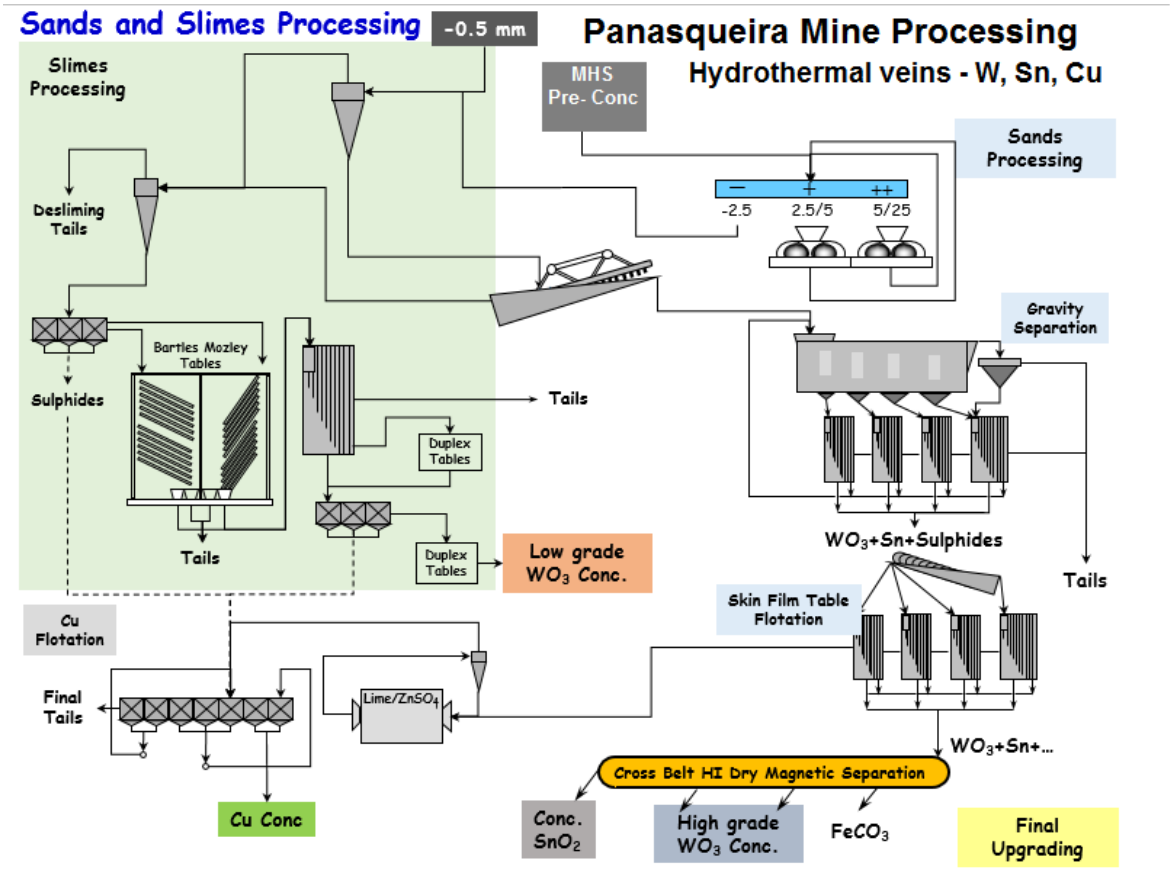


Figure 2.7– Processing plant of sands and slimes (Leite, 2017)

Currently, underground exploration, milling processes and MT piles account to approx. 7,000,000 m^3. There are two ponds, one active and one inactive, located in Barroca Grande with 1,193,885 m^3 of MT (Candeias *et al.*, 2014). In Table 2.2 it is visible that Panasqueira mines have an extended life with a considerable annual production of MTU's representing a good source of W.

Table 2.2 – Panasqueira mines characteristics (Adapted from Lefebvre et al., 2016)

Project Specifications	
Company/ Operator & Stock Exchange	Beralt Tin and Wolfram Portugal
Ore Resources Measured	9.54 Mt[2]
WO_3 grade (%)	0.22
Operating Cost/ MTU[1] (€)	130-140
Annual Production MTU'S WO_3	85,000 to 95,000
Mine life	10 years

[1] Conversion factor: MTU = 10kg, therefore 100 MTU = 1 t WO_3 contains 0,79 W.
[2] 1 Mt = 1,000,000 t

2.2 Tungsten

W is a stable transition metal found in nature. It is stored in high concentrations as waste product from mines, industries, agricultural and military activities (Erdemir *et al.*, 2017), however this element is considered to be toxic to the organisms causing breath problems (Erdemir *et al.*, 2017). W is a greyish-

white lustrous metal (Figure 2.8) with the highest melting point (3683 K), the lowest vapor pressure (1 x 10^{-8} mm Hg at 2400 K) of all metals, withstands corrosion strength and at temperatures over 1650 °C (Bilewska, 2016) and the highest tensile strength of 100,000 – 500,000 psi at room temperature (PowerStream, 2017; Midwest Tungsten Service, 2018).

Figure 2.8 – Tungsten metal (CRM Aliance, 2016)

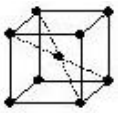
Magmatic-hydrothermal processes combined with granitic intrusions usually form W deposits. This type of deposits can be found within the peripheral part of the intrusive itself (greisen, porphyry, stock work and vein deposits), or in its vicinity (stock work, vein and skarn deposits). These deposits are often linked with tin or molybdenum mineralization (Schmidt *et al.*, 2012).

The European Union (EU) revealed a list of raw materials with a high risk of scarcity and economic relevance in order to guarantee their safe, sustainable and economic exploitation (EU, 2017). The identification of 27 critical raw materials (CRM) by the EU Commission aims to encourage their production and the promotion of new innovative recycling methods and activities that may contribute to circular economy in Europe (EU, 2017). W was introduced in the EU CRM list in 2017, with an end-of-life recycling input rate of 42 %. The W EU main supplies are given by Russia (50 %), Portugal (17 %), Spain (15 %) and Austria (8 %) (EU, 2017).

Chemistry

The extent of complexation of metals depends mainly on the amount of metal ions, complexed ligands and pH in solution. Thus, the total metal content of a solution is the sum of free metals plus the sum of all metal species it can form (Quina, 2005). The chemical and physical characteristics which can influence the behavior of W are listed in Table 2.3 (Lourenço, 2008).

Table 2.3 – Chemical and physical characteristics of W (NCBI, 2018)

General properties			***Physical properties***			***Atomic properties***
Cristal structure	*Element category*	*Molecular weight (g/mol)*	*Melting point (K)*	*Boiling point (K)*	*Heat of Vaporization (kcal/g-atm)*	*Oxidation states*
 Body centered cubic	Transition metal	183.84	3683	5803	1150	2-, 1-, 0, 1+, 2+, 3+, 4+, 5+, 6+

As shown in Table 2.3, W has nine oxidation states where the 6+ is the most stable. The speciation forms mainly emerge from an acid pH (Figure 2.9). WO_3 is the most common form in the environment and is present in solutions with pH bellow 2. W has acid-resisting properties and is easily soluble in mixtures of HF and HNO_3 (Flink & Jones, 1931). W can be transformed in complexes depending on its oxidation state. The main groups of complexes and resultant complexes are summarized in Table 2.4.

Table 2.4 – W complexes (Adapted Parish, 1966)

Type	**W oxidation state**	**W complexes**
Halides and oxyhalides complexes	W (V)	$[WO_xF_x]^{x-}$; $[WO_3F_2H_2O]^-$ $[WF_x]^-$;$[WO_xCl_x]^-$ $[WOBr_x]^{x-}$; $[W_xBr_x]^{x-}$
Cyano complexes	W (IV); W (V); W (II); W(III)	$[W(CN)_4(OH)_4]^{2-}$ $[W(CN)_4(OH)_3(H_2O)]^{3-}$ $W(CO)_6$
Thiocyanato complexes	W (IV); W(V)	WCl_6 ; WO_xClx $[W(OH)_3(NCS)_3]^-$ $W(NCS)_6$; $WO(NCS)_x$

In solution, W complexes are quickly decomposed and stabilized by high concentrations of chloride ions. One major product of the decomposition is $[W_2Cl_9]^{3-}$ (Parish, 1966). On the other hand, the adsorption of sulfate ions on metallic W surface results in the electronic structure modification. It also blocks oxygen reduction reaction, which is already low in cationic dissolution in electrochemical processes (Tunic *et al.*, 2011).

In nature, W is found in primary minerals like scheelite ($CaWO_4$), hübnerite ($MnWO_4$), ferberite ($FeWO_4$) or wolframite ($[Fe/Mn]WO_4$) and its mobility increases under alkaline conditions (Schwertberger, 2016).

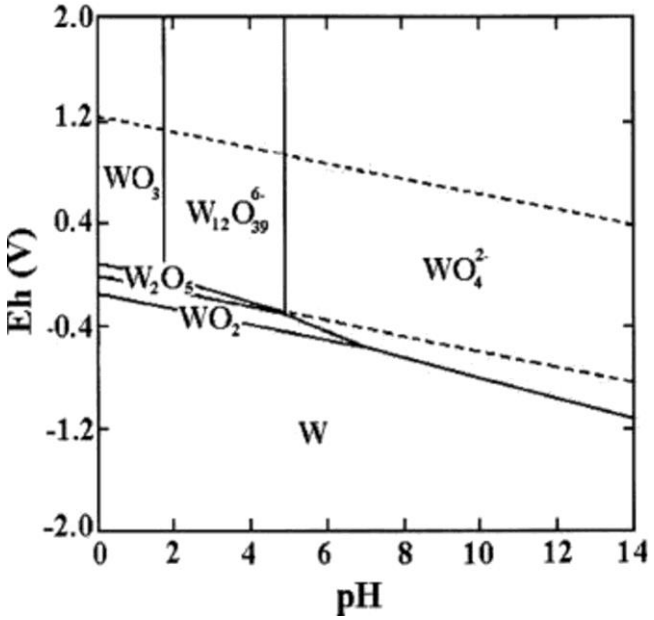


Figure 2.9 - Effect of pH on tugsten speciation (Flink & Jones, 1931)

Production

It is estimated that 87,000 t of mined W are extracted over the world annually. The principal W production takes place in China (82-85 %), Russia (5 %) and Canada (3.5 %). In Europe only four mines are still operating and one of them is in Portugal (Panasqueira, Covilhã). At Panasqueira mine, the ore deposit type is classical, with a content of ferberite or hubnerite mineralization. However, the total production of Panasqueira (Portugal), Los Santos (Spain), Mittersill (Austria) and Drakelands (UK) represents less than 1 % of the global production of W (Lefebvre *et al.*, 2016).

There are primary and secondary sources of W. The primary sources are minerals like wolframite and scheelite. The secondary resources are generated as a result of the extraction and processing of ores and minerals, as show on Figure 2.10. These residues can be divided into waste rock, MT, coal refuse, wash slimes and spent oil shale (Oeqvist, 2016).

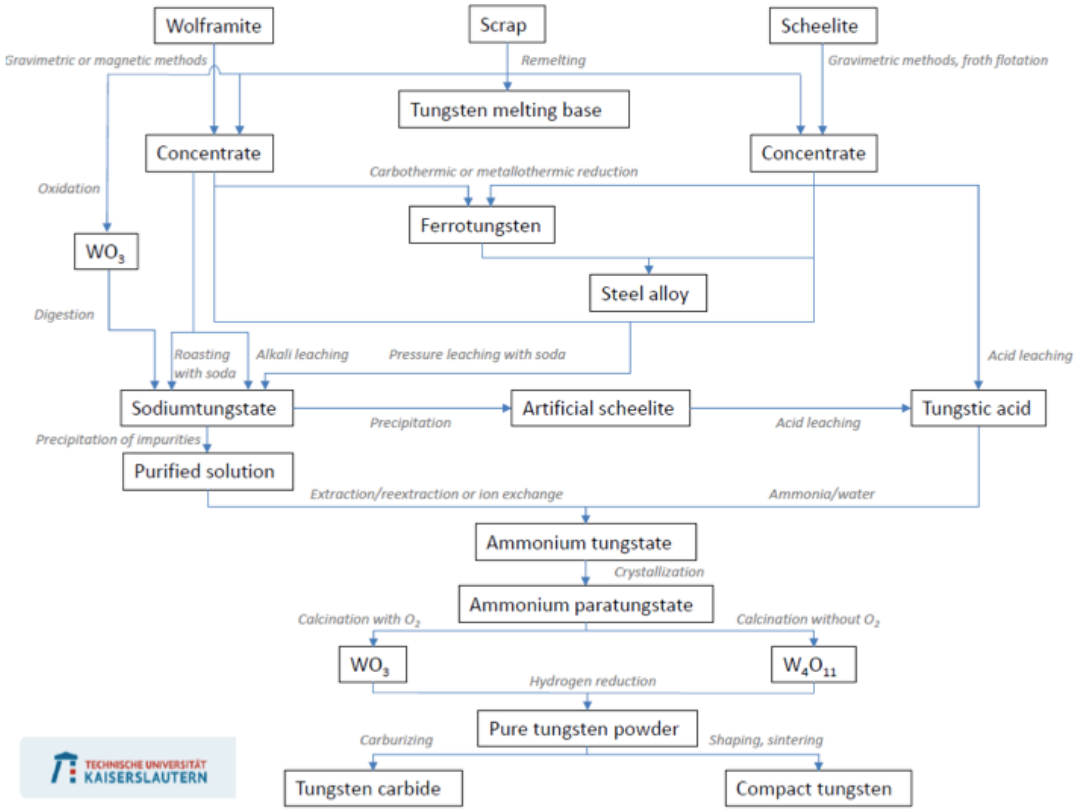


Figure 2.10. – W processing scheme (Oeqvist, 2016)

Applications

Throughout the world there are several applications of W. In 2010 there was a consumption of 71,000 t of virgin W and 95,000 t of secondary sources of W consumption including scrap (Lefebvre *et al.*, 2016). Cemented carbides dominate the market due to applications in steel tools, high speed steels and creep-resistant steels (Lefebvre *et al.*, 2016). W is mainly used for the production of hard materials (alloy and steel) based on tungsten carbide (WC) and less than 10 % is used in chemical compounds (Lambert, 2016)

W is an essential component for these tools manufacturing because of its high melting point, low coefficient of thermal expansion and lower vapor pressure than any non-alloyed metal. W is the heaviest metal with a gold-like density, a high modulus of compression, wear resistance, tensile strength and thermal and electrical conductivity (Bilewska, 2016).

As show in Figure 2.11, these materials are obtained in different stages of W processing. The highest concentrations (65-75 % WO_3) are directly used in steel manufacture. WC and alloys are produce from a low concentrate form of WO_3 (Yang *et al.*, 2016).

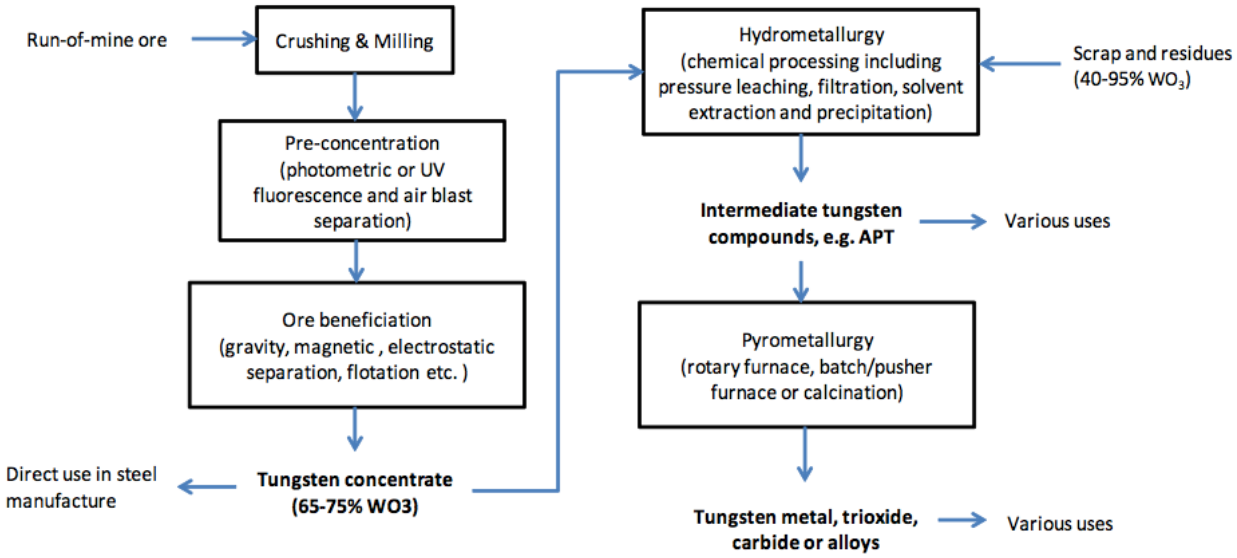


Figure 2.11- Stages of W processing for different materials (Yang et al., 2016)

WC represents a group of hard and wear resistant refractory composites where the hard carbide particles are bonded together by a ductile and resistant binder matrix. W has a high cost (20 € to 2,050 € per kg), being only used in operational parts for this reason. W is applied in mining, construction and metal-working (e.g. drill bits, machine tools for shaping metals, wood, composites, plastics and ceramics) (Bilewska, 2016; Midwest Tungsten Service,2018).

W is usually alloyed with high-speed steels which allows high productivity levels in metal curing. In superalloys, its high corrosion resistance is suitable for aerospace applications (Bilewska, 2016). Pure W mine products are used as light bulb filaments, vacuum tubes and heating elements. W powder is used in electric and electronic industries and some alloys include Cu and Ag for electrical contacts production (Bilewska, 2016).

Exportation

W has been considered economically important throughout the last years and its price also increased (Figure 2.12). W demand raised from 62,550 t in 2005 to 82,500 t in 2015 and the major consumer of W is China (64 %), followed by Europe (14 %) (Lefebvre *et al.*, 2016).

Figure 2.12 - Price variation of W (InfoMine, 2018)

In 2010, W ore reserves were estimated in 2.8 million t of W metal, where more than 60 % of these supplied were located in China. There were created new exportation restrictions during 2008 and 2013 and since 2015-2016 mines in Drakelands (UK) and Nui Phao (Vietman) became active (Lefebvre *et al.*, 2016).

W can be substituted by other compounds, although in most applications there is a loss of performance or a cost increase. In WC, W can be replaced by Mo, Ti, ceramics depleted uranium or hardened steel (Bilewska, 2016). As show in Figure 2.13 the three major applications of W have a high cost and will affect materials performance if a replacement of W occurs.

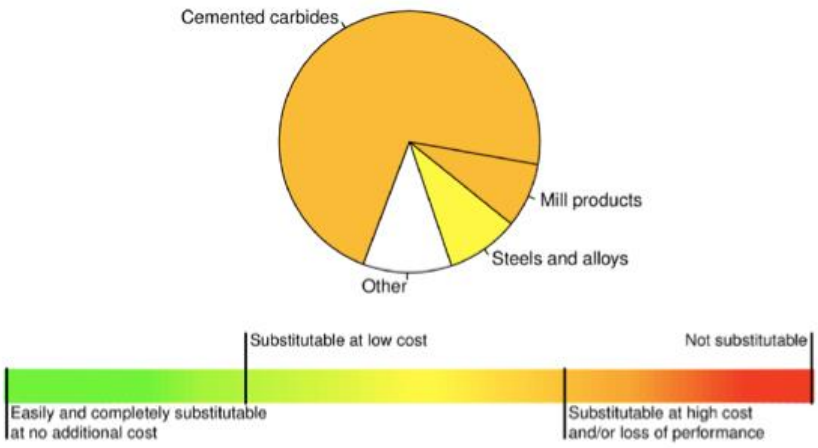


Figure 2.13 - Tungsten replacement analysis (Bilewska, 2016)

Recycling

The replacement of W is not always feasible. Thus, recycling is an attractive way to achieve environmental and economic benefits type of scrap. 2.5 presents different kinds of recycling depending on the type of scrap.

Table 2.5 - Tungsten recycling types (Adapted from Kurylak et al., 2016)

Type	***Specification***
Home scrap	Results during the material production. Its manufacture or fabrication can be reinserted directly into the process
New scrap	Results during fabrication and manufacturing. It cannot be recycled and it is transferred to the scrap market
Old scrap	Fragments in products that have achieved the end-of-life
Functional recycling	The metal in a discarded product is separated and sorted to obtain recycled fractions which are returned to raw material production process generating metals or metal alloys
Non-functional recycling	The metal is collected as old scrap and incorporated with a large-magnitude material stream as a tramp or impurity elements
Losses	The metal is not completely captured by any of the previous recycling flows

The recycle efficiency of a metal can be measured in three levels: Old scrap collection rate (CR); Functional recycling (EOL-RR: End-of-life – Recycling Rate) and Old scrap in the recycling flow (OSR) (Kurylak *et al.*, 2016). According to the same authors (Kurylak *et al.*, 2016), W has the highest recycling efficiency when old scrap is introduced in the flow (Table 2.6).

Table 2.6 – Recycling efficiency (Kurylak et al., 2016)

Refractory Metal	**Functional recycling (%)**	**Old Scrap collection rate (%)**	**Old scrap in the recycling flow (%)**
W	>10-25	>25-50	>50

W in scrap represents about 30 % of W from primary and secondary raw materials. The W-bearing scrap can be categorized as new scrap during the production of these materials and consumption and old scrap when the product reaches its end-of-life. The new scrap is collected because it cannot be recycled inhouse and old scrap is recycled depending on scrap availability from the collection system. Predominant recycled scrap includes cemented carbide scrap, heavy metal steel/alloy scrap and mine products from metal powder scrap, which are basically in accordance with the primary use (Kurylak et al., 2016).

Other materials like burnt-out lamps, electric contacts/devices, electrodes, bullets and surface coating materials are examples of other W-bearing wastes. Its recycling is difficult because they are dissipative

and so far there is no efficient way to collect them (Kurylak *et al.*, 2016).

Methods to recover W

There are various methods to process WC scrap and to recover W, such as the hydrometallurgical route, oxidation and electrochemical process. In the hydrometallurgical route, WC is immersed into leaching agents to dissolve the matrix. The main advantages of this process are the directly production of metal carbide and the low number of operations involved, saving time and energy (Katiyar et al., 2014). Table 2.7 shows some examples done after hydrometallurgical route to recovery metals from WC scrap.

Table 2.7- Hydrometallurgical processes for metals recovery from WC scrap (Adapted from Katiyar et al., 2014)

Leaching agent	***Temperature (ºC)***	***Type of scrap***	***Recovery/product***
Glacial acetic acid	118	Cemented carbide scrap	WC powder
HCl	140-195	Cemented carbide scrap	W metal
H_2SO_4	160-330	Scrap of cemented	W metal
HCl	55-85	Scrap of cemented	W
NaOH	120	Metal carbide scrap	WC

The oxidation is a leaching method used in scrap of WC. This material is first heated above the melting point of cobalt, which causes the swelling and generates a porous mass on cooling. The porous metal carbide scraps are then subjected to mechanical reduction to produce a fine powder of WC (Katiyar *et al.*, 2014). Some methods to process WC scrap following thermal oxidation are described in Table 2.8.

Table 2.8 - Thermal oxidation methods for treatment of WC scrap (Adapted from Katiyar et al., 2014)

Type of scrap	***Temperature (ºC)***	***Process***
Hard metal Heavy metal WC alloys	900	W is recovered using molten salt mixture of hydroxide and sodium sulfate.
Cemented WC	825	Oxidized product digested in 20-40 % alkali metal hydroxide to form alkali metal tungstate
W containing materials	680-700	Oxidation with sodium nitrate and leached with $CaCl_2$ and form crystalline calcium tungstate. Tungstic acid formed by 80-180 gpl HCl leaching.
WC	600-1050	Dissolution in solution of NaOH followed by spray drying to form precursor compound

In the electrochemical process the scrap acts as anode and graphite or platinum are used as cathode (Katiyar *et al.*, 2014). Table 2.9 shows the different conditions used in this process to obtain W.

Table 2.9 - Electrochemical processing for WC scrap recycle (Adapted from Katiyar et al., 2014)

Types of scrap	***Electrolyte***	***Current density***	***Recovery/product***
W alloy	NaOH	250 /Am^2 450 /Am^2	90 % W dissolution
W	NaOH	2.74 /$A.cm^2$	Tungstate
WC 6 % cobalt alloy	H_3PO_4	-	Co and W
Scraps of sintered metal carbide	HNO_3	-	Co and W
Hard metal scrap	10 % HNO_3	-	WO_3
Cemented carbide WC-87 %	HNO_3	-	W and Co
WC scrap	Aqueous ammonia	-	Co metal and WO_3

2.3 Arsenic

Arsenic is a toxic metalloid and widely distributed in the earth's crust. This metalloid occurs naturally in soils, rocks, water and air and it is usually combined with one or more elements, such as oxygen, sulfur or chlorine (WHO, 2001a; Mandal & Suzuki, 2002; Chou & De Rosa, 2003).

Arsenic can be found in a range between 1.5 to 3 mg/kg (Mandal & Suzuki, 2002), being the 20th element more abundant in earth's crust (NAS, 1977 in WHO, 1981) and the 12th element more abundant in the human body (Mandal & Suzuki, 2002). However there are natural or man-made sources as identified in Figure 2.14.

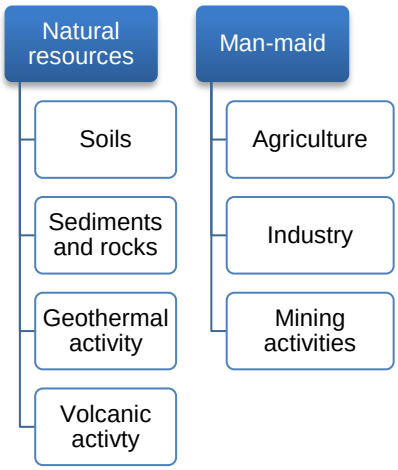


Figure 2.14 - Identification of natural and man-made sources os As (Correia, 2008).

Arsenic contamination in natural waters is the main concern on a global scale (WHO, 2001b). Figure 2.15 shows several countries where As incidents have been reported due to mining and mineralization, e.g. Bangladesh, West Bengal (India), inland of Mongolia (China) and Taiwan (Jain *et al.*, 2000; Chakraborti *et al.*, 2002; Ng *et al.*, 2003).

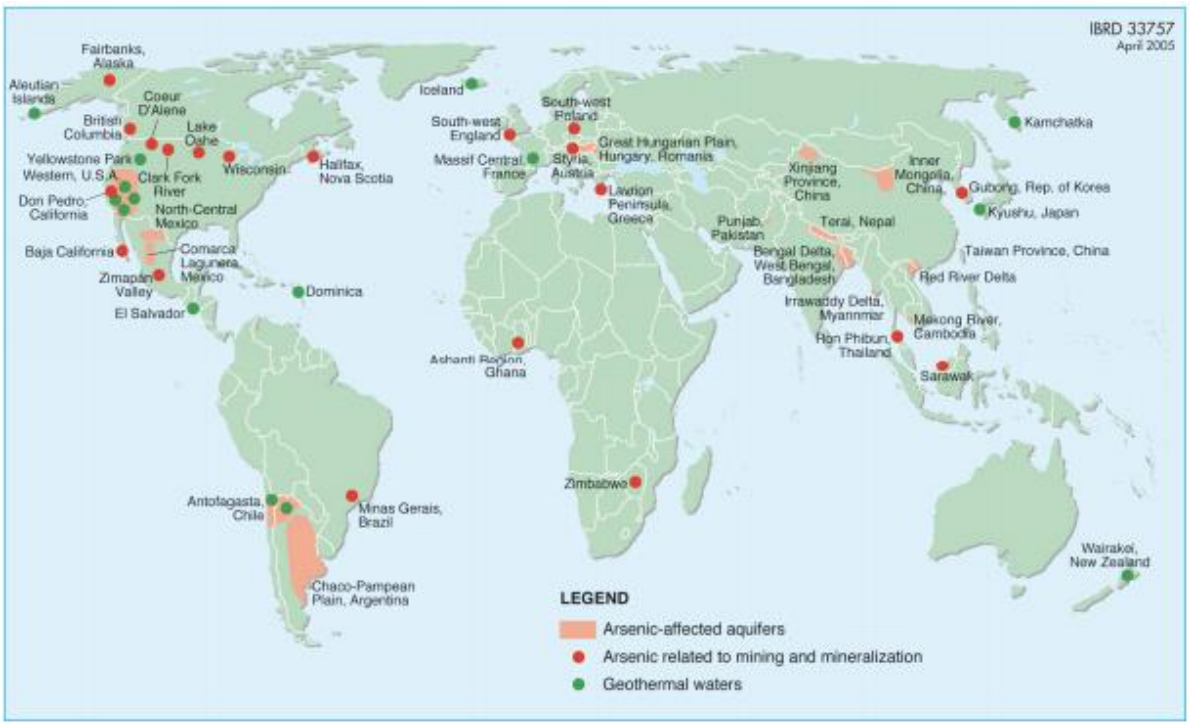


Figure 2.15 - Wolrd distribution of As contaminations and sources (Correia, 2008)

Arsenic is not only harmful to the environment but also for public health because of its toxicity and its bioaccumulable behavior through the food chain (WHO, 2001a). WHO targeted a limit in 1993 of As concentration in water for human consumption below 10 µg As/L and in 2007, Portugal also targeted this value (Decreto Lei nº 152/17 of 7th Dezember, from Ministério do Ambiente, 2017).

The inhalation and ingestion of As causes acute and severe toxic effects. The consequences of the exposure to As are cardiac and hypertension problems. Since the major concentration of As is in the water for consumption, gastric problems are also associated. In long-term exposition, problems in the kidney and liver can appear since these organs perform the function of filtering and excreting the residue of the liquid phase (Correia, 2008).

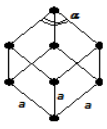
Figueira *et al.* (2007) carried out a study to evaluate the As exposure risk in Portugal. The authors concluded that the places where As concentration in drinking water was over 10 µg/L were in the north-east and interior center. This conclusion was related to the high number of groundwater abstractions, predominantly granite or schist lithology and to quartzite rocks (Matschullat, 2000 in Figueira *et al.*, 2007). In the north of Portugal, quartz is often associated with sulfur minerals, which can contain high levels of As and be easily leached (Morgada *et al.*, 2008).

High concentrations of As may also occur in areas close to mining activities, even if they are no longer active. The drainage water from the mines and the residues are typically acid and it may contain levels of dissolved As up to 48,000 µg/L (Welch *et al.*, 1988 in EPA, 2000b).

Chemistry

Table 2.10 summarizes chemical and physical properties of As. Its leaching behavior is one of the major mechanisms by As can enter in the ecosystems harming the environment and humans.

Table 2.10 – Chemical and physical characteristics of As (NCBI, 2018)

General properties			***Physical properties***			***Atomic properties***
Cristal structure	*Element category*	*Molecular weight (g/mol)*	*Melting point (K)*	*Boiling point (K)*	*Heat of Vaporization (kcal/g-atm)*	*Oxidation states*
 Rhombohedral	Metalloid	74.99	885	885	11.2	3-,0, 3+, 5+

The main As species are pentavalent arsenate (As^{5+}) and trivalent arsenite (As^{3+}), represented in Figure 2.16 as H_3AsO_4 and H_3AsO_3, respectively, in a pH below 2. These As forms are not stable in soil at long term. Arsenic can be found as poorly crystalline As-bearing solids, As-sorbed species and organic forms of As, mainly methylated compounds and carbohydrate derivative (Morin & Calas, 2006).

Elementary arsenic is not soluble in water, but inorganic As trivalent and pentavalent have a solubility of 37 g/L at 20 ºC and 302 g/L at 12.5 ºC, respectively (Danish Ministry of the Environment, 2014). In soil, As can form insoluble complexes with iron, aluminum and magnesium oxides. This type of arsenic, mixed with insoluble complexes, is immobile, although in the reduction state the arsenite is predominant and the complexes formed are mobile (Danish Ministry of the Environment, 2014).

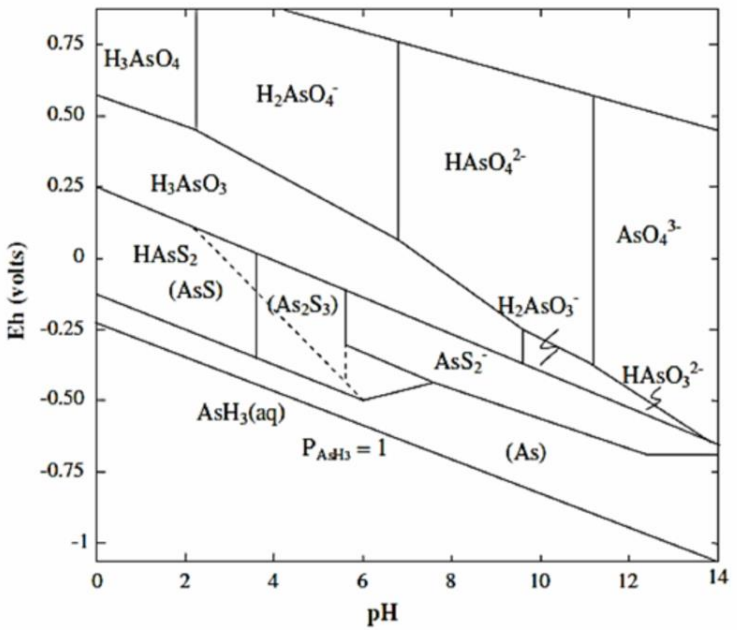


Figure 2.16 - Effect of pH on arsenic speciation (Nicomel et al., 2016)

Production

The largest producers of As are China, Russia, France, Mexico, Germany, Peru, Namibia, Sweden and the United States of America. These countries hold about 90 % of world production as can be seen in Table 2.11 (WHO, 1981; Nelson 1977 and US Department of the Interior Bureau of Mines, 1973 in Mandal & Suzuki, 2002; Edelstein, 201).

Arsenic Trioxide (AsO_3) is recovered from the smelting or baking of non-ferrous minerals ore or concentrates. However, dust and smelting residues with high As concentrations in hot air are normally processed for commercial AsO_3 (Reese, 2000).

Table 2.11–Principal producers of As (Adapted from Edelstein, 2016)

Countries	***Production of AsO_3 (t)***	
	2014	**2015**
China	25,00	25,000
Morocco	8,800	8,500
Russia	1,500	1,500
World total (rounded)	36,400	36,000

Applications

Trade data indicates that USA, with an estimated demand of more than 24,000 t in 2000, will probably remain the world's largest consumer of As. More than 95 % of the As consumed was estimated to be in its primary form AsO_3, for the production of wood preservatives. However, As is also applied to herbicides for weed control, as a metalloid additive to improve corrosion resistance and tensile strength in copper alloys, and as a minor additive to increase the strength of posts and grids in lead-acid storage batteries (Reese, 2000). Table 2.12 presents As main applications.

Table 2.12- Principal applications of As in different sectors (Adapted from Correia, 2008)

Sector	***Uses***
Wood	Wood preservatives
Agriculture	Insecticides, fungicides and other pesticides, defoliants, peeling agents
Agro-livestock and poultry farming	Food additives, disease prevention agents, anti-parasites, algicides
Medicine	Anti-syphilitic drugs, chemotherapy, treatment oftrypanosomiasis, amoebiasis and sleep disease
Industry	Glass, electrophotography, catalysts, pyrotechnics, dyes and soaps, ceramics, pharmaceutical substances, alloys (automotive welding and radiators), battery plates, solar cells, light emitting diodes on digital watches

Recycling

Arsenic can be recycled from the manufacture of gallium arsenide (GaAs), semiconductors and water from wood treatment, where it is used as chromium copper arsenide (CCA). Although boards, relays and circuit breakers may contain As, recycling is a difficult process because As is mixed with other metals (Edelstein, 2016).

Methods to remove As

Considering MT interact directly with soil and water, Table 2.13 describes remediation methods for both matrices.

Table 2.13 – Methods to remove As from water and soil (Adapted from Shrestha, 2011; Lim et al. 2014)

Water		***Soil***	
Method	*Resume*	*Method*	*Resume*
Oxidation	Conversion of arsenite into arsenate by oxidation with oxygen (O_2), hypochlorite (HClO), permanganate ($HMnO_4$) and hydrogen peroxide (H_2O_2).	Soil washing	Contaminated soil washed with different concentration of chemicals such as sulfuric acid, nitric acid, phosphoric acid, and hydrogen bromide.
Coagulation	Precipitation: formation of insoluble compounds; Co-precipitation: incorporation of soluble As species into a growing metal hydroxides phases; Adsorption: electrostatic binding of soluble As to external surfaces.	Additives (surfactants, co-solvents, etc.)	Improves the efficiencies of soil flushing using aqueous solutions as water solubility is the controlling mechanism of contaminant dissolution.
Ion exchange	A pre-oxidation converts arsenite into arsenate and since the ion exchange process is less dependent on pH of water arsenate is removed.	Coagulation and filtration	This method is economic but often displayed efficiencies <90 %
Membrane techniques	Low-pressure membranes such as microfiltration and ultrafiltration; High-pressure membranes such as nanofiltration and reverse osmosis. This process depends on pH and the presence of other.	Intrinsic bioremediation	The degradation of As occurs by naturally occurring microorganisms. More suitable for remediation of soil with a low level of contaminants.
		Engineered bioremediation	Optimization of the environmental conditions to promote the proliferation and activity of microorganisms. This is more favorable in highly contaminated areas.

2.4 Electrodialytic process

The electrodialytic (ED) process has proved to be an efficient method to remove metals from solid porous matrices (Hansen *et al.*, 2004). ED process is commonly applied to remove metals and results from a combination of charged species movement (electrokinetic process) and electrodialysis (Ribeiro & Rodríguez-Maroto, 2006).

In the electrokinetic (EK) process a low level direct current (DC) is applied, passing by a pair of electrodes in a system with charged particles and promoting the movement of contaminants (Guedes *et al.*, 2014). The dislocation of particles happens because of mainly three mechanisms: electromigration, electroosmosis and electrophoresis (Ribeiro & Rodríguez-Maroto, 2006).

The main difference between ED and EK processes are the use of ion exchange membranes to separate the contaminated matrix from the electrodes compartments: ED uses them while EK uses passive membranes instead (Ribeiro & Rodríguez-Maroto, 2006).

In a three compartment ED cell (3C), the electrodes are placed in the compartments at both ends where the electrolyte solutions circulate (Figure 2.17). The contaminated matrix is placed in the central compartment separated by ion exchange membranes. The anion exchange membrane (AN) separates de anode from the central compartment, and a cation exchange membrane (CAT) divides the central compartment from the cathode end, allowing the passage of anions and cations, respectively (Guedes *et al.*, 2014). The use of ion exchange membranes increases the efficiency of removal because the membranes have good conducting properties, decreasing power consumption and providing good chemical stability over an extensive pH range (Ribeiro & Rodríguez-Maroto, 2006).

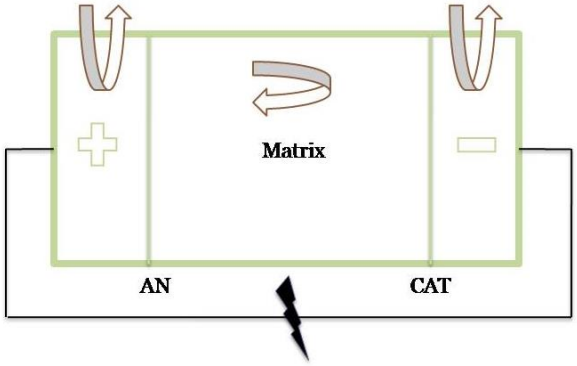


Figure 2.17- Schematic representation of the three compartment electrodialytic cell (3C).
AN – anion exchange membrane; CAT – cation exchange membrane

Electromigration

Electromigration is the movement of ions through water or moist soil, when an electric field is applied (Kelsh, 1996). This mechanism occurs in matrices with soluble charged species, such as heavy metal cations. Positive ions move in the direction of the cathode and negative ions in the direction of the anode end (Ribeiro & Rodríguez-Maroto, 2006).

The migration flux, J_m is given by:

$$J_m = u * \phi_e \quad \textbf{(2.1)}$$

Where:

u* and c are respectively the ionic mobility and concentration of species, and *Φe* the gradient of electric potential.

The current efficiency of electromigration of specific ionic species is expressed as the proportion of electrical charge carried by the species of interest, relative to the amount of charge carried by all charged species in solution (Ribeiro & Rodríguez-Maroto, 2006). This is the most important transport mechanisms for ions in porous media. The electromigration flux is dependent on the ionic mobility, tortuosity factor, porosity of the material and ions charge (Acar, 1993).

Electroosmosis

Electroosmosis describes the mass flux of pore fluid relative to soil particles under the influence of an electric potential gradient (Ribeiro & Rodríguez-Maroto, 2006). This mechanism is more efficient in the removal of uncharged and/or weakly dissociated organic contaminants, such as phenols (Ribeiro *et al*, 1999).

When an electric field is applied in a wet matrix, the flow-direct usually promotes the movement of cations in direction to the cathode and anions to the anode. When the ions migrate, they carry their water of hydration and they exert a viscous drag on the pore fluid around them (Ribeiro & Rodríguez-Maroto, 2006).

Electromigration of species usually occurs from the anode to the cathode because the species diffuses in a double layer that is often positively charged, e.g. soil. However, if there is a low range of pH values, the charge is performed in opposite direction, which can cause a change in the electroosmotic flow (Jensen, 2005; Ribeiro & Rodríguez-Maroto, 2006).

The electroosmotic flux, J_{eo}, is described by the following equation:

$$J_{eo} = -k_e c \phi e \quad \textbf{(2.2)}$$

Where K_e is the electroosmotic permeability of soil, c the concentration of species, and *Φe* the gradient of electric potential.

The electroosmotic transport of water should be low to ensure the matrix volume to maintain a wet interface between the soil and the membrane (Ribeiro & Rodríguez-Maroto, 2006).

Electrophoresis

Electrophoresis is the movement of a charged colloid under an applied electric field. The colloids are

attracted to one electrode and replied by other. The negative charged particles move towards the anode end and the positive charged towards the cathode end (Ribeiro & Rodríguez-Maroto, 2006).

Diffusion

Diffusion is the movement of species under a chemical concentration gradient in porous media and free solutions. The diffusion can be expressed by Fick's law, where its coefficient must be obtained by correction, considering the porosity and the tortuosity effects. This can decline the movement in more than one order of magnitude (Ribeiro & Rodríguez-Maroto, 2006).

The diffusive flux in soils, J_d, is given by:

$$J_d = -D * \nabla c \quad \textbf{(2.3)}$$

Where:

D* – Effective diffusion coefficient

∇c - Concentration gradient

Usually this is a secondary transport and can be important only in some areas of the soil where the gradients are higher (Ribeiro & Rodríguez-Maroto, 2006).

Electrodialysis

Electrodialys is a movement derivate from the presence of exchange membranes. As CAT and AN are permselective, their use increases transport efficiency of species from the cathode or anode. The flux of the electrolytes does not circulate between the two electrodes compartments and the matrix is continuously emptied of anions and cations, until there are no ions to be transported. The resistance will increase until a certain level and then it will become constant (Ribeiro *et al*, 1999).

The membranes should have a high exchange capacity to maximize the fluxes of counter-ions and minimize electrical resistance, high selectivity for opposite charged ions and high permeability in order to save electricity during the transportation (Ribeiro & Rodríguez-Maroto, 2006).

Reactions in the electrode compartments

In an ED cell, the electrolyte can be continuously recirculated in a closed system, through a peristaltic pump (Guedes *et al.*, 2015). The reactions at the electrodes are key factors for the variation of pH values. Therefore, the electrodes must be inert (e.g. carbon, platinum or titanium) to guarantee that they will not take part in the electrode reactions (Nystrøm, 2001).

The electric current applied favors the occurrence of electrolysis of water at the electrodes, generating an acidic media at the anode and an alkaline media at the cathode (Ribeiro & Rodríguez-Maroto, 2006). Water electrolysis is given by the following equations:

Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ **(2.4)**

Cathode: $4H_2O^- + 4e \rightarrow 2H_2 + 4OH^-$ **(2.5)**

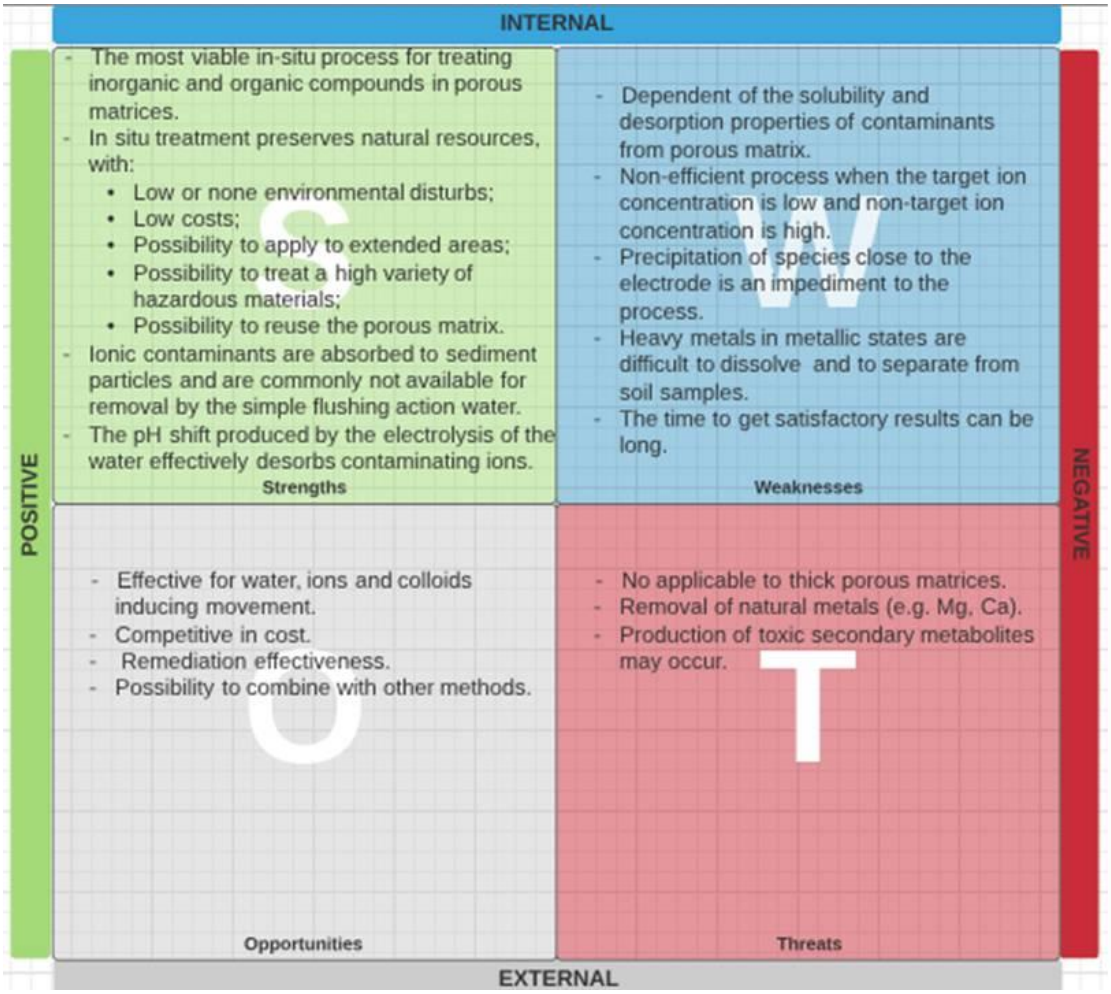
If chlorides are present in the electrolyte (anolyte), chloride gas is produced.

Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ **(2.6)**

SWOT analysis of the ED process

The ED process has benefits and limitations. To analyze the main outcomes of this process, a SWOT (strengths, weaknesses, opportunities and threats) analysis was carried out, as seen in Table 2.14.

Table 2.14 - SWOT analysis of ED process (Adapted from Gardner, 2005 in Almeida, 2015)



2.4.2 Metal speciation of MT from Norway before and after electrodialytic extraction

Submarine MT disposal (STD) has been used as an alternative for disposal on land. They have several environmental effects that can change depending on the site and on metal binding. In Repparfjorden, in Kvalsund, Northern Norway there is a STD site, where between 1972 and 1978 the Cu mining resulted in the release of approximately 1,000,000 t of Cu-enriched MT. In many cases, it has been used a

sequential extraction to measure how metals are bounded in sediments/ soils, considering that these sediments are from the old and new deposit (Pedersen *et al.*, 2017).

To analyze the concentration of Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, As, Cd, Cr, Cu, Ni, Pb and Zn, the sediments were dried at 105 ºC (1.0 g) and HNO_3 (9 M, 20 mL) was added prior to be submitted to a digestion process (Norwegian standard NS4770) at 200 kPa, 120 ºC during 30 min. Then solid particles were removed by vacuum filtration and the liquid was diluted to 100 mL. The liquid was evaluated by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) to measure metal concentrations. The conductivity was measured after drying the sediments and then mixed with distilled water for 1 h. After it was used a radiometric analytical electrode to analyze the parameter (Pedersen *et al.*, 2017).

For these experiments it was used two different setup cells, both with two compartments to perform electrodialysis extraction as represented in Figure 2.18. This configuration was chosen to explore electrodes reactions to ensure acidifying (A) or alkalifying (B) the suspension. The acid/base extraction was made with 10 samples of dried sediment (5 g) with HNO_3 (25 mL) or NaOH (25 mL) in different concentrations and in constant stirrer (Pedersen *et al.*, 2017).

Ion-exchange membranes were used to prevent transport of ions between the two cell compartments, and the application of a CAT in the acidifying electrodialysis cell prevented the hydroxyl ions from the electrolysis reaction on the cathode from entering the suspension. By applying an AN in the alkaline electrodialysis cell, protons from electrolysis reactions on the anode were similarly prevented from entering the compartment with the suspension (Pedersen *et al.*, 2017).

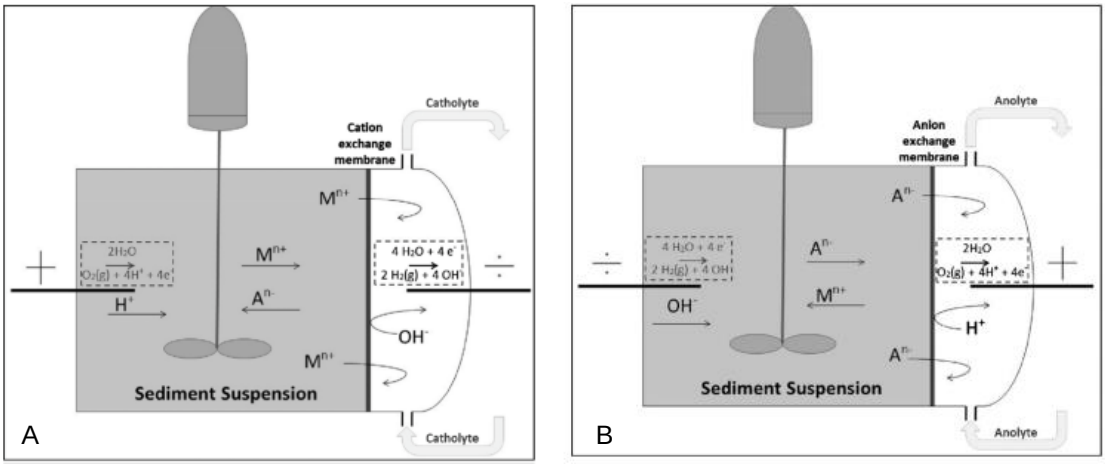


Figure 2.18–Electrodialysis. A: acidic electrodialysis B: alkaline electrodialysis (Pedersen et al., 2017)

This study shows differences in metal concentrations between the fresh tailings and the aged sediments. This happens because the origin of rock can be different. The electrodialytic extraction is significant in fresh tailings but not in the aged ones, since there are presently no prospects of dredging and treating of the aged sediments. Tailings have high concentrations of carbonates. Thus, the time needed to acidify the matrix is more extensive than to alkalify the tailings (Pedersen *et al.*, 2017).

These experiments demonstrated highest removals of metals in the acidic electrodialytic treatment. In the alkaline electrodialysis most of the dissolved metals (>90 %) were found in the cathode compartment, demonstrating that metals can form complexes. In the anode compartment were found 97 % of the Cu, 60–85 % of Fe, Mg and Mn, 30 % of the Cr, and 2 % of the Al. In the acidic electrodialysis, approximately 30 % of the metals in the liquids are kept in suspension because of the fast change in pH, promoting the dissolution of carbonate (pH <4) and resulting in large amounts of desorbed metal that did not pass across the ion exchange membrane. In the cathode compartment, 15 % of the Cu, 30 % of the Mg, 60 % of Mn and less than 3 % of Al, Fe was found (Pedersen *et al.,* 2017).

The electrolysis reactions at the anode end provided oxidation conditions and resulted in the release of metals bound in sulfides. Extracting Cu from the recently processed MT by alkaline and acidic electrodialysis improves mobilization and affects minerals stabilization in the tailings to a lesser degree. This indicates that the electrodialysis can be designed for targeted removal of Cu, while limiting the mobilization of other metals from the tailings (Pedersen *et al.*, 2017).

2.5 Analytic techniques

2.5.1 W and As determination

Microwave assisted acid digestion

According to Environmental Protection Agency (EPA), the method 3051 A was designed to mimic extraction using conventional heating with concentrate nitric acid (HNO_3), or nitric acid and hydrochloric acid (HCl). This technique provides a multi-element extraction for further application of spectroscopic methods, such as inductively coupled plasma – atomic emission spectrometry (ICP-AES) (EPA, 2007).

The operation principle for microwave assisted digestion systems is the preservation of the sample compounds and the reagents reaction under their boiling point, while increasing pressure and temperature though microwave energy (Yang *et al.*, 2017). Table 2.15 presents a sum-up of advantages and limitations of the microwave assisted acid digestion.

Table 2.15 - Advantages and limitations of microwave assisted acid digestion (Adapted from: Yanget al., 2017)

Advantages	***Limitations***
Short term technique.	Insufficient extraction selectivity.
Multi-sample digestions.	Extract must be separated from the "post-extraction residue".
Precision on a range of low abundance elements.	It is necessary to carry out a cleaning program.
Automatic operation.	The cooling time of the bottles can be long.
Does not generate acid steam.	

Inductively coupled plasma- atomic emission spectrometry

Inductively coupled plasma- atomic emission spectrometry (ICP-AES) allows a multi-element analysis. This analysis is conducted under a reduced number of samples, low reagent needs and low waste generation. With this technique it is also possible to analyze different metals contents in simultaneous, improving the sample throughput (Martínez *et al.*, 2018).

ICP-AES can analyze dissolved samples, varying from solutions containing high salt concentrations to diluted acids. The source used to dissociate the sample into its constituent atoms or ions is based on the exciting of ions to a higher energy level. When the compounds return to their ground state, they emit photons with a characteristic wavelength, which depends on the present elements. The emitted wavelength is recorded by an optical spectrometer (Philips, 2013).

Ionic Chromatography

The process of chromatography using ion exchange is based in an eluent loading, sample injection, sample separation, elution (movement thought the column) of analyte A and elution of analyte B (Wenzel, 2018).

Initially the eluent is continuously introduced into the column creating a flow through the column. Then the sample that contains the analyte A and analyte B is injected and keeps moving through the column. Analyte A and B remain in the column surface and some zones are created which separate the analytes. With the presence of eluent, the existent flow promotes the elution of analyte A and then analyte B of the column, separating both (Wenzel, 2018).

3 Material and methods

The Figure 3.1 represents the methodology applied for the dissertation experimental work. In this chapter all the materials and methods used are presented.

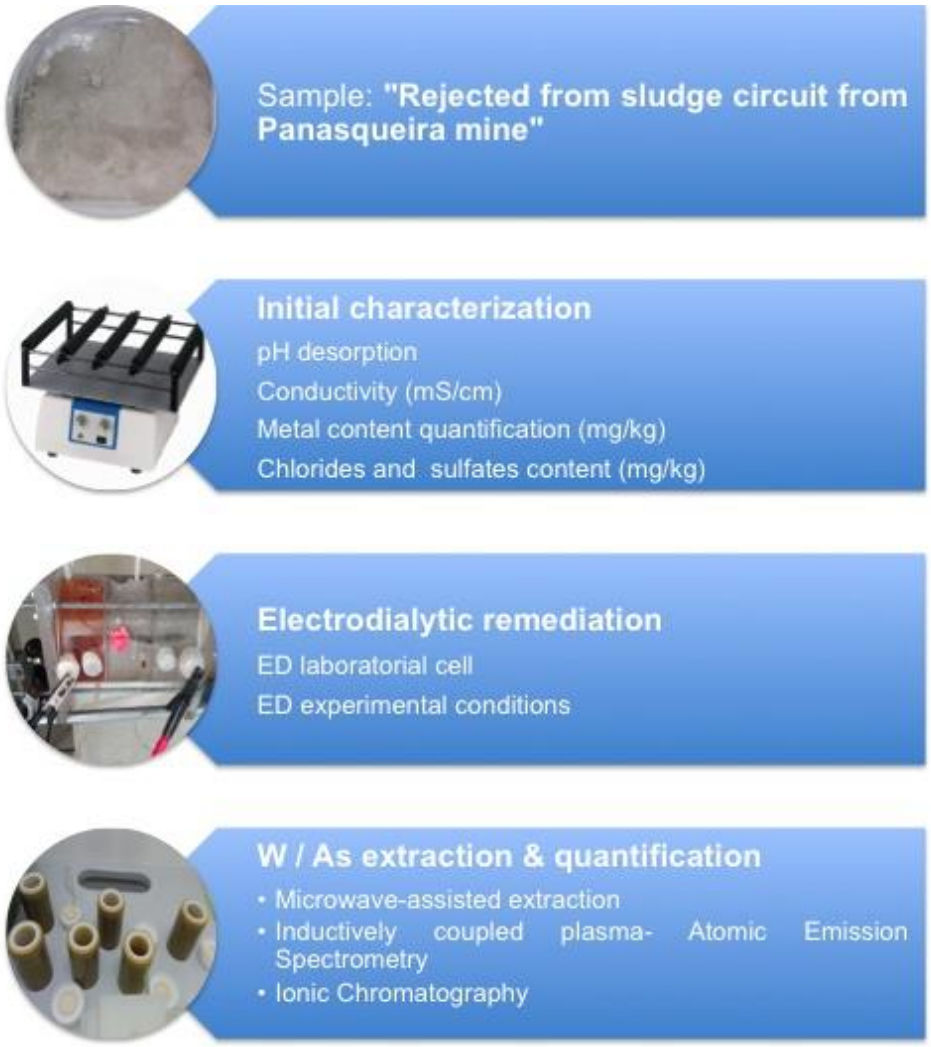


Figure 3.1 – Applyed methodology

3.1 Initial characterization

pH desorption

To determine the pH influence in As and W desorption, 2.5 g of MT were suspended in 12.5 mL of different concentrations of HNO_3 and NaOH with deionized H_2O to have solutions with pH between 1 and 14 (Table 3.1). The suspensions were placed at a shaking table for one week at room temperature. At the end of the experiment, the pH was measured with a 744 pH meter, Metrohm. The suspensions were filtered by vacuum using 0.45 µm filters and As and W concentrations were determinate by ICP-AES analysis, as explained in chapter 2.5.1.

Table 3.1- Reagents used for pH desoption tests

Reagents	
NaOH concentration (M)	*HNO_3 concentrations (M)*
	1.0
	0.7
1.0	*0.5*
0.5	*0.3*
0.05	*0.1*
0.01	*0.08*
	0.05
	0.01

Conductivity

The conductivity of the samples depends on the number of conductive particles present in the liquid phase. To determine the conductivity, 5 g of the sample were mixed with 12.5 mL of H_2O and then placed in a shaking table for 24 h at room temperature. After shaking for 24 h, the conductivity of the samples was measured with a Horiba Iaquatwin equipment, in mS/cm.

Quantification of W and As content

To quantify the initial content of W and As microwave assisted acid extraction was done according to EPA method 3051 A. Thus, 0.5 g of MT were placed in a vessel with 3 mL of HCl and 9 mL of HNO_3 and placed in a microwave from Milestone Ethos (Bergamo, Italy). At the end, the samples were diluted (1:25) and filtered by vacuum using 0.45 μm filters. As and W concentrations were determined by ICP-AES analysis, as explained in the section 2.5.1.

Chlorides and sulfates content

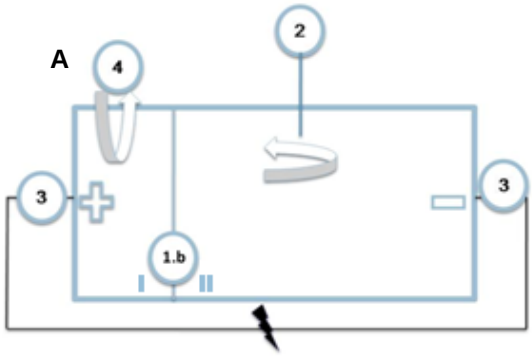
To quantify the content of chlorides and sulfates, 5 g of MT were mixed with 25 mL of deionized H_2O and then placed in a shaking table for 24 h, at room temperature. The samples were after filtered by vacuum, using 0.45 μm filters and further analyzed in ionic chromatography (DIONEX ICS-3000 equipment).

3.2 Electrodialytic experiments

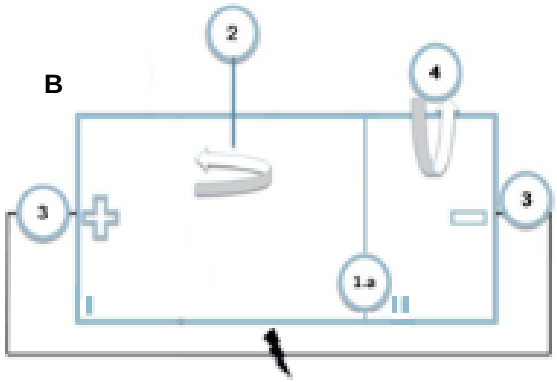
ED laboratorial cell

The experiments were carried out in a two (2C) and three (3C) compartment ED cell. All compartments have an internal diameter of 8 cm, a length of 10 cm in the sample compartment and a length of 5 cm in the electrolyte compartments. The electrodes were applied in each compartment, except when a 3C setup was used (the central compartment does not have an electrode). Electrodes are made of platinized titanium bars with a 3 mm diameter and a length of 5 cm (Bergsøe Anti Corrosion A/S,

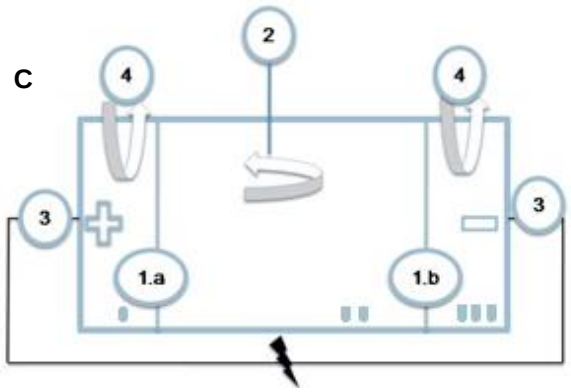
Herfoelge, Denmark). Commercial cation and anion exchange membranes (AR204 SZRA B02249) from ionics were also used to separate the compartments. The compartment where the sample was placed was also equipped with a stirrer. Figure 3.2 schematically represents the ED cell setups tested in the present dissertation.



I- Anode compartment (Electrolyte); II- Cathode compartment (MT)



I- Anode compartment (MT); II- Cathode compartment (Electrolyte)



I- Anode compartment; II- Central compartment (MT); III- Cathode

Figure 3.2 – Schematic representation of the ED cell: 1 - Ion exchange membrane; 2 - Stirrer; 3 - Electrodes (+ anode; - cathode; 4 - Recirculation system of electrolytes. A) Two compartment cell with a anion exchange membrane (1.b); B) Two compartment cell with an cation exchange membrane (1.a); C) Three compartment cell

To maintain a constant current a power supply was used (Hewlett Packard E3612A, Palo Alto, USA) and the voltage was monitored (Kiotto KT 1000H multimeter). Before each experiment new electrolyte was prepared (10^{-2} M $NaNO_3$ with pH 7). During the experiments, the electrolyte recirculated in the anode compartment (Figure 3.2 A) or in the cathode compartment (Figure 3.2 B) in a 2C ED cell, and in the anode and cathode compartment in a 3C ED cell (Figure 3.2 C). A peristaltic pump was used (Watson-Marlow 503 U/R, Watson-Marlow Pumps Group, Falmouth, Cornwall, UK) to ensure the constant recirculation of the electrolyte (3 mL/min).

ED experiment conditions

The MT compartment was field with 39 g of sample and 350 mL of deionized H_2O (L/S=9). A funnel was placed in the stirrer hole and the mixture was poured through it. Table 3.2 summarizes the experimental conditions carried out. Nine experiments were performed (some in duplicated) with different current intensities, cell setups, agents added to the sample and time. All the experiments were performed in a fume hood at room temperature.

The experiments were carried out in two stages, aiming the highest W recovery and As removal. First, the best configuration cell setup was chosen from the three tested ones (E1-E3). In a second step, three different adjuvants A, B and C, intentionally not specified due to intellectual property issues, were added to the MT solution to study the elements solubilization rate (E4-E7).

Table 3.2 – Experimental conditions used

Experiment	***Current (mA)***	***Cell setup***	***Agent added***	***Time (days)***	***n***
Control 1	0	Figure 3.2 A	H_2O	10	2
Control 2	0	Figure 3.2 B	H_2O	14	2
E1	100	Figure 3.2 B	H_2O	14	2
E2	1	Figure 3.2 C	H_2O	14	2
E3	50	Figure 3.2 A	H_2O	7	2
E4	100	Figure 3.2 B	Adjuvant A*	10	1
E5	100	Figure 3.2 B	Adjuvant B* + H_2O	10	1
E6	100	Figure 3.2 B	Adjuvant C*	14	1
E7	100	Figure 3.2 B	Adjuvant A* + H_2O	10	1

*Adjuvants A, B and C are not explicit due to intellectual property issues still to be solved.

During the experiments pH, conductivity and voltage were controlled twice a day in the MT and in the electrolyte compartments. To measure the pH and conductivity, samples from the MT were taken from the cell to a beaker and, after the measurement, returned to the cell. The same procedure was done for the electrolyte, although 10 mL were daily collected for further analysis in ICP-AES.

At the end of each experiment, the volume (mL) of the electrolyte was measured. The MT compartment content was dropped in to a beaker and weighted. The MT mixture was filtrated under vacuum to separate the solid (MT) from the liquid phase (water or adjuvant). Then, the liquid phase volume was also measured and reserved to posterior analysis in ICP-AES. The solid phase was also weighted and dried at room temperature for one week. Afterwards, microwave-assisted extraction was applied to the dried samples and the resulted liquid was analyzed in ICP-AES.

The membranes and electrodes were soaked in HNO_3, 1M and 5M, respectively, for 24 h to promote the removal of W and As that was attached. Then, the volumes of acid were measured, and the mixture was filtrated under vacuum to remove the solid content. The liquid was reserved for further analysis in ICP-AES.

3.3Analytical methodologies

Microwave assisted acid extraction

According to EPA method 3051 A, the determination of W and As concentration in the solid (MT) was done by mixing 9 mL of HNO_3 and 3 mL of HCl with 0,5 g of dry sample. Using a Microwave from Milestone Ethos (Bergamo, Italy), it was set a program with a length of 45 min that achieves 195 ºC and 10 bar in 15 minutes. Then, the temperature and pressure are kept constant for the following 15 minutes. During the last 15 minutes, the system returns to normal conditions and, at the end, the samples were collected from the microwave, filtered through a filter (pore size 0.45 µm) and diluted for further analysis in ICP-AES.

Inductively coupled plasma- Atomic Emission Spectrometry

As explained in chapter 2.5.1, this method allows a multi-element analysis of different metals, improving the sample throughput (Martínez et al., 2018). The ICP-AES Horiba Jobin-Yvon Ultima, equipped with generator RF (40,68 MHz), monochromator Czerny-Turner with 1,00 m (sequential), automatic sampler AS500 and dispositive CMA (Concomitant Metals Analyser), was used to analyse W and As (mg/L) in all liquid samples obtained at the end of each experience (liquid phase, electrolyte, extraction from solid phase). This method has detection limits for W and As quantification of 15 ± 7 µg/L and 8 ± 3 µg/L, respectively.

Ionic Chromatography

As explained in chapter 2.5.1, this method allows the separation of different analytes. In this study, Ionic chromatograph DIONEX ICS-3000, equipped with conductivity (CD), electrochemical (ED), Photodiode Array (PDA) and refraction index (RI) detectors, was used to quantify chlorides and sulfates (mg/L) in liquid samples.

3.4Statistical analysis

To validate the results obtained during the experiments, significant differences between the samples were evaluated through ANOVA tests. It was applied one-way ANOVA Tukey Test at 95%, with a confidence level of $p< 0.05$ by using GraphPad software (version prism 7). The statistically significant differences among W and As distribution were done within the cell compartments (different samples in the same experiment and between different experiments for the same sample).

4 Results and discussion

4.1Initial characterization

As reviewed in chapter 2.1, MT ranges from sand to silt-clay in particle size and the sample studied has a silt-clay texture (Figure 4.1). Therefore, Panasqueira MT are characterized by low permeability, poor aeration, high plasticity and high adhesiveness when wet and toughness when dry (Gerard, n.d.).

Figure 4.1 – Sample of Panasqueira MT (sample kindly provided by Professor José António Almeida from DCT NOVA)

As shown in Figure 4.2, the composition of the MT is predominantly characterized by silica (22.91 %), sulfur (15.61 %), iron (13.59 %), aluminum (9.68 %) and potassium (4.77 %). The elements in study have a representation of 0.94 % and 0.23 % of As and W, respectively.

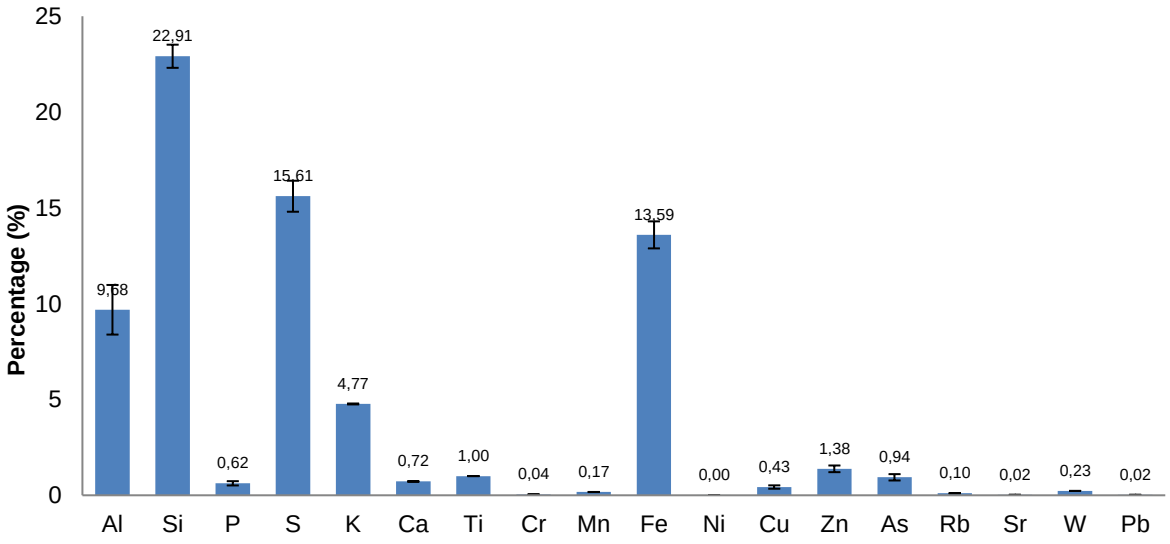


Figure 4.2 – Panasqueira mines MT composition (results kindly provided by Professor José António Almeida from DCT NOVA)

To verify how different conditions may influence MT remediation process, an initial characterization of Panasqueira MT samples was carried out at RESOLUTION Lab and the W and As content, pH, conductivity, chlorides and sulfates are summarized in Table 4.1.

Table 4.1 – Initial characterization

Parameter	***Value***
W content (mg/kg)	496.7 ± 66.8
As content (mg/kg)	3657.7 ± 444.5
pH	4.5 ± 0.9
Conductivity (mS/cm)	0.4 ± 0.3
Chlorides (mg/kg)	0.1 ± 0.1
Sulfates (mg/kg)	5.4 ± 0.1

MT samples without treatment have As contents of 3658 ± 445 mg/kg, while W shows lower amounts (497 ± 67 mg/kg), being these samples also characterized by low conductivity (0.37 ± 0.32 mS/cm).

The content of chlorides and sulfates was analyzed and, as explained in chapter 2.2, chlorides ions stabilize W and sulfate ions create modifications at metallic W electronic structure (Parish, 1966), influencing the electrochemical efficiency. As show in Table 4.1, sulfate contents are higher than chlorides. Thus, a low percentage of W recovery is expected due its interaction with sulfates.

4.1.1 pH desorption

Desorption tests were carried out in order to understand W and As desorption from the MT sample. Figure 4.3 and 4.4 show, respectively, W and As concentration in the aqueous phase in function of pH. There are pH ranges where W and As concentration desorption is higher.

These tests demonstrated that W desorption from MT was higher at low pH (0.31), where 12.89 mg/L were solubilized. On the other hand, As desorption from MT archived a maximum at a pH value of 0.62, where 649.7 mg/L were solubilized. However, it is visible a rise of pH desorption curve at alkaline solutions with a maximum of 14.43 tested.

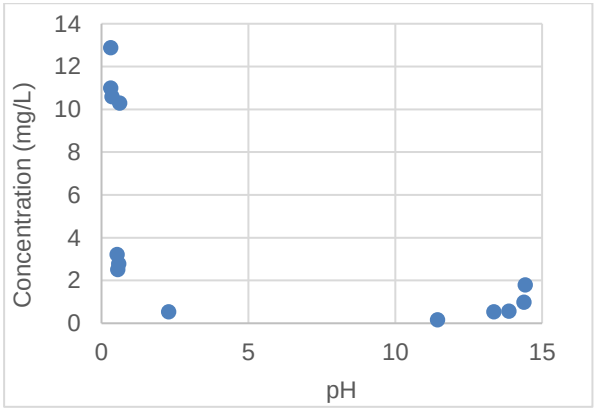


Figure 4.3 - W pH desorption

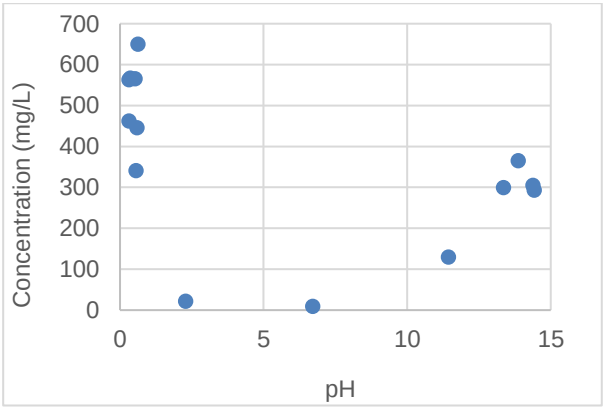


Figure 4.4 - As pH desorption

As reviewed in chapter 2.2, AsO_3 and WO_3 are the most common forms of As and W in MT, respectively, in an acid media. Previous studies showed these As and W forms are soluble at pH below 2, verifying the results of the desorption tests (Morin & Calas, 2006). However, as reviewed previously some

complexes can be formed and since there are a few studies related with those forms of W and As, this may be the explanation of the raising of the curve at alkaline pH.

Electrodialytic experiments

4.1.2 pH and conductivity variation along the experiments

Table 3.2, section 3, summarizes the experiments carried out in this study. During the ED assays, twice a day the pH of the electrolyte was registered. This control was done to monitor the solubilization and subsequent movement of the ions by pH variation.

Analyzing Figure 4.5, it is visible that E3 achieved high pH values (> 10) in the MT solution. This happened due to the cell setup, which promoted the generation of OH^- ions in the cathode end. In previous studies, Crespo (2015) proved that exists a higher desorption of heavy metals at low pH and it needs a period of at least two days to decrease the pH and to start removing the metals.

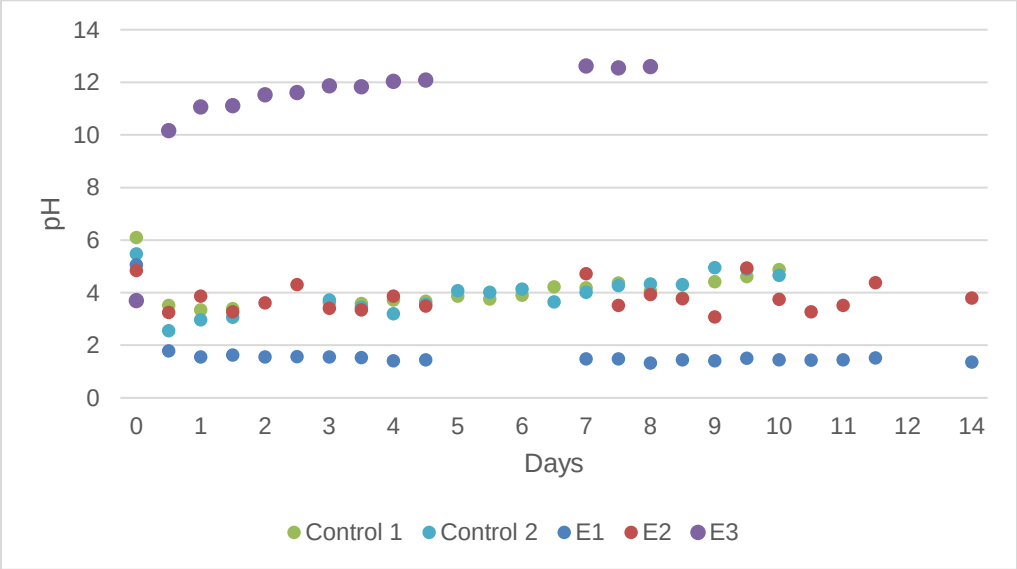


Figure 4.5 – MT solution pH measured during the experiments.

Figure 4.6 represents pH variations in the electrolyte compartment. It is possible to verify a distribution along all the pH range. Experiments, such as E3, where the electrolyte was placed in the anode compartment, H^+ ions are generated decreasing the pH, while the pH in the MT compartment increases. On the other hand, when the electrolyte is placed in the cathode, OH^- ions are generated and the pH increases and the pH in the MT compartment decreases, as verified in E1 and E2.

E2 was carried out in a 3C cell and the pH variations between the anode and cathode compartment were higher in E2- (anode end) and lower in E2+ (cathode end). The conductivity was low (< 5 mS/cm) during the experiment, which was reflected in the voltage (1 mA). This may be explained by the long length of the cell and thickness of the matrix, however there were accomplished some results in W recovery and As separation. In addition, the sample conductivity is low (0.4 ± 0.3 mS/cm), decreasing the ability of the matrix to conduct an electric current.

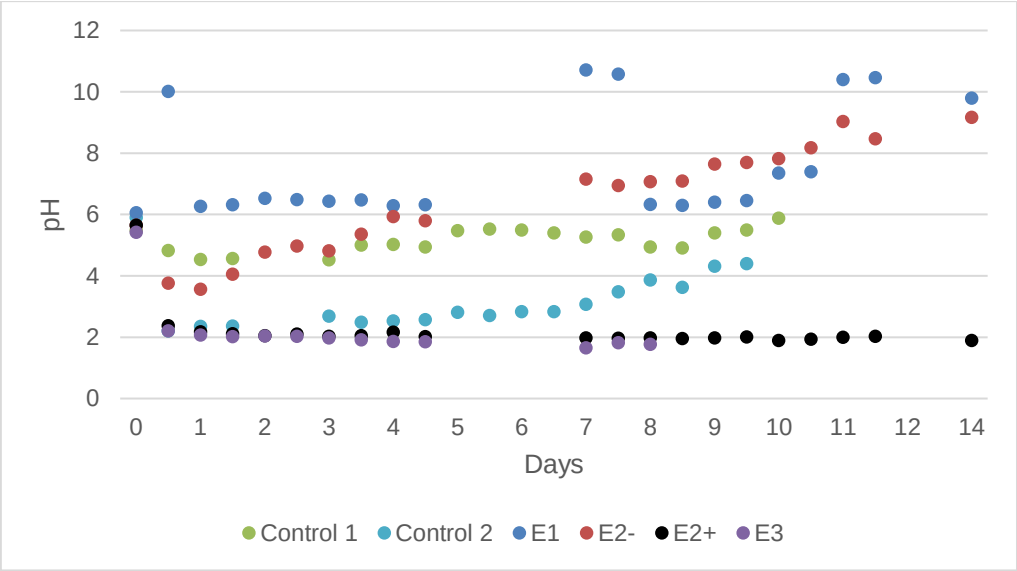


Figure 4.6 - Electrolyte pH measured during the experiments.

Twice a day the conductivity of the MT solution (Figure 4.7) and of the electrolyte (Figure 4.8) was monitored. This variation is due to the cell conditions, the presence of adjuvants and the composition of the MT.

The experiment with a higher conductivity in MT solution was E5 (80 – 118 mS/cm) and in the electrolyte was E6 (up to 39 mS/cm). The assays where adjuvants were used shew a higher conductivity in the MT with values between 37 and 118 mS/cm. The use of adjuvants also helped to decrease the pH of the solution. In this sense, the solubilization of the metals was faster as well as the conduction of the electric current, promoting an increase of the conductivity and consequently highest W recovery and As separation rates.

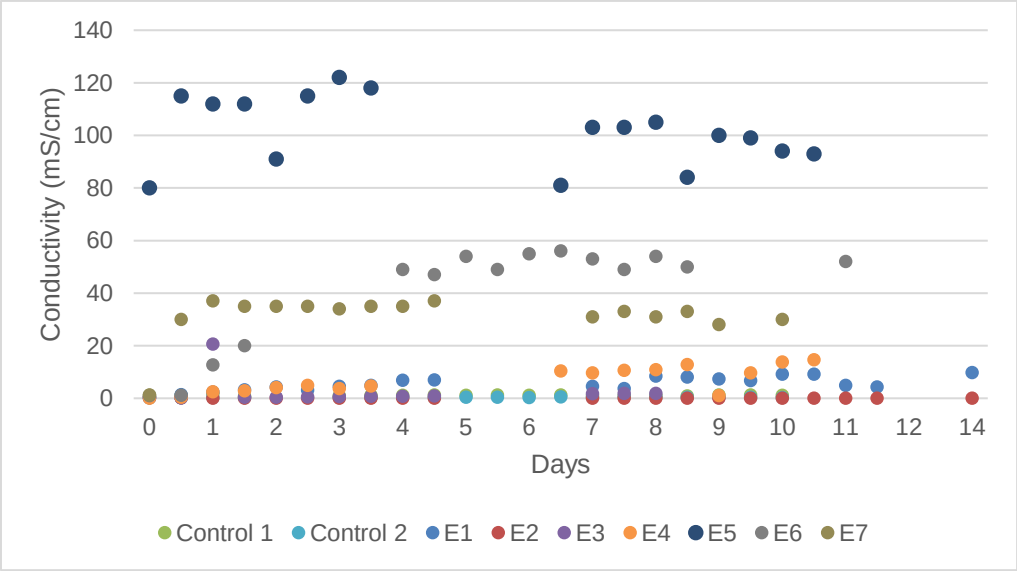


Figure 4.7 – MT solution conductivity measured during the experiments.

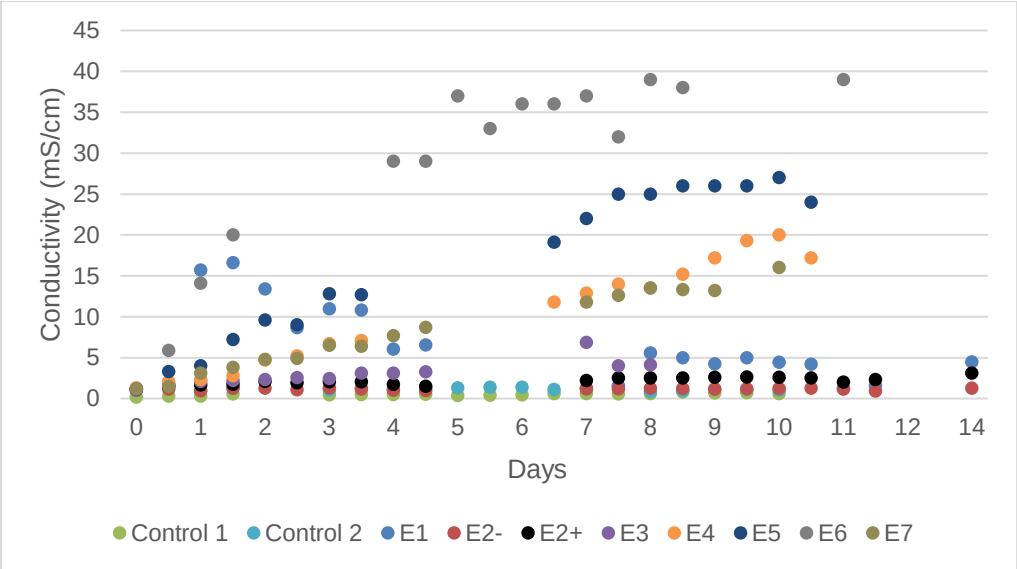


Figure 4.8 - Electrolyte conductivity measured during the experiments.

4.1.3 W and As distribution in the ED cell

To analyse the distribution and movement results of W and As in the ED cell compartments, the cell was divided in three sections: electrolyte (A), MT (B) and liquid phase (C). According to Figure 4.9, electrolyte compartment includes the membrane, electrode and electrolyte, MT compartment is constituted by MT samples, the electrode and liquid phase, where the liquid phase was analysed separately from the other components.

The removal rate of the elements was done considering the quantification of W and As in 1, 2, 3, 5 and 6 (Figure 4.9). The presence of W and As in the electrolyte (6), was also assessed, designated by recover (W) and separation (As).

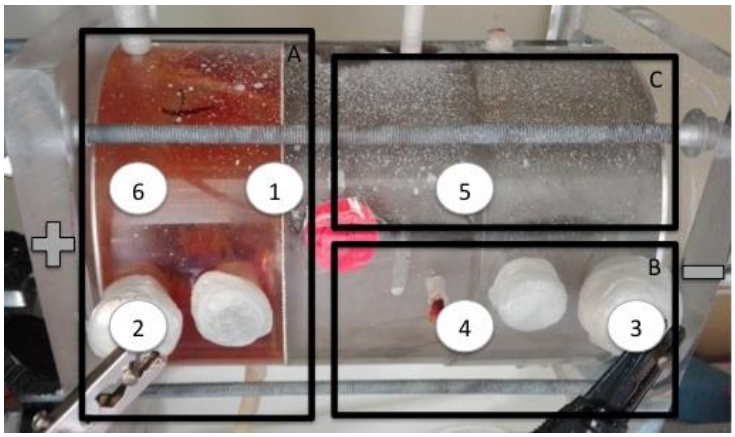


Figure 4.9 – 2C ED cell setup; 1- membrane, 2- electrode +; 3- electrode -; 4- MT; 5- liquid phase and 6- electrolyte; A- electrolyte, B- MT and C- liquid phase

As shown in Figure 4.10, in several experiments W did not move from MT compartment, such as in control 1, control 2, E1, E2 and E3. However, in E5 38 % of W content was solubilized into the liquid phase. The representatively of W in the electrolyte compartment is low (< 1 %) in all experiments, although E5, an experiment where an adjuvant was applied, 0.87 % of W was found in the electrolyte compartment. This experiment (E5) has shown high conductivity in the MT compartment, which favors

the metals transportation.

The electrolyte compartment is constituted by the electrolyte and the membrane. In some cases, W contents were found in the membrane, as observed in E1, with 0.6 ± 0.7 % of W in the membrane, corresponding to the electrolyte compartment percentage. This shows that the tested cell setup promotes the solubilization of metals but does not benefit the migration between compartments. On the other hand, E3 has 0.18 ± 0.04 % of W found in the electrolyte.

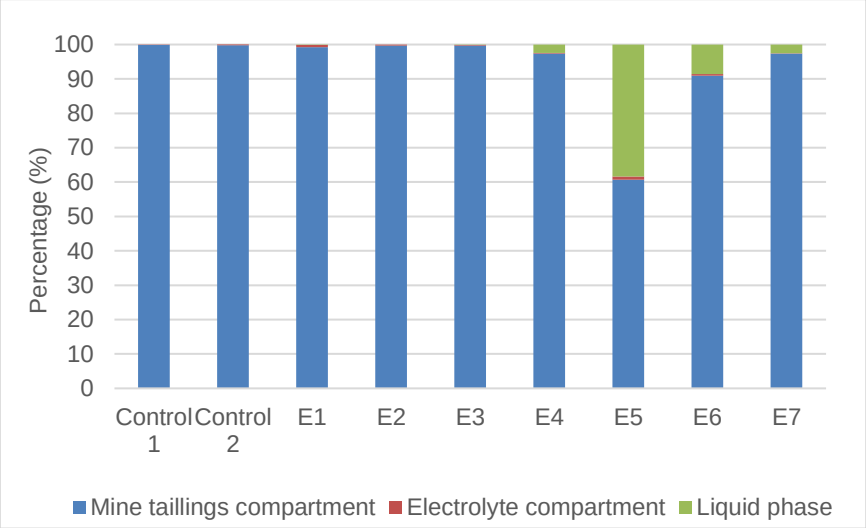


Figure 4.10 – W compartment distribution

Analyzing As distribution, the percentage of As in the MT compartment is low (<55 %), except in E2 and E3, with 85 ± 12 % and 75 ± 21 %, respectively. It is visible in Figure 4.11 that E1, E4 and E5 had the highest percentages of As in the liquid phase, with 62 ± 3 %, 46 ± 1 % and 75 %, respectively. In the electrolyte compartment, the content of As was higher than W, where E3 and E4 contained 24 ± 21 % and 14 % of As, respectively.

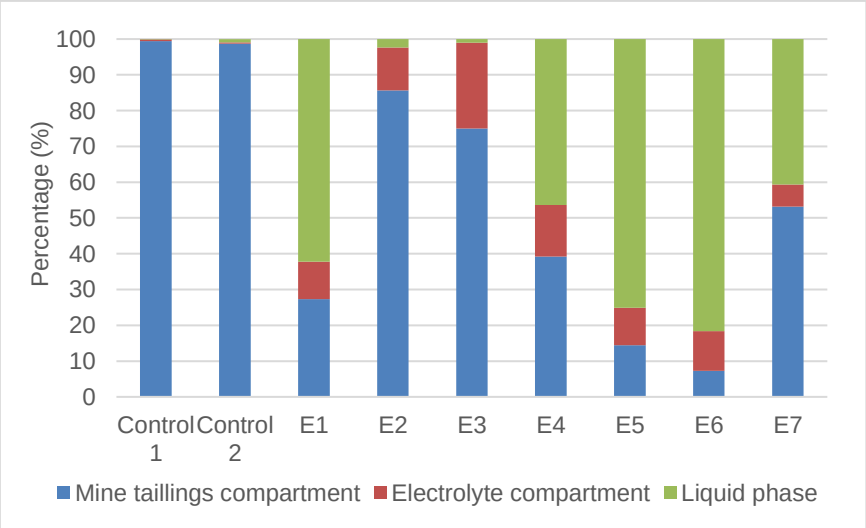


Figure 4.11 – As compartment distribution

4.1.4 W recovery and As separation in the ED cell

Two experiments were performed as control tests, with no current application (0 mA). These results are shown in Table 4.2 Since there is no current, the only factor influencing the process is the stirrer which promotes W and As suspension in the solution. According to Crespo (2015), the mobilization of the elements is faster when the suspension is stirred, promoting direct contact of metals and metalloids with the acidic solution.

As previously explained at chapter 3, the experiments were carried out in two stages. First, the best cell setup was achieved. As shown in Table 4.2, the assay with the highest recovery rate of W (0.15 %) and As separation (23.51 ± 21.33 %) was E3, an 2C cell with AN.

Table 4.2 - W recovery and As separation rate and compartment distribution at the end of experiments C1, C2, E1, E2 and E3

		Control 1	Control 2	E1	E2	E3
W	MT (%)	99.92 ± 0.01 bcefhijklnoqr	99.82 ± 0.06 bcefhijklnoqrtuz1	99.27 ± 0.80	99.73 ± 0.09 bc	99.67 ± 0.01 bcef
	Electrolyte (%)	0.08 ±0.01 adglmps	0.21 ± 0.01 adglmpsvy	0.60 ± 0.72 a	0.27 ± 0.08 ad	0.18 ± 0.04 adg
	Liquid phase (%)	< DL adglmps	< DL adglmpsvy	0.13 ± 0.08 a	< DL ad	0.15 ± 0.05 adg
	Recovery rate (%)	< DL adglmpsvy2	< DL adglmpsvy2	< DL adglmpsvy2	< DL adglmpsvy2	0.15 adglmpsvy2
As	MT (%)	99.46 ±0.24 bcefhijklnoqrtu	98.75 ±0.29 bcefhijklnoqrtuwxz1	27.35 ± 11.53 ad	85.65 ± 12.29 bcefghijk	75.01 ± 21.72 bcefhijkno
	Electrolyte (%)	9.39 ± 0.07 adglmpsy	0.31 ± 0.19 adglmpsvy2	10.41 ±8.24 adg	12.00 ± 10.04 adglm	23.93 ± 20.73 adglmp
	Liquid phase (%)	0.14 ± 0.17 adglmpsy	0.93 ± 0.08 adglmpsvy2	62.24 ± 2.68 abcdefghijk	2.35 ± 1.08 adglm	1.05 ± 0.99 adglmp
	Separation rate (%)	0.24 ±0.14 adglmpsvy2	0.21 ± 0.08 adglmpsvy2	0.63 ± 0.77 adglmpsvy2	10.37 ± 13.94 adglmpsvy2	23.51 ± 21.33 adglmpsvy2

DL – Detection Limit

Statistics tests: values statistically significantly different at $p < 0.05$ (95 % confidence interval) comparing to: a E1 W MT(A); b E1 W Electrolyte (B); c E1 W Liquid phase (C); d E2 W MT (D); e E2 W Electrolyte (E); f E2 W Liquid phase (F); g E3 W MT (G); h E3 W Electrolyte (H); i E3 W Liquid phase (I); j E1 As MT (J); k E1 As Electrolyte (K); l E1 As Liquid phase (L); m E2 As MT (M); n E2 As Electrolyte (N); o E2 As Liquid phase (O); p E3 As MT (P); q E3 As Electrolyte (Q); r E3 As Liquid phase (R); s Control 1 W MT (S); t Control 1 W Electrolyte (T); u Control 1 W Liquid phase (U); v Control 2 W MT (V); w Control 2 W Electrolyte (W); x Control 2 W Liquid phase (X); y Control 1 As MT (Y) ; z Control 1 As Electrolyte (Z) ; 1 Control 1 As Liquid phase (1); 2 Control 2 As MT (2).

(values under the detection limit were considered 0 for statistic test)

Studies carried out by Peppicelli *et al.* (2018) have shown that acid generation induces alterations in metals distribution and does not improve its removal but its repartition towards more available fractions. It needs to be considered that W atomic configuration has four unfilled shells at orbital d, so there are four electrons available to interact with other elements (Gällström *et al.*, 2012). Due to this characteristics W electrons can be mixed with electrons from other elements and complexes can be formed.

The variation of separation and recovery rates of As and W, respectively, during the experiments is presented in Figures 4.13, 4.14, 4.15 and 4.16. As represented in Table 4.2, E3 was the only experiment where a recovery rate of W was detected (0.15 %). However, analyzing Figure 4.15, W was detected in the electrolyte only at day seven. This could happen due to the low conductivity in the MT compartment and the increase of the conductivity over 5 mS/cm after day six in the electrolyte compartment. Also, in alkaline electrodialysis (sample in the cathode) most of the dissolved metals (>90 %) can be found in the cathode compartment, demonstrating metals can form complexes (Pedersen *et al.*, 2017)

In E1, W was not detected in the electrolyte at the end of ED process. However, during the experiment (Figure 4.12), there was an increment of the recovery rate between day two and eight. This demonstrated solubilization of W occurred, but CAT did not allow the passage of W to the electrolyte probably due the complex formation. Since chromium (Cr) and W belong to the same column of the periodic table it is expected the same behavior during the application of ED. Gonçalves (2015) described that 5 % to 13 % of Cr was adsorbed by the membranes during ED and, after the ED process, 63 to 90 % of Cr was found in the matrix of study (soil), which corroborate the present results.

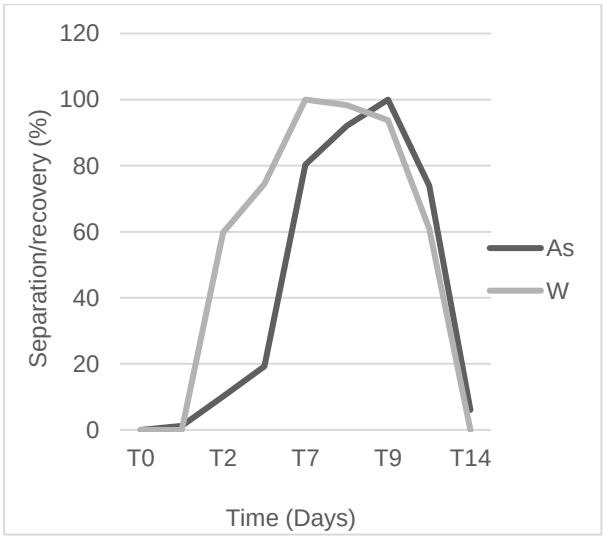


Figure 4.12 - As separation and W recovery, E1

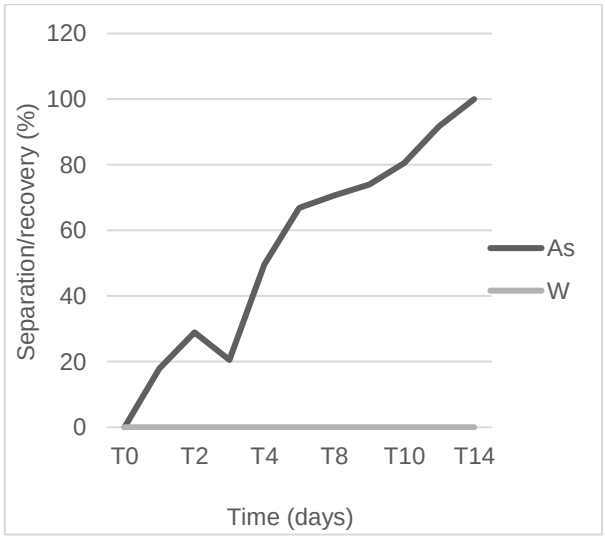


Figure 4.13 - As separation and W recovery, E2+

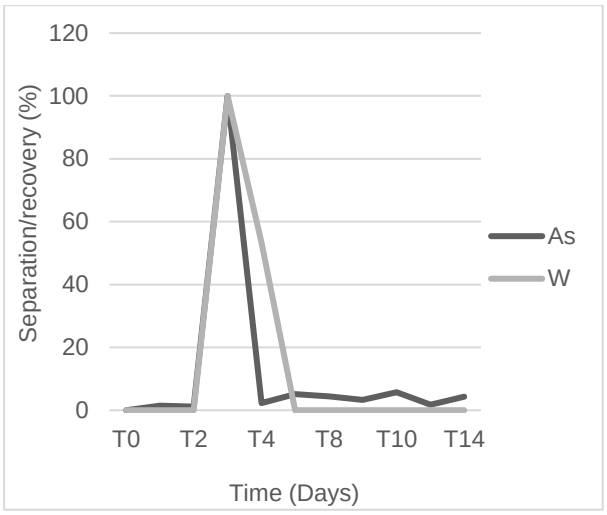


Figure 4.14 - As separation and W recovery, E2-

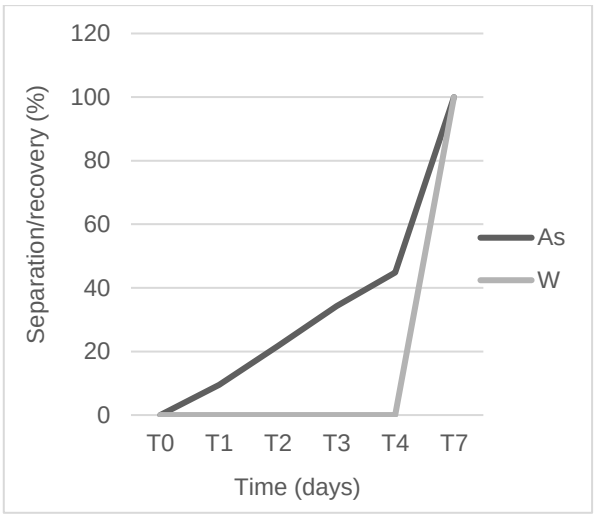


Figure 4.15 - As separation and W recovery, E3

Table 4.2 shows the results for As separation. Comparing Figure 4.13, 4.14, 4.15 and 4.16, E3 reached the highest value of As (1.51 mg/kg) in seven days. The analysis over time allows to perceive that long running times are not viable, since the best results were obtained in seven days. Other experiments (e.g. E1) do not shown recovery/separation rates improvements after day eight.

Despite the results, where a cell setup with 2C and AN proved to be the one that promotes the highest recovery and removal rates of W and As, respectively, this cell setup was not stable in the presence of adjuvants, due to its acidic media. This increased the pH gradient between the compartments and the electrolyte passed into the sample compartment during some experiments. Therefore, the cell setup used for the experiments preformed at this second step was a 2C cell with CAT, to understand the metals solubilization and the membrane behavior.

The results of the addition of adjuvants are represented in Table 4.3 The experiment with the highest W recovery (0.64 %) and As separation (9.48 %) rate was E5, where adjuvant B was mixed with H_2O and MT. The quantities of W and As in the electrolyte compartment does not match the recovery/separation rate of W and As. This happens due to the heterogeneity of the sample and the membrane type. As explained previously, a CAT does not favor the passage of W complexes, since these have in their majority negative charge.

As shown in Table 4.3, E4, E6 and E7 have more than 90 % of W content in the MT, demonstrating that adjuvant A and adjuvant C do not improve the efficiency of the ED process. It is possible to verify that As was removed from MT with rates below 50 %. However, most of As content in each experiment was stabilized in the liquid phase, proving that ED was successful in As solubilization but not in its migration to electrolyte compartment.

Table 4.3 - W recovery and As separation rate and compartment distribution

		E4	E5	E6	E7
W	MT (%)	97.41	60.72	90.91	97.47
	Electrolyte (%)	0.10	0.85	0.51	0.07
	Liquid phase (%)	2.48	38.41	8.57	2.52
	Recovery rate (%)	< DL	0.64	< DL	< DL
As	MT (%)	39.23	14.46	7.31	53.16
	Electrolyte (%)	14.42	10.40	11.04	6.20
	Liquid phase (%)	46.35	75.14	81.66	40.64
	Separation rate (%)	8.91	9.48	1.82	3.81

DL – Detection Limit

Analyzing Figure 4.16, W was not recovered in the electrolyte although As was successfully separated with a continuous increase along the time, up to 0.23 mg/kg. E5 was the experiment among the adjuvants with greatest results, with a W recovery rate of 0.64 % and As separation rate of 9.48 %. As shown in Figure 4.17, W started to migrate towards the electrolyte compartment from day three and As was continually separated from day one.

In E6, for eight days, 0.02 mg/kg (25 %) of As were separated and in the last three days more 0.06 mg/kg (75 %) of As (Figure 4.18) were found in the electrolyte. The last days were more efficient due to the increment of the conductivity in the electrolyte, reaching the maximum of 39 mS/cm. Analyzing W content, the maximum rate was accomplished at day four with 0.003 mg/kg of W in the electrolyte compartment.

Figure 4.19 represents the variation of W and As in E7. This experiment was not successful in terms of W recovery. Although, As was continually separated until day seven, reaching a separation of 0.17 mg/kg (95 %) of As. Afterwards, 5 % of As content was separated after seven days, showing that one week is enough to remediate MT under these conditions.

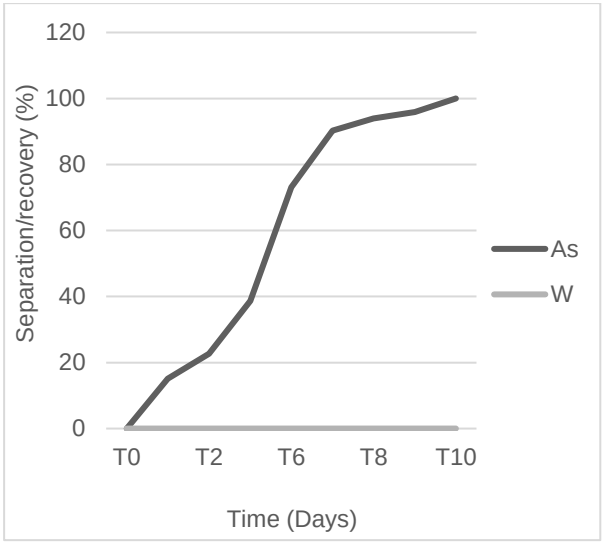


Figure 4.16 - As separation and W recovery during time, E4

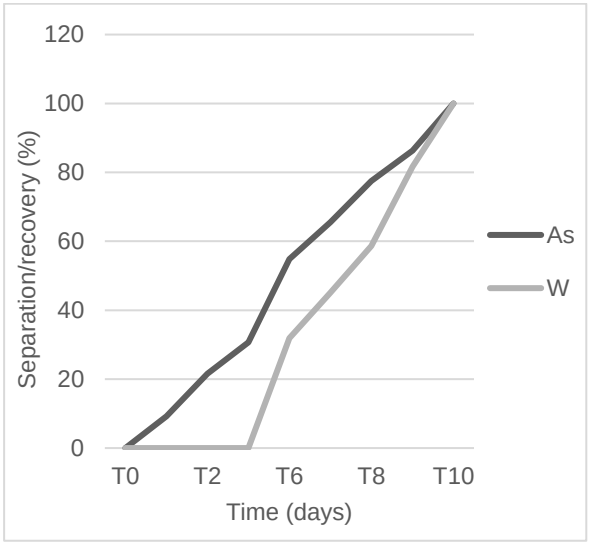


Figure 4.17 - As separation and W recovery during time, E5

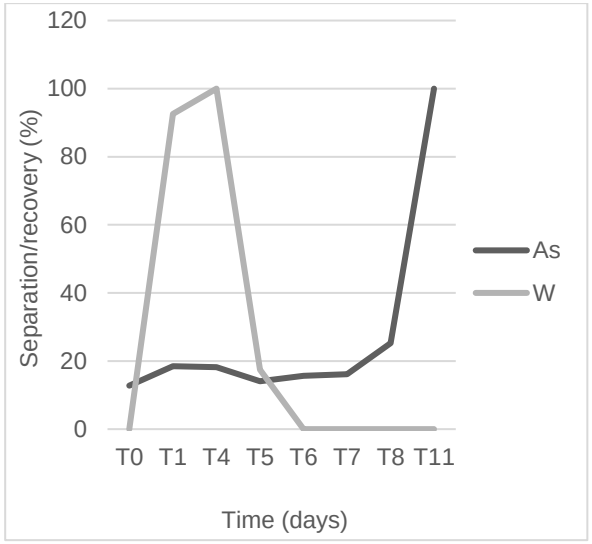


Figure 4.18 - As separation and W recovery during time, E6

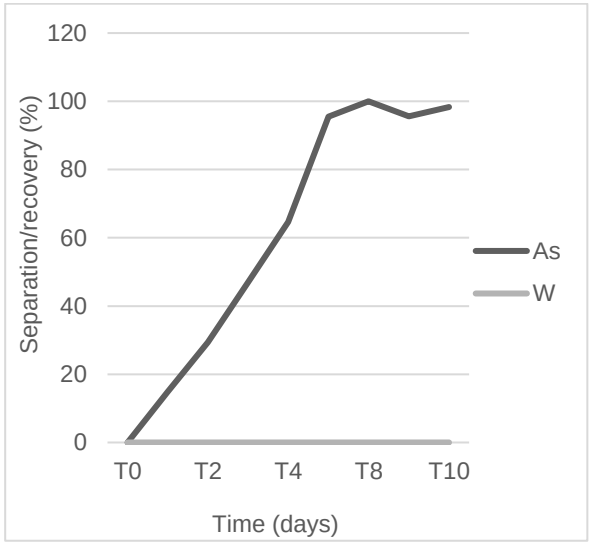


Figure 4.19 - As separation and W recovery during time, E7

According to Guedes (2015), there are mobile and mobilizable forms of As, where the mobile forms are more available in the ecosystem and are more susceptible to leach. The application of EK reduces the content of mobilizable forms of As, proving that EK affects As by changing soil fraction characteristics and consequently decreasing the mobilizable As present or by making it mobile and removing it towards the electrode compartments.

Comparing experiments with and without adjuvants, it is noticeable that occurred a higher solubilization in experiments with adjuvants than in experiments without adjuvants. In E5, an experiment without adjuvant, it was possible to solubilize 38.41 % of W and 75.14 % of As, more 38.27 % of W and 74.09 % of As than in E3, an experiment without adjuvant. Herewith, it is proved that adjuvants increased the efficiency of the ED process in W recovery and As removal and further studies should be carried out.

As shown in Figure 4.20, experiments with adjuvants (e.g. E4, E5 and E6) have high amounts of chlorides. This can influence the results, once the presence of these elements can stabilize W (as reviewed in chapter 2.2). In the other hand, E1, E2 and E3 have amounts of chlorides below 0.50 mg/kg increasing the difficulty of the ED process, since W are more susceptible to form complexes.

E4 stands out in the sulfate's analyses, with 214.04 mg/kg. This was the experiment with adjuvant with the lowest recovery/separation rate, where 97 % of W and 39 % of As remained in MT compartment. E3, the experiment without adjuvant with greatest results (W recovery of 0.15 % and As separation of 23.51 ± 21.33) had a consumption of sulfates, meaning that a cell setup 2C AN promotes the mobilization of W complexes and electronic altered W forms. E5, the experiment with adjuvant solubilized 2.07 mg/kg of sulfates. Therefore, adjuvant B reactions promoted W solubilization.

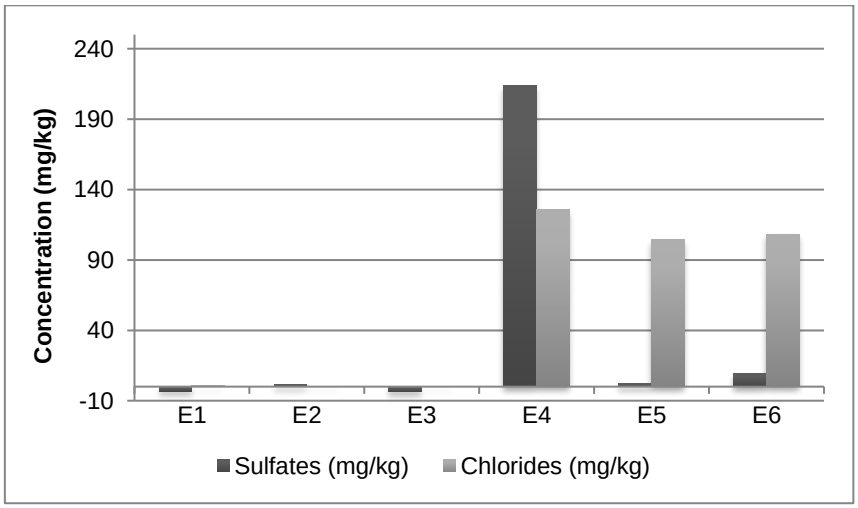


Figure 4.20 – Degradation of sulfates and chlorides in relation to control experiment

4.2 Energy and material costs

After the study of the effectiveness of the ED process for As removal and W recovery, an energy consumption analysis was carried out as well as other costs associated to the process. For that, energy and material costs used during each experience performed were considered.

The energy consumption was determinate according to equation 4.1 (Tran & Drogui, 2013).

$$E_c = \frac{U_c \times I + t}{1000} \quad \textbf{(4.1)}$$

Where:

E_C– Energy consumption (kWh)

U_C– Cell voltage (V)

I – Applied current (A)

t – Treatment time (h)

Considering the material needed for an ED test, which is listed in Table 0.1 in appendix, the total cost reached a value of 2,037.53 €. The energy consumption was measured in the power supply, in the peristaltic bomb and in the stirrer. An energy monitor 3000 voltcraft was used for energy determinations. Considering an electric cost of 0.1616 €/ kWh (EDP, 2018), Table 4.4 shows the costs per assay and its removal/recovery rates.

Table 4.4- Cost per assay

Exp.	***Consumption (kWh)***	***Energy Cost (€/kg)***	***W recovery***		***As removal***	
			Rate (%)	**kWh/ kg W recovered**	**Rate (%)**	**kWh/ kg As recovered**
Control 1	12.51	51.84	<DL	-	0.53	1556.17
Control 2	12.51	51.84	<DL	-	1.24	118.25
E1	18.27	75.72	<DL	-	72.71	2.93
E2	19.51	80.85	<DL	-	14.32	15.76
E3	9.72	40.30	0.15	751.63	25.41	4.51
E4	12.91	53.49	<DL	-	60.83	2.48
E5	12.62	52.30	0.64	230.57	85.56	1.73
E6	14.14	58.61	<DL	-	92.74	1.78
E7	12.69	52.59	<DL	-	47.40	3.17

*Detection Limit

Analysing the results, long periods of running time, E1 and E2, have higher energy consumptions (18.27 kWh and 19.51 kWh, respectively). As expected, short periods of running time, E3 with seven days, had the lowest energy consumption (9.72 kWh), saving 37.99 ± 2.57 €/kg comparing to E1 and E2. Comparing the energy costs associated to each experiment with the results obtained, E3 has the lowest cost (40.30 €/kg) and energy consumption (9.72 kWh). However, in experiments with adjuvants, E5 had the lowest consumption (52.36 kWh) and the highest W recovery (0.64 %). The experiment with adjuvant, with the highest As removal rate (92.74 %) was E6. However, this experiment had the highest energy consumption (14.14 kWh) and has shown to be inefficient to W recovery.

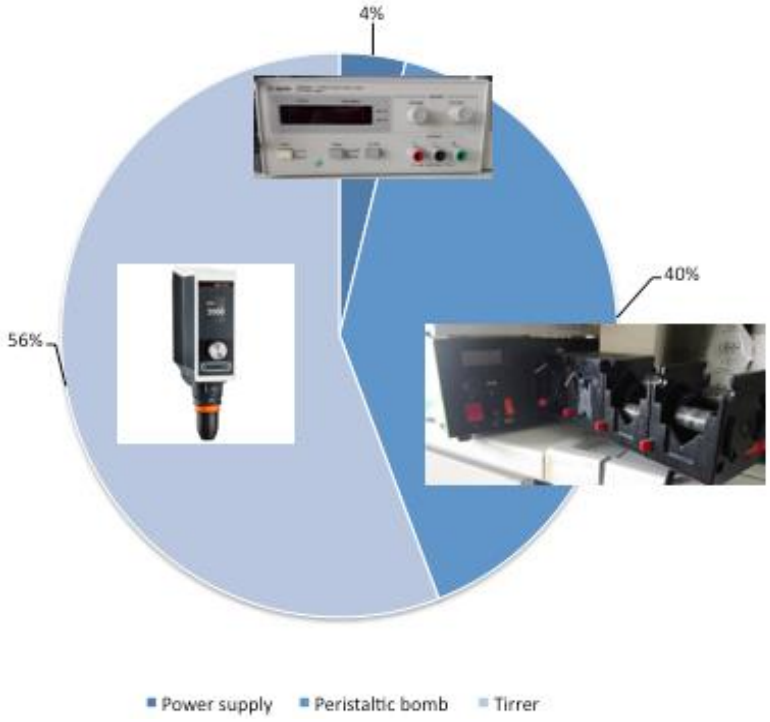


Figure 4.21 – Consumption distribution

According to Guedes (2015), the electrolyte conditioning with NaOH increases As removal and decreases energy consumption. This may be the reason why the power supply has the lowest energy consumption of all the three components in study, with the maximum of 2 kWh per experiment. The stirrer has the highest energy consumption (7.27 to 10.17 kWh per assay) as shown in Figure 4.21. Even when the consumption of the power supply is combined with the bomb, the energy consumption (6.13 ± 0.36 kWh) is lower than the stirrer (7.75 ± 1.58 kWh).

5 Conclusions

This dissertation aimed to develop an electro-based technology able to recover W and remove As from Panasqueira mine tailings. This is a challenging topic, not only due to the presence of high amounts of harmful metals in the study matrix, but also because there are few studies related to W recovery and no work referring to W and ED process application.

A successful treatment envisaging the W recovery and As removal from mine tailings as a secondary raw material source would allow not only the decommission of W from the UE critical raw materials List but also the prevention of further leaching behaviors from these residues. Studying their mobility, it may guide to a safer use of this source reducing the impact in the environment and public health.

W recovery from MT was affected by the presence of compounds in solutions such as sulfates and chlorides and the formation of complexes, such as $[W_2Cl_9]^{3-}$. E3 achieved a W recovery rate of 0.60 ± 0.72 % in the electrolyte (anode). The use of an adjuvant (E5) promoted the solubilization of 38 % of W in the liquid phase although its migration into the cathode compartment was not successful.

Generally, As separation reached higher rates than W recovery. The experiment with the highest removal rate was E3, without the presence of an adjuvant, with 23 ± 21 % of As found in the electrolyte and 1 % of As in the liquid phase. However, E4 with adjuvant A, reached 14 % of As in the electrolyte and 46 % of As in the liquid phase. In spite of this, E5, the experiment with adjuvant B, promoted the solubilization of 75 % of As into the liquid phase.

The results show the application of the ED process for W recovery is difficult due to the low migration rate of W to the electrolyte compartment. On the other hand, ED proved to be efficient for As removal (93 % in E7) and As separation (23.51 % in E3). The best cell setup for W recovery and As removal from MT is a 2C with AN and the use of adjuvant B increased the process efficiency.

The energy balance showed the experiments with the highest W recovery and As removal rates had the lowest energy consumption (9.72 kWh, E3 without adjuvant and 12.62 kWh, E5 with adjuvant B). The study of the equipment used in each experiment showed that the stirrer had the highest energy consumption (7.75 ± 1.58 kWh) and the higher acquisition cost (899 €) corresponding to 44 % of the total material costs.

6 Future developments

The application of the ED process for As separation from MT proved to be efficient. However, for W recovery this process had shown some difficulties. In this way, future studies can focus on the improvement of the process efficiency. It is relevant to understand what W and As complexes are formed and at which pH are easily desorbed (acid or alkaline) and at the same time knowledge more about W ED behaviour. Also, for further considering up-scaling it is important to contemplate environmental, social and economic aspects of the process.

During the experiments carried out, it was verified that an ED cell with 2C and AN was the setup with the best results. However, this cell setup proved to be instable in the presence of adjuvants. It makes sense to study how to reduce pH gradient in a 2C AN cell setup without interferences in the process with adjuvants, stabilizing it for a longer time period.

In a cell of 2C and a CAT, the application of adjuvant B promoted an efficiency increase of the process. For that reason, it should be interesting to test a 2C cell with AN and deep the knowledge about adjuvant characterization and ED interferences.

The experiments with the best recovery/removal rates were E3, which ran for seven days, and E5, where a CAT was used and adjuvant B was mixed for ten days. However, these experiments only had visible migration/solubilization phenomena occurring after day three. Therefore, it could be interesting to test an ED cell with 2C and an AN, with the electrolyte in the cathode compartment and the MT in the anode compartment, in order to promote the solubilization of W and As during seven days. After that, the poles may be switched for more seven days to promote the migration of the compounds into the anode compartment. This experiment should be tested with and without an adjuvant.

Further studies related with energy consumption and acquisition costs of the stirrer should be developed in order to optimize the process, searching for more eco-friendly and economic alternatives. It would also be interesting to develop statistical studies and mathematical models for the process optimization.

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Appendix

Table 0.1 – Material especification used for energy costs

	Designation	***Quantity***	***Cost per unit (€)***	***Cost per cell (€)***
Tools/ auxiliary materials	Pliers	2	2.19	4.38
	Volumetric pipettes	1	4.17	4.17
	Pompete	1	8.90	8.90
	Gobelés	3	7.90	23.70
	Spatulas	1	3.90	3.90
	Electrolyte jar	2	34.79	69.58
	Flasks	21	0.63	13.23
	Pasteur pipettes	3	0.05	0.15
	Trays	1	3.70	3.70
	Gloves (box)	1	6.75	6.75
	Paper	1	25.90	25.90
	Cells (acrylic)	1	60.27	60.27
	Electrodes	2	5.83	11.67
	Membranes	2	1.25	2.51
	Parafilm	1	4.00	4.00
	Pump	1	530.00	530.00
	Recirculation tubes	4	1.89	7.56
	Stirrer	1	899.00	899.00
	Screws	4	2.72	10.86
	Washers	4	0.11	0.44
	Nuts type A	4	0.28	1.12
	Nuts type B	4	0.13	0.53
	Sealing rubbers	4	5.04	20.16
	Power supply	1	383.81	383.81
	Crocodiles and wire	2	0.66	1.33
	$NaNO_3$	1	0.19	0.19
		Total cost		2037.53