HERAKLION 2019

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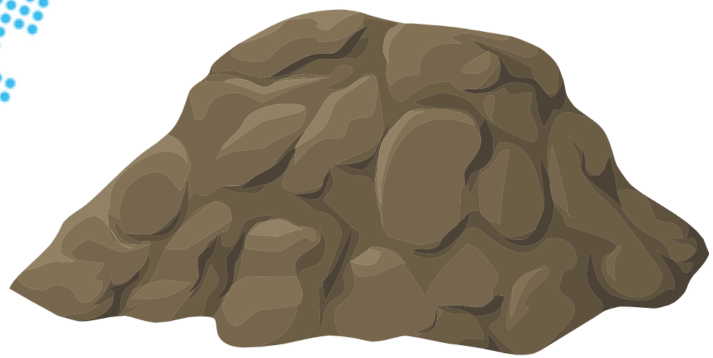
TUNGSTEN RECOVERY AND ARSENIC REMOVAL FROM SECONDARY RESOURCES DEEP EUTETIC SOLVENTS IN THE ELECTRODIALYTIC PROCESS

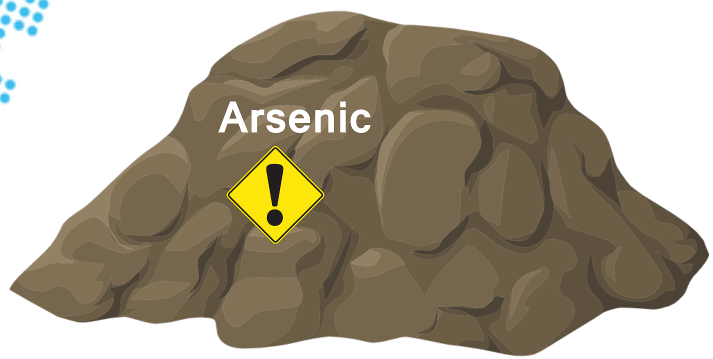
Castro-Gomes, Mud collection at Panasqueira Mine, 2018

Panasquiera Mine, Covilhã, PT



Mining residues

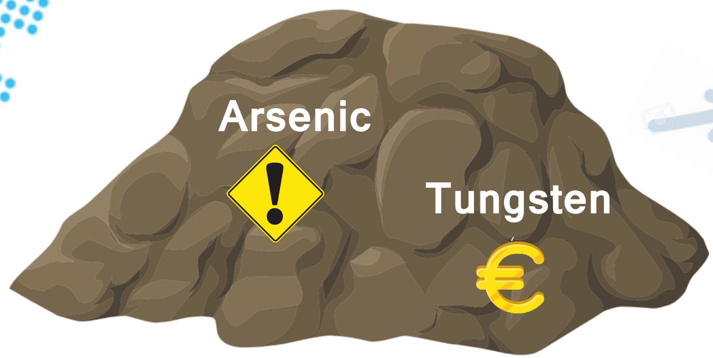
Panasqueira Mine, Covilhã, PT



Mining residues


Panasqueira Mine, Covilhã, PT
Arsenic
Tungsten
Mining residues

Panasqueira Mine, Covilhã, PT

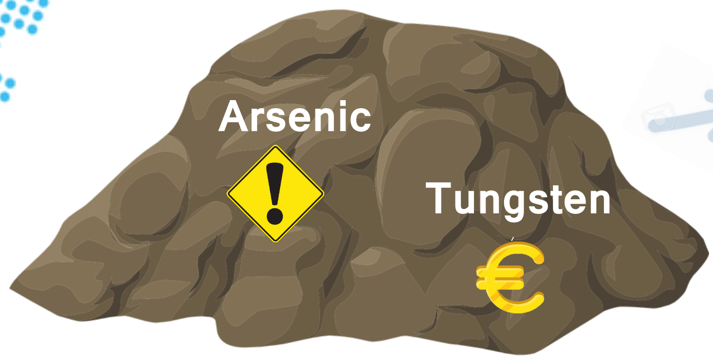


Mining residues

How to remove harmful compounds & recover critical raw materials from secondary resources?

SCOPE

Panasqueira Mine, Covilhã, PT



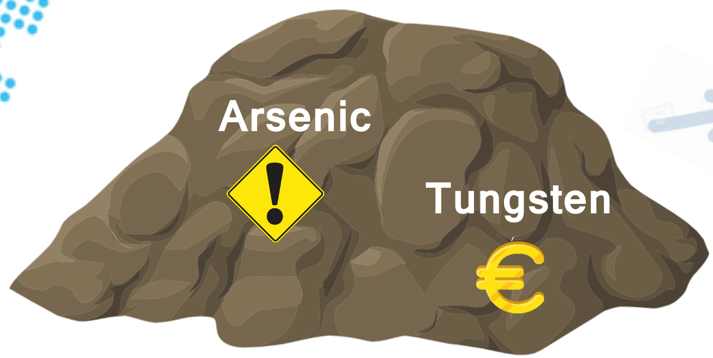
Mining residues

How to remove harmful compounds & recover critical raw materials from secondary resources?

Electro-based technologies

Deep Eutetic Solvents

Panasqueira Mine, Covilhã, PT



Mining residues

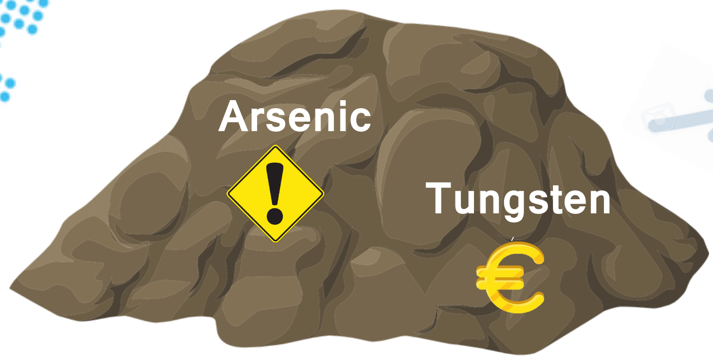
How to remove harmful compounds & recover critical raw materials from secondary resources?

Electro-based technologies

Deep Eutetic Solvents

Both techniques combined!

Panasqueira Mine, Covilhã, PT



Mining residues

How to remove harmful compounds & recover critical raw materials from secondary resources?

Electro-based technologies

Deep Eutetic Solvents

Both techniques combined!

Treated mining residues for reuse in the construction sector

MATRIX CHARACTERIZATION

Castro-Gomes, Mud collection at Panasqueira Mine, 2018

Sample

Rejected fraction from sludge circuit (tube output; pumped directly to the Panasqueira dam)

→ **Low conductivity**

0.8 ± 0.4 mS/cm

→ **Acidic pH**

5.3 ± 0.5

→ **Arsenic content**

As: 1675 ± 564 mg/kg

→ **Tungsten content**

W: 130 ± 31 mg/kg

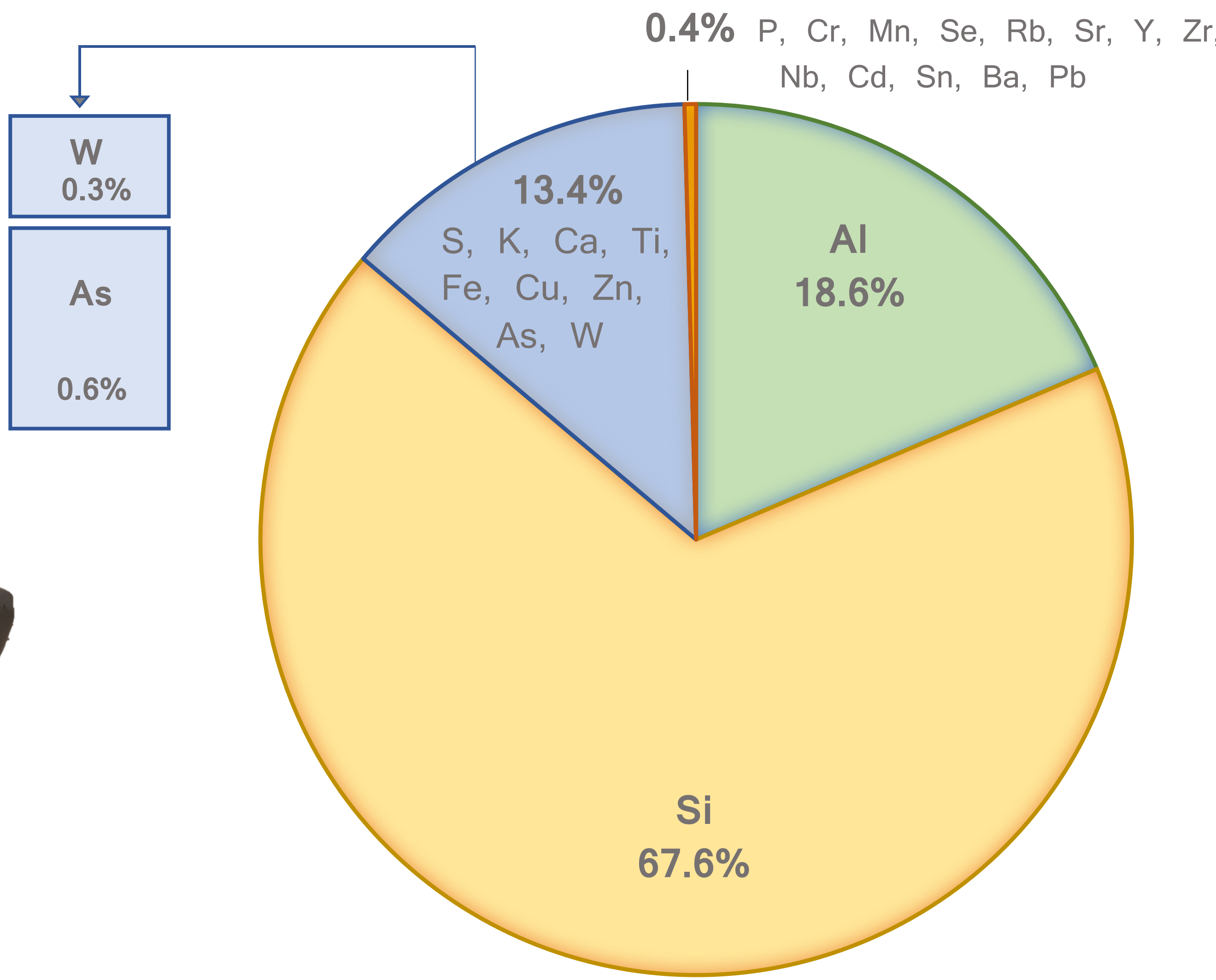
→ **Other elements of interest**

Cu: 731 ± 270 mg/kg

Sn: 38 ± 9 mg/kg

MATRIX ELEMENTS

X-Ray Fluorescence (XRF)
Semi-Quantitative Data (%)



XRF spectrometer

Acids, amides, amines and alcohols as liquid ≤ 100 °C
↑
Deep Eutetic Solvents (DES) = Quaternary ammonium or metal salt + Hydrogen bond donor (HDB)

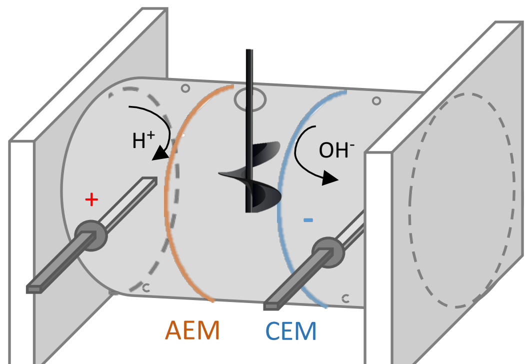
	Ionic Liquids	**Deep Eutetic Solvents** (natural products)
Low price	X	✓
Low toxicity	X	✓
100% atom economy	X	✓
Biodegradable	X	✓
Low vapor pressure	✓	✓
Low volatility	✓	✓

Acids, amides, amines and alcohols as liquid ≤ 100 °C
↑
Deep Eutetic Solvents (DES) = Quaternary ammonium or metal salt + Hydrogen bond donor (HDB)

Why DES?

	Ionic Liquids	**Deep Eutetic Solvents** (natural products)
Low price	X	✓
Low toxicity	X	✓
100% atom economy	X	✓
Biodegradable	X	✓
Low vapor pressure	✓	✓
Low volatility	✓	✓

➔ **Electrokinetic (EK)** and **Electrodialytic (ED)** treatments consist in a low current density (mA/cm^2) application between a pair of electrodes to promote removal/separation of substances, with an ionic exchange membrane interposed in the ED treatment



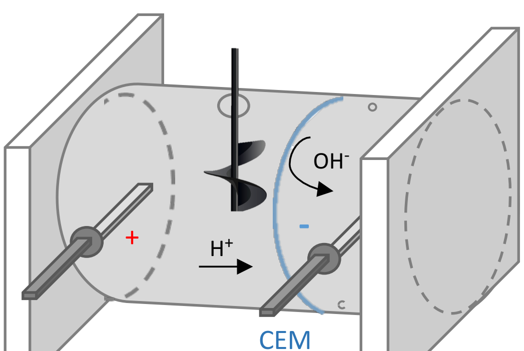
(A)

(A) 3 compartments ED cell

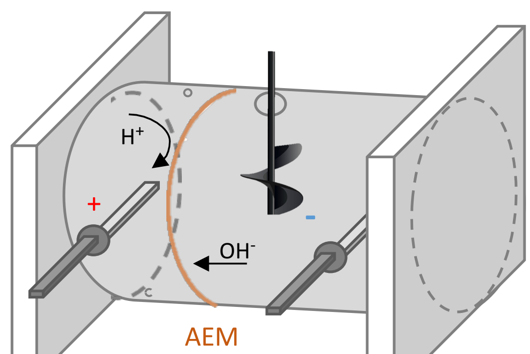
(B) & (C) 2 compartments ED cell

AEM - Anionic exchange membrane

CEM - Cationic Exchange membrane

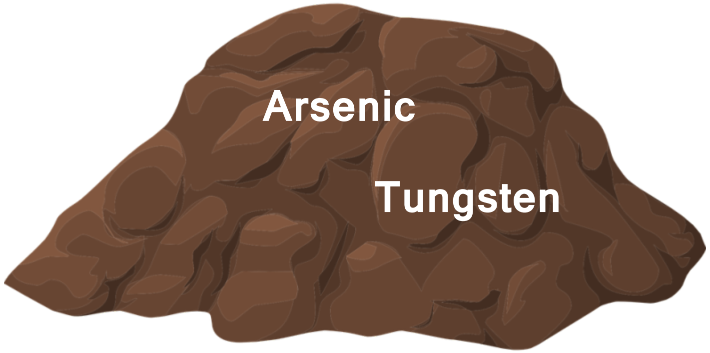


(B)



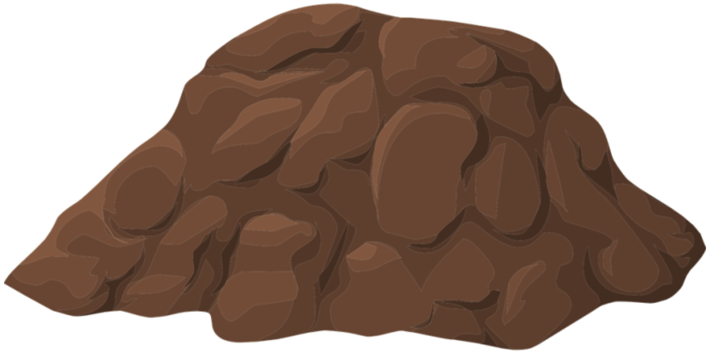
(C)

GOALS



Mining residues (MR)

GOALS

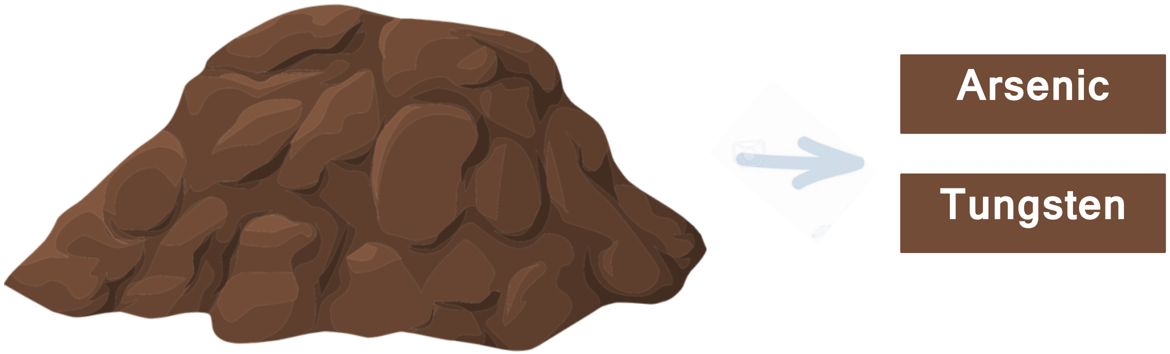


Mining residues (MR)

Arsenic

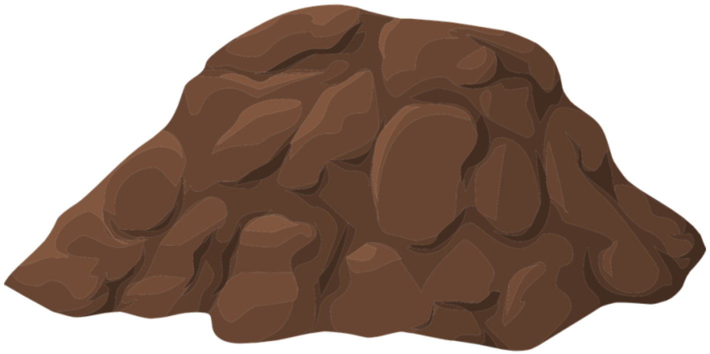
Tungsten

GOALS



Mining residues (MR)

1 Selection of the most efficient DES for As and W extraction from the matrix



Mining residues (MR)

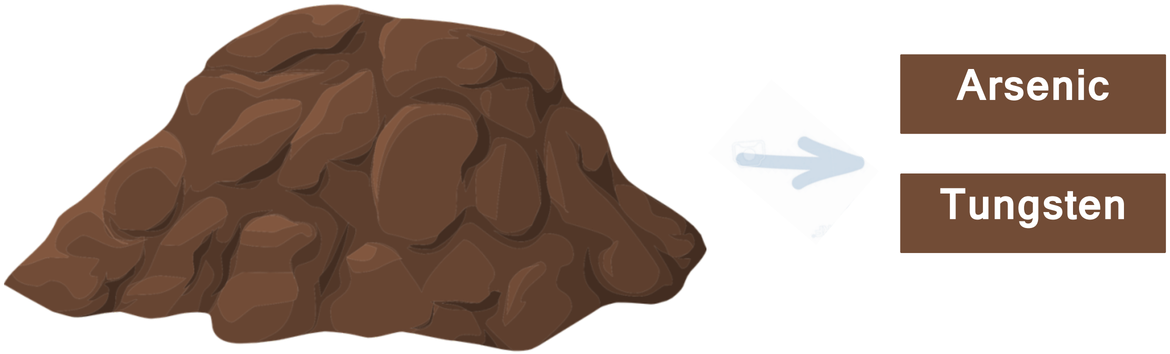
Arsenic

Tungsten

1 Selection of the most efficient DES for As and W extraction from the matrix

2 Potential of the EK process combined with DES to improve As and W extraction from the matrix

GOALS



Mining residues (MR)

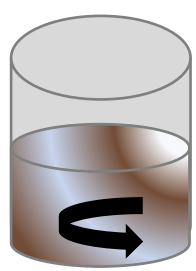
1. Selection of the most efficient DES for As and W extraction from the matrix
2. Potential of the EK process combined with DES to improve As and W extraction from the matrix
3. Feasibility of the ED process to separate As and W in a compartment apart from the matrix

METHODOLOGY

1 Selection of the most efficient DES for As and W extraction from the matrix

DES tested

- ➔ **ChCl:MA** - Choline Chloride:Malonic Acid (1:2)
- ➔ **ChCl:OA** - Choline Chloride:Oxalic Acid (1:1)
- ➔ **ChCl:LA** - Choline Chloride:Latic Acid (1:2)
- ➔ **PA:U** - Propionic Acid:Urea (2:1)



Liquid/solid = 9

Stirring

10 days

DES + MR

2 Potential of the EK process combined with DES to improve As and W extraction from the matrix

DES tested with higher As and W extraction

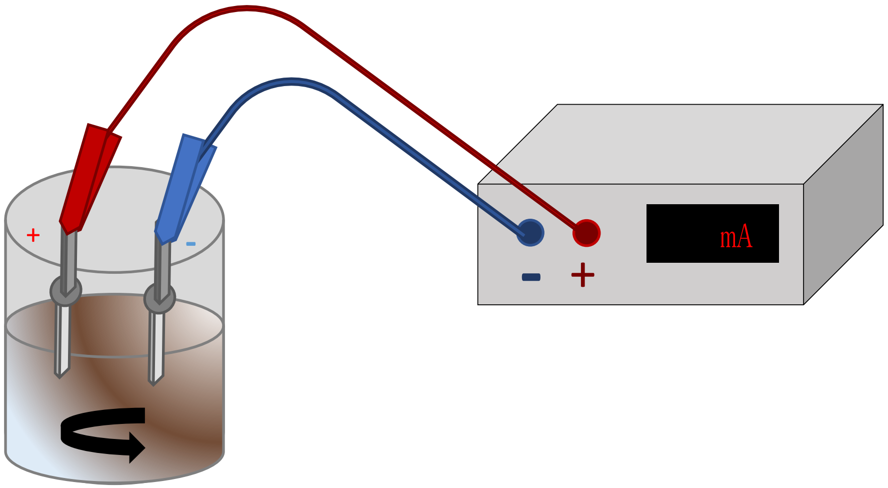
- → **ChCl:MA** - Choline Chloride:Malonic Acid (1:2) ↑**As**
- → **ChCl:OA** - Choline Chloride:Oxalic Acid (1:1) ↑**W**

50 & 100 mA

Liquid/Solid=9

Stirring

4 days



DES + MR +H_20

(1.5% ChCl:MA & 1.5% ChCl:OA)

3 Feasibility of the ED process to separate As and W in a compartment apart from the matrix

DES tested with higher As and W extraction

- ➔ **ChCl:MA** - Choline Chloride:Malonic Acid (1:2) ↑**As**
- ➔ **ChCl:OA** - Choline Chloride:Oxalic Acid (1:1) ↑**W**

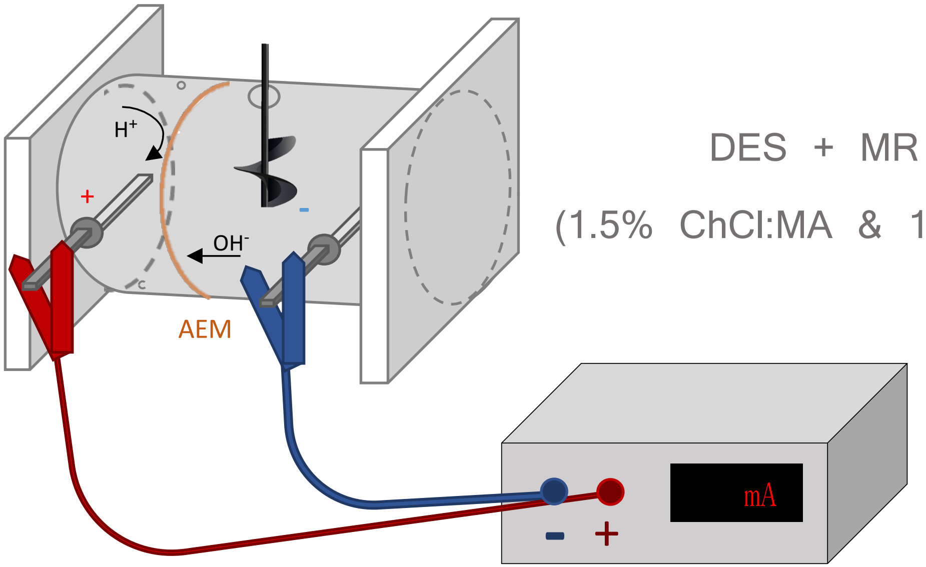
50 & 100 mA

Liquid/Solid=9

Electrolyte 0.01 M $NaNO_3$

Stirring

4 days

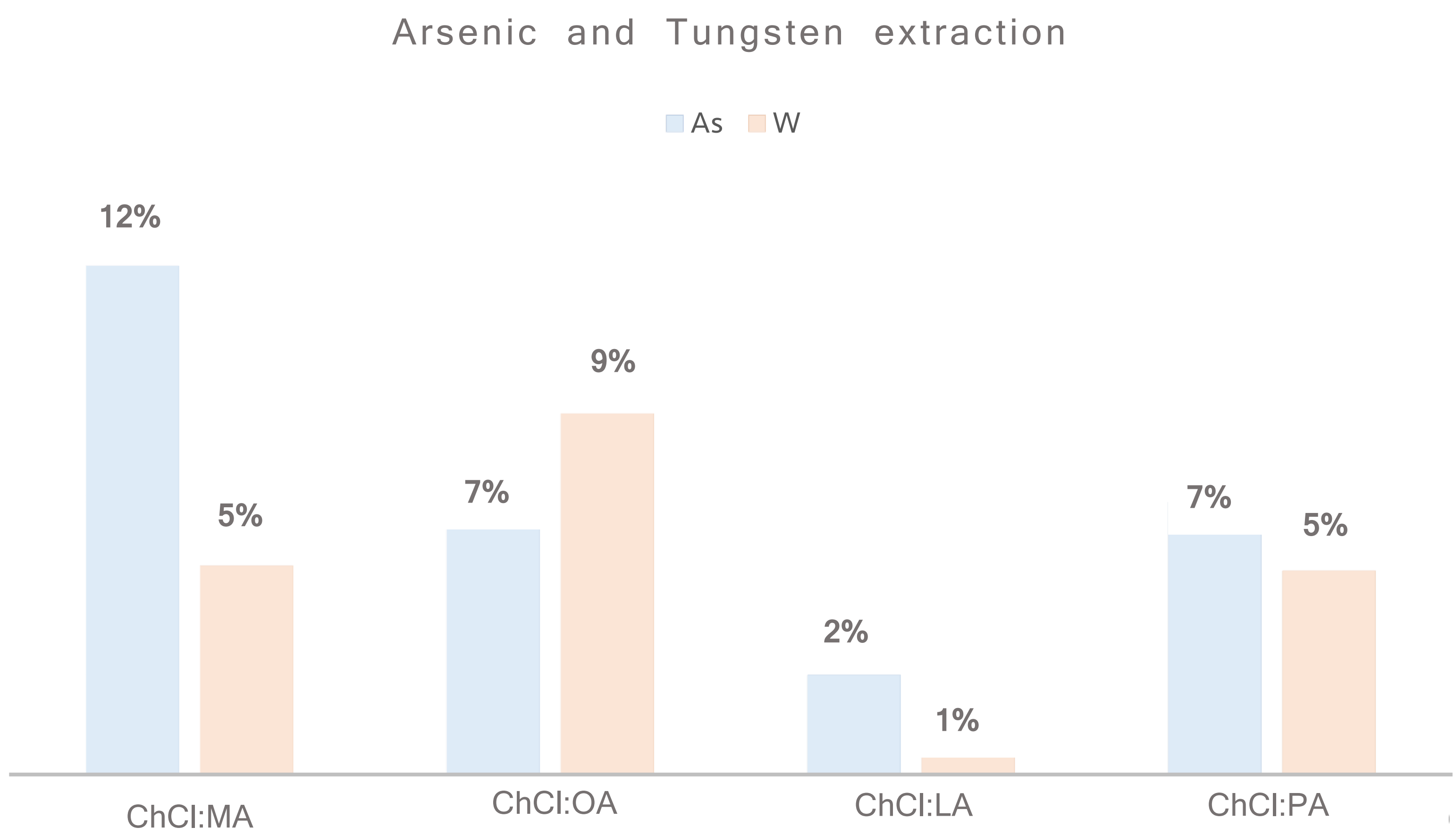


DES + MR +$H_2$0

(1.5% ChCl:MA & 1.5% ChCl:OA)

RESULTS & DISCUSSION

1 Selection of the most efficient DES for As and W extraction from the matrix



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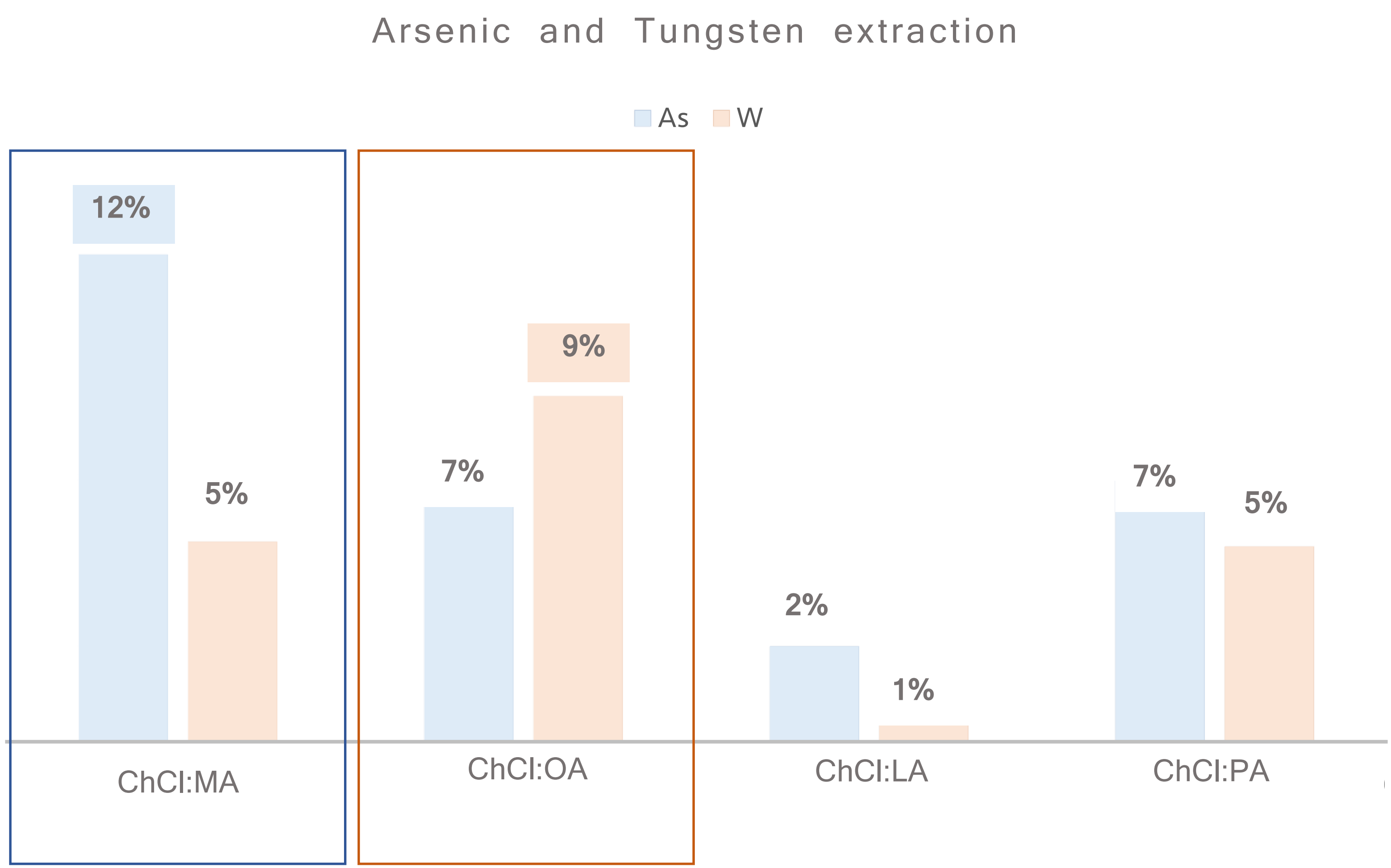
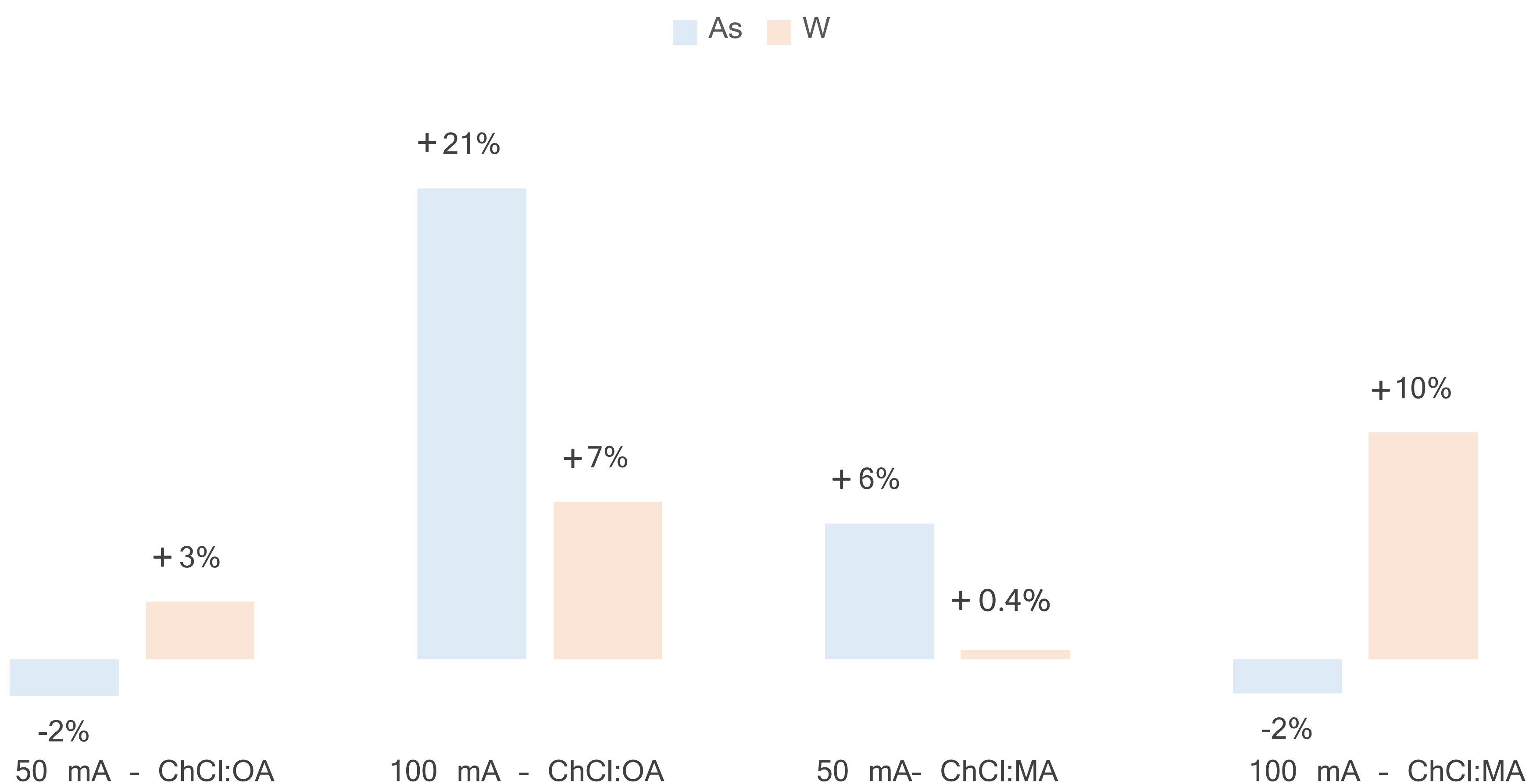


2 Potential of the EK process combined with DES to improve As and W extraction from the matrix

Extraction percentages in relation to DES experiments without current



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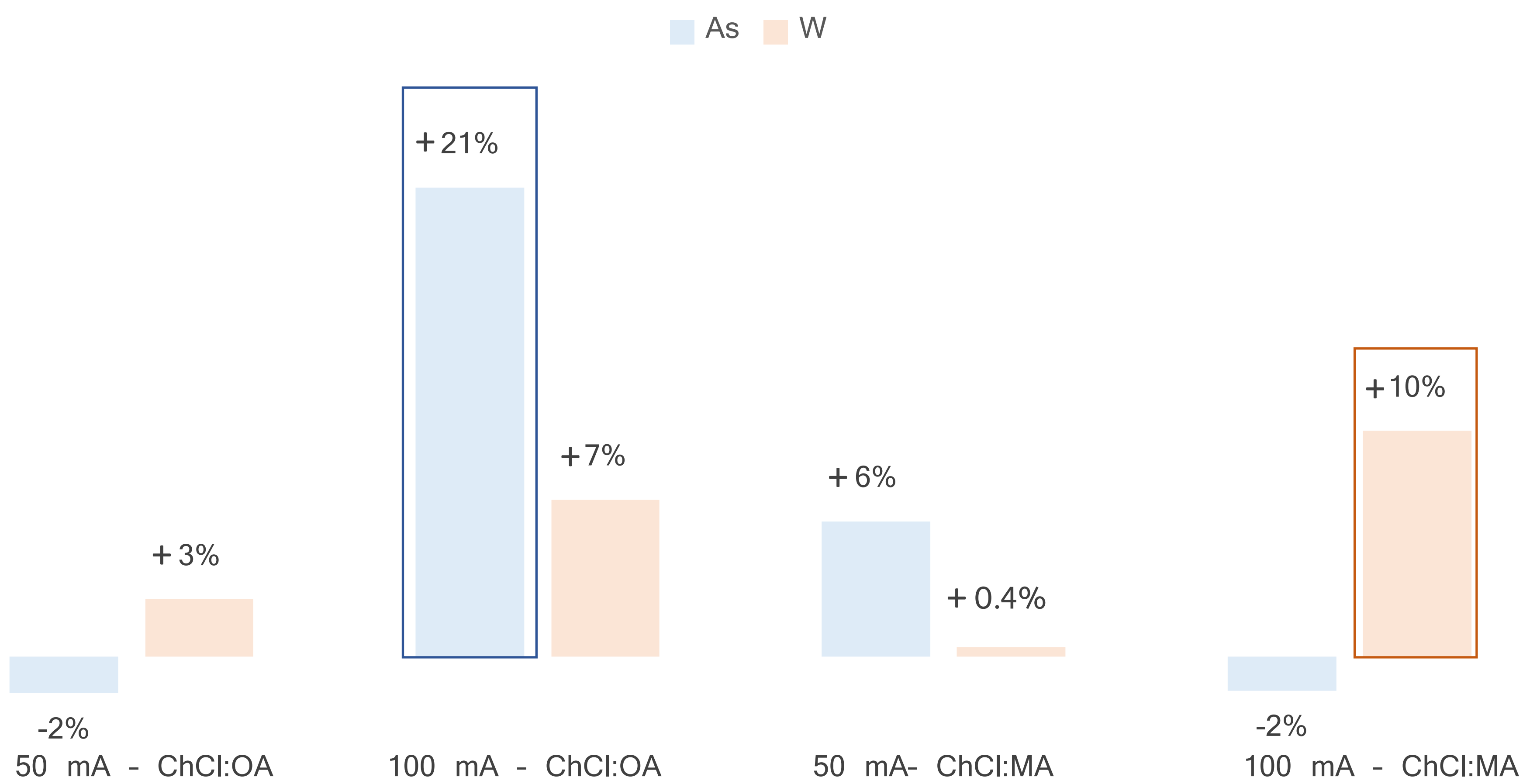
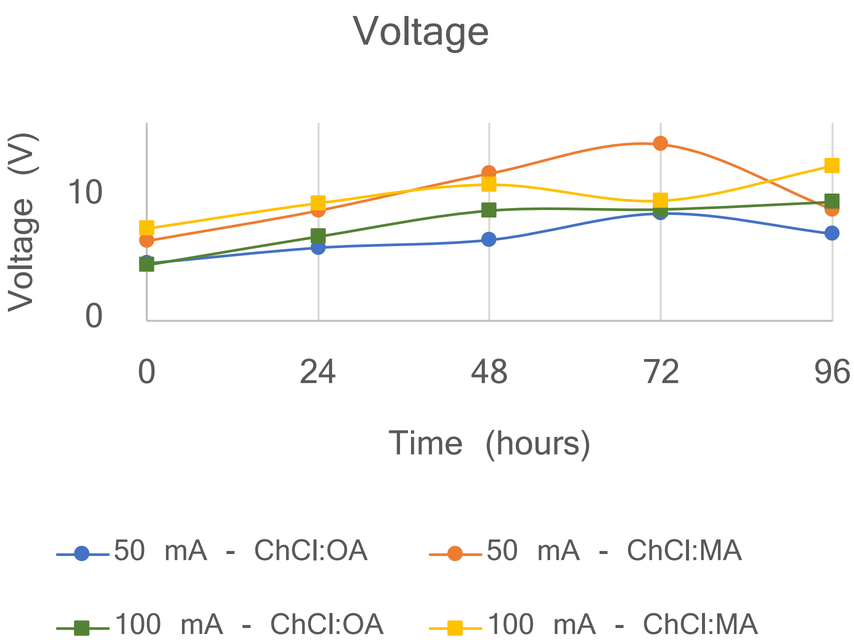
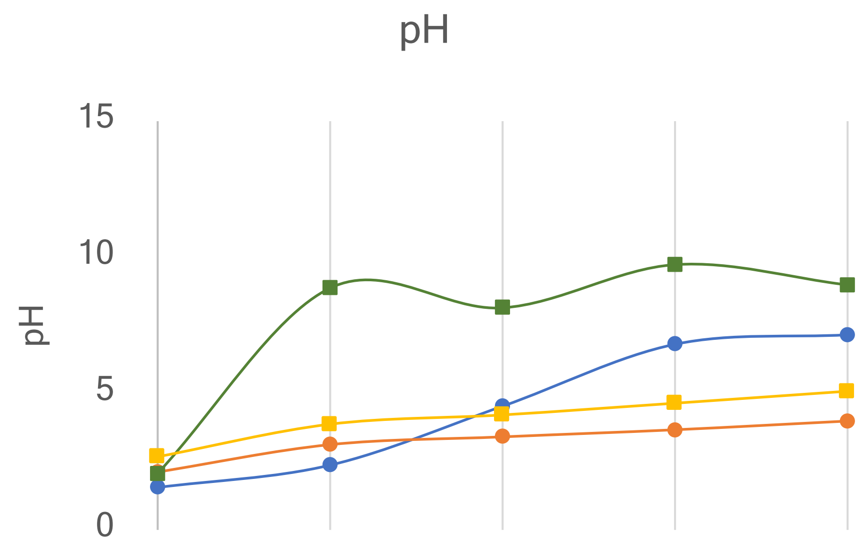
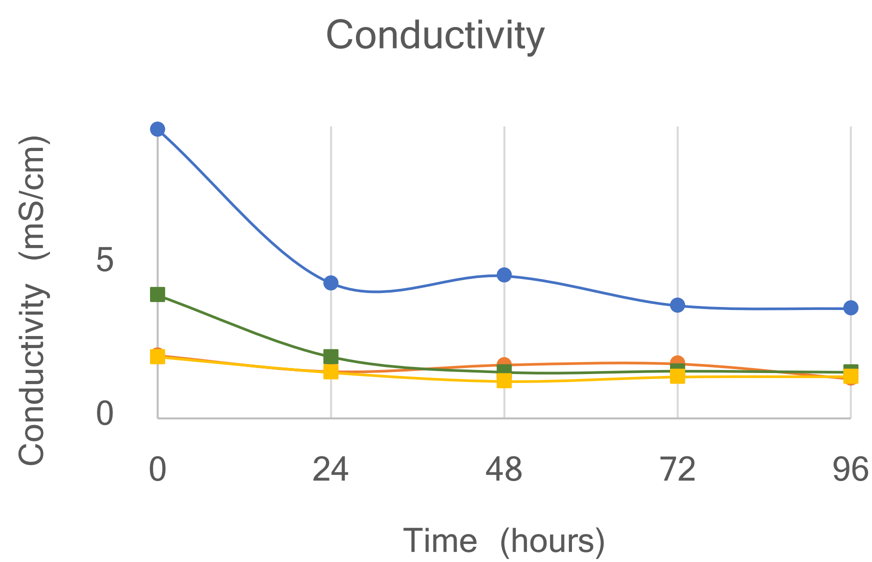


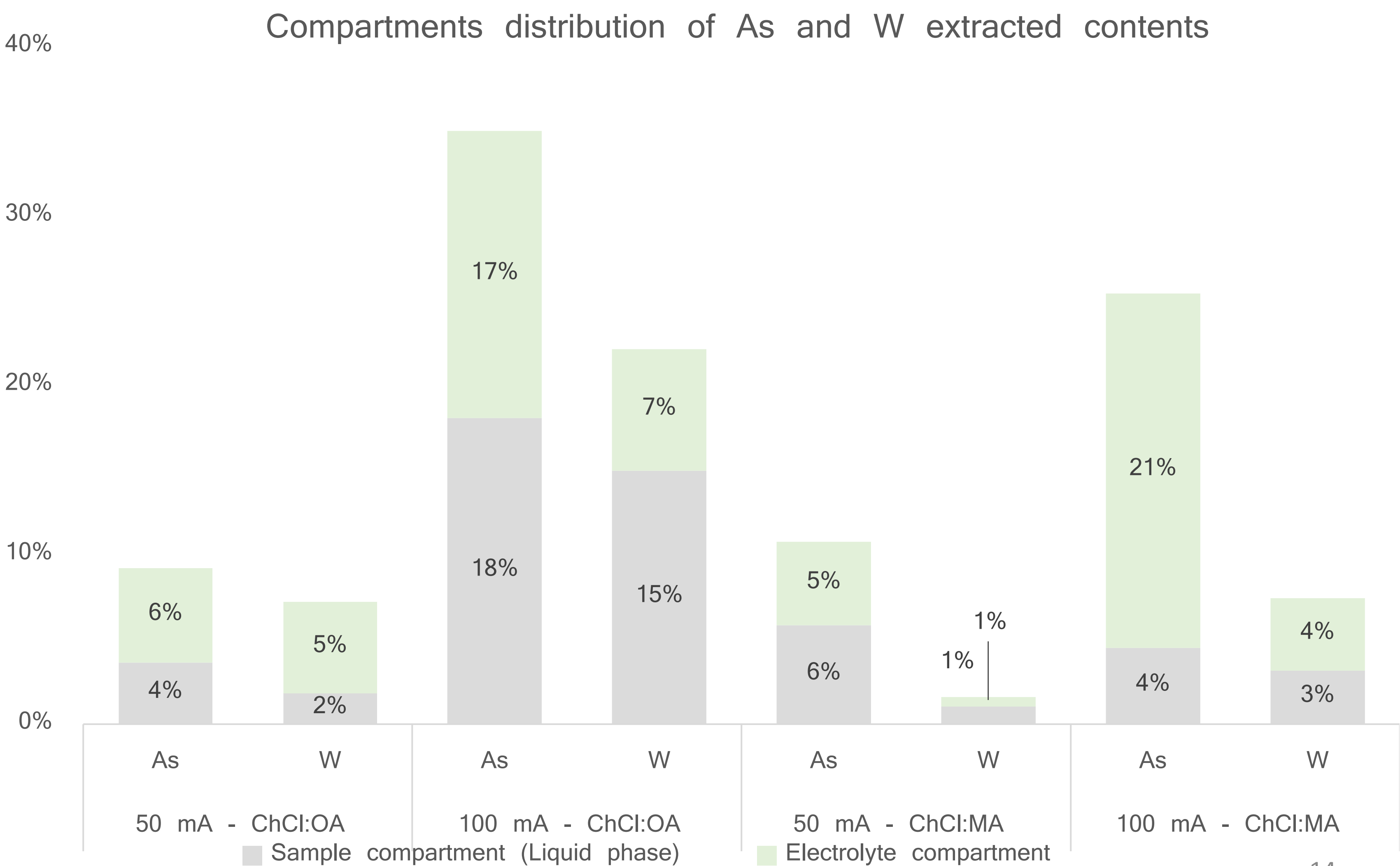
VOLTAGE, pH & CONDUCTIVITY CONTROL





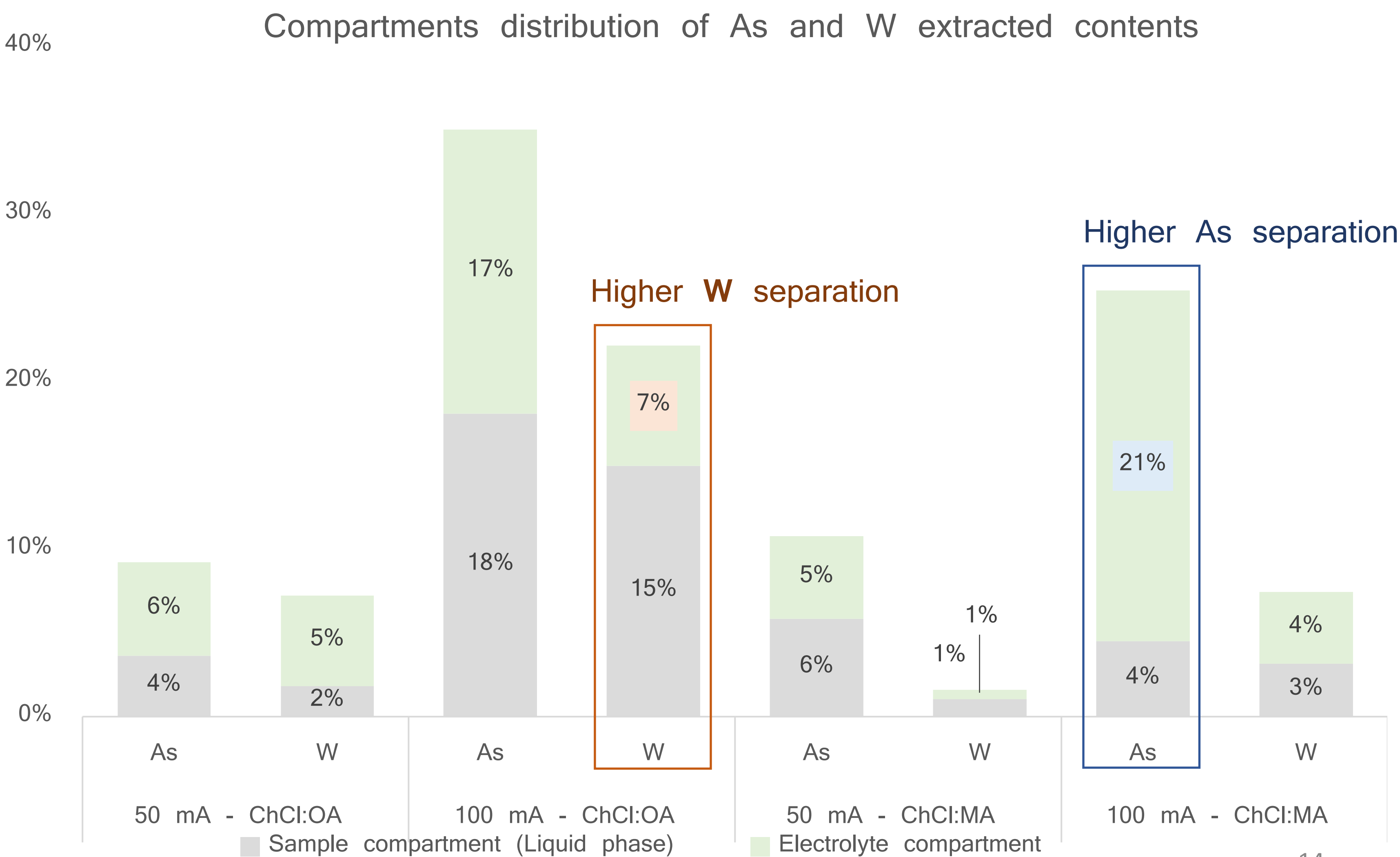


3 Feasibility of the ED process to separate As and W in a compartment apart from the matrix



Removed - Liquid phase + electrolyte contents; Separated - electrolyte content

3 Feasibility of the ED process to separate As and W in a compartment apart from the matrix



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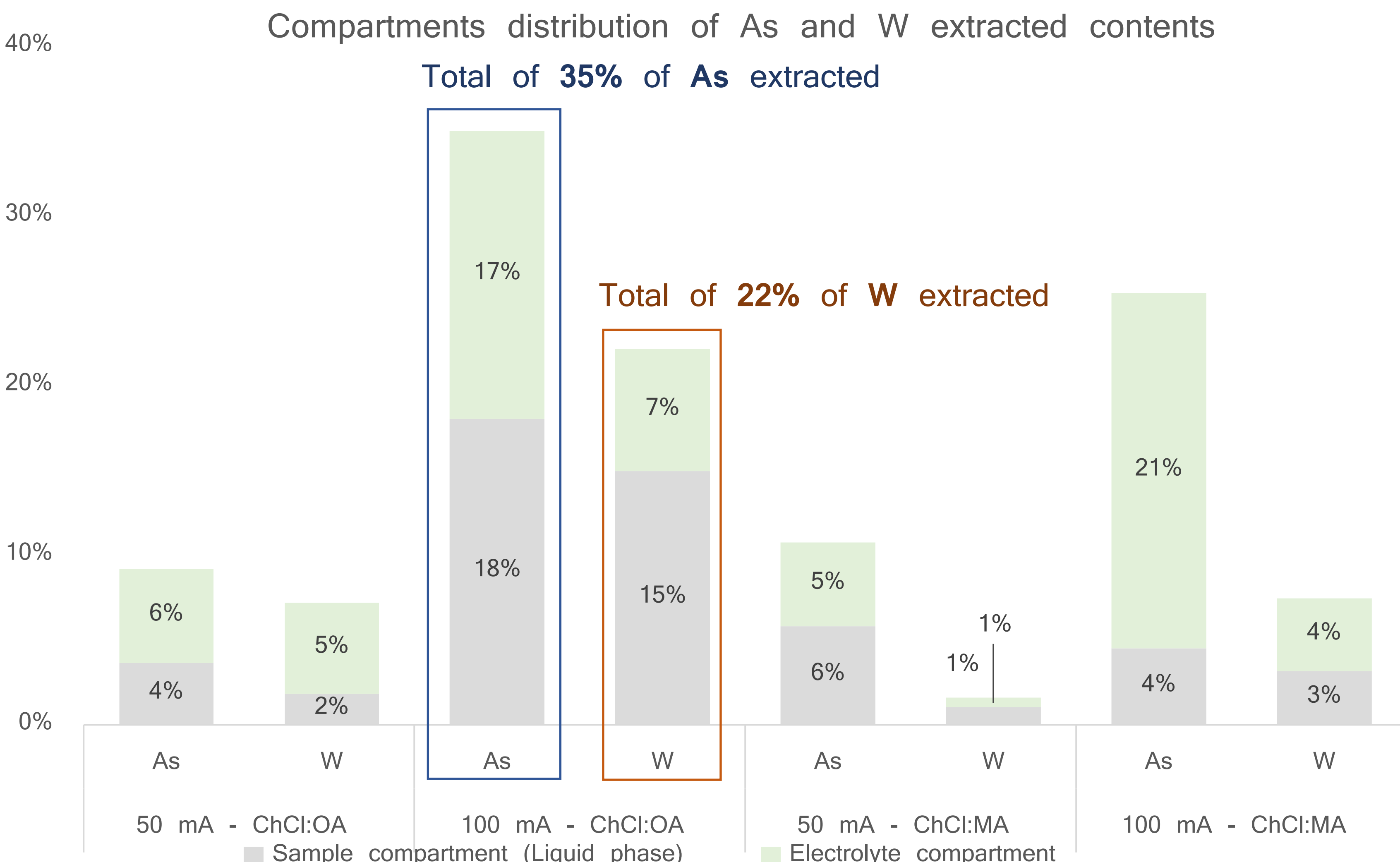
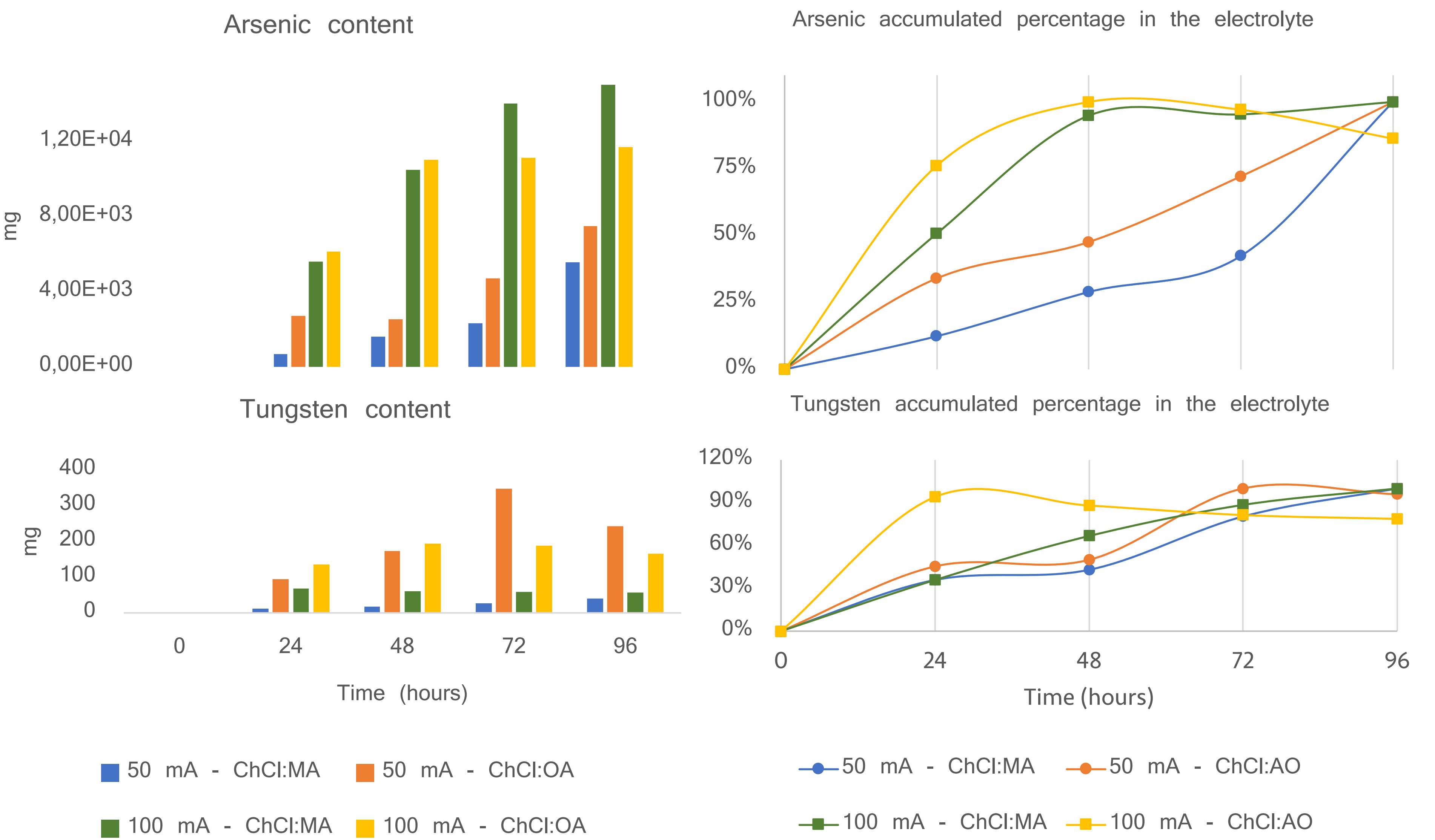


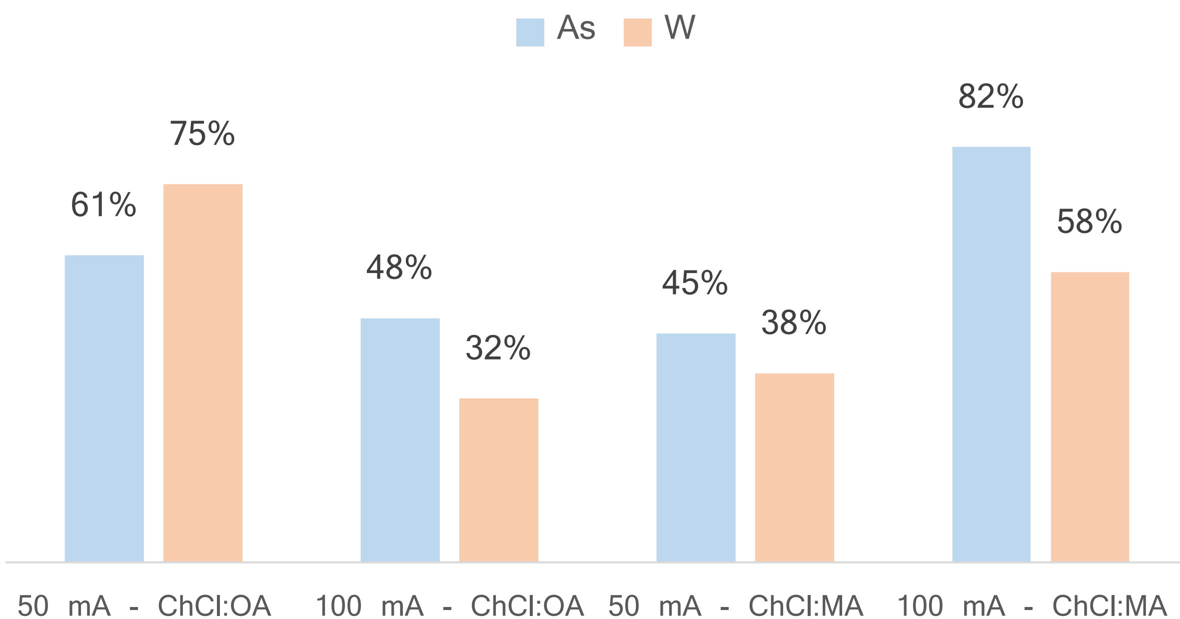
Removed - Liquid phase + electrolyte contents; Separated - electrolyte content

ELECTROLYTE BEHAVIOR

Mass and Percentage of elements reaching the electrolyte along the experiments



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



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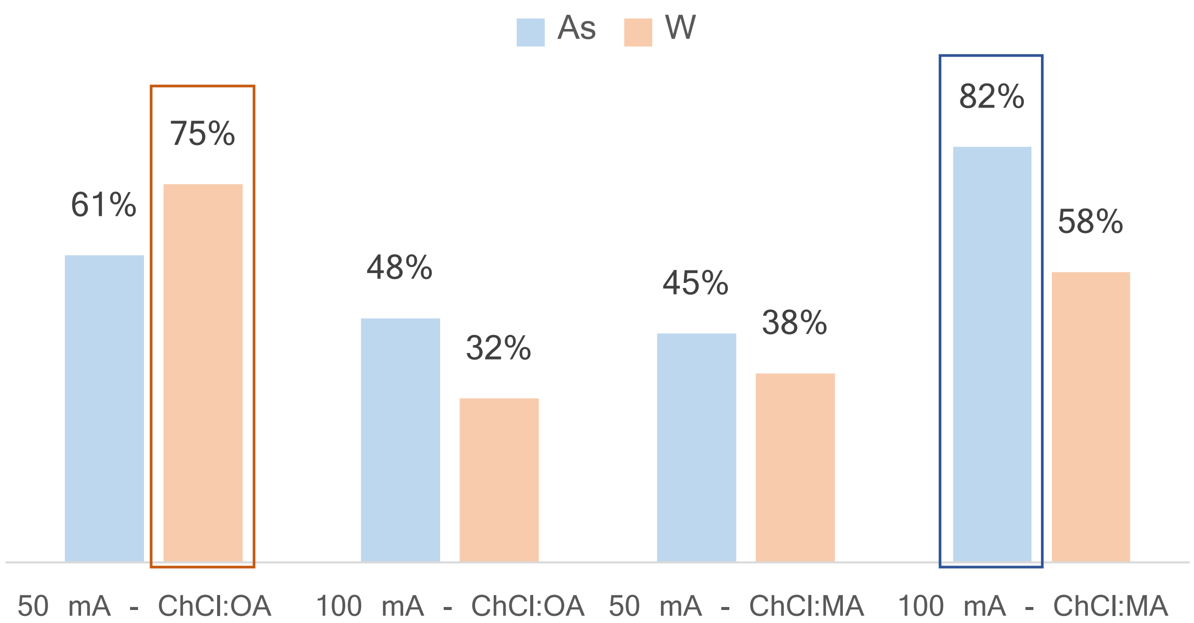
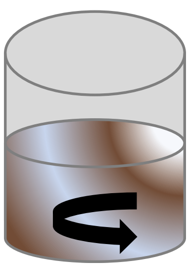


1 Selection of the most efficient DES for As and W extraction from the matrix

→ Different DES demonstrated higher extraction efficiencies for different elements

- ChCl:MA (1:2) extracted a maximum of 12% for As
- ChCl:OA (1:1) extracted a maximum of 9% for W

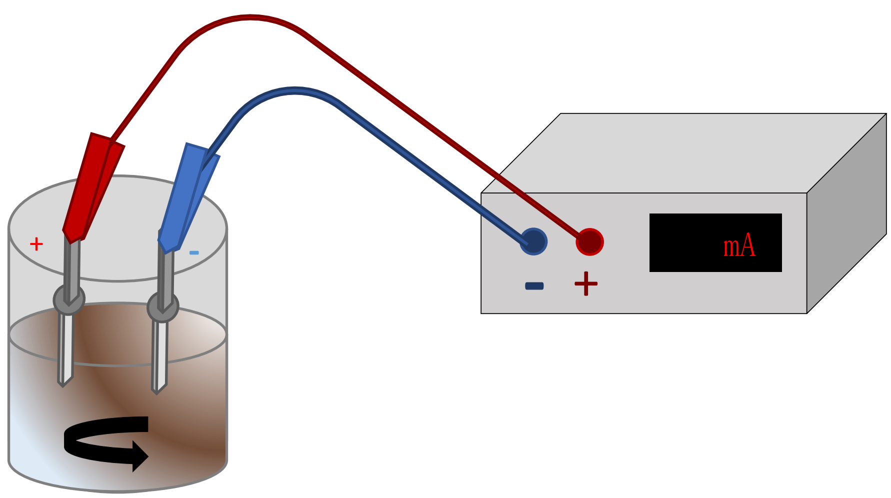


2 Potential of the EK process combined with DES to improve As and W extraction from the matrix

→ Deep Eutetic solvents and EK treatment synergy potentiated the extraction

- As extraction increased 21% (100 mA, ChCl:OA)
- W extraction increased 10% (100 mA, ChCl:MA)

Compared to DES experiments with no current

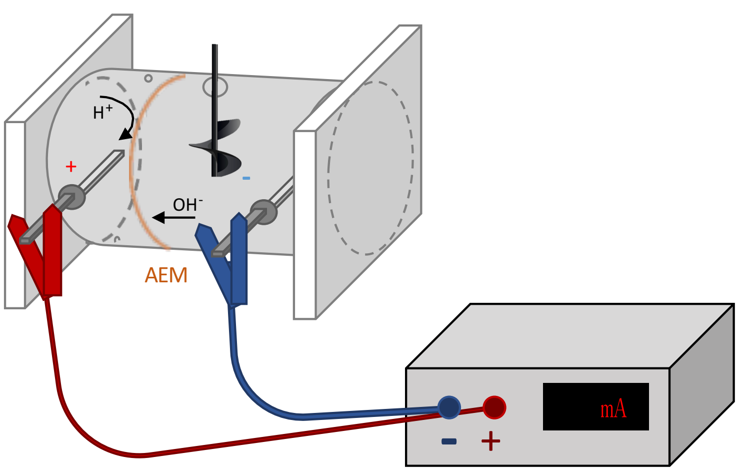


CONCLUSIONS

3 Feasibility of the ED process to separate As and W in a compartment apart from the matrix

➔ ED treatment enable to separate As and W, improving the migration of the elements from the matrix to the electrolyte compartment

- From the total As extracted, 82% (100 mA, ChCl:MA) migrated to the electrolyte
- From the total W extracted, 75% (50 mA, ChCl:OA) migrated to the electrolyte



Thank you!

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ACKNOWLEDGMENTS

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