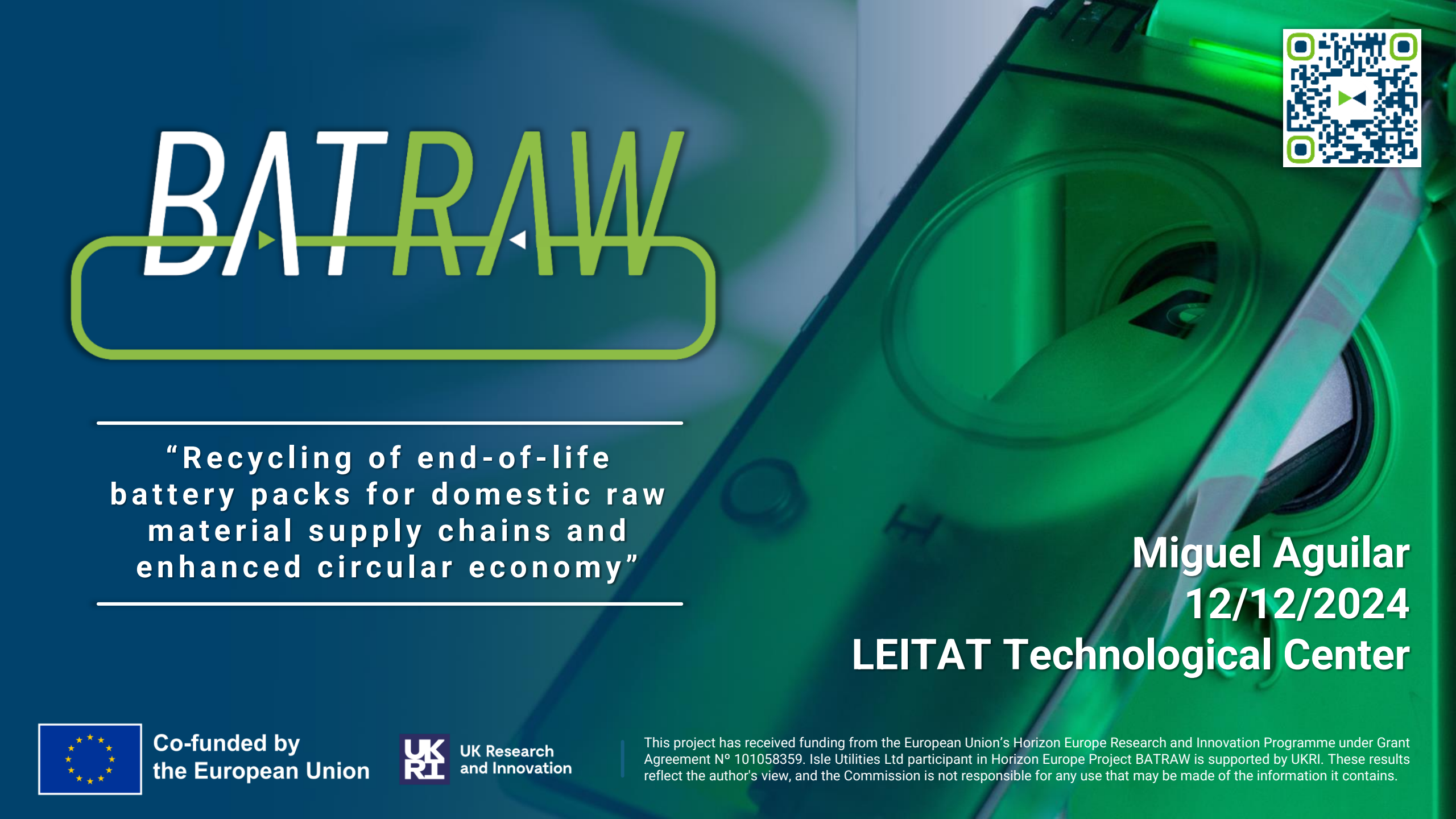


BATRAW

"Recycling of end-of-life battery packs for domestic raw material supply chains and enhanced circular economy"

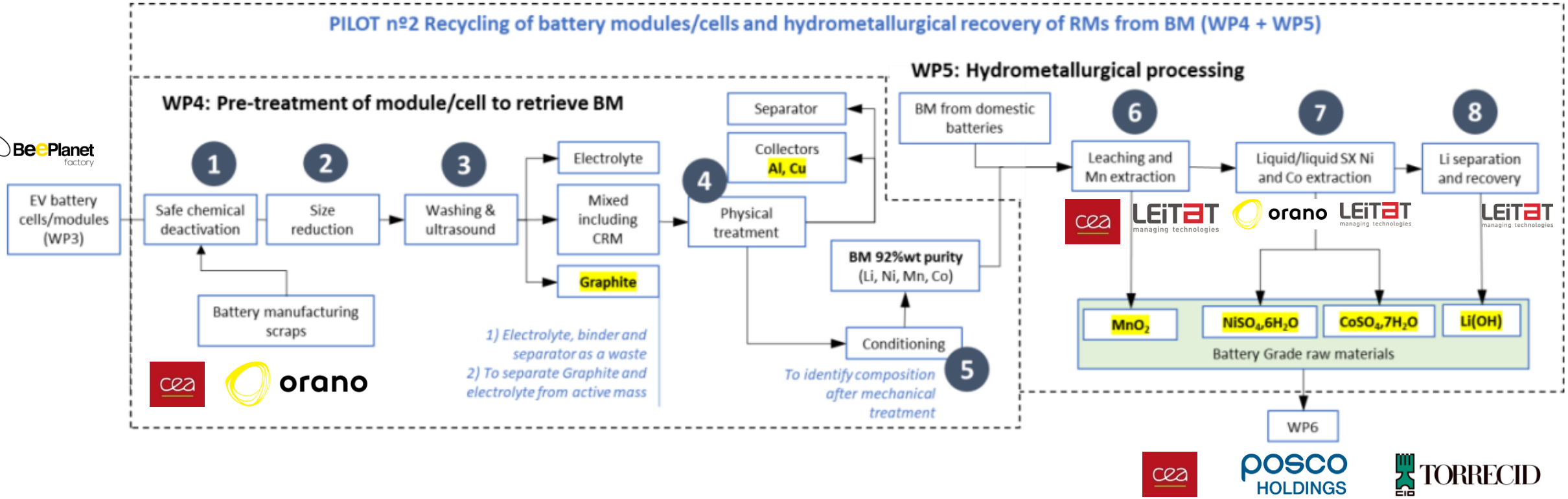
Miguel Aguilar
12/12/2024
LEITAT Technological Center

Co-funded by the European Union

UK Research and Innovation

This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

Pilot 2: Recycling and RM recovery (ORANO, France)



BATRAW

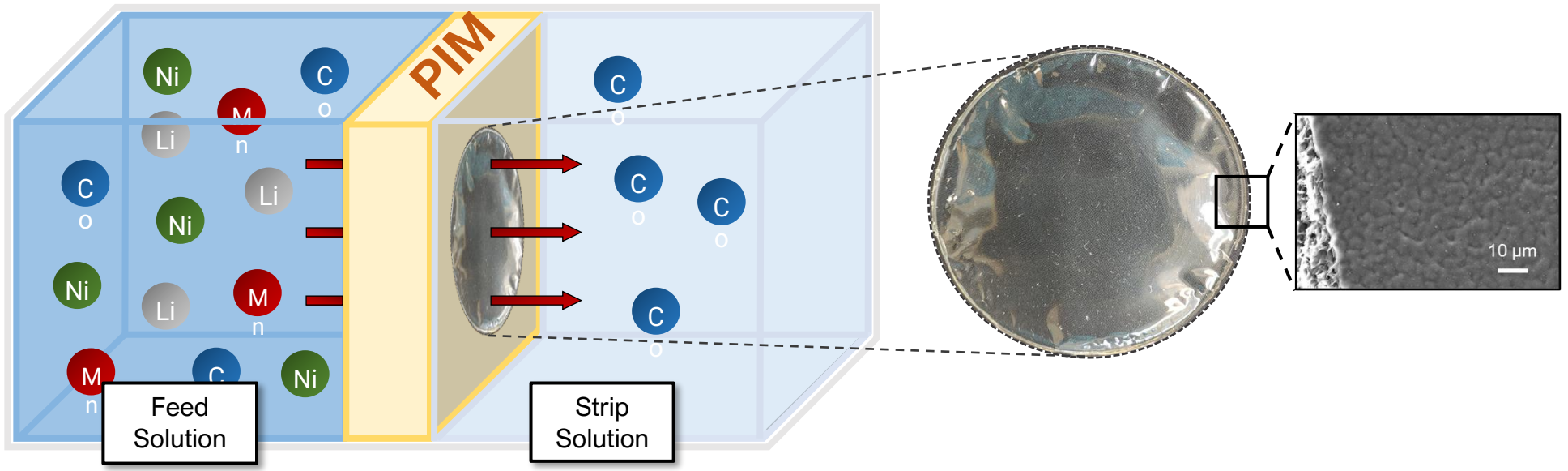
Co-funded by the European Union

UK Research and Innovation

This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

Polymer inclusion membrane

- Polymer inclusion membranes (PIMs) are **dense and hydrophobic**.
- The extractant (ionic liquid) is **embedded within the polymer structure**.
- The extractant forms a **complex with the target metal** present in the feed solution.
- Through **diffusion**, the metal is transferred across the membrane to a stripping solution (in an acidic or basic medium).
- This process can theoretically continue until **all the target metal is extracted**, as long as the initial conditions are maintained.

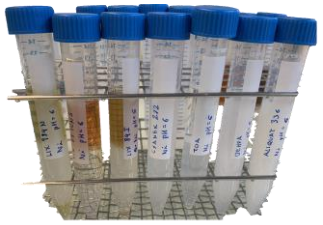


Co-funded by the European Union
UK Research and Innovation
This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

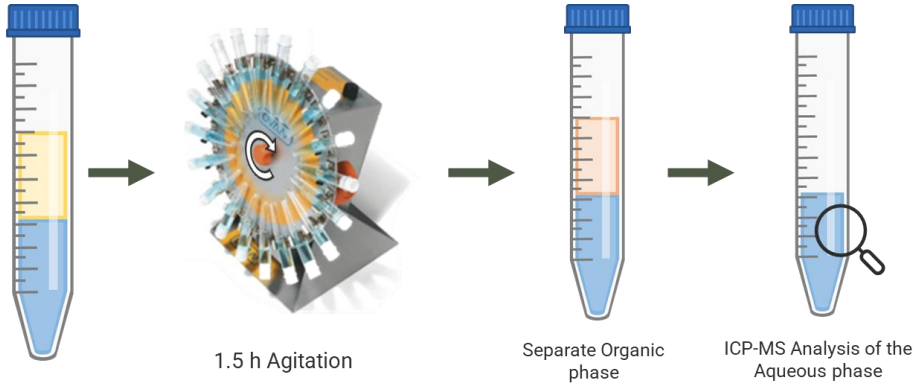
Liquid-liquid extraction

Extractant Evaluation → PIM development and characterization → PIM evaluation

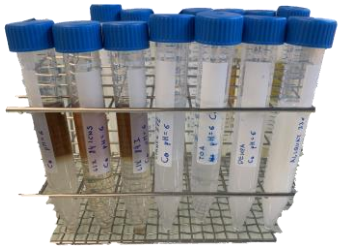
METAL EXTRACTION



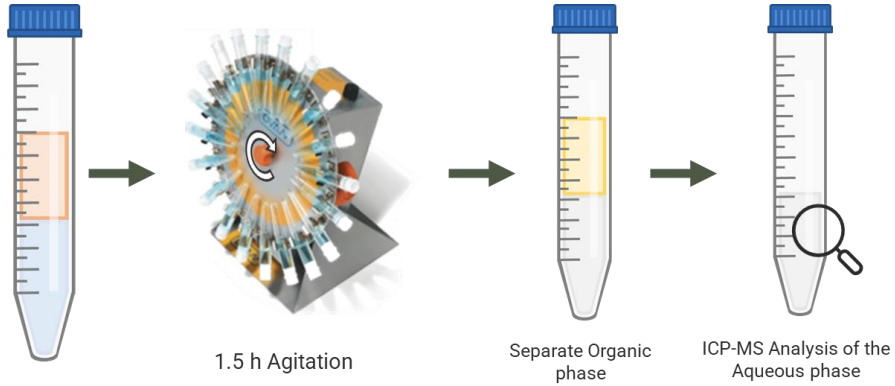
5 mL **Extractant** (Organic phase)
+
5 mL **Metal** solution 100 ppm (Aqueous phase)



METAL STRIPPING



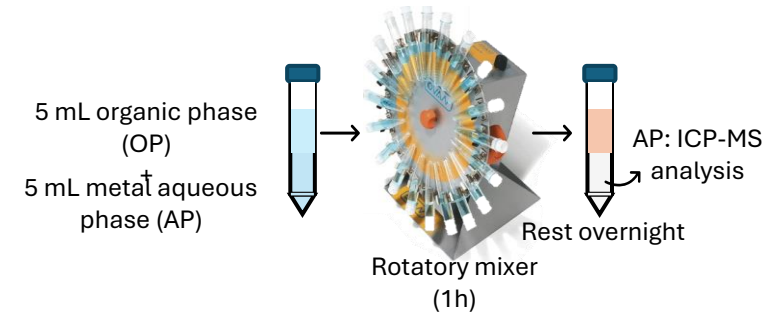
5 mL **Extractant** (Organic phase + Metal)
+
5 mL **Stripping solution** (Acid/Basic phase)



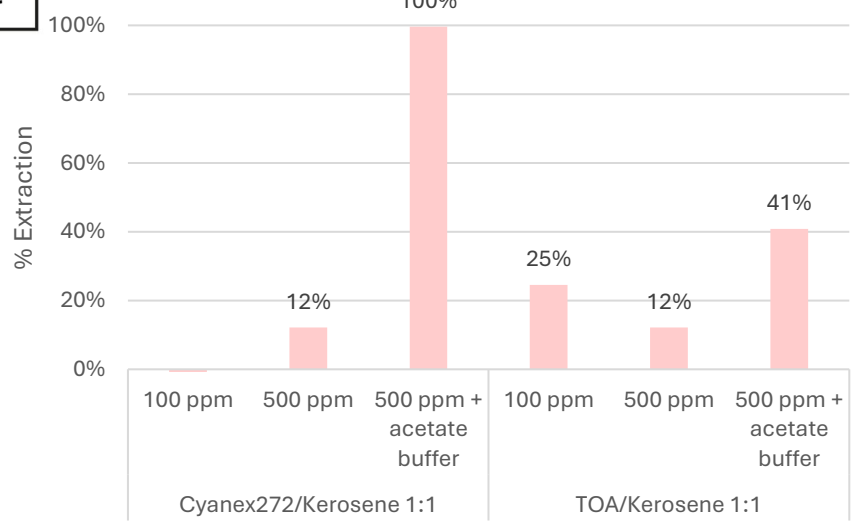
Co-funded by the European Union
UK Research and Innovation
This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

Results

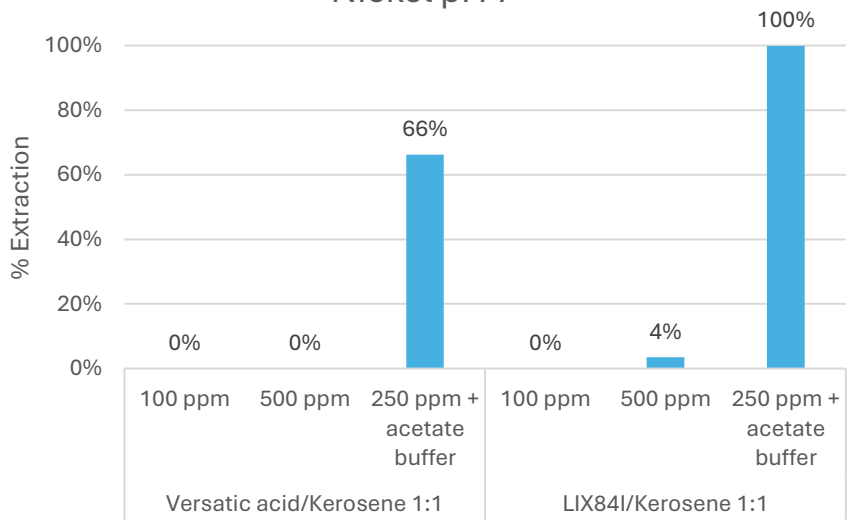
Liquid-liquid extraction: extractant selection



27 Co Cobalt 58.933



28 Ni Nickel 58.693



- 100 % extraction has been achieved for Co (Cyanex 272/kerosene 1:1) and Ni (LIX84I/kerosene 1:1)
- All the studied extractants evaluated by L-L extraction had enhanced extraction capacity in the presence of acetic acid/acetate buffer.

Co-funded by the European Union

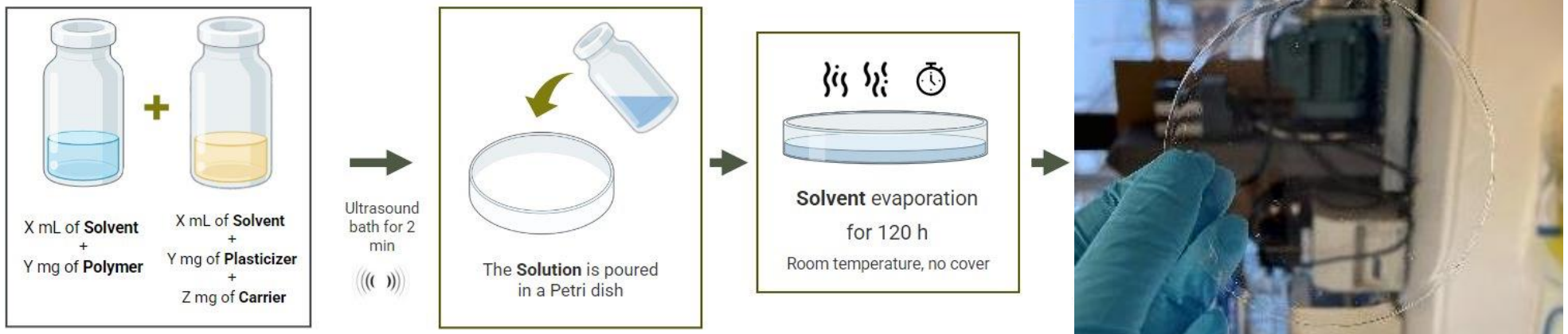
UK Research and Innovation

This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

Polymer inclusion membrane developing

Membrane fabrication

Extractant Evaluation → PIM development and characterization → PIM evaluation



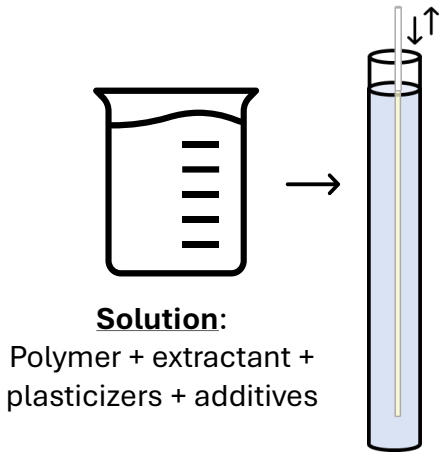
- More tan 150 PIMs with several compositions were developed

Co-funded by the European Union
UK Research and Innovation
This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

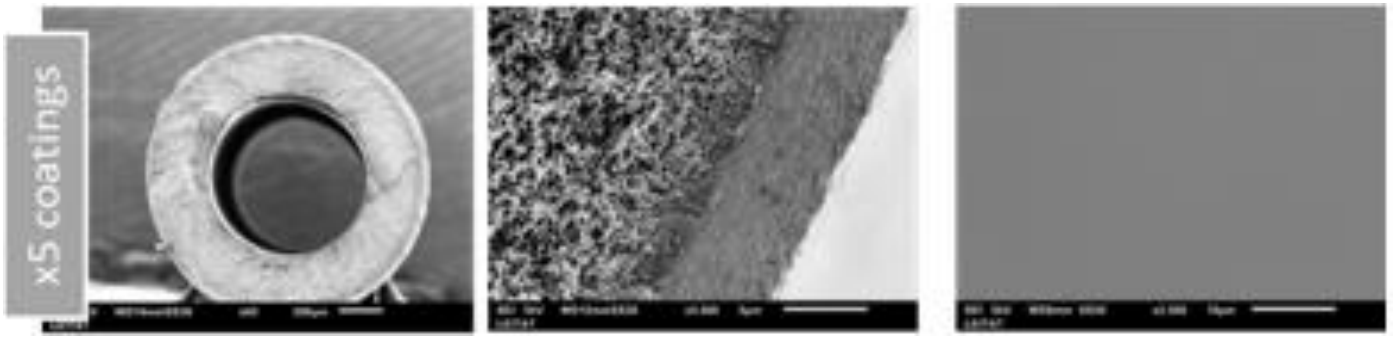
Polymer inclusion membrane developing

Membrane fabrication

Extractant Evaluation → PIM development and characterization → PIM evaluation



Solution:
Polymer + extractant +
plasticizers + additives



Module fabrication

Area = 27.8 cm^2

Co-funded by the European Union

UK Research and Innovation

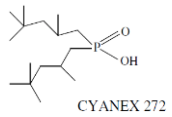
This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

Polymer inclusion membrane developing

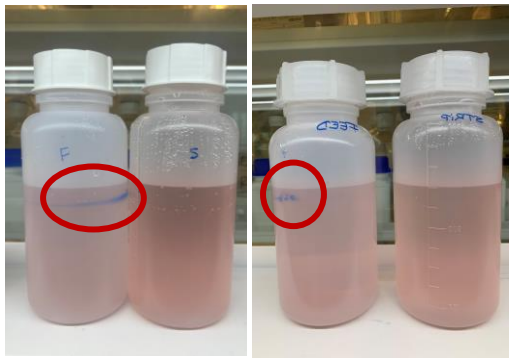
27 Co Cobalt 58.933

Extractant Evaluation → PIM development and characterization → PIM evaluation

Membrane	Composition	Thickness (µm)	% Co(II) Extraction / 30h
PIM-4.5a-10mL	25.6% CTA + 29.3% Cyanex 272 + 39.9% 2NPOE + 5.2% TBP	52 ± 7	55
PIM-4.5-a.1-10mL	↑Cyanex 272	41 ± 8	74
PIM-4.5-a.1-20mL	25.5% CTA + 35% Cyanex 272 + 34.2% 2NPOE + 5.3%TBP	71 ± 12	45
PIM-4.5-a.2-10mL	↑TBP	37 ± 7	61
PIM-4.5-a.2-20mL	25.5% CTA + 29.3% Cyanex 272 + 35.2% 2NPOE + 10% TBP	85 ± 12	64



Experimental conditions
Feed: 0.0085 M Co pH 6 (acetic acid/acetate buffer)
Strip: H_2SO_4 1.5 M
Flow: 152 mL/min



Feed and strip solutions after experiment with blue precipitation.

- Increasing Cyanex 272 content in the PIM, increases the Co extraction from 55 % to 74 %, but also increase the precipitation of $[Co\text{-}Cyanex272]_n$.

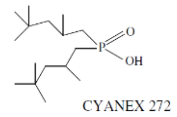
BATRAW
Co-funded by the European Union
UK Research and Innovation
This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

Polymer inclusion membrane developing

27 Co Cobalt 58.933

Extractant Evaluation → PIM development and characterization → PIM evaluation

Membrane	Composition	Thickness (µm)	% Extraction Co(II) / 30h	Initial flux J_0 (mol/m²·h)
PVC-4.5-A-10mL-2	42.5% PVC + 48.7% Cyanex 272 + 8.8% TBP	16 ± 3	27	0.036
PVC-4.5-E-10mL-2	26% PVC + 29% Cyanex 272 + 5% TBP + **40% DOA**	25 ± 3	48	0.051
PVC-4.5-G-10mL-1	26% PVC + 29% Cyanex 272 + 5% TBP + **40% BTS**	38 ± 7	82	0.102
PVC-4.5-A-30mL-2	42.5% PVC + 48.7% Cyanex 272 + 8.8% TBP	54 ± 16	22	0.020
PVC-4.5-B-30mL-1	26% PVC + 29% Cyanex 272 + 5% TBP + **40% 2NPOE**	63 ± 15	84	0.036
PVC-4.5-G-30mL-1	26% PVC + 29% Cyanex 272 + 5% TBP + **40% BTS**	80 ± 7	74	0.051



CYANEX 272

Experimental conditions

Feed: 0.0085 M Co pH 6 (acetic acid/acetate buffer)

Strip: H_2SO_4 1.5 M

Flow: 152 mL/min

Feed and strip solutions after experiment with less blue precipitation.

- Changing the CTA base polymer for PVC, we are able to maintain the extractant inside the polymer structure avoiding the formation of blue precipitate and also increasing Co recovery from **74% to 82%.**

BATRAW

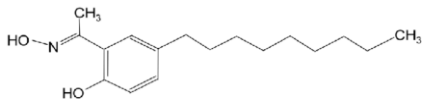
Co-funded by the European Union

UK Research and Innovation

This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

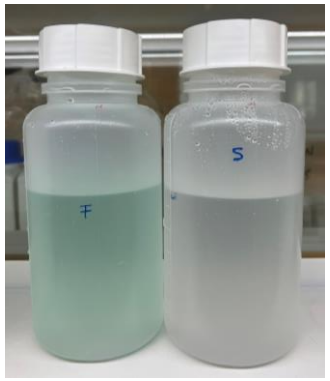
Extractant Evaluation → PIM development and characterization → PIM evaluation

28
Ni
Nickel
58.693



Membrane	Composition	Thickness (µm)	% Extraction Co(II) / 30h	Initial flux J_0 (mol/m²·h)
PIM-10.1-A-10mL	30 % CTA + 40 % LIX-84I + 30 % TBP	40 ± 4	60	0.026
PIM-10.1-B-10mL	30 % CTA + 40 % LIX-84I + 30 % 2NPOE	60 ± 14	0.5	0.001
PIM-10.1-C-10mL	30 % CTA + 40 % LIX-84I + 30 % TBEP	33 ± 7	0.2	0.005
PIM-10.1-D-10mL	30 % CTA + 40 % LIX-84I + 30 % DOA	33 ± 4	0.1	0.005

Experimental conditions
Feed: 0.0085 M Ni pH 6 (acetic acid/acetate buffer)
Strip: H_2SO_4 1.5 M
Flow: 152 mL/min



Feed and strip solutions after experiment, there was no color change

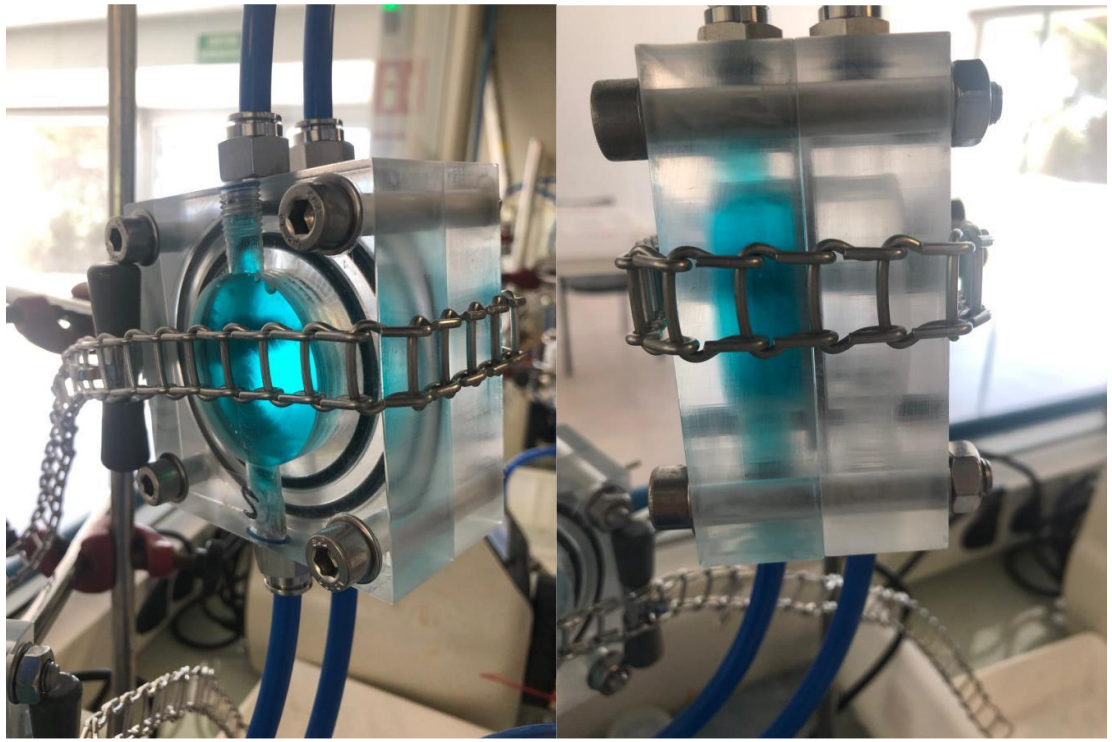
- Versatic acid PIM did not exhibit nickel, extraction ability at pH 7 without the addition of the acetic acid/acetate buffer.
- Different test with LIX-84I + Several plasticizers (2NPOE,TBEP, DOA and TBP)
- The membrane PIM-10-A with LIX84-I and TBP presents good recovery rates for Ni

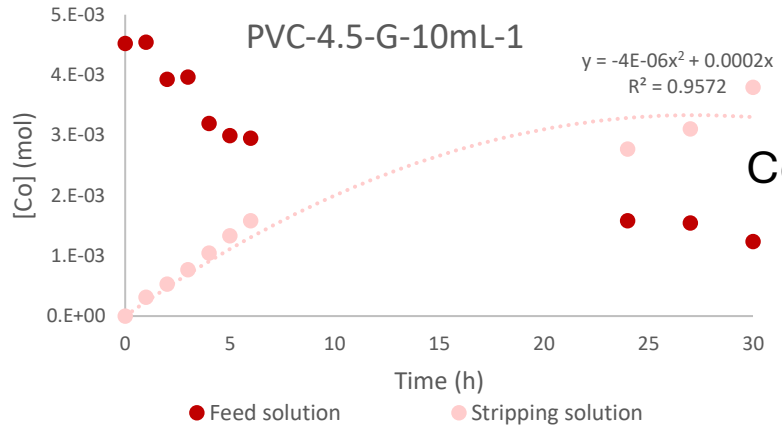
BATRAW
Co-funded by the European Union
UK Research and Innovation
This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

Polymer inclusion membrane developing

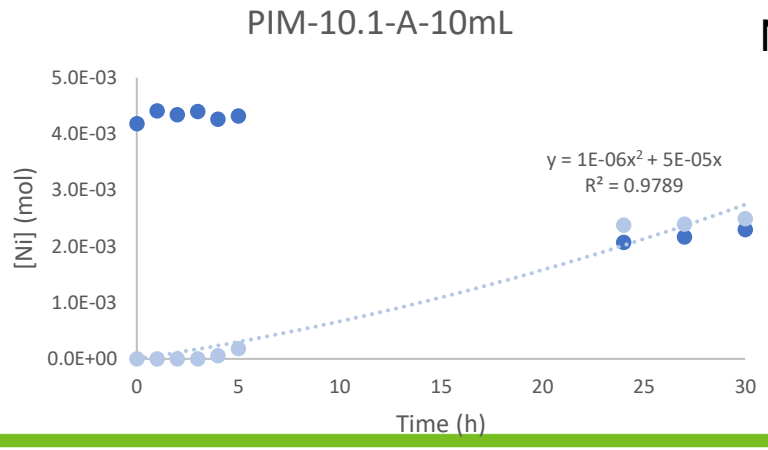
LEITAT managing technologies

Extractant Evaluation → PIM development and characterization → PIM evaluation





Co Extraction: **82%**



Ni Extraction: **60%**

BATRAW

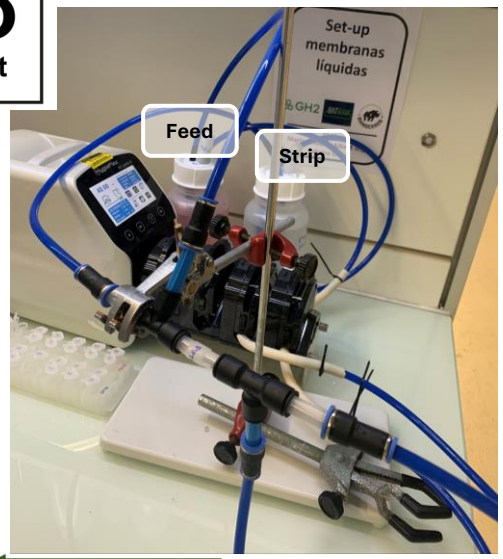
Co-funded by the European Union

UK Research and Innovation

This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

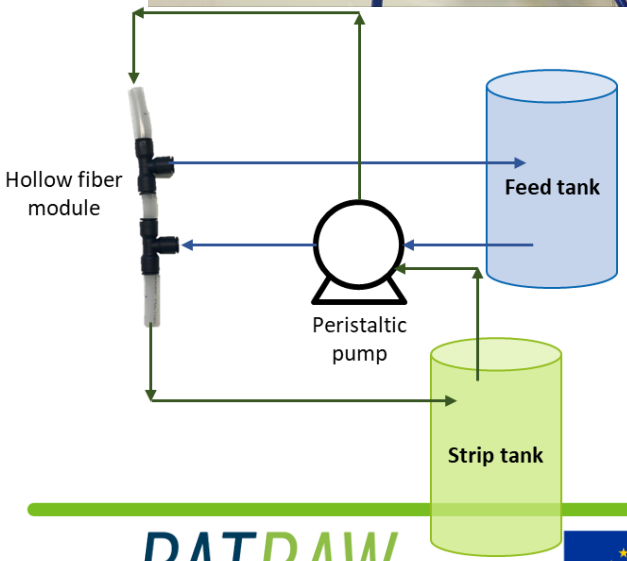
Liquid membrane evaluation: Hollow fiber PIMs

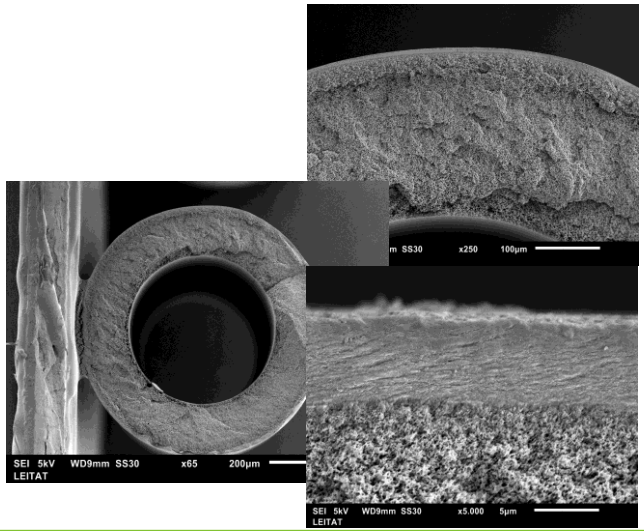
27 Co Cobalt 58.933

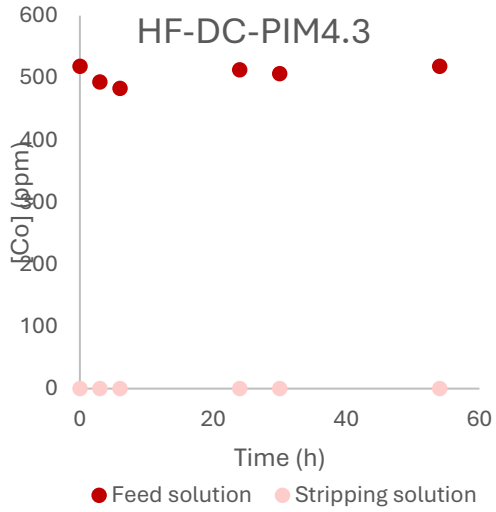


Experimental conditions
Feed: 0.0085 M Co pH6 (acetic/acetate buffer)
Strip: H_2SO_4 1.5 M
Flow: 152 mL/min

Membrane	Extractant	Plasticizer	Supporting membrane	Coating thickness (µm)	Active area (cm^2)	Co(II) %Extraction after 30h
HF-DC-PIM-4.3	Cyanex 272	2NPOE + TBP	PVDF	6 (3 coatings)	27.8	0
HF-DC-PIM-4.4	Cyanex 272	2NPOE	PVDF	8 (7 coatings)	23.7	0
HF-DC-PIM-4.5a	Cyanex 272	2NPOE + TBP	PVDF	4 (10 coatings)	22.9	0
HF-DC-PIM4.5e	Cyanex 272	TBEP + TBP	PVDF	8 (10 coatings)	24.5	0







- All manufactured modules showed no extraction ability.
- PIM-4.5a solution presented good extraction abilities, but the contact between stripping phase and the PIM coating needs to be improved.

BATRAW
Co-funded by the European Union
UK Research and Innovation
This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

Selectivity results using ORANO PLS

Liquor	ORANO PLS			ORANO_Mn_Raffinate			ORANO_Co_Raffinate		
pH	6.58	6.60	6.56	2.78	2.77	2.79	6.67	6.70	6.70
	6,6			2,8			6,7		

Liquor Code	Li (g/L)	Na (g/L)	K (g/L)	Co (g/L)	Mn (g/L)	Ni (g/L)	Al (g/L)	Cu (g/L)	Fe (g/L)
ORANO_PLS_1	5.3	30.6	0.3	8.6	10.4	19.2	<0.01	<0.001	<0.001
ORANO_PLS_2	4.6	27.3	0.2	7.5	9.4	18.9	<0.01	<0.001	<0.001
ORANO_PLS_3	5.0	29.7	0.2	8.4	10.0	18.8	<0.01	<0.001	<0.001
Mn_Raffinate_1	4.2	37.2	0.1	6.8	<0.001	19.4	<0.01	<0.001	<0.001
Mn_Raffinate_2	5.5	39.8	0.2	7.3	<0.001	18.8	<0.01	<0.001	<0.001
Mn_Raffinate_3	4.6	41.3	0.2	7.3	<0.001	19.1	<0.01	<0.001	<0.001
Co_Raffinate_1	4.7	50.2	0.2	<0.001	<0.001	18.5	<0.01	<0.001	<0.001
Co_Raffinate_2	5.4	56.3	0.3	<0.001	<0.001	21.6	<0.01	<0.001	<0.001
Co_Raffinate_3	4.7	48.9	0.3	<0.001	<0.001	18.8	<0.01	<0.001	<0.001

- Cobalt in Mn_Raffinate
- Nickel in Co_Raffinate

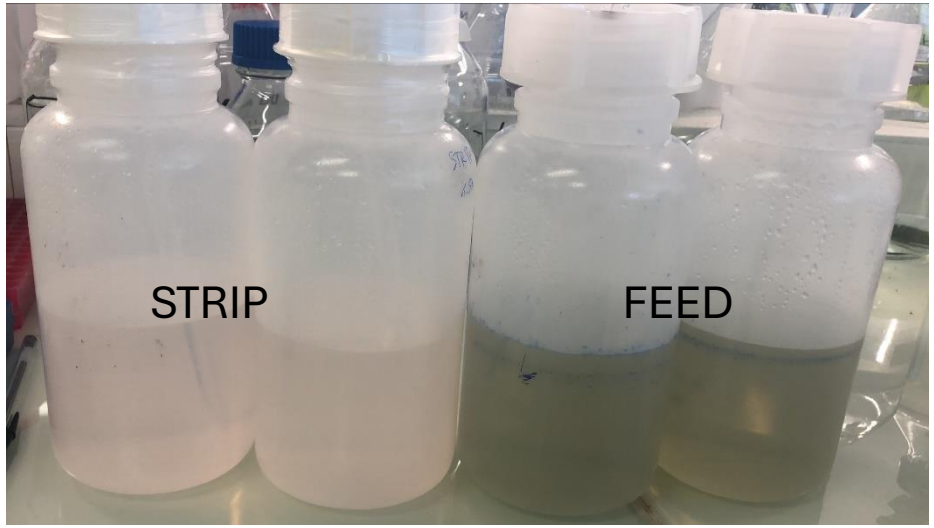
- **Membrane selection:**
- *Mn_Raffinate:* PVC-4.5-G-10ml-1 membrane, efficient for Co recovery and selective against Ni.
- *Co_Raffinate:* PIM-10.1-A-10ml membrane, specific for Ni recovery.

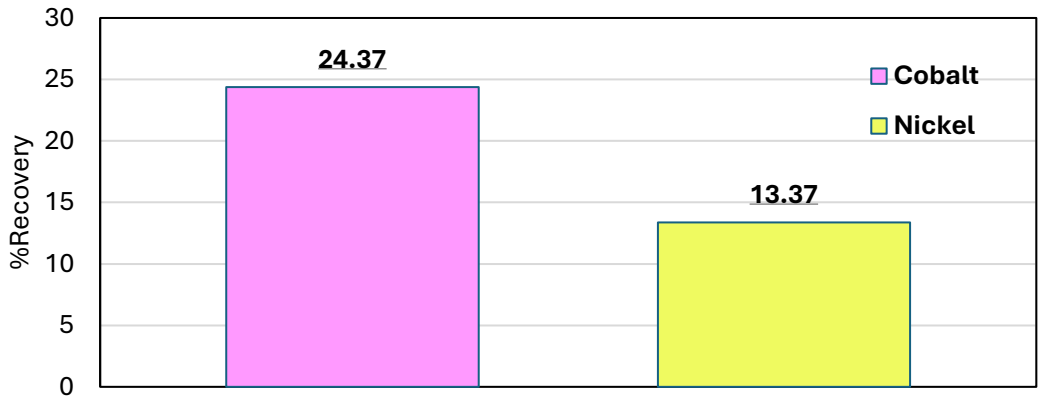
BATRAW
Co-funded by the European Union
UK Research and Innovation
This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

Selectivity results using ORANO LEACHEATES

- **Mn_Raffinate Evaluation:**
- 24% Co recovery with PVC-4.5-G-10ml-1 after 24h.
- The pinkish color in the stripping stream indicated the presence of Co^{2+} ions.
- Recovery dropped from 84% (synthetic) to 24% (liquor) due to Cyanex-272 acidifying the pH from 6 to 1.5, halting Co transport.

Synthetic solutions used an acetate buffer for pH stability, which is impractical for larger-scale systems with higher volumes.





- **Co_Raffinate Evaluation:**
- 13% Ni recovery with PIM-10.1-A-10ml after 24h.
- Recovery was lower (60% vs. 13%) between synthetic and liquor streams due to the absence of a buffer in the liquor, leading to less pH stability and reduced metal transport efficiency.

RESULTS

- 1,74 g of Cobalt y 2,8 g of Nickel transfered in 24h.
- **37 g/m²·h Co and 60 g/m²·h Ni**

BATRAW
Co-funded by the European Union
UK Research and Innovation
This project has received funding from the European Union's Horizon Europe Research and Innovation Programme under Grant Agreement Nº 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI. These results reflect the author's view, and the Commission is not responsible for any use that may be made of the information it contains.

BATRAW

Miguel Aguilar
Researcher at LEITAT Technological Center

Thank you for your attention!

Special acknowledgements to Maria Uriburu

Co-funded by the European Union

UK Research and Innovation