The extraction of elements from secondary mining resources in electrodialytic systems

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J Almeida, JM Paz-Garcia, JM Rodríguez-Maroto, EP Mateus, AB Ribeiro

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Problem

Population growth implied the need of more raw materials to serve inhabitants

- ✓ Low ore grades promoted high disposal rates of residues at mining sites
- ✓ The processes involved release intense CO_2 emissions
- ✓ Overexploitation of primary ore resources generated **raw materials scarcity**

Tungsten (W)

Critical raw material included in EU list (2020) as one of the 30 Critical Raw Materials

Transition metal used in

Cement carbide

Alloys

Steels

✓ Primary sources of W are **scheelite** ($CaWO_4$) and **wolframite** $(Fe,Mn)WO_4$

Secondary mining resources

The Panasqueira Mine, Covilhã, Portugal

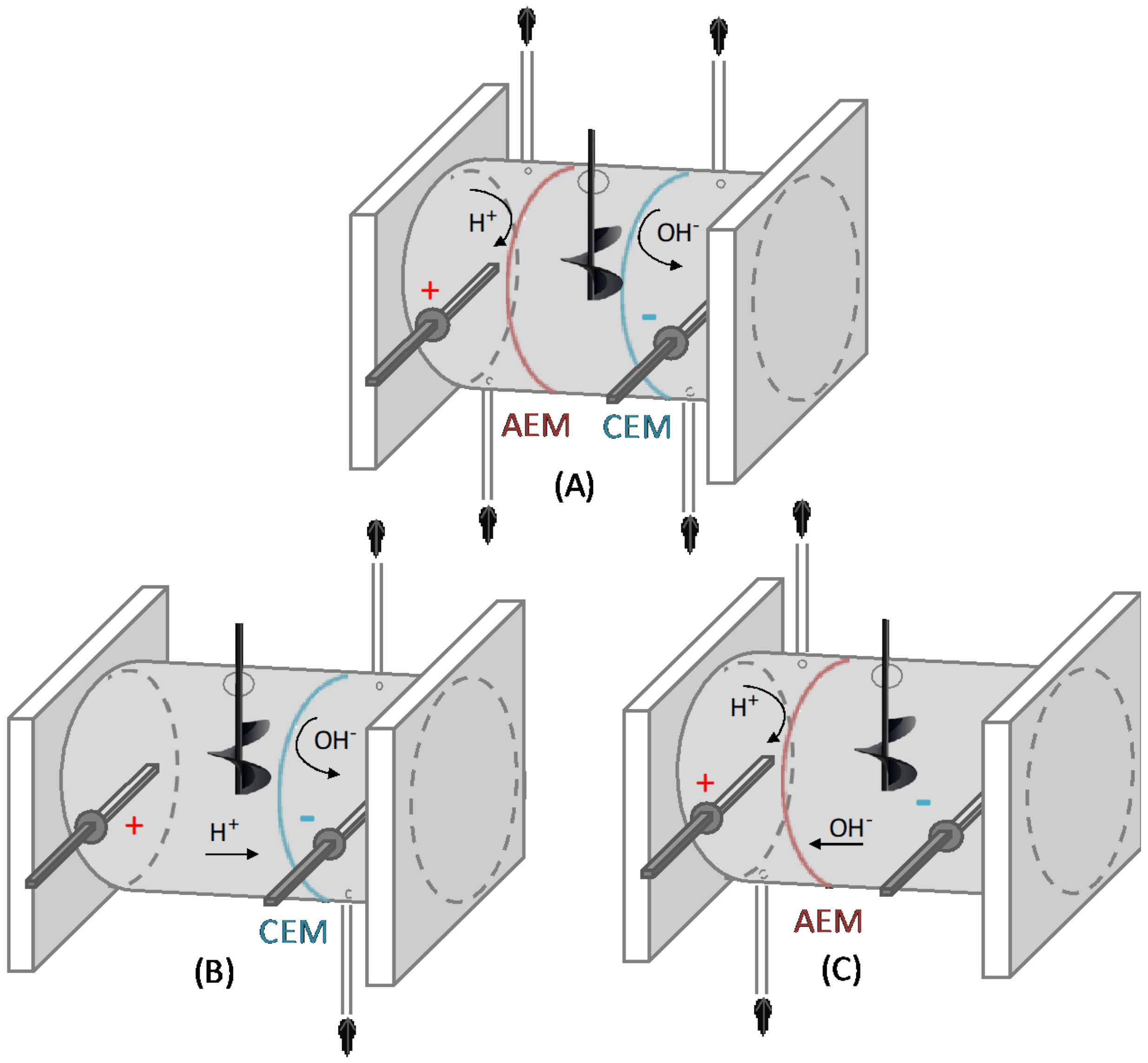
- ✓ Secondary source of critical raw materials - W
- ✓ Presence of contents of Arsenic (As), a harmful metalloid

The challenge

To develop sustainable strategies to recover W and remove As from secondary resources

Electrodialytic process (ED)

The ED technology is applied to remove inorganic and/or organic substances from liquid and solid matrices



Based on the application of a low-level current intensity, between pairs of electrodes, the removal of substances from a matrix is promoted

- ✓ Ion exchange membranes are used to separate the contaminated matrix
- ✓ The water electrolysis at inert electrodes generates an acidic media at the anode (H^+) and an alkaline media at the cathode (OH^-)

Deep eutectic solvents (DES)

Natural solvents applied for the extraction of metals from environmental matrices

DES = Quaternary ammonium or metal salt + hydrogen bond donor[1]

[1] Acids, amides, amines, and alcohols as liquid < 100 °C

	Ionic liquids	Deep eutectic solvents (natural products)
Low price	✗	✓
Low toxicity	✗	✓
100% atom economy	✗	✓
Biodegradable	✗	✓
Low vapor pressure	✓	✓
Low volatility	✓	✓

Goals

Electrodialytic technologies and DES were tested to:

1. **Extract elements from Panasqueira mine secondary resources**

2. **Understand the species behavior in the reactor and improve the efficiency of the ED system**

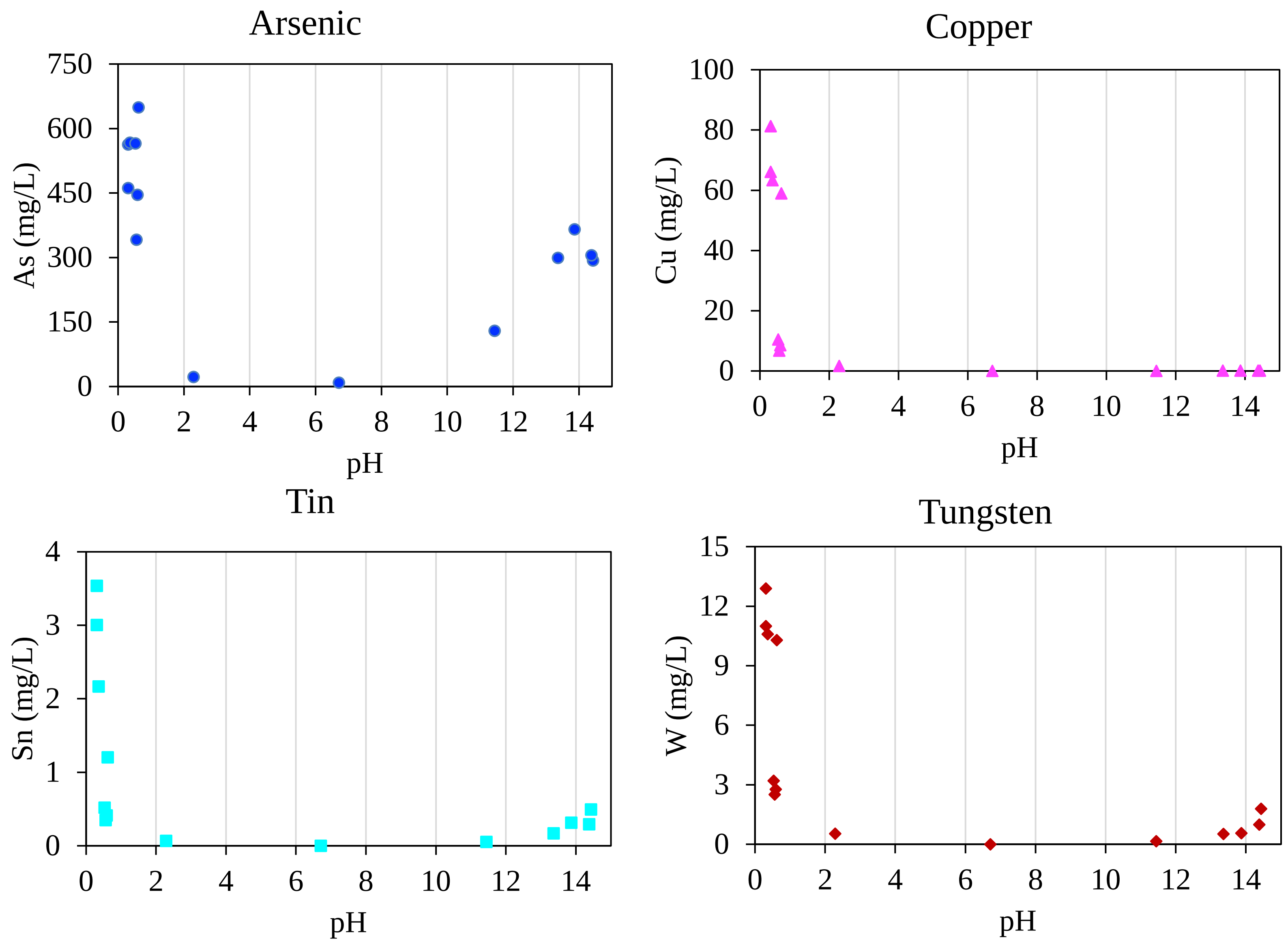
Sample characterisation

Rejected fraction from the sludge circuit, that is directly pumped to the Panasqueira dam

Conductivity	0.8 ± 0.4 mS/cm
pH	5.3 ± 0.5
Arsenic	1675 ± 564 mg/kg
Tungsten	130 ± 31 mg/kg
Copper	731 ± 270 mg/kg
Tin	38 ± 9 mg/kg

Desorption tests of the mining residues

✓ Generally, elements desorption from mining residues were higher at pH values below 2

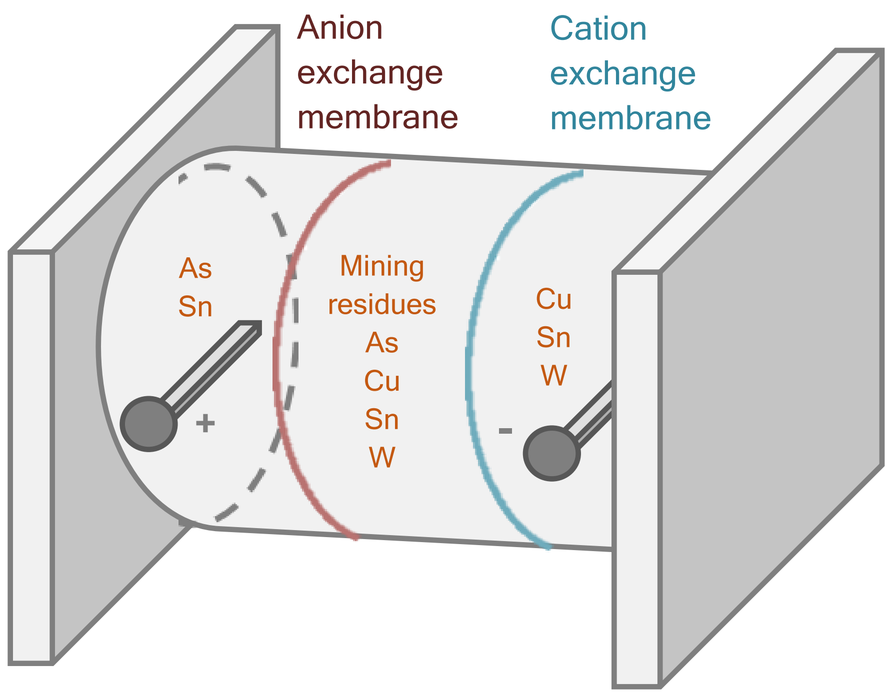


Application of the electrodialytic technology to mining residues

Electrodialytic process tested for As, Cu, Sn and W extraction from mining residues

Highest extraction of elements achieved in a system including

- ✓ 3 compartment reactor
- ✓ 5 days of experiment
- ✓ Current intensity of 100 mA
- ✓ NaCl as supporting electrolyte due to the low conductivity of the sample (0.3 mS/cm)



(DTU concept)

Extraction ratios

As → 63%

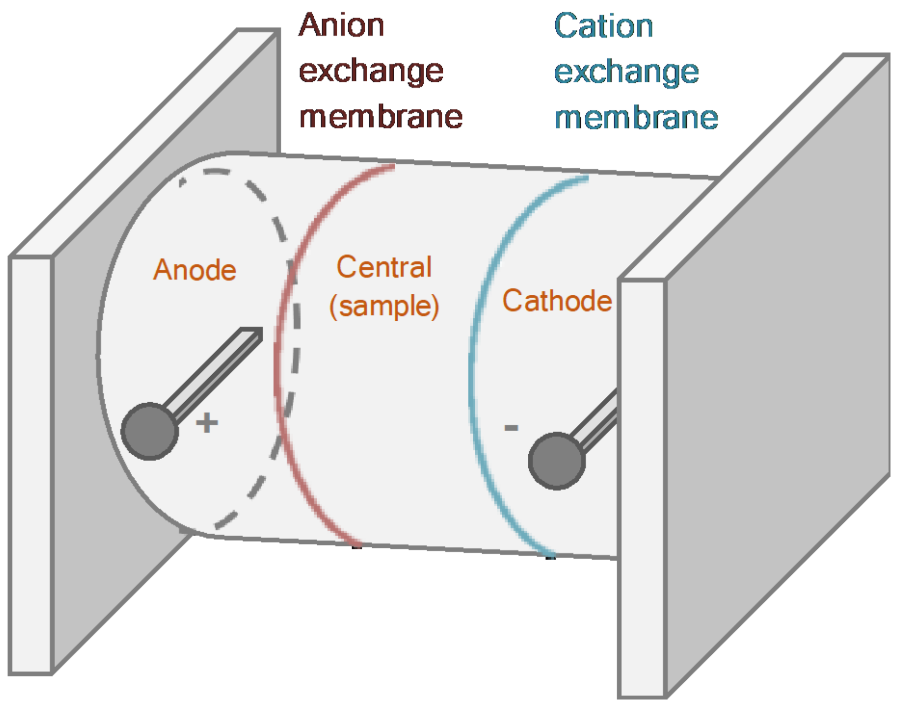
Cu → 13%

Sn → 10%

W → 13%

Application of the electrodialytic technology to mining residues

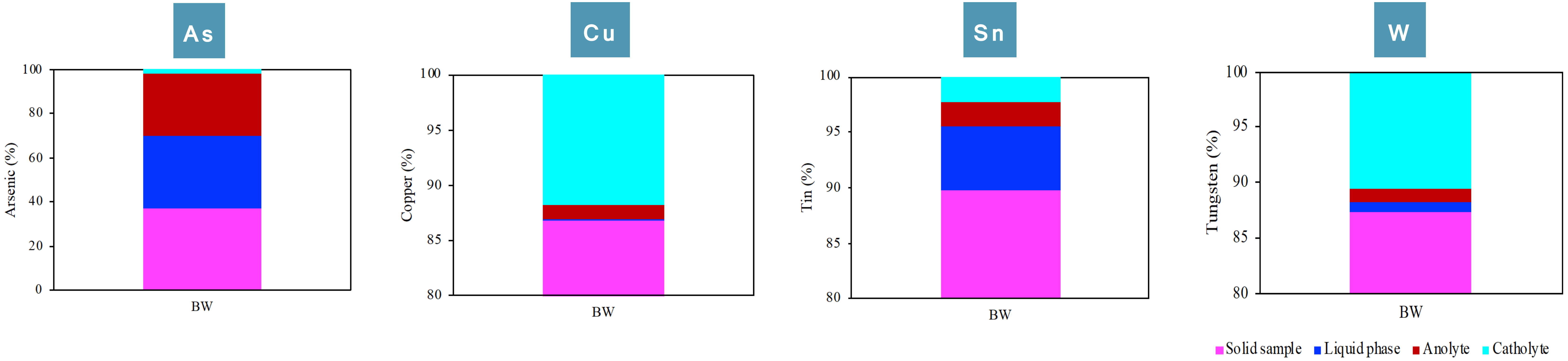
Electrodialytic process tested for As, Cu, Sn and W extraction from mining residues



Compartment	pH		Conductivity (mS/cm)		Voltage (V)	
	initial	final	initial	final	initial	final
Cathode	6.8 ± 0.2	12.5 ± 0.5	0.7 ± 0.1	6.3 ± 1.6		
Central (sample)	5.3 ± 0.7	4.5 ± 1.0	12.6 ± 1.6	3.8 ± 1.2	29.2 ± 9.1	16.2 ± 1.4
Anode	6.8 ± 0.2	1.5 ± 0.1	0.7 ± 0.1	13.5 ± 1.6		

Application of the electrodialytic technology to mining residues

As, Cu, Sn and W distribution in the ED reactor after the ED experiments



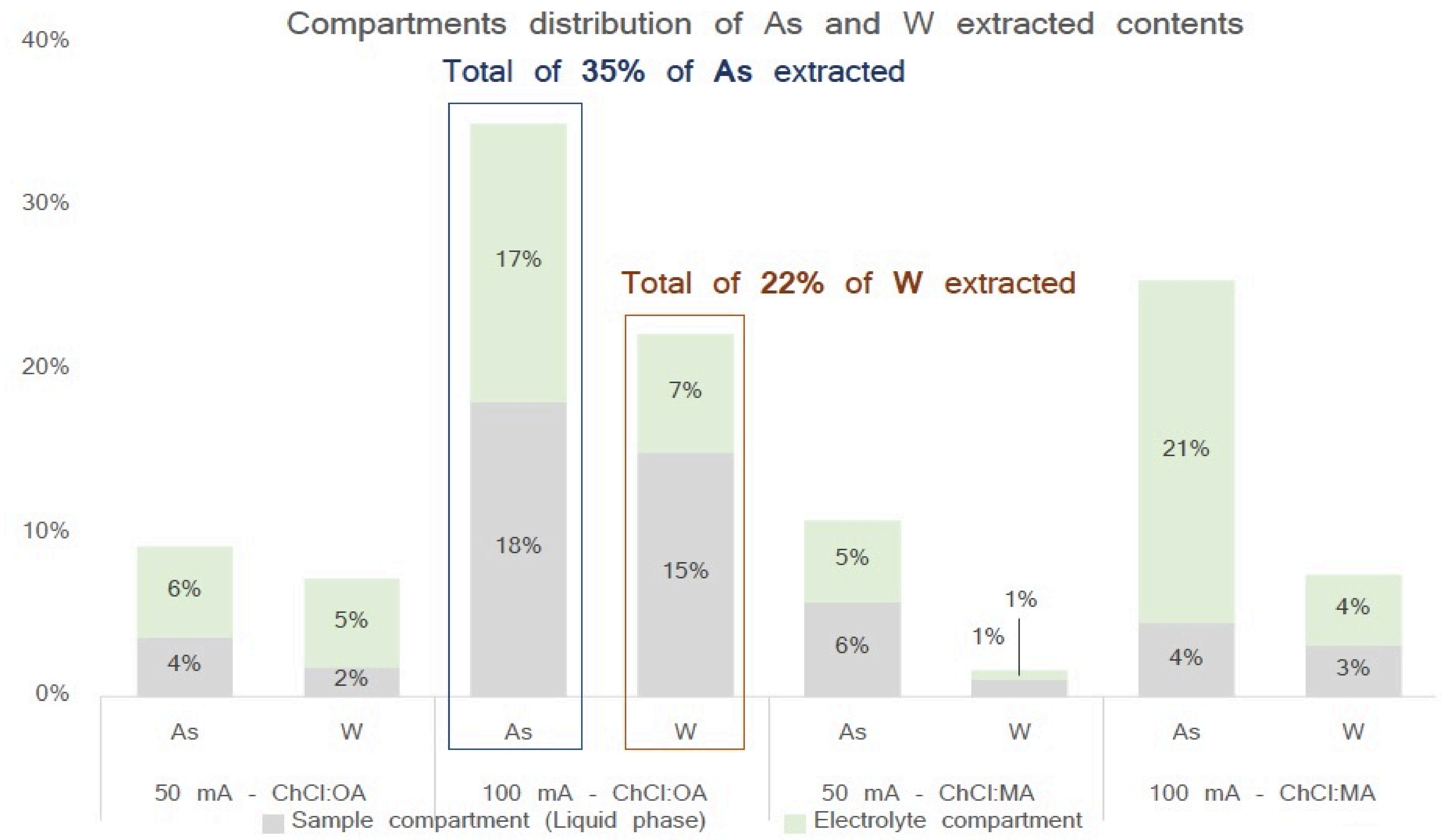
- ✓ As was detected in the anolyte (28%)
- ✓ Cu (12%) and W (11%) were mainly detected at the anode end
- ✓ Sn was detected in both electrolyte compartments in the same proportion (2%)

Application of the electrodialytic technology and DES to mining residues

Extraction of W and As from mining residues

Tested combinations for Arsenic and Tungsten extractior

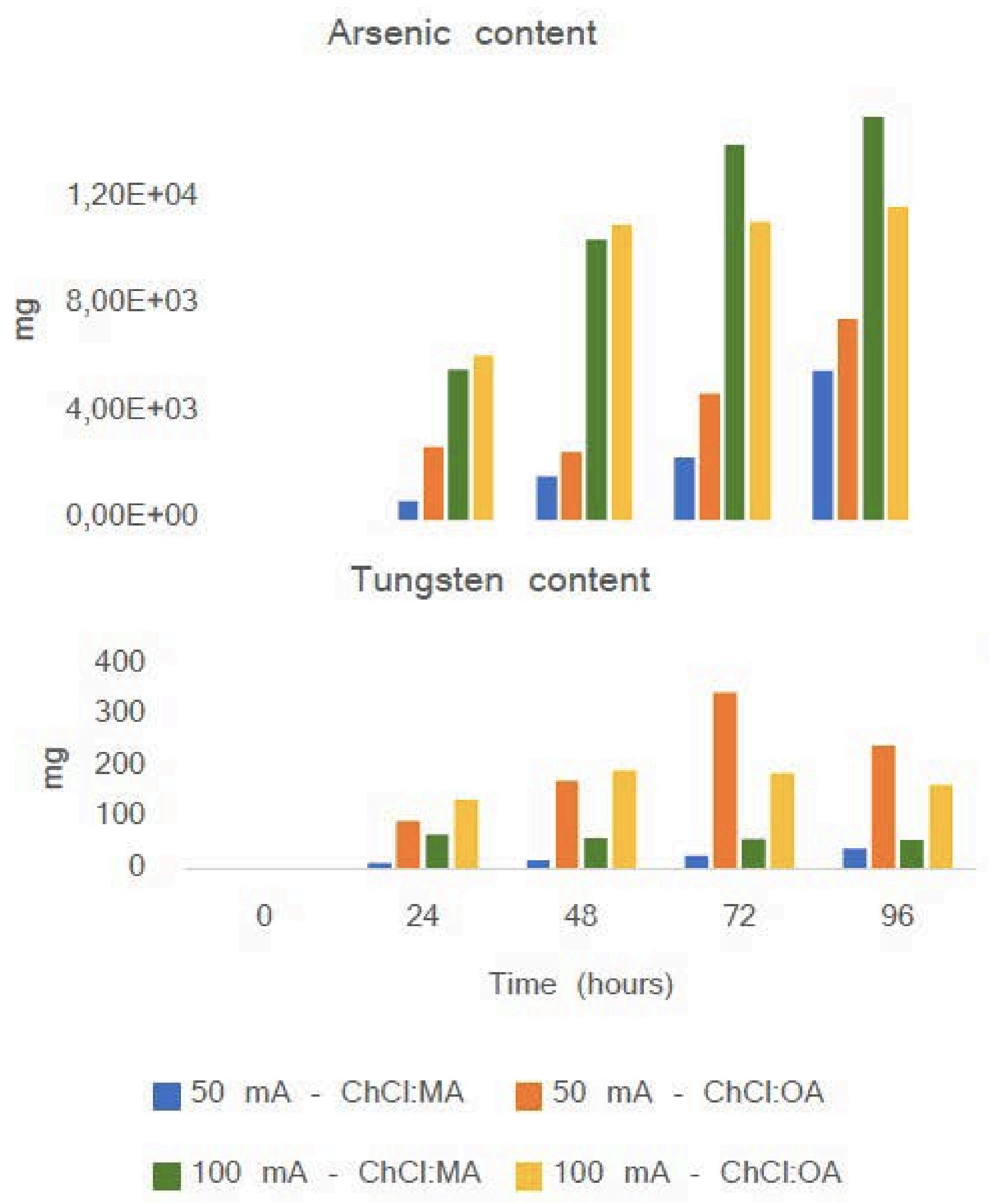
- ✓ **Choline chloride/ malonic acid (1:2)**
- ✓ **Choline chloride/ oxalic acid (1:1)**
- ✓ Choline chloride/ lactic acid (1:2)
- ✓ Propionic acid/ urea (2:1)

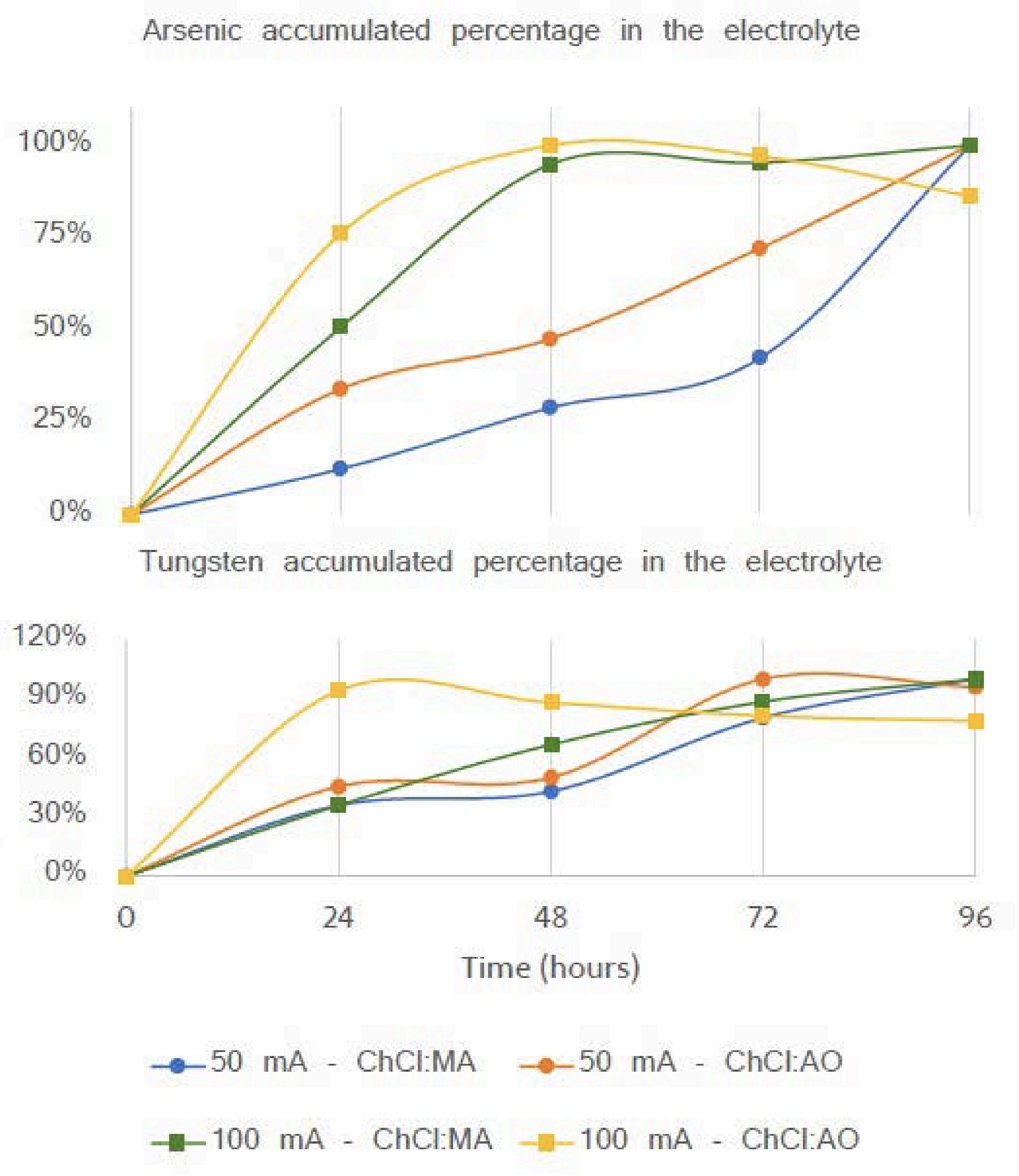


Coupling ED and DES promote the extraction of 35% of As and 22% of W

Application of the electrodialytic technology and DES to mining residues

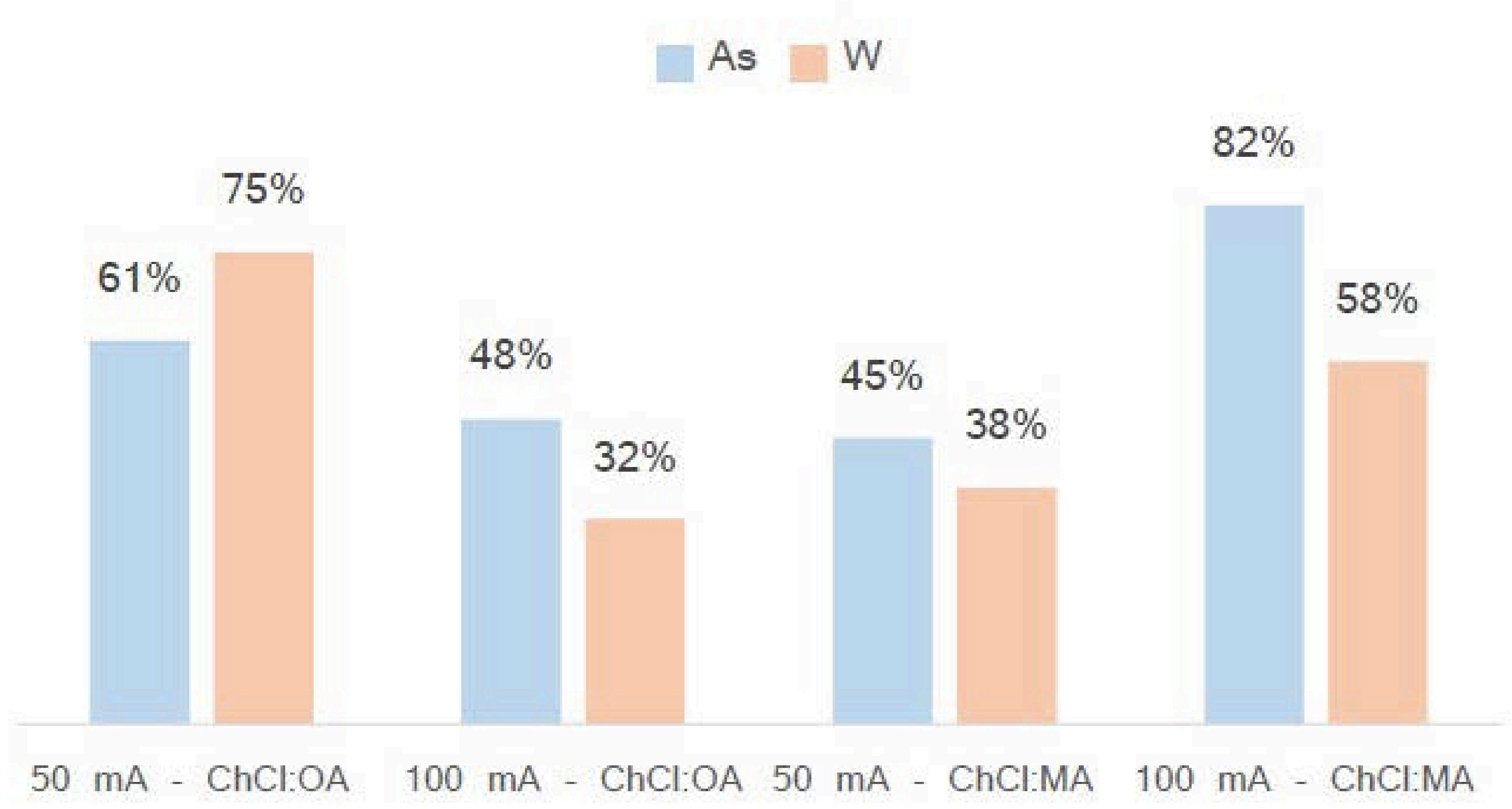
Mass and percentage of As and W reaching the electrolyte along the experiments





Application of the electrodialytic technology and DES to mining residues

Percentage of elements from the total As and W extracted that reached the electrolyte



Conclusions

- ✓ The reuse of mining residues can decrease consumption of primary resources and promote improvements in the sustainability of mining industries
- ✓ The application of the electrodialytic process and DES suggests new possibilities for the recovery of critical raw materials and the removal of harmful compounds from secondary mine resources
  - ✓ Different DES demonstrated higher extraction efficiencies for different elements
  - ✓ DES plus ED process synergy may potentiate the extraction of elements
  - ✓ ED treatment promote the separation of As and W, improving the migration of the elements from the matrix to the electrolyte compartment

Thank you!

Js.almeida@campus.fct.unl.pt

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