tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

WATER PROOF

WaterProof Final Workshop: From Waste(water) CO_2 to Formic Acid

Acidic deep eutectic solvents (ADES) synthesis and application to recover metals from wastewater sludge and incineration ashes

TECNALIA RESEARCH & INNOVATION, 22nd October 2026, Amsterdam

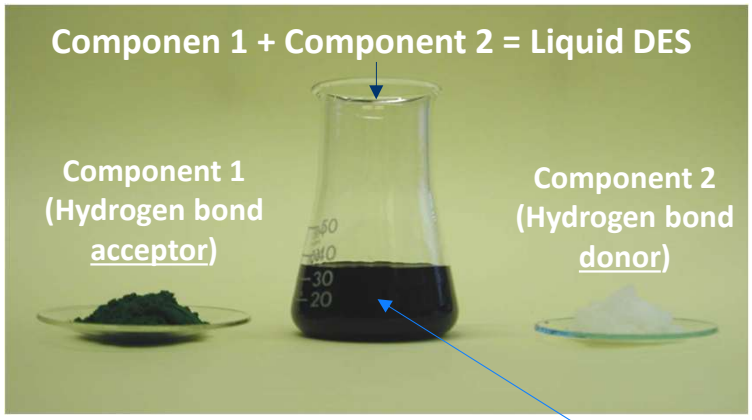
The WaterProof Project receives funding from the Horizon Europe Framework Programme under the Grant Agreement Number 101058578.

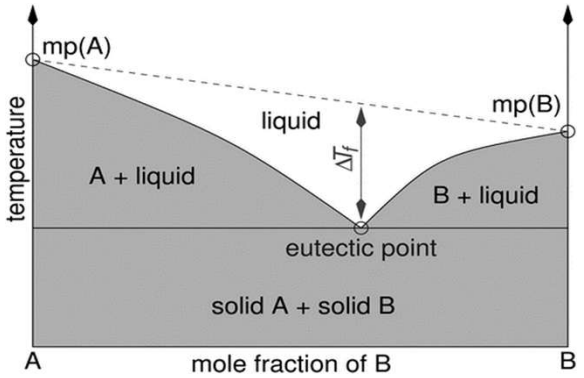
Funded by the European Union

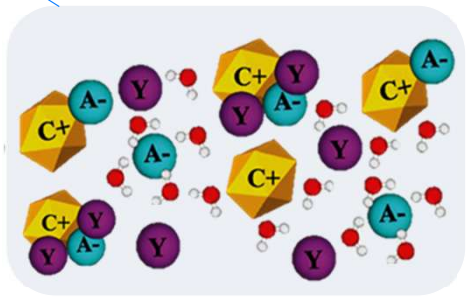
Acidic deep eutectic solvents (ADES) synthesis

WHAT is a Deep Eutectic Solvent (DES)?

Deep Eutectic Solvents (DES) are formed from a eutectic mixture of two components, one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA).







Most relevant properties

- Easy preparation
- Low-cost precursors
- Biodegradable
- Recyclable
- Non-flammable
- Excellent solvent & reaction media
- Can be selective solvent

WATERPROOF project:
Formic acid=HBD → Acidic DESs

**REFERENCE: Chem. Rev. 2014, 114, 21, 11060–11082*

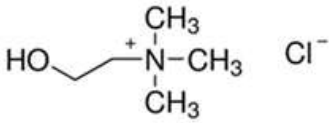
ADES synthesis

Commercial formic acid and HBAs at several molar ratios

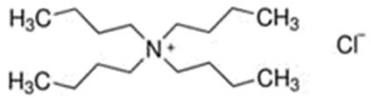
→ 1st **DES formation**: Evolution of physical state upon temperature

→ 2nd Aspect of synthesized ADES at **room temperature** (melting point)

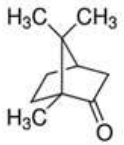
Hydrogen Bond Acceptors (HBAs)



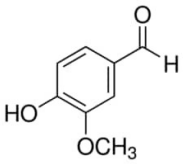
Choline Chloride
(ChCl)



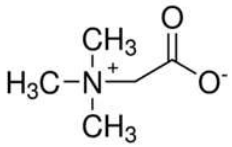
TetraButylAmmonium Chloride
(TBAC)



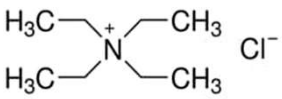
Camphor
(CP)



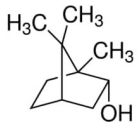
Vanillin
(Van)



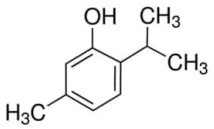
Betaine
(BT)



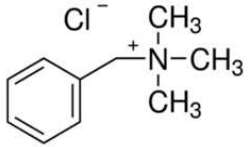
TetraEthylAmmonium Chloride
(TEAC)



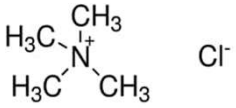
(-)-Borneol
(Bor)



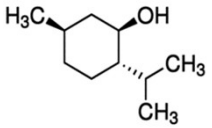
Thymol
(Thy)



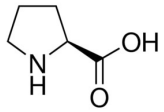
BenzylTriMethylAmmonium Chloride
(BTMAC)



TetraMetylAmmonium Chloride
(TMAC)



Menthol
(MT)

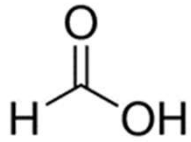


L-Proline
(Pro)

Formic acid (HBD)

Commercial grade
(Scharlau 98-100)

Different HBA/FA **molar ratios**:
1/0.5, 1/1, 1/1.5 *and* ***1/2***



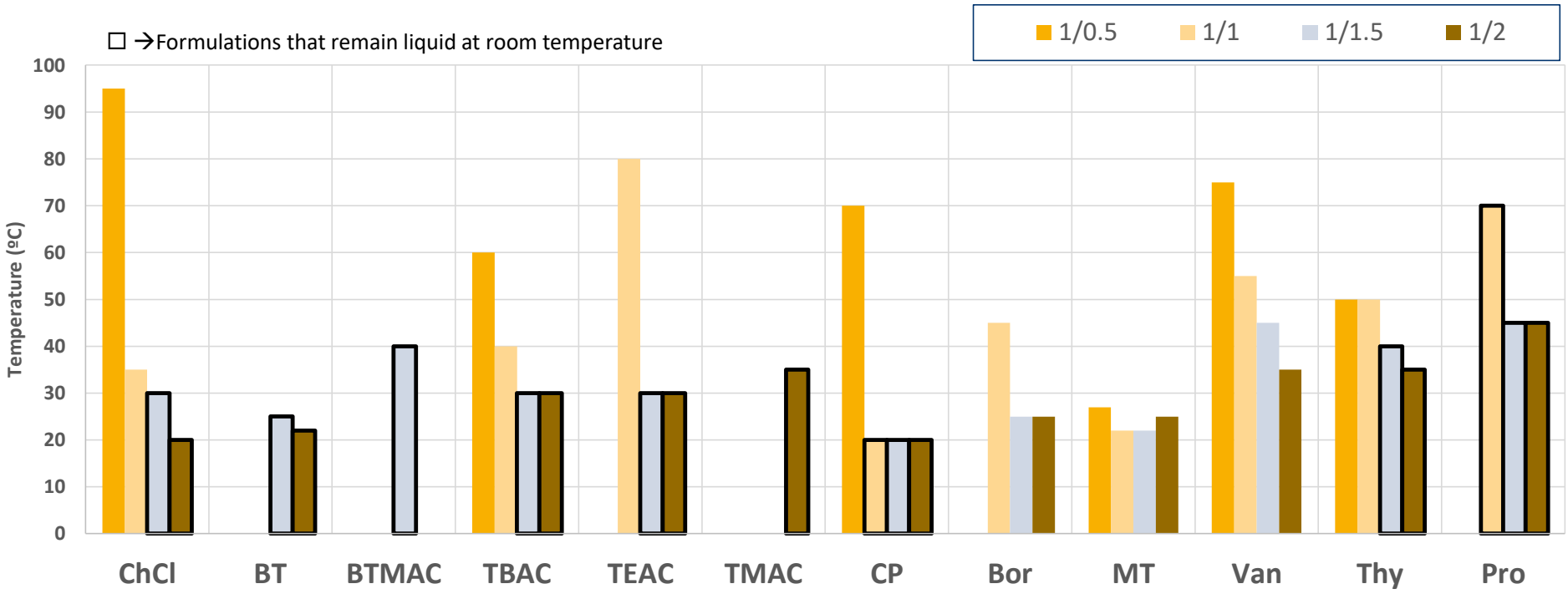
ADES synthesis

Commercial formic acid and HBAs at several molar ratios

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→ 2nd Aspect of synthesized ADES at **room temperature** (melting point)

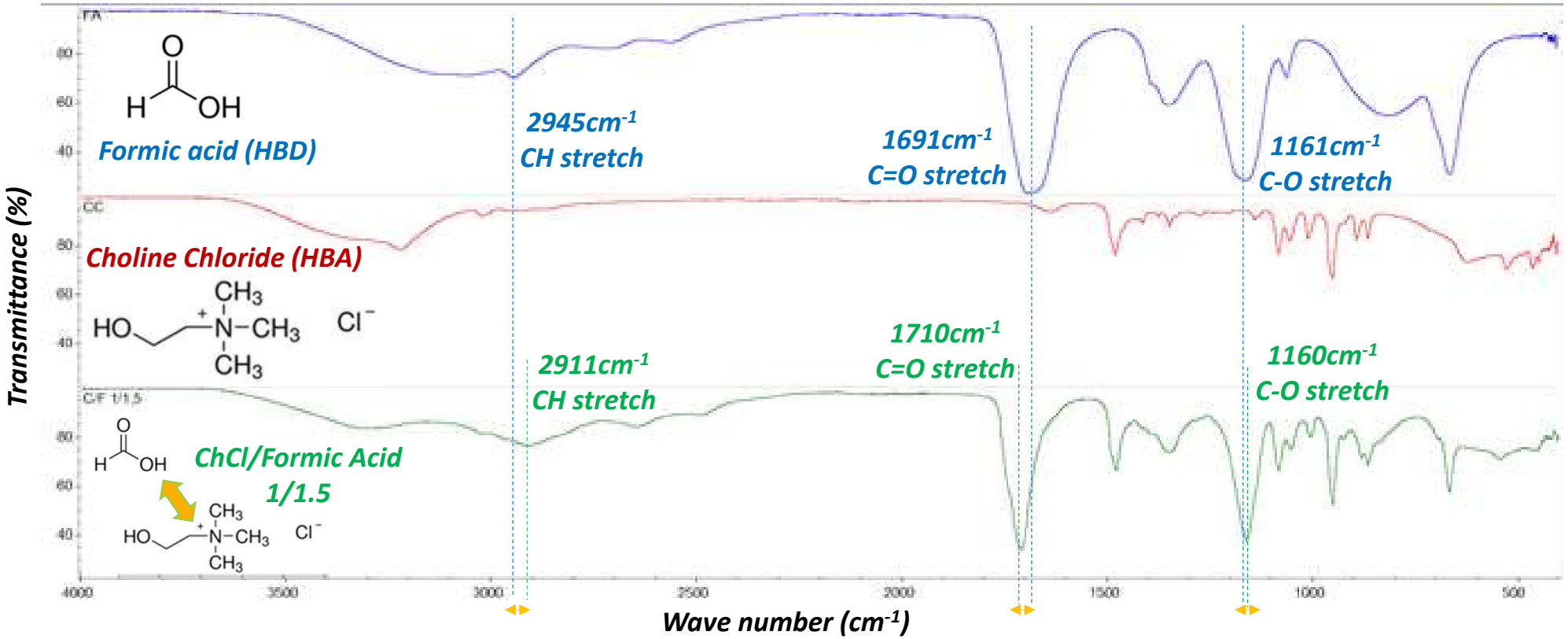
ADES synthesis temperature: different HBAs and HBA/FA ratios



ADES characterization: Molecular interactions

→ **FTIR** spectroscopy (Molecular vibrations: characteristic absorptions in the IR range: 4000-400cm^{-1})

- In case of interactions, such as hydrogen bonding → shifts in bands/peaks expected



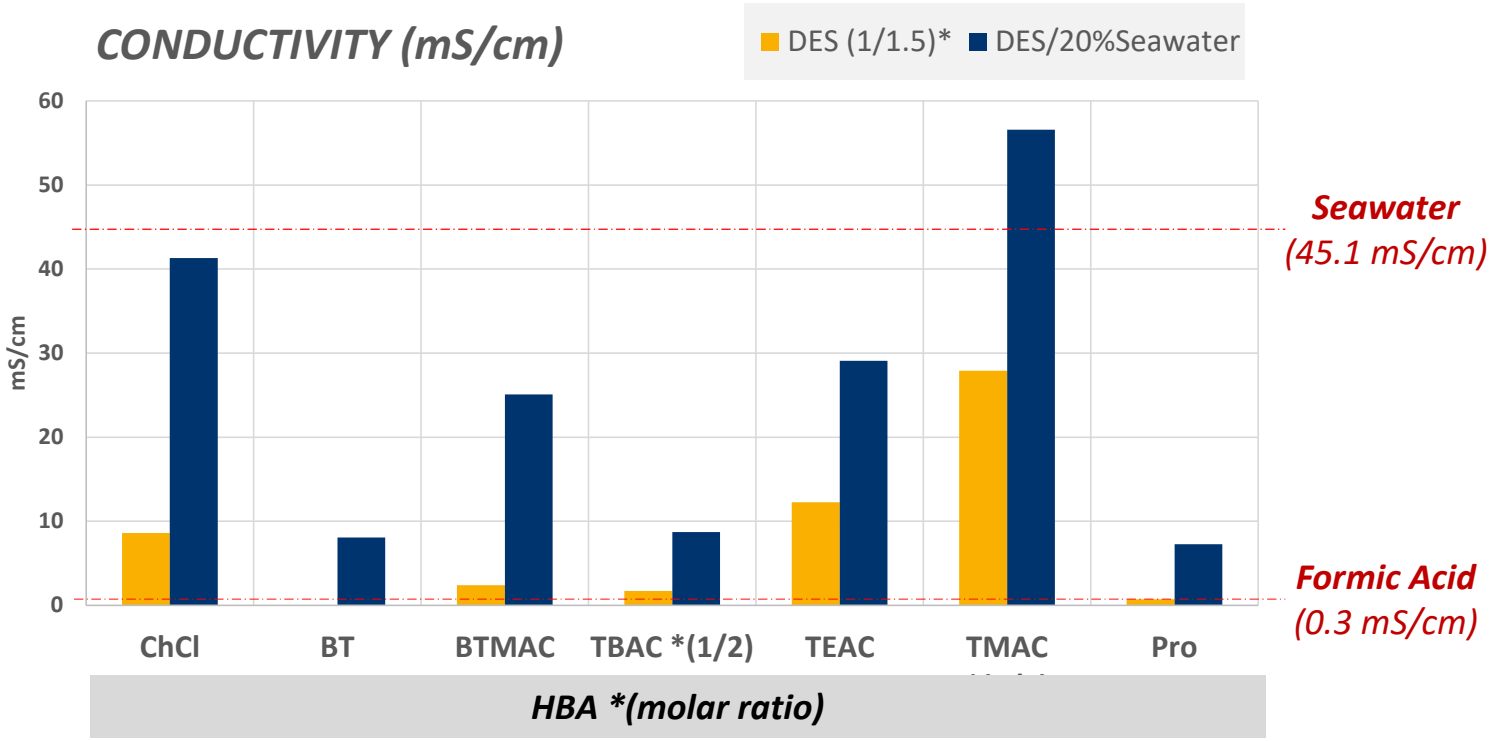
ADES characterization: Physicochemical properties

→ **Physicochemical properties** of synthesized ADESs and ADES+Seawater (80/20) formulations.

- Density, viscosity, conductivity, electrochemical properties, thermogravimetric analysis (TGA, TGA-FTIR)

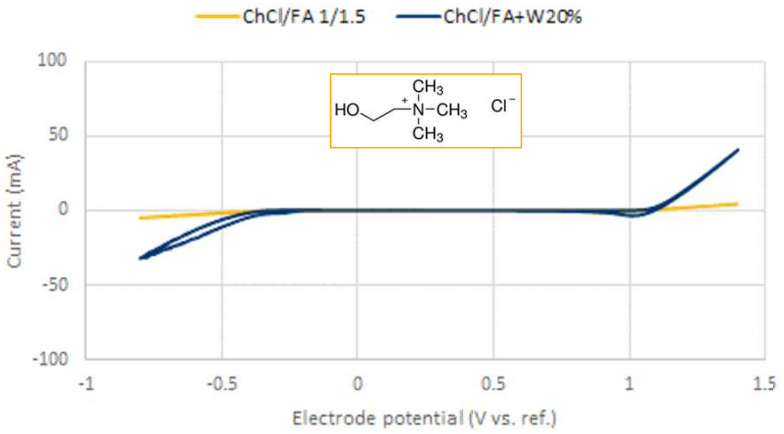
Characterized formulations (homogenous and stable at RT):

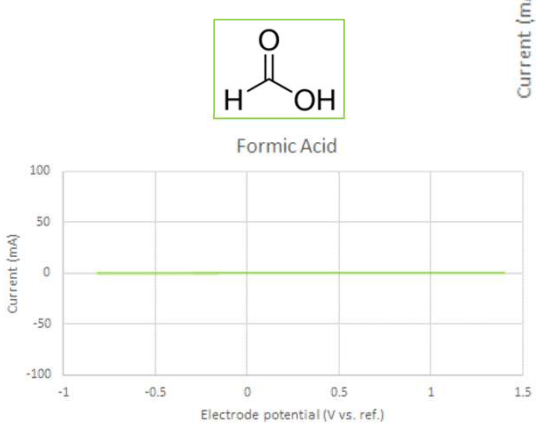
- ***DES*** *(HBA/FA with 1/1.5 molar ratio, except for [*]: 1/2 selected stable ratio)*
- ***DES/Seawater*** *mixture (80/20 weight basis ratio)*

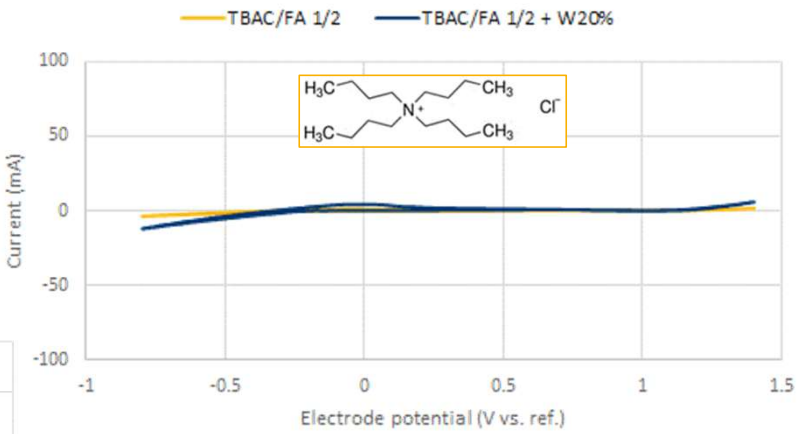


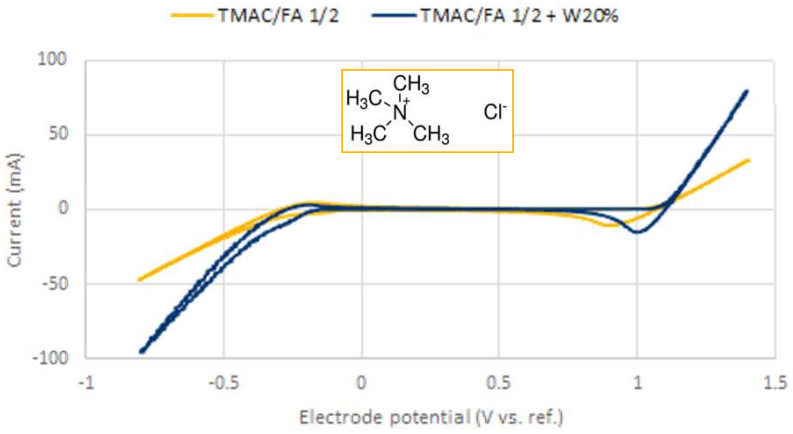
ADES characterization: Electrochemical properties

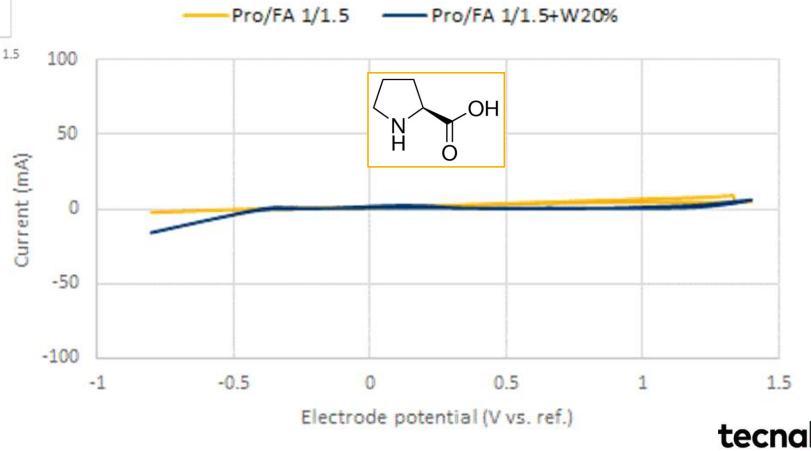
<u>Electrochemical characterization</u>: **Cyclic voltammetry** (several cycles between *-0.8V and +1.4V*)











ADES for metal recovery from waste streams

ADES for metal recovery

Characterization







	Zn	Cu	As	Cd	Cr	Hg	Pb	Ni	Fe
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%
Waternet	1237	618	7.6	<1	37	0.7	82	24	1.7

	Zn	Cu	Si	Al	Ca	Fe	Mg	Mn	Ni	Pb	Cr
	mg/kg	mg/kg	%	%	%	%	%	mg/kg	mg/kg	mg/kg	mg/kg
HVC filtercake	7078	2237	9.2	3.2	22.4	2.5	1.6	1125	177	1943	492

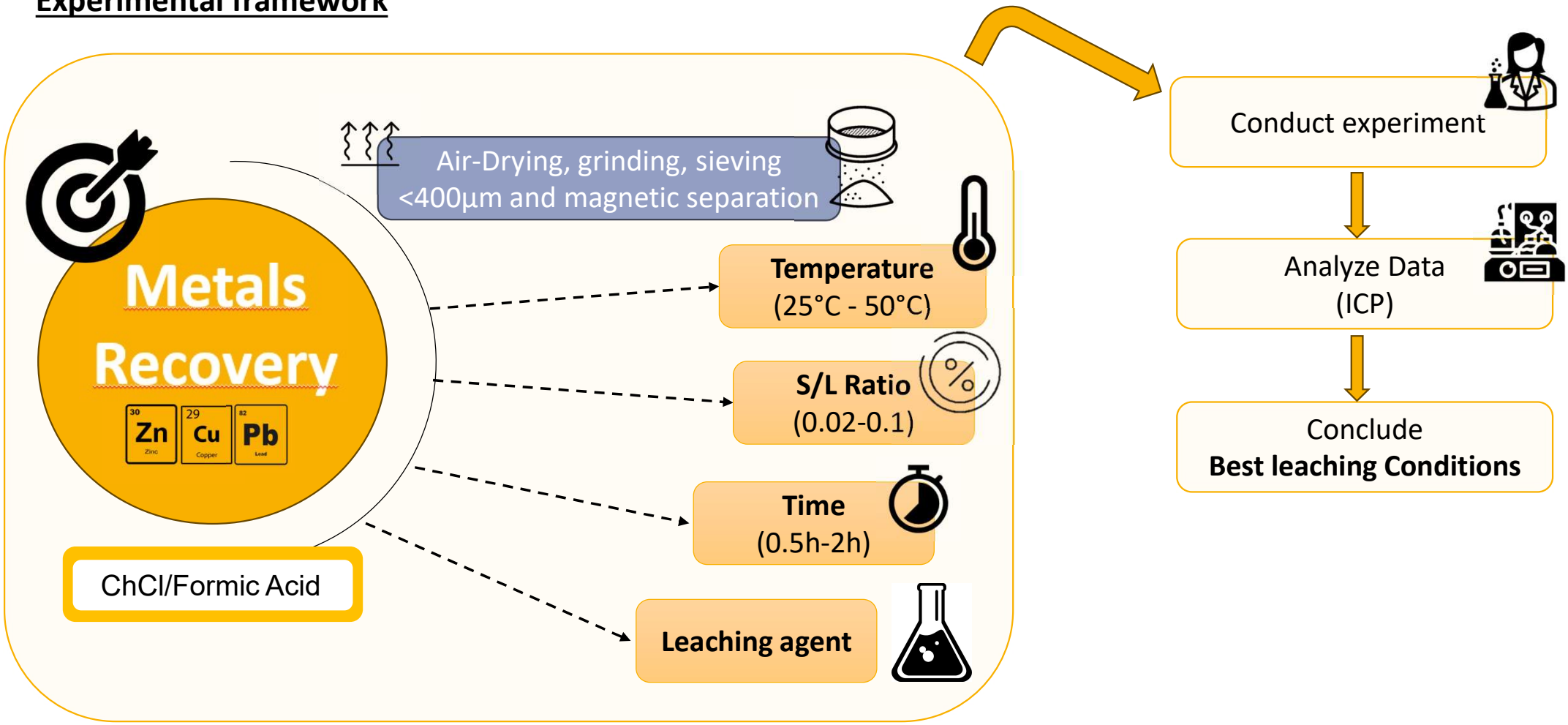
	Zn	Cu	Si	Al	Ca	Fe	Mg	Mn	Ni	Pb	Cr
	mg/kg	mg/kg	%	%	%	%	%	%	mg/kg	mg/kg	mg/kg
HVC Sand	2992	2999	26.5	4.7	10.7	5.4	1.4	0.1	214	1943	603

Sample	Dry matter	Ash content	pH (1/5)*	Conductivity (1/5)*
	%	% d.w.		mS/cm
Waternet	24.23	29.19	7.23	2.64
HVC Filtercake	54.31	88.39	12.48	16.77
HVC Sand	76.71	97.95	11.86	7.11

**MiliQ water dilution used to determine pH and conductivity*

ADES for metal recovery: **Conventional leaching**

Experimental framework



ADES for metal recovery: **Conventional leaching**

Experimental Results

Input material: **WATERNET sludge**

Initial solid composition

Zn mg/kg	Cu mg/kg	Pb mg/kg
1237	618	82

Optimization of operating conditions (ChCl/FA)

			% Extraction		
Temperature	Time	S/L Ratio	Zn	Cu	Pb
°C	h	w/w	%	%	%
37.5	1.25	0.06	70.8	30.6	24.4
37.5	1.25	0.06	85.1	44.7	38.0
25	2	0.02	84.4	43.1	57.4
25	0.5	0.1	66.2	10.8	8.2
50	0.5	0.1	50.1	22.5	13.8
25	2	0.1	53.6	21.3	12.9
25	0.5	0.02	38.5	10.7	12.9
50	2	0.02	43.8	10.1	12.9
50	1.25	0.02	31.7	10.4	14.7
50	2	0.1	58.7	18.8	12.2

Best conditions: 25 °C; 2h; S/L 0.02

Optimization of leaching agent (25 °C; 2h; S/L 0.02)

	% Removal		
Leachants	Zn	Cu	Pb
	%	%	%
DES (ChCl/Formic Acid)	85.4	44.1	57.4
HCl 0.2M	93.1	77.5	87.8
Formic Acid 0.2M	94.4	75.5	72.6
DES (ChCl/Formic Acid) + NaCl 0.5M	95.9	95.0	89.8

DES + NaCl 0.5M vs. other leachants:

- ❑ Enhanced Metal Removal Efficiencies
- ❑ Reduced Acid Quantities
- ❑ Minimized Environmental Impact
- ❑ Enhanced Stability

ADES for metal recovery: **Conventional leaching**

Experimental Results

Input material: **HVC Sand**

Initial solid composition

Zn	Cu	Fe	Mg	Ni	Pb	Cr
mg/kg	mg/kg	%	%	mg/kg	mg/kg	mg/kg
2992	2999	5.4	1.4	214	1943	603

Optimization of leaching agent (25 °C (or *50ºC); 2h; S/L 0.02)

LEACHANTS	Extraction yield (%)						
	Zn	Cu	Fe	Mg	Ni	Pb	Cr
0.2M HCl	68	5,3	30,9	30,9	12	49,1	17,6
0.2M FA	52,7	33,3	21,4	35,6	0	43,9	0
FA (98%)	42,1	18,8	20,9	19,6	17,2	56,7	20
80/20 DES/0.5MNaCl *	59,6	56,4	32,2	34,6	29,2	65,1	18,3

No single leaching agent outperforms the others across all metals. Each reagent has a distinct strength, but the **DES/0.5M NaCl** system stands out as the most versatile. If the goal is **multi-metal recovery** (especially Cu, Ni, and Pb — the metals of greater environmental and industrial relevance), the **80/20 DES/0.5M NaCl** system is the most promising option. It avoids the critical failures of the other reagents (0% Ni or Cu) while maintaining competitive yields for Zn and the rest.

ADES for metal recovery: **Conventional leaching**

Experimental Results

Input material: **HVC filtercake**

Initial solid composition

Cu	Zn	Pb	P	Mg
mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
2053	6138	1711	5869	16413

Optimization of leaching agent (25 °C (or *50°C); 2h; S/L 0.02)

LEACHANTS	Extraction yield (%)				
	Cu	Zn	Pb	P	Mg
0.2M FA	51.5	69.9	26.4	2.5	61.2
0.2M HCl	62.3	75.7	50.2	24.4	70.4
DES (ChCl/FA)	58.2	68.7	74.7	30.5	43.1
80/20 DES/W	77.7	76.5	88.3	73.1	65.4
80/20 DES/W *	88.9	77.8	89.9	66.6	71.5

80/20 DES/W is clearly superior for multi-metal recovery

It achieves the highest or near-highest extraction for **Cu (77.7–88.9%)**, **Pb (88.3–89.9%)**, and **P (66.6–73.1%)**, while remaining competitive for Zn and Mg. No other reagent comes close for these three metals.

ADES for metal recovery: **Conventional leaching**

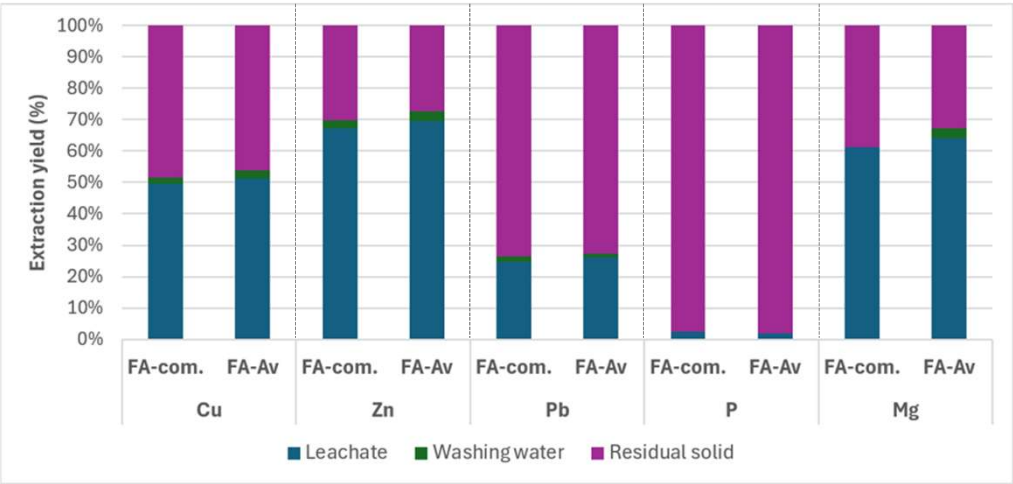
Experimental Results

Input material: **HVC filtercake**

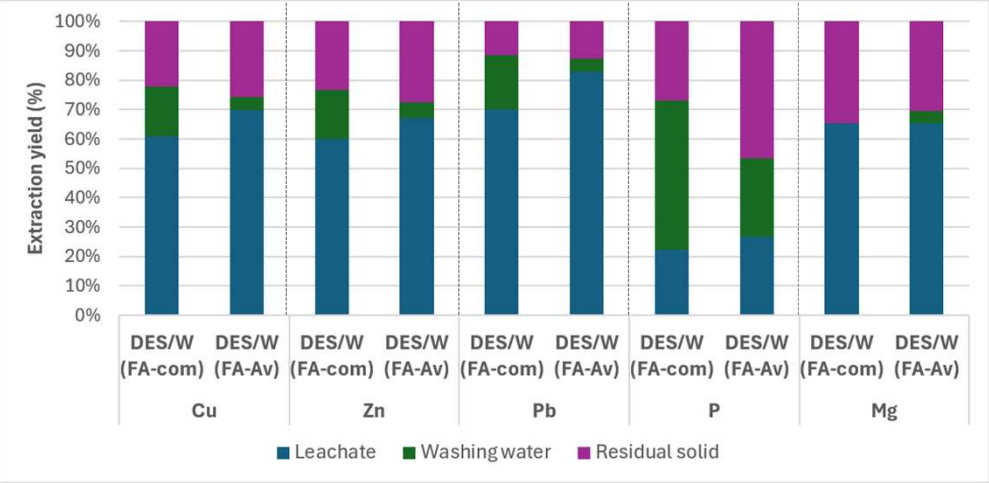
Initial solid composition

Cu	Zn	Pb	P	Mg
mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
2053	6138	1711	5869	16413

Formic Acid: Commercial vs Avantium (25 °C; 2h; S/L 0.02)



Comparison of leaching experiments with 0.2M commercial formic acid (FA-com) vs. 0.2M Avantium-formic acid (FA-Av)

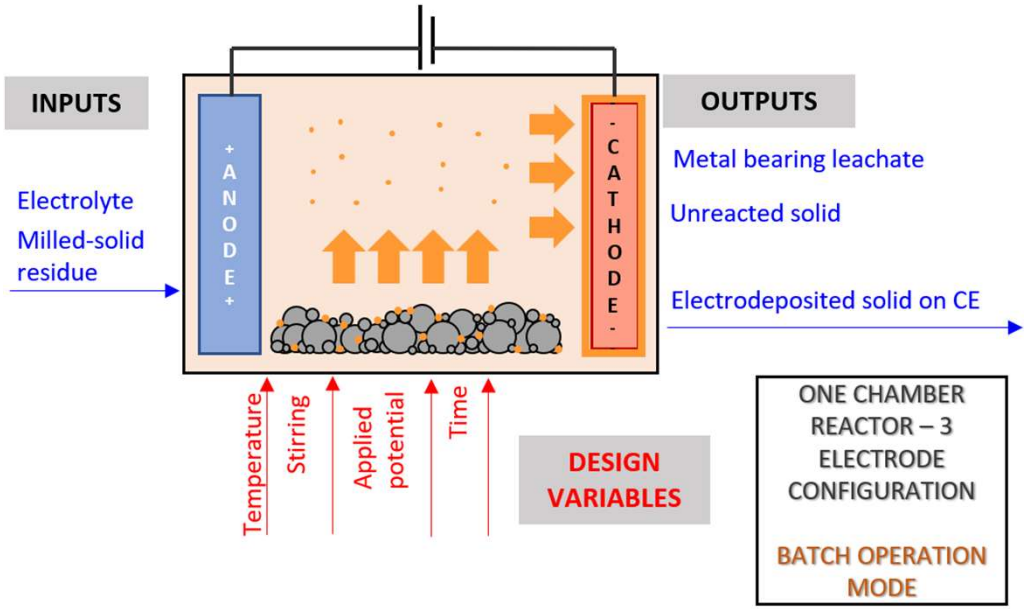


Comparison of leaching experiments with commercial formic acid-based DES/W mixture vs. Avantium-Formic acid-based DES/W mixture (80/20DES-FAAv/W)

Across every metal and in both systems (pure FA and DES/W), **commercial FA (FA-com)** and **Avantium FA (FA-Av)** give nearly identical leachate + wash yields. The green/Avantium acid is a **drop-in replacement** for the commercial product with no loss in metal recovery — the relevant variable is the *acid chemistry/medium*, not its supply source.

ADES for metal recovery: **Electroleaching**

Concept



COMPONENT	REAGENTS
ELECTROLYTE	DES (80%) + aqueous solution (20%)
➢ DES	ChCl/FA
➢ AQUEOUS SOLUTION	0.5M NaCl

ELECTRODE	MATERIAL
WORKING ELECTRODE (Anode)	Boron Doped Diamond (BDD)
COUNTER ELECTRODE (Cathode)	Graphite
REFERENCE ELECTRODE	Ag/AgCl (KCl sat.)

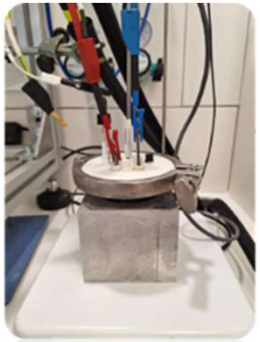
- ELX introduces an electrified electroleaching process that replaces chemically intensive leaching with in-situ generation of oxidant species, delivering a step-change in efficiency, cost, and sustainability.
- By producing oxidants electrochemically, the process reduces external reagent consumption by 30–60% compared to conventional hydro- and solvometallurgical routes, while operating under milder conditions.

ADES for metal recovery: **Electroleaching**

Electroleaching set-up

Lab-scale (≈ 80 ml)



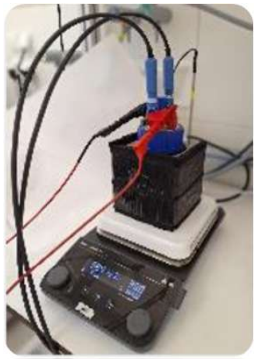




POTENTIOSTAT used at LAB scale

Intermediate scale (≈ 360-500 ml)







POWER SUPPLY used at INTERMEDIATE scale



pH, ORP and temperature probes for continuous monitorization

- WATERPROOF project: 80-500 ml scale.
- Possibilities of working at higher scale (≈2-4 L).

ADES for metal recovery: **Electroleaching**

Electroleaching results at LAB-scale (≈80 ml)

Waternet sludge

- Problems **mixing the solid and the liquid** and **foam formation** → Probably due to the presence of some organic compounds.
- Almost a complete **extraction of Cu, Pb and Zn (≈90%)** when 2.4 V vs NHE is applied under 50ºC for 2 h.
- Practically all the **leached elements remained in the leachate** (not electrodeposited on the cathode). The foaming might have negatively affected to the electrodeposition.





Foam formation during reaction with Waternet sludge

Calcination

	Cu	Pb	Zn	P	Mg
Sample	mg/kg	mg/kg	mg/kg	%	%
NON-CALCINATED	462	64	956	3,8	1,9
CALCINATED	1729	279	3665	16,7	8,1

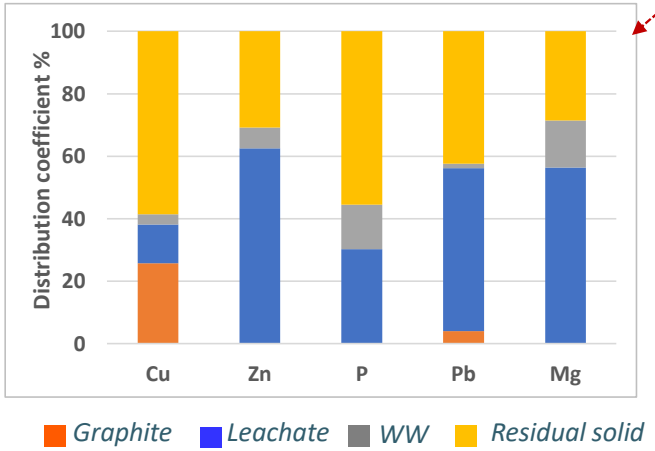
WATERNET sludge CALCINATED



PARAMETER	CONDITIONS
Electrolyte	ChCl/Formic acid 1:1.5 + NaCl
Ratio liquid/solid	50
APPLIED POTENTIAL (V)	+ 2.4 V vs. SHE (2.2 V vs Ag/AgCl)
TIME (h)	2 h
TEMPERATURE (°C)	50 (T_{max} = 55°C)
STIRRING (rpm)	350

	Cu	Zn	P	Pb	Mg
Conventional leaching (%)	51	66	42	58	67
Electroleaching (%)	41	69	45	58	71

NO foam formation!



- The removal of organic fraction allowed the correct completion of the process. Lower extraction yields compared to non-calcinated sample most likely due to higher metal concentration in input material.
- Moderate simultaneous electrodeposition was possible. Cu mainly deposits on the cathode. Zn, Mg and Pb mainly remains in leachate.

ADES for metal recovery: **Electroleaching**

Electroleaching results at LAB-scale (≈80 ml)

HVC filteracke

Cu	Pb	Zn	P	Mg
mg/kg	mg/kg	mg/kg	mg/kg	%
2053	**1711**	**6138**	**5869**	**1,6**

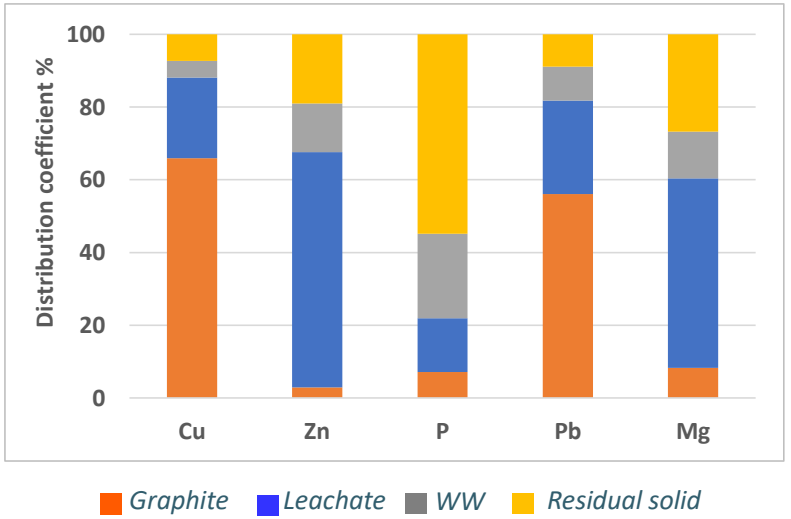
PARAMETER	CONDITIONS
Electrolyte	**ChCl/Formic acid 1:1.5 + NaCl**
Ratio liquid/solid	**50**
APPLIED POTENTIAL (V)	**+ 2.9 V vs. SHE** (2.7 V vs Ag/AgCl)
TIME (h)	**2 h**
TEMPERATURE (°C)	**50** (T_{max} = 105°C)
STIRRING (rpm)	**350**

	Cu	Zn	P	Pb	Mg
Conventional leaching (%)	89	78	67	90	72
Electroleaching (%)	93	81	45	91	73

- Similar extraction yields compared to conventional leaching but ELX enables the simultaneous electrodeposition of Cu and Pb → separation strategy.
- Zn and Mg mainly remains in the leachate.



Solid deposited on cathode after ELX for HVC filtercake



ADES for metal recovery: **Electroleaching**

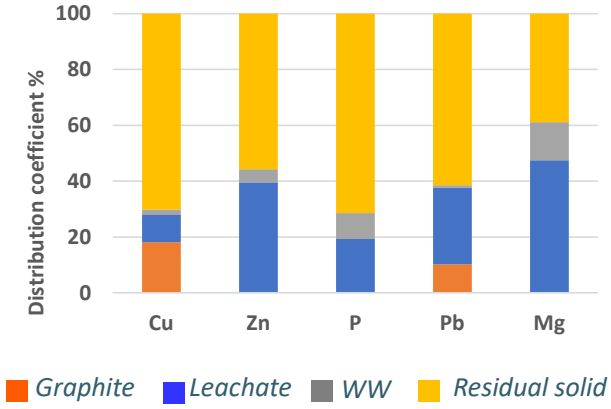
Electroleaching results at MEDIUM-scale (≈500 ml)

Waternet sludge - CALCINATED

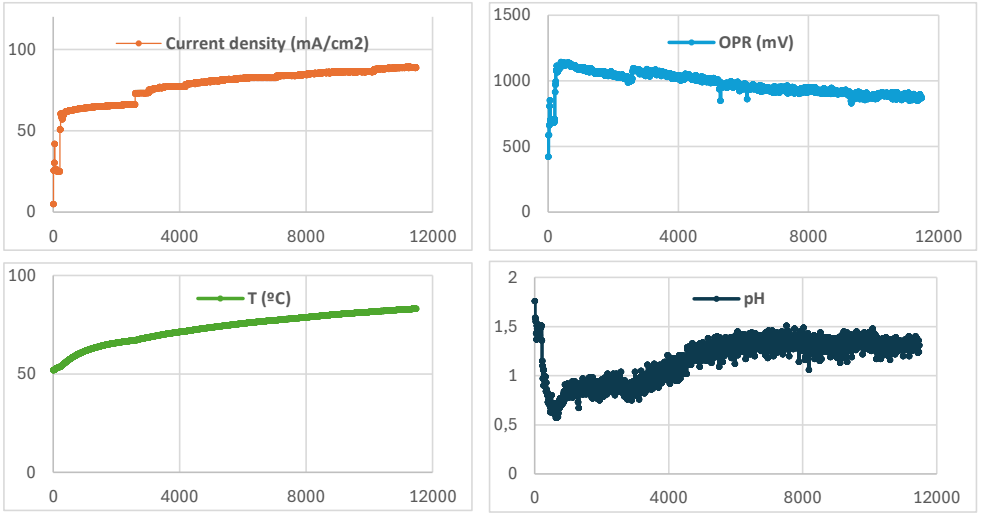
	Cu	Pb	Zn	P	Mg
	mg/kg	mg/kg	mg/kg	%	%
CALCINATED*	1771	242	3753	15,4	7,4

PARAMETER	SMALL SCALE	HIGH SCALE
Electrolyte	ChCl/Formic acid 1:1.5 + NaCl	ChCl/Formic acid 1:1.5 + NaCl
Ratio liquid/solid	50	20
APPLIED POTENTIAL (V)	+ 2.4 V vs. SHE	+ 8 V (CELL voltage)
TIME (h)	2 h	3 h
TEMPERATURE (°C)	50	50
STIRRING (rpm)	350	250

SCALE	Cu	Zn	P	Pb	Mg
SMALL (%)	41	69	45	58	71
MEDIUM (%)	30	44	29	39	61



- Lower extraction yields at medium scale, but it could be related to the liquid/solid ratio (lower at high scale).
- Similar trend in the simultaneous electrodeposition of metals. Moderate electrodeposition of Cu (and slightly Pb) on the cathode. Extracted Zn, Mg and P mainly remain in the leachate.
- Longer times could increase the extraction and simultaneous electrodeposition of Cu at lower liquid/solid ratio.



- Continuous monitoring of the operating parameters allows to track the evolution of the reaction over time and thus adjust and optimise the operating conditions.

ADES for metal recovery: **Electroleaching**

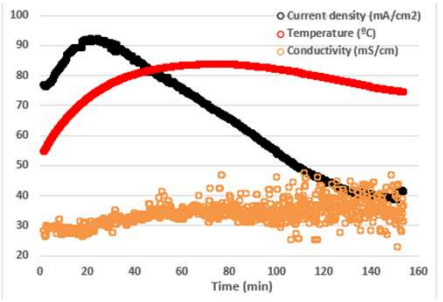
Electroleaching results at MEDIUM-scale (≈500 ml)

HVC filteracke

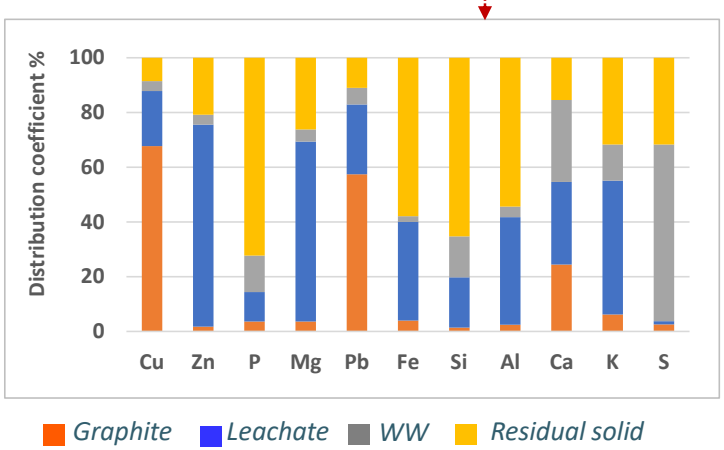
Cu	Zn	P	Pb	Mg
mg/kg	mg/kg	mg/kg	mg/kg	%
2053	6138	5869	1711	1.6

Fe	Si	Al	Ca	K	S
%	%	%	%	%	%
2.52	9.19	3.18	22.4	1.01	3.91

PARAMETER	SMALL SCALE	MEDIUM SCALE
ELECTROLYTE	ChCl/FA 1:1.5 + NaCl	ChCl/FA 1:1.5 + NaCl
SCALE	≈60 ml	≈500 ml
APPLIED POTENTIAL (V)	+ 2.9 vs SHE (WE)	+ 10 V (cell)
TIME (h)	2 h	2.5 h
TEMPERATURE (°C)	50	50
STIRRING (rpm)	350	350
RATIO LIQUID/SOLID	50	20



SCALE	Cu	Zn	P	Pb	Mg
SMALL (%)	93	81	45	91	73
MEDIUM (%)	90	79	27	88	74



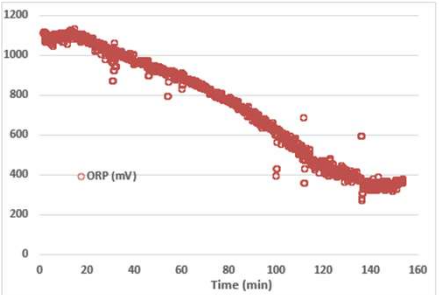
- Similar extraction yields at medium scale, except for P.
- Similar trend in the simultaneous electrodeposition of metals. Cu and Pb primarily recovered at the cathode via electrodeposition. Zn and Mg mostly remain in the leachate .

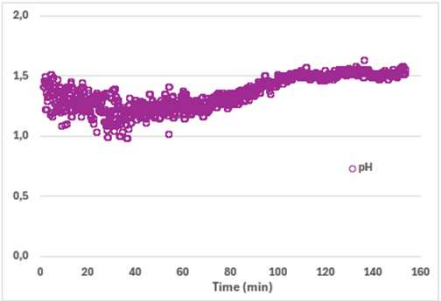


Leachate obtained during ELX.

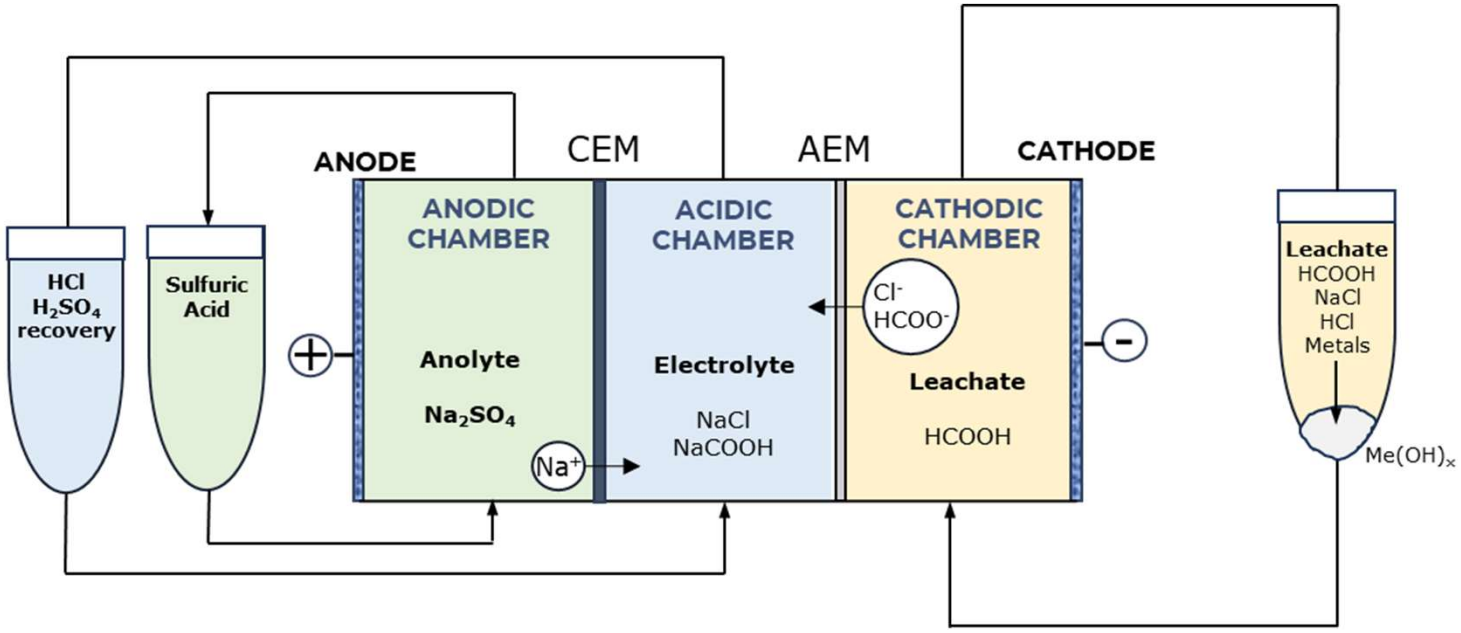


Solid electrodeposited on graphite during ELX.





Electrochemically-assisted formic acid recovery



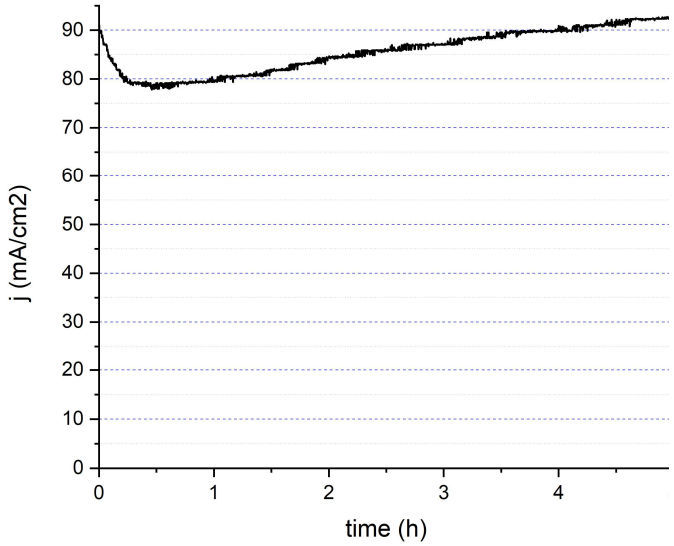
- Best results were achieved with a 3-chamber ED cell, where the leachate is fed to the cathodic chamber
- Formic acid is recovered in the acidic chamber (central compartment)
- To prevent further migration of undissociated formic acid to the anodic chamber, a sodium sulfate solution was used in anolyte, favouring Na+ migration against protons.
- This setup was tested for:
  - **Synthetic samples.**
  - **Real electroleachates**

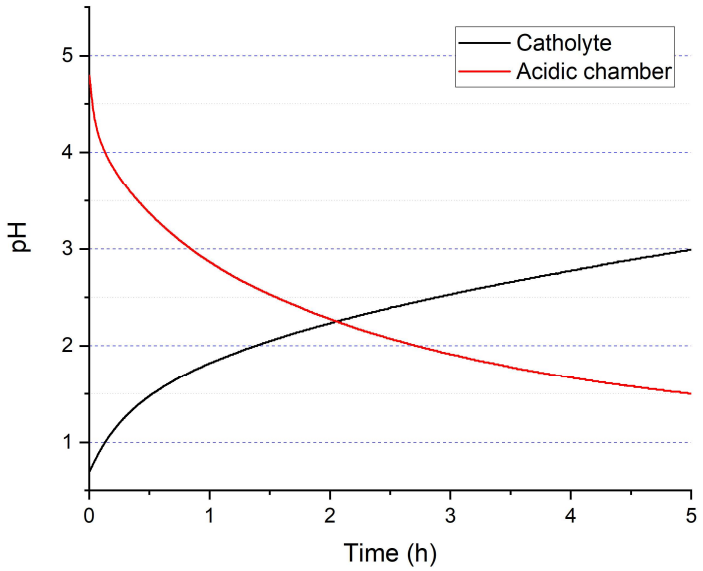
ADES for metal recovery waste streams

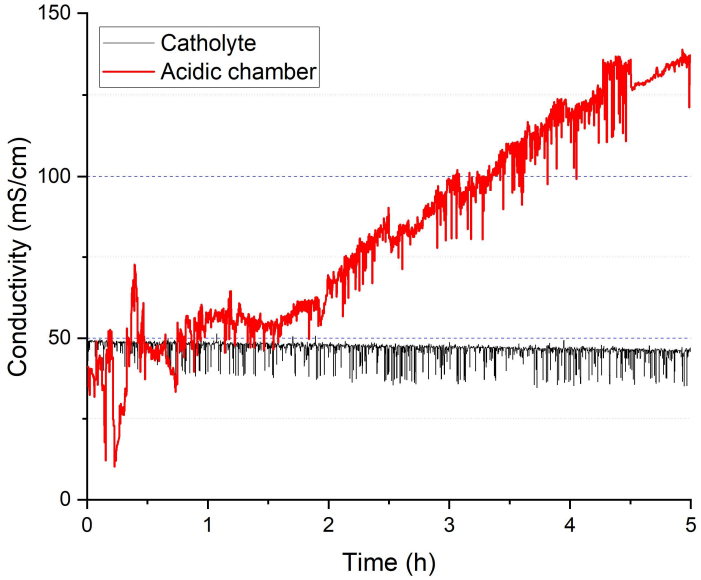
Synthetic sample

	Cu	Zn	Na	FA	Cl-	SO_4^{2-}
WF-Synth4	1,0	2,0	2,4	298	165	0

All concentrations in g l^{-1}







		Anolyte	Acidic chamber electrolyte	Catholyte
Conductivity mS/cm	**Before**	27,7	41,3	41,0
	After	50,5	137,3	38,0
pH	**Before**	5,56	5,37	0,68
	After	0,94	0,72	3,01

- Ecell 10V. Current density was stabilized at 85 mA·cm^{-2}
- Normal behaviour was observed:
  - Acidic chamber: Conductivity increases. pH slightly decreases
  - Catholyte: pH increases

ADES for metal recovery waste streams

Synthetic sample

	Cu	Zn	Na	FA	Cl-	SO_4^{2-}
WF-Synth4	1,0	2,0	2,4	298	165	0

All concentrations in g l^{-1}

BALANCE (CATIONS AND ANIONS)

All in mg

	Inputs			Outputs			Total Inputs	Total Outputs
	Anodic chamber	Acidic chamber	Cathodic chamber	Anodic chamber	Acidic chamber	Cathodic chamber		
Cu	0	0	197	0,00	7,9	45,9	196,7	53,77
Zn	0	0	404	0,26	25,7	345,0	404,5	370,9
Na	2114	6,3	482	826,7	1373,8	471	2602,0	2671,8
FA	0	0	59580	0,0	3557,6	50825	59580,0	54382,7
Cl	0	0	33000	0,0	5037,2	23959	33000	28996

- Cu and Zn dissapear from catholyte due to precipitation in the cathode. No precipitate appeared in Solution.
- Some Cu, Zn migrates to the acidic chamber combined with Cl- or formiate.
- Na migrates from anodic chamber to acidic chamber.
- FA and Cl migrates from catholyte to acidic chamber.

BALANCE (TOTAL WEIGHT)

All in g

	Inputs			Outputs			Total Inputs	Total Outputs
	Anodic chamber	Acidic chamber	Cathodic chamber	Anodic chamber	Acidic chamber	Cathodic chamber		
Weight	200,435	204,3150	220	187,98	222,3	197,6	624,9	607,84

ADES for metal recovery waste streams

Electroleachate

Real sample W-260303 (yellow)

Cu	Zn	P	Mg	Ca	K	Na	FA	Cl-
0,009	0,1	2,2	2,2	1,0	0,2	2,7	253	153

All concentrations in g l^{-1}

All in mg

	Inputs			Outputs			Total Inputs	Total Outputs
	Anodic chamber	Acidic chamber	Cathodic chamber	Anodic chamber	Acidic chamber	Cathodic chamber		
Na	2401	4,3	533	312,1	2047,9	579	2937,7	2939,3
FA	0	0	50540	148,7	24941,3	33342	50540,0	58432,2
Cl	0	0	30610	11,1	19461,1	13683	30610	33155

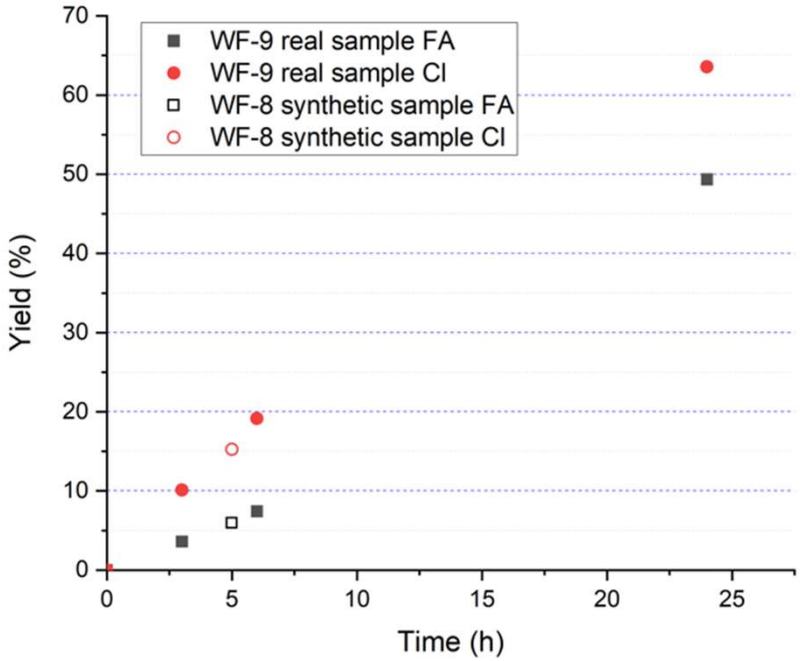
	Inputs			Outputs			Total Inputs	Total Outputs
	Anodic chamber	Acidic chamber	Cathodic chamber	Anodic chamber	Acidic chamber	Cathodic chamber		
Weight	205,329	202,8160	225	144	291,7	193,4	633,1	629,24

- Formate and chloride ions migrates to the acidic chamber, while sodium migrates at high rate from the anodic chamber to the acidic chamber.
- Some formic acid was found in the anolyte, but the total balance does not suggest missing formic acid in the anolyte due to oxidation.

ADES for metal recovery waste streams

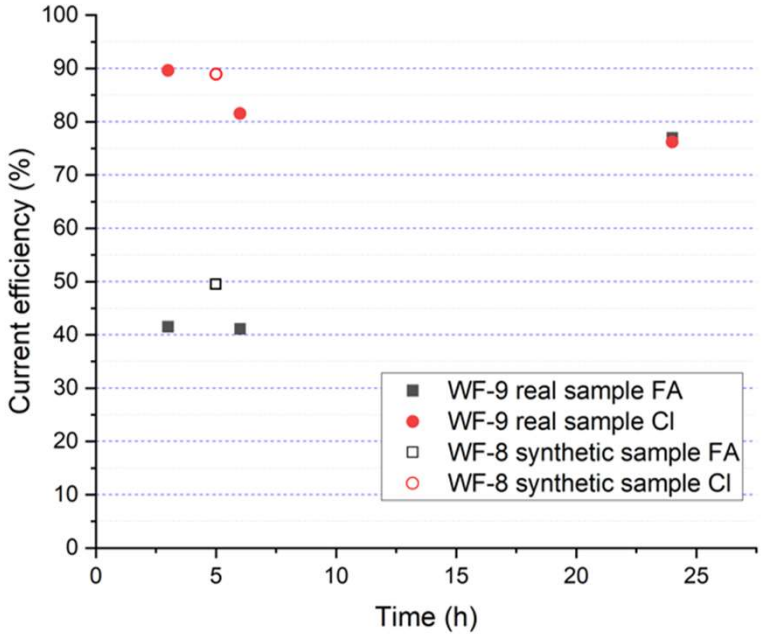
Electroleachate vs **Synthetic sample**

FA and chloride migration from catholyte to acidic chamber
Based in acidic chamber concentrations



- 50% Formic Acid yields in 24 yields, higher formic acid yields are expected when fouling is avoided
- Similar performance with synthetic and real samples

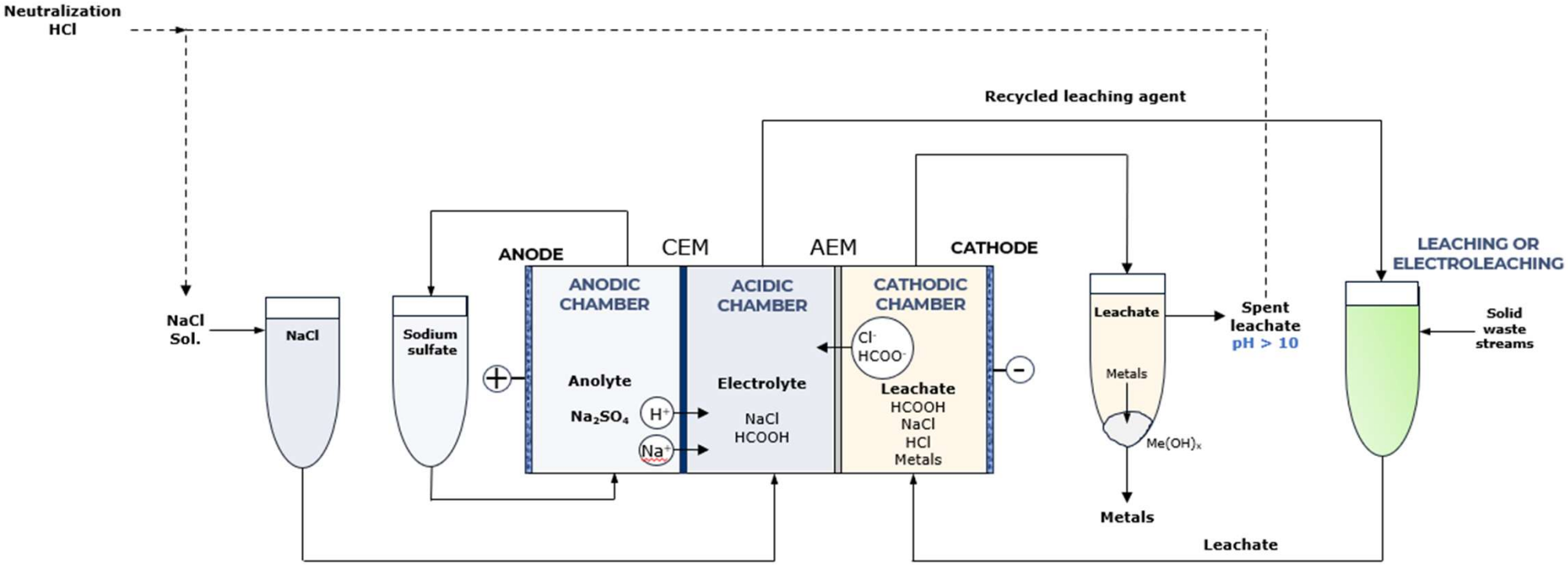
FA and chloride migration from catholyte to acidic chamber
Based in acidic chamber concentrations



- Chloride migration is favoured against formate ion.
- Undissociated formic acid can also migrate due to diffusion.

NEW CONCEPT

- Metals recovery
  - Coupling Leaching/Electroleaching and membrane electrolysis to recover metals and solvents



ADES for metal recovery: **Conclusions**

Key achievements:

- Development of a **bio-based deep eutectic solvent (DES) leaching route** based on formic acid, confirming its suitability as sustainable leaching media, replacing conventional mineral acids with a **biodegradable, non-flammable, and recyclable** medium.
- **Effective recovery of Cu, Zn, and Pb** from wastewater sludge and incineration ashes was demonstrated via both **conventional leaching and electroleaching**.
- Application of **electrodialysis-based recovery module** that regenerates formic acid from spent leachates, closing the material loop between leaching and solvent regeneration.
- **Conventional leaching:**
  - The optimized DES/FA formulation (ChCl/FA + 0.5 M NaCl) achieves **>95% Cu and Zn extraction** under mild conditions (50 °C, 2 h, S/L 0.02), while simultaneously **reducing acid consumption** and the overall environmental footprint.
  - This low-temperature, low-reagent approach delivers **selective metal dissolution** from complex waste streams (wastewater sludges, incineration ashes) without the need for high-pressure or high-purity acid infrastructure.
- **Electroleaching:**
  - The electrified electroleaching process can replace chemically intensive leaching with in-situ generation of oxidant species, reducing external reagent consumption by 30–60% compared to conventional hydro- and solvometallurgical routes.
  - Crucially, part of the dissolved metals can be simultaneously electrodeposited on the cathode, reducing downstream separation steps and associated energy use by 20–40%.
  - Medium-scale trials (~500 ml) confirmed process scalability, with continuous monitoring enabling real-time optimization.
- **Electrodyalisis:**
  - This **zero-chemical-replenishment** strategy reduces the life-cycle cost of the leaching medium and eliminates secondary effluent streams, aligning the overall process with the **circular economy** principles targeted by WaterProof.
  - Combined with metal recovery, the electrodialysis module delivers a **fully integrated, closed-loop ADES process,** from waste to metals and recycled solvent.

Any questions?

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tecnalia

MEMBER OF BASQUE RESEARCH
& TECHNOLOGY ALLIANCE