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EUROMEMBRANE 2021

High Pressure Reverse Osmosis shows promising perspectives for the Treatment of Electroplating Wastewater and Trivalent Chromium

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“This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 958454”.

Outline

- **Electroplating plastics & the IntelWATT project**
- **Analysis of real Cr III) electroplating rinse waters**
- **Recovery of electrolyte: Reverse osmosis trials**
- **Concentrate Reuse: Electroplating tests via Hull cell tests**

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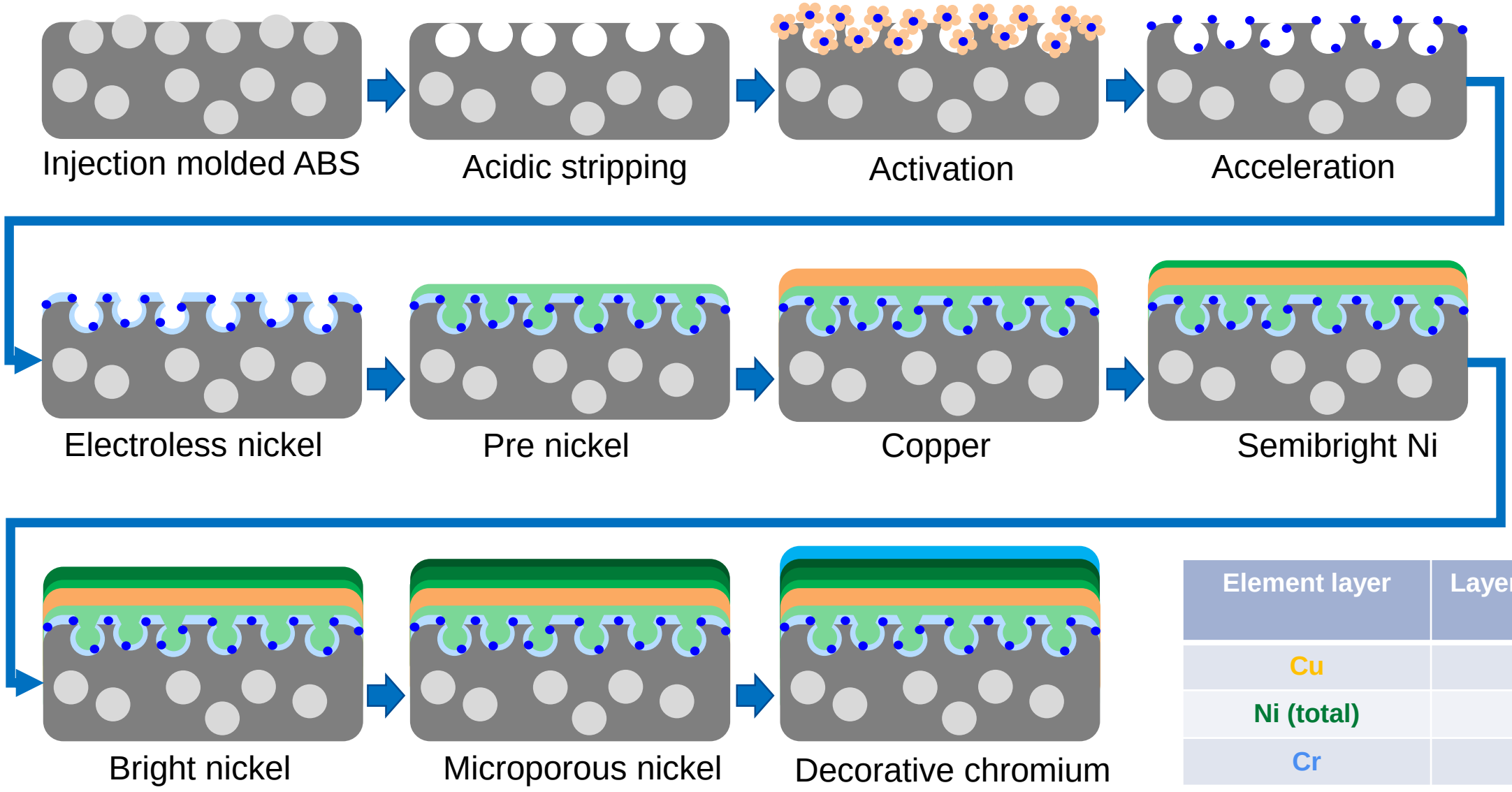
The electroplating of ABS plastics



Element layer	Layer thickness / µm
Cu	25
Ni (total)	15
Cr	0.3-0.8

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Electroplating line in Solingen, Germany

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The waste water treatment to date

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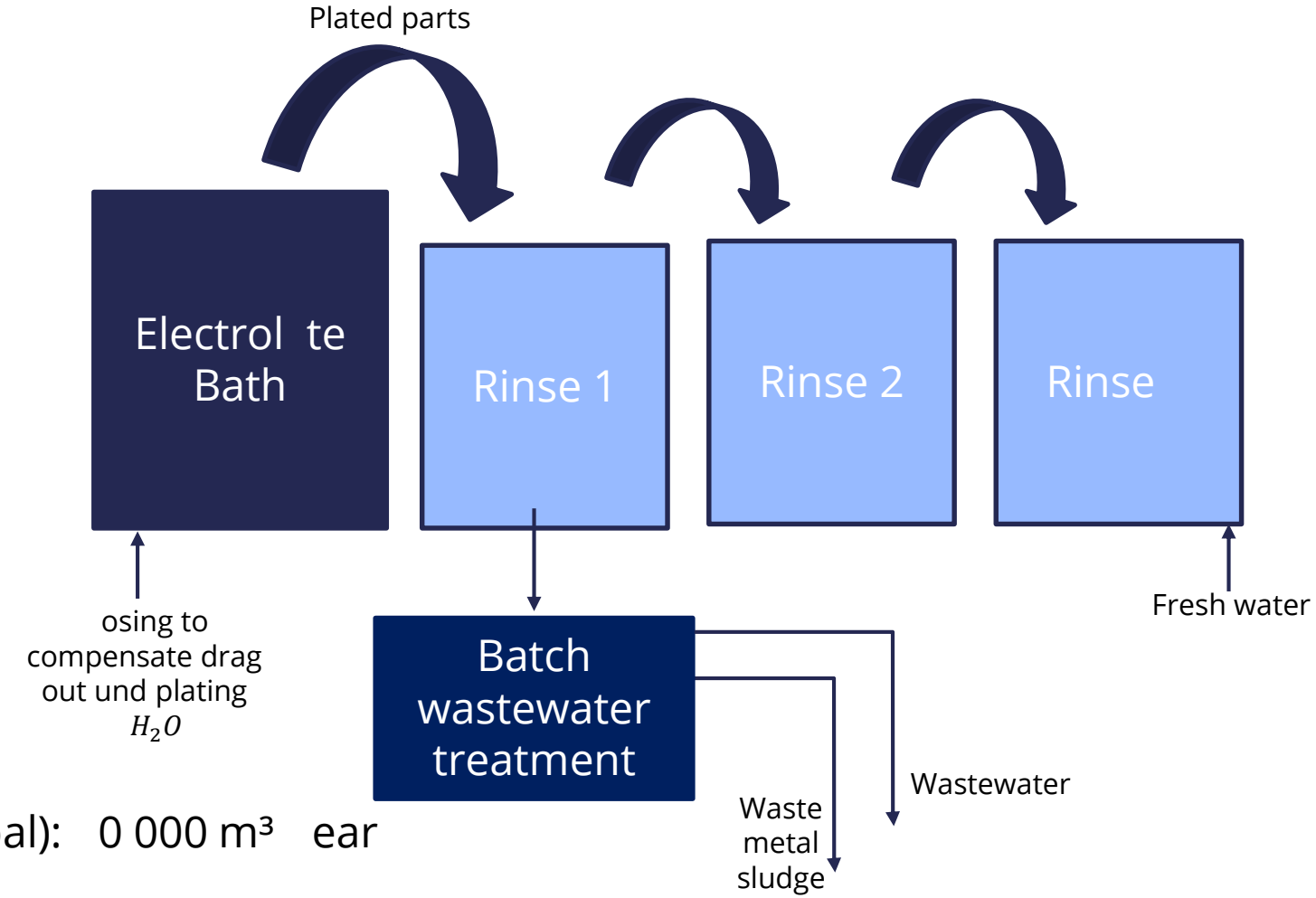

Needed rinse water b B GmbH (global): 0 000 m³ ear

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The intelWATT approach

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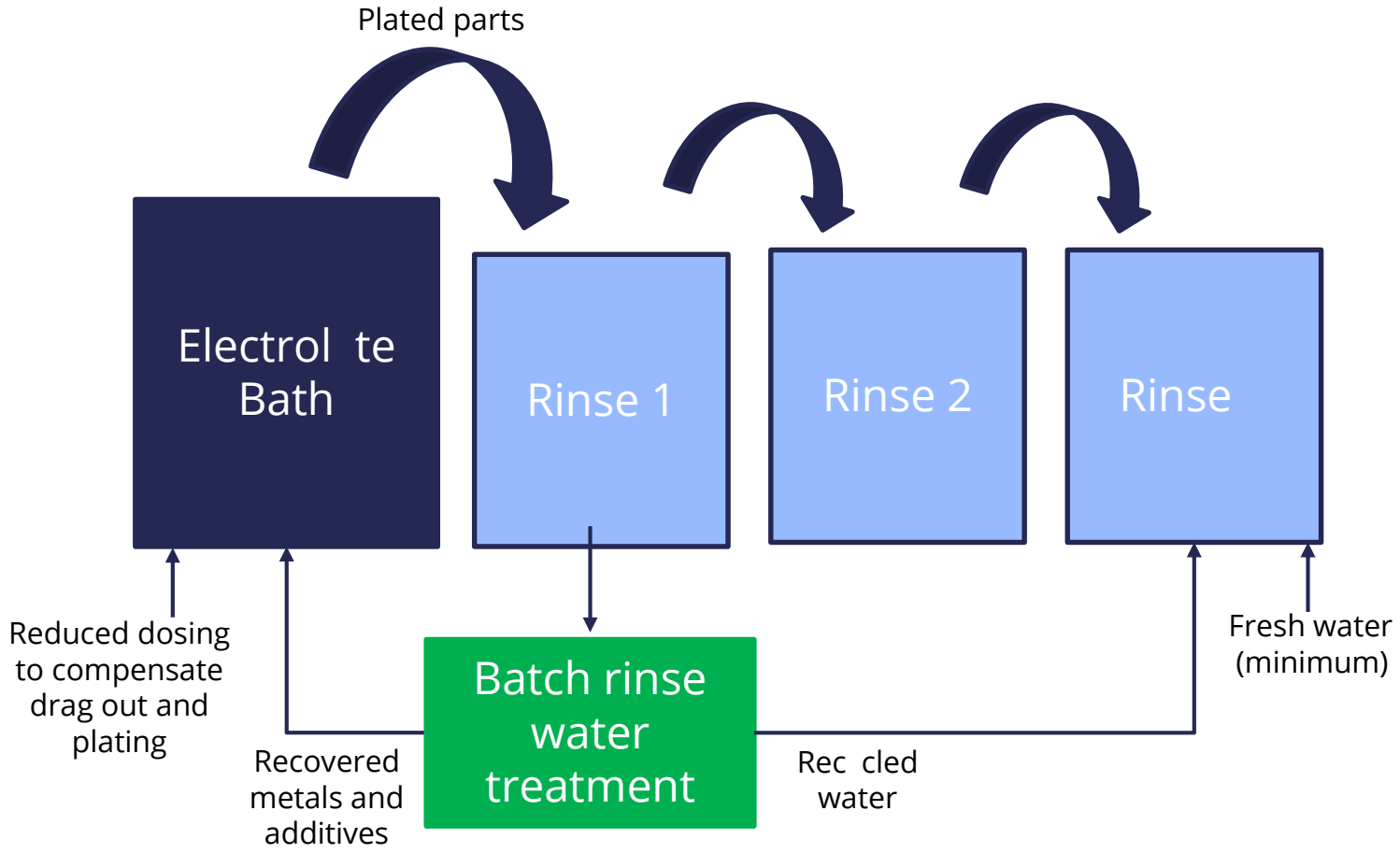

Project Goal: TRL8 membrane-based plant: 95% metal recovery, 65% water recovery

Requirements

Quality parameters for RO permeate recycling in rinsing baths

Quality Parameter	Unit	Lower limit	Upper limit	Measurement Method
pH value		5	8	pH meter
Surface Tension	mN m	0	2	Tensiometer
Chromium ( )	mg L	0	10	CP OES
Nickel	mg L	0		CP OES
Copper	mg L	0		CP OES
Boric cid	mg L	0	100	CP OES
Sulfate	mg L	0	150	CP OES Titration
Malic cid	mg L	0		HPLC
Chloride	mg L	0	50	Titration
Total Organic Carbon	mg L	0	15	ifference method

Quality parameters for RO concentrate* re-use in electroplating baths

Quality Parameter	Unit	Lower limit	Upper limit	Measurement Method
pH value		.5	.9	pH meter
Surface Tension	mN m	0	50	Tensiometer
Chromium ( )	g L	8	12	CP OES
Nickel	mg L	0	15	CP OES
Copper	mg L	0		CP OES
Boric cid	g L	80	110	CP OES
Sulfate	g L	80	150	CP OES Titration
Malic cid	g L	0.	2.5	HPLC

equal to electrol te parameters

Cr(III) electrolyte recovery by RO: Predicted challenges and issues to overcome

- Unknown components and concentrations in real electroplating rinse water
- Surfactants blocking the membrane
- High TOC content: Fouling
- Cr stallization of boric acid on the membrane (solubilit limit 55 g L 25°C)
- Feed pH ≤ 5: Low membrane rejection of protonated (neutral) boric acid

Quantification of main inorganic components in real electroplating rinse waters

Via ICP-OES and TOC difference method

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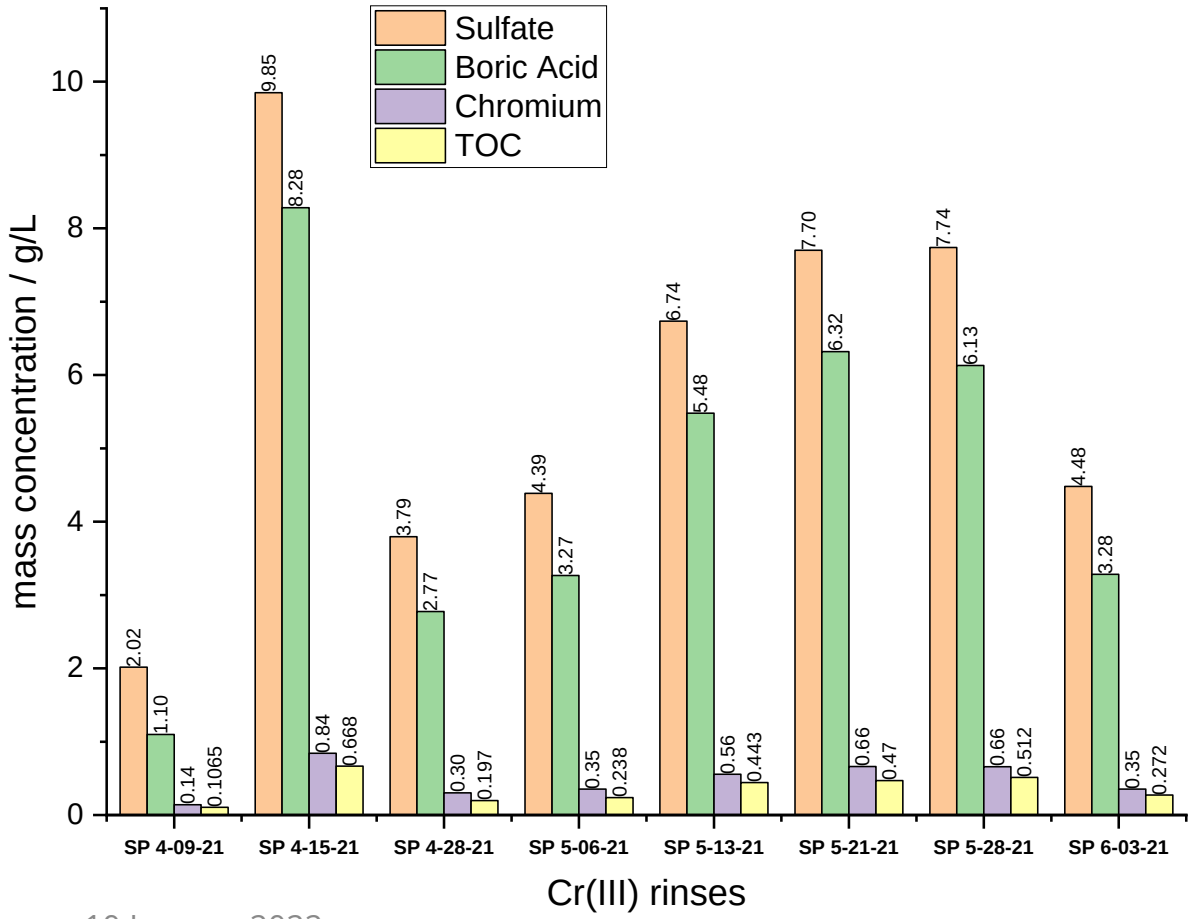
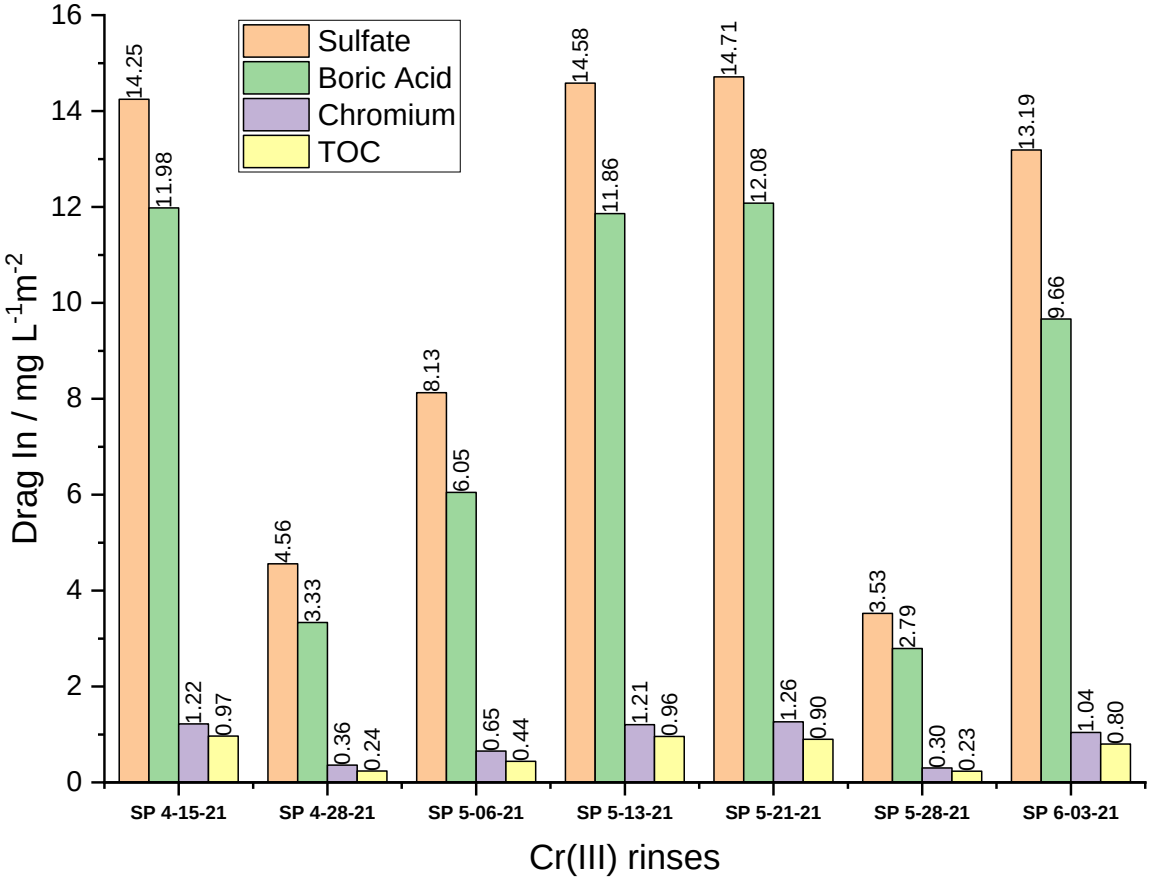
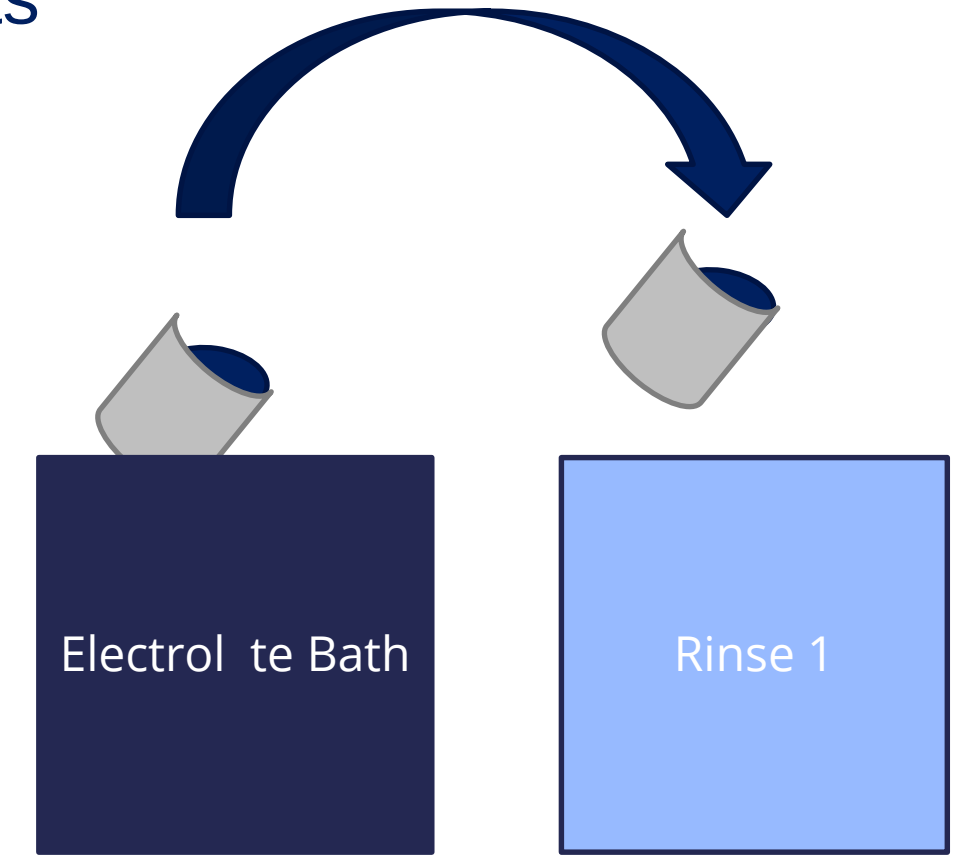
ICP-OES of real Cr(III) bath rinses + TOC



Sample	β Cr)/ g/L	β SO_4^{2-})/ g/L	β $B(OH)_3$)/ g/L	β Ni)/ mg/L	TOC /mg/L
SP 4-09-2021	0.14	2.02	1.10	2.58	106.5
SP 4-15-2021	0.84	9.85	8.28	8.84	668
SP 4-28-2021	0. 0	. 9	2.	2.5	197
SP 5-06-2021	0. 5	4. 9	.2	.21	238
SP 5-13-2021	0.5	. 4	5.48	4. 2	443
SP 5-21-2021	0.	. 0	. 2	5.45	470
SP 5-28-2021	0.	. 4	.1	5.48	512
SP 6-03-2021	0. 5	4.48	.28	.9	272
$\bar{x} \pm \Delta x$	0.48 ± 0.23	5.83 ± 2.58	4.58 ± 2.35	4.60 ± 1.94	363.3

Relative drag-in of inorganic components





Reverse osmosis for the recovery of electrolyte from rinse water

Characterization of the process

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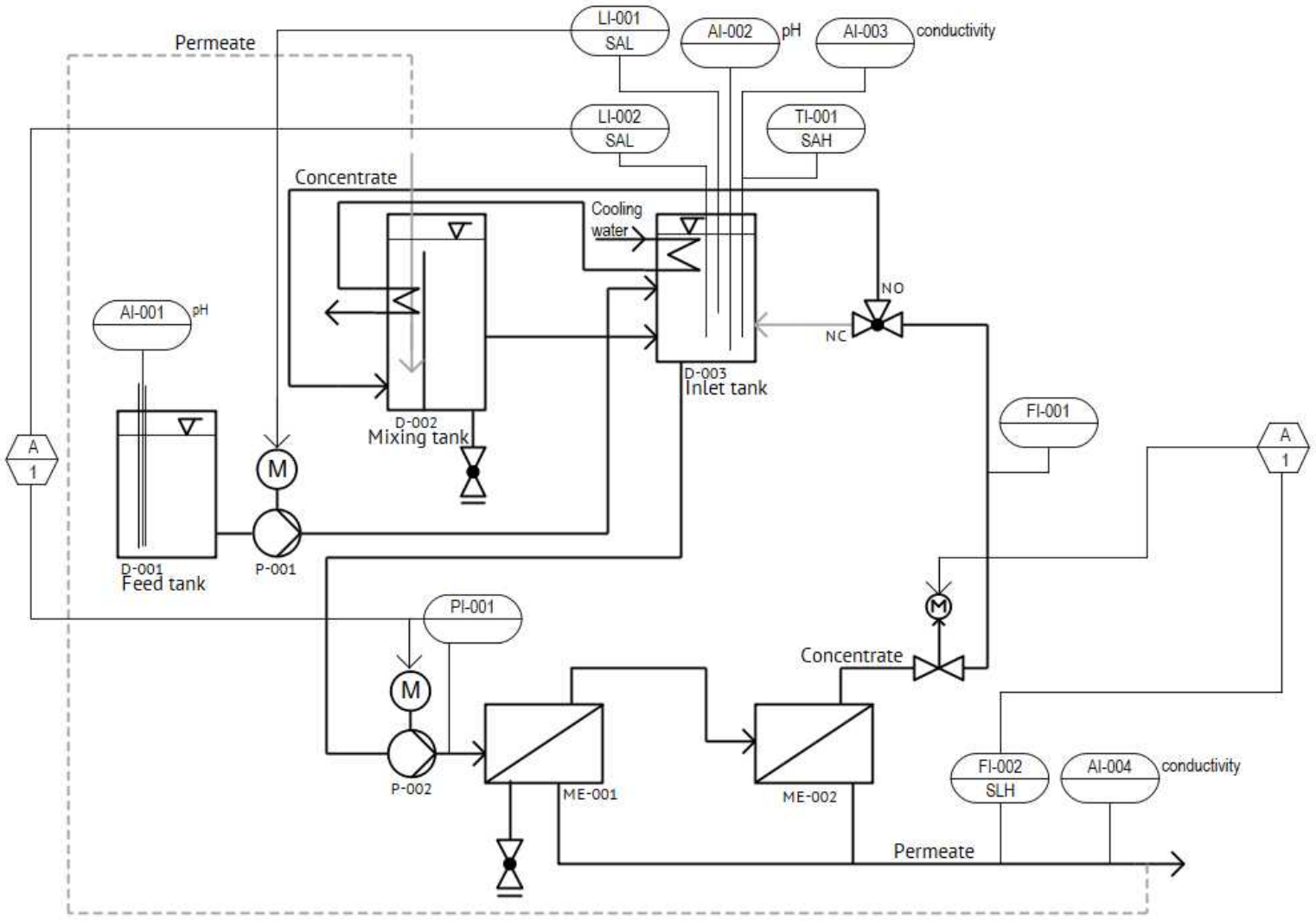
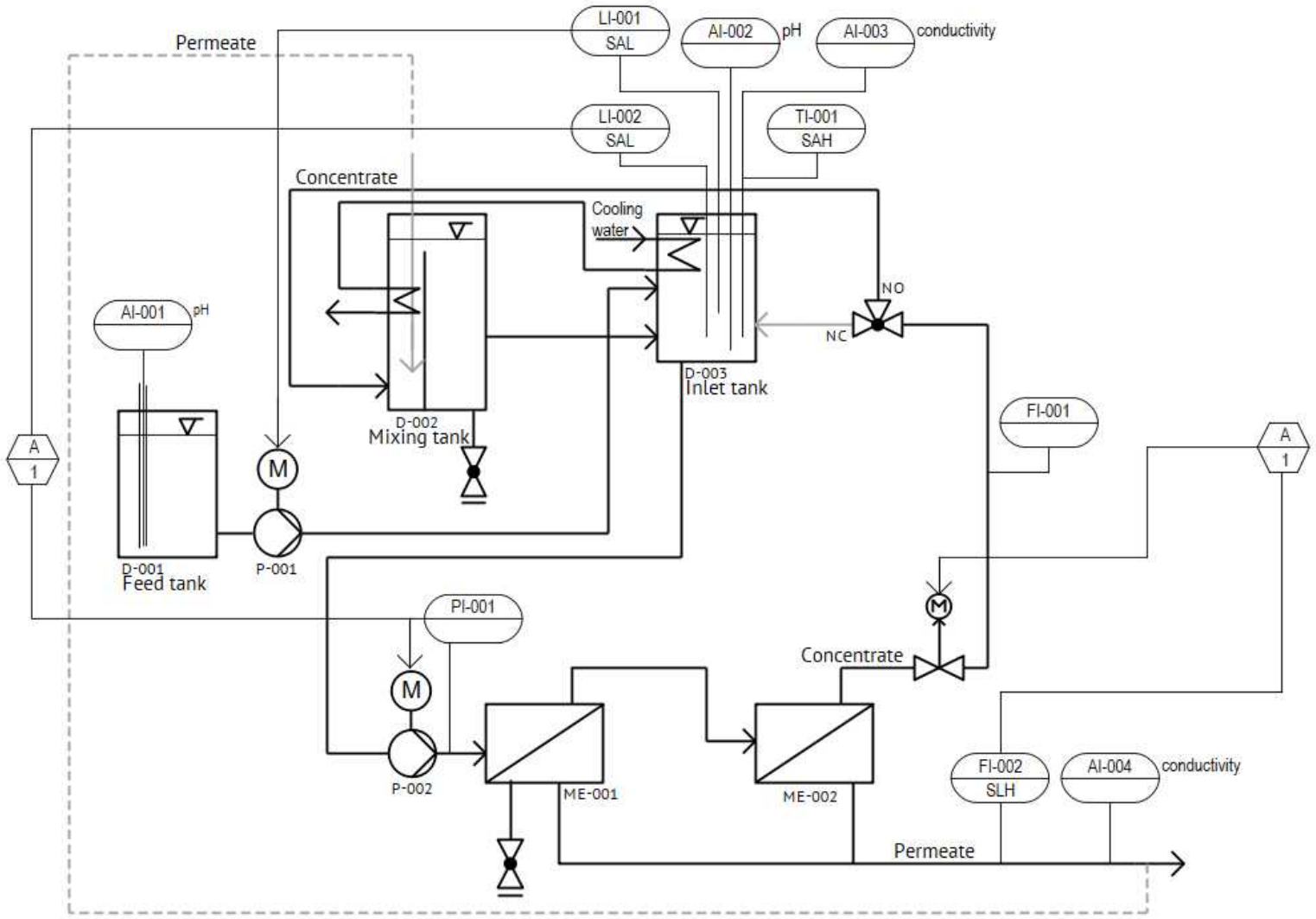
RO lab plant


Permeate
LI-001
SAL
AI-002
pH
AI-003
conductivity
LI-002
SAL
TI-001
SAH
Concentrate
Cooling
water
NO
NC
AI-001
pH
D-003
Inlet tank
D-002
Mixing tank
FI-001
A
1
A
1
M
D-001
Feed tank
P-001
PI-001
M
Concentrate
M
P-002
ME-001
ME-002
FI-002
SLH
AI-004
conductivity
Permeate

RO trials

Parameter	Value
T °C	25
p_{max} bar	80
$pH_{initial}$	4.
J_{max} L m²·h	0
$v_{crossflow}$ m s	0.25
$A_{M;total}$ cm²	1 0
$A_{plant;inner}$ cm²	≈ 4251

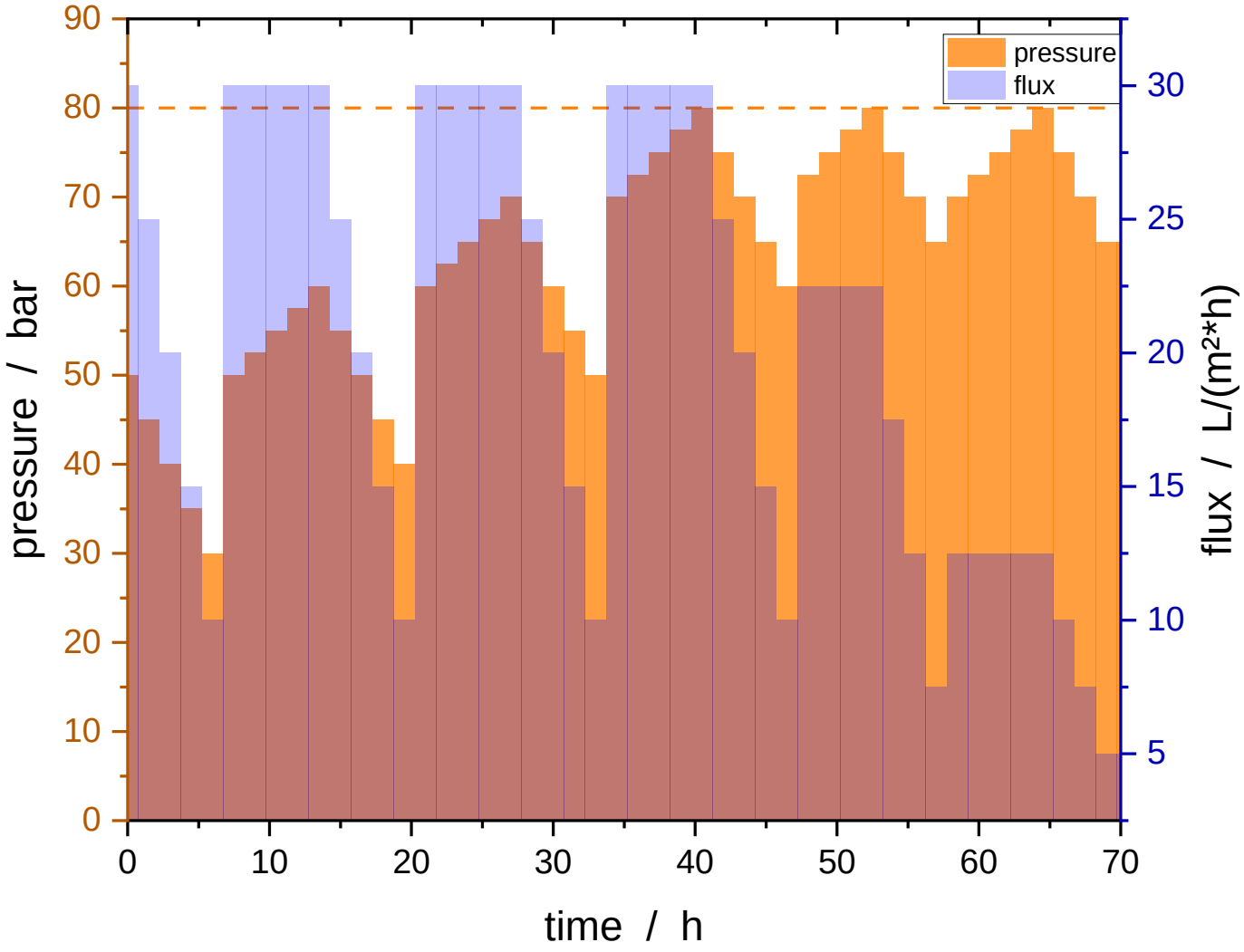
Feed: iluted Cr( ) Electrol te
(8 of initial concentration 0. 5 g L Cr)
Membrane: **SW30 DuPont-Filmtec**



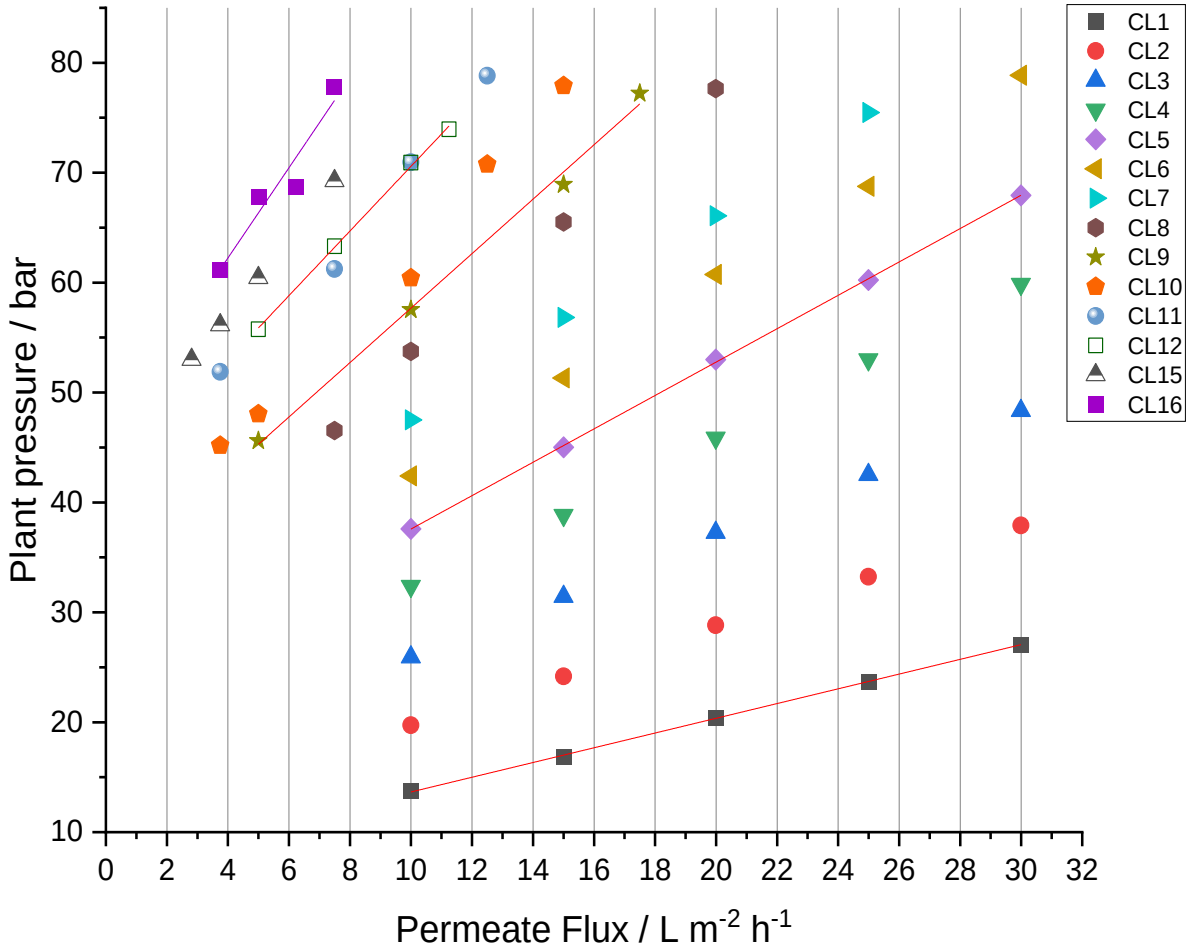
DOE: Increasing the concentration of artificial Cr(III) rinse water

Parameter	Value
T °C	25
p_{max} bar	80
$pH_{initial}$	4.
J_{max} L m²·h	0
$v_{crossflow}$ m s	0.25
$A_{M;total}$ cm²	1 0
$A_{plant;inner}$ cm²	≈ 4251

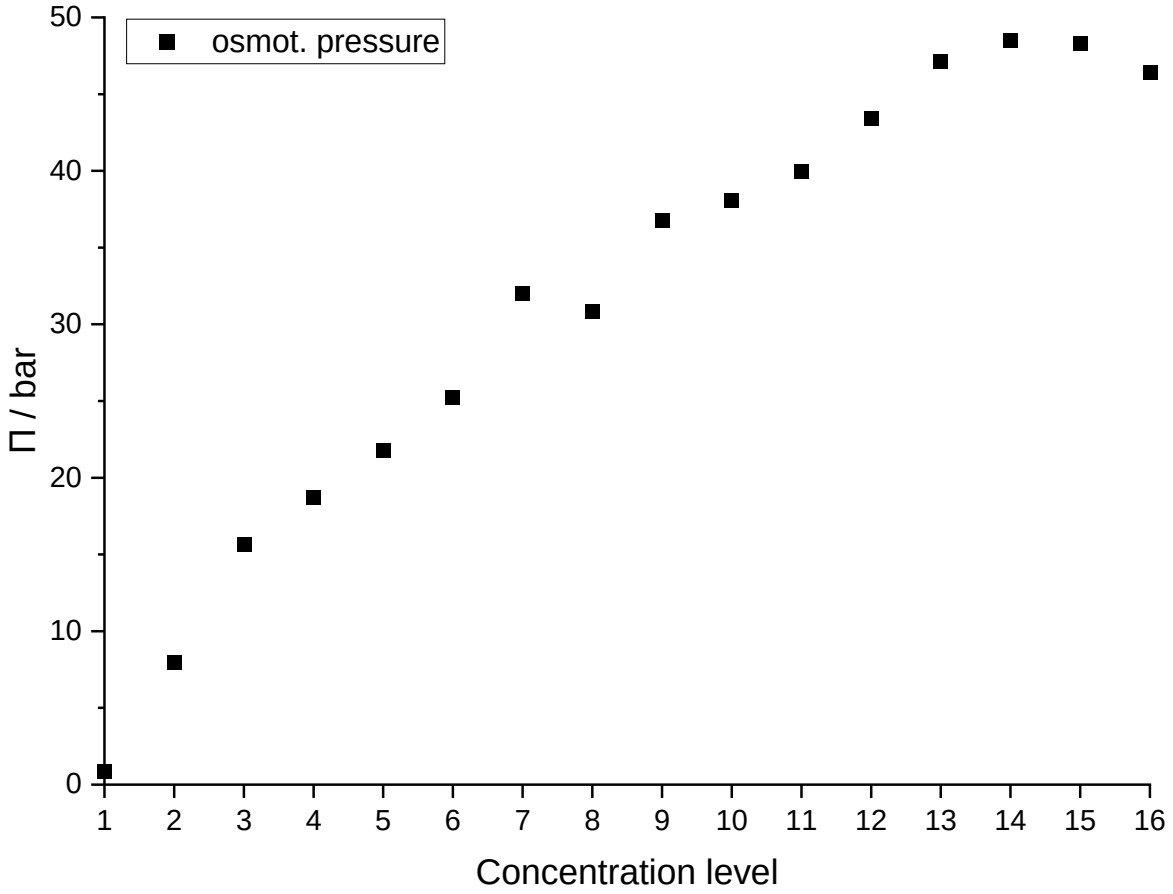
Feed: iluted Cr( ) Electrol te
(8 of initial concentration 0. 5 g L Cr)
Membrane: **SW30 DuPont-Filmtec**



Plant Pressure-Flux diagram

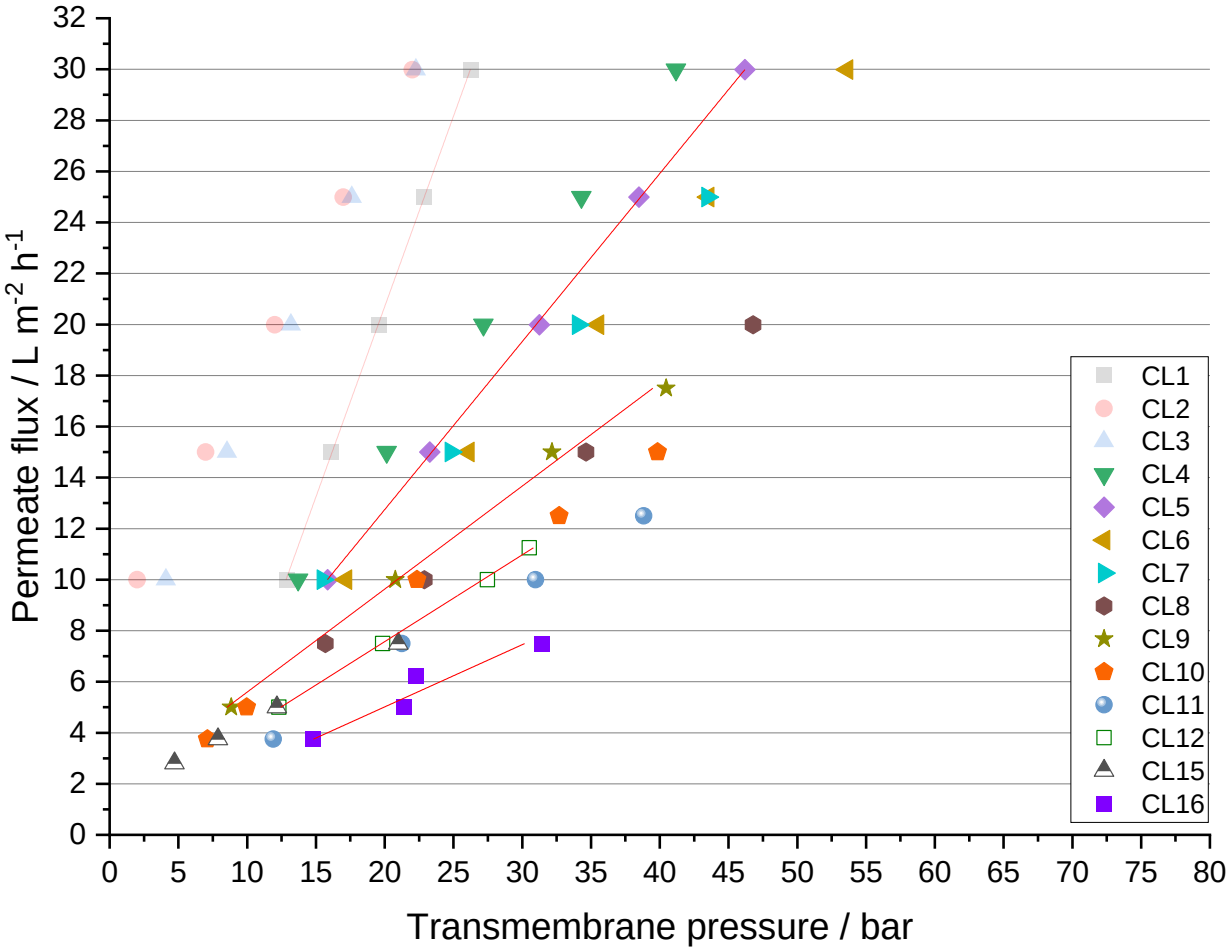


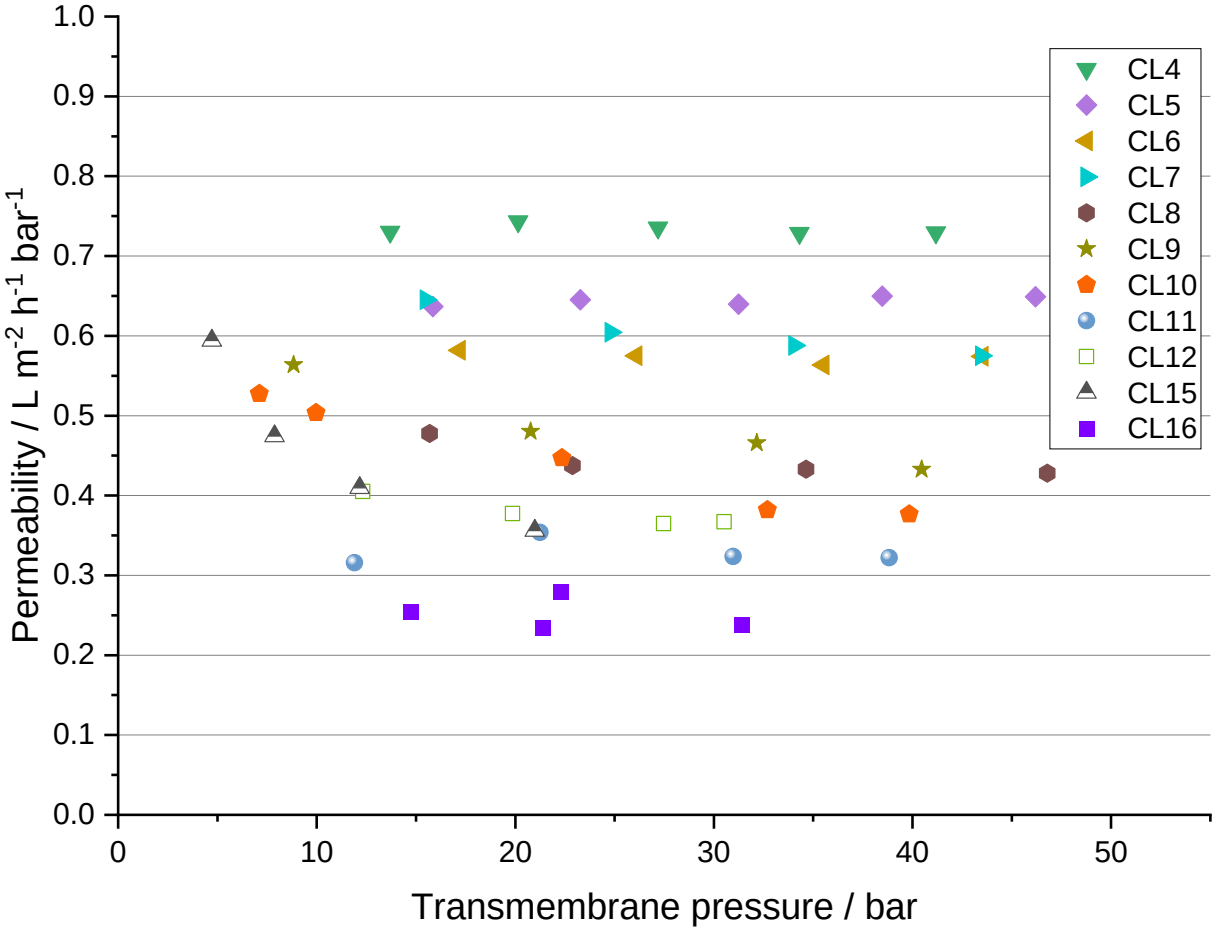
Osmotic pressure of RO concentrates



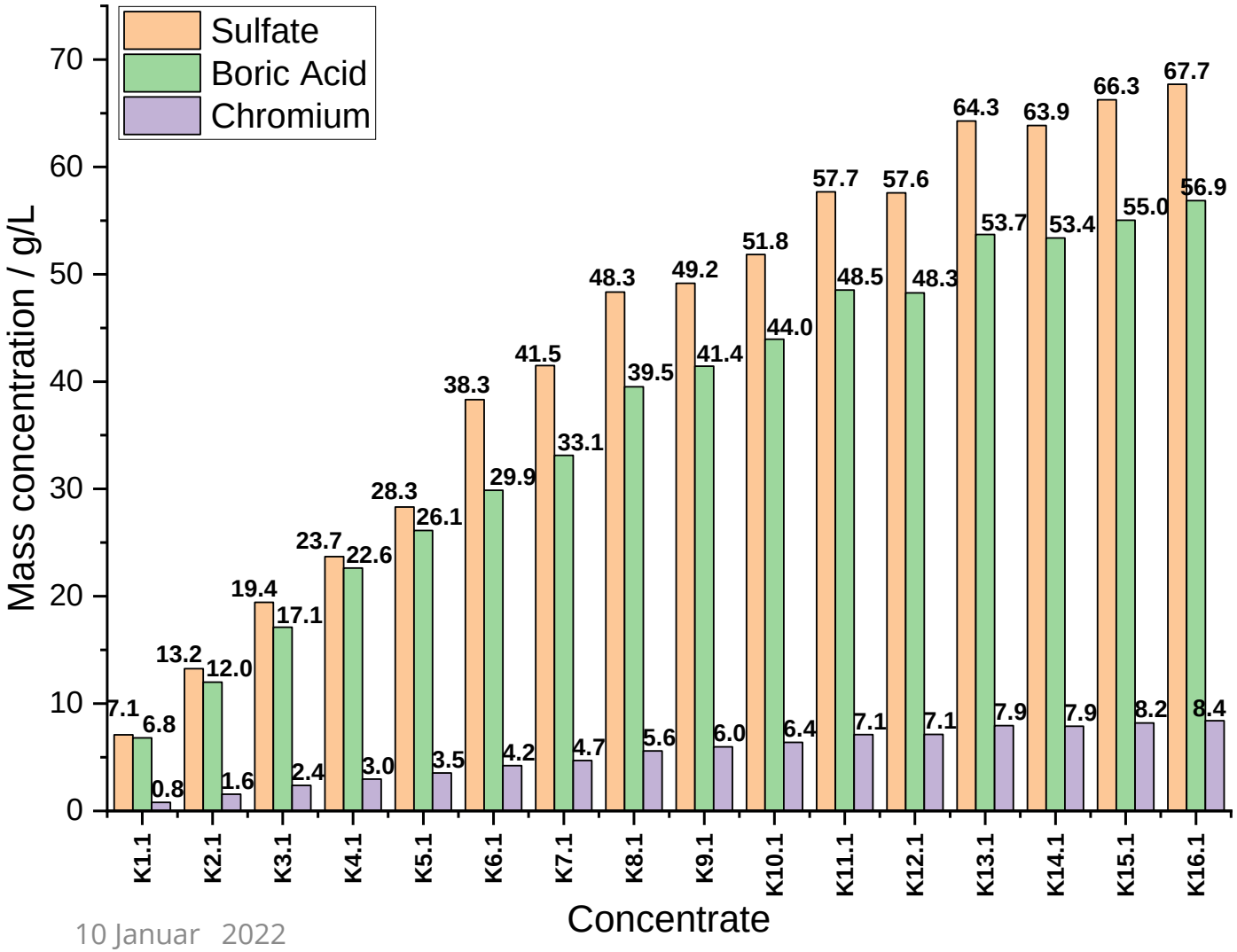
Measured with vapor pressure osmometer

Permeate flux and Permeability in dep. of the Transmembrane pressure





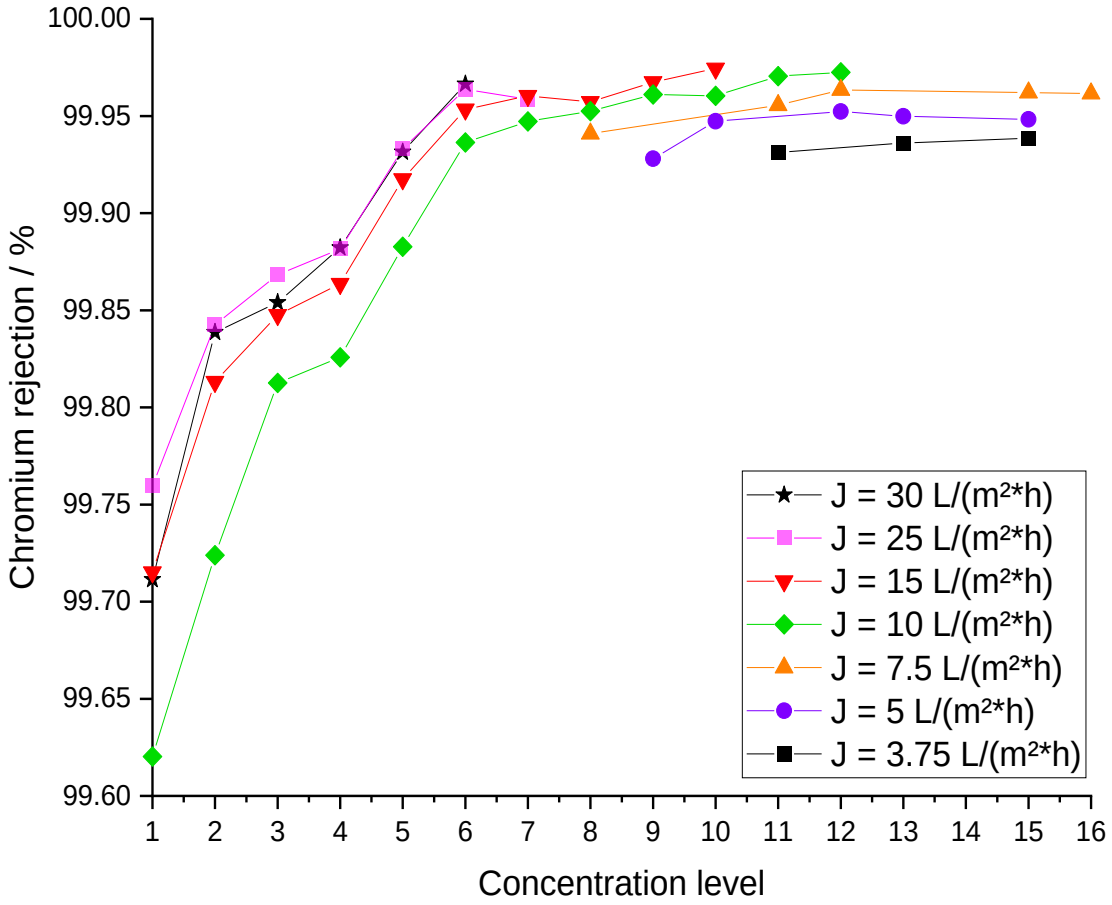
ICP-OES analysis of RO concentrates

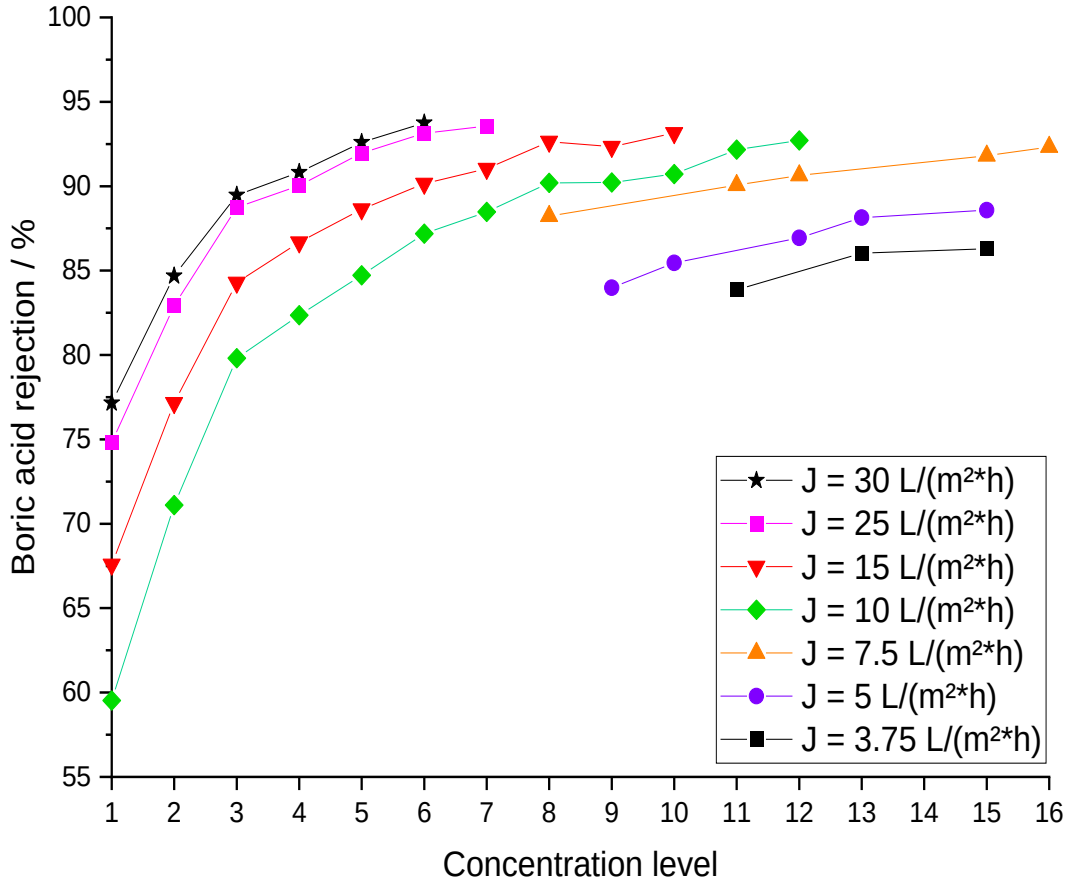


	β Cr) / g/L	β $B(OH)_3$) / g/L	β SO_4^{2-}) / g/L	γ / mN/m	pH
Cr III) Electrolyte	8-12	80-110	80-150	30-50	3.5-3.9
HPRO feed	0.75	3.55	7.12	72.0	4.7
Concentrate K16.1	8.39	56.89	67.72	63.7	3.85

Concentrate Permeate

Rejection of chromium and boric acid





RO membrane after use – fouling!

But: Pilot plant will run in batch: Cleaning is taken into account

	NaCl rejection / %	Permeate flux / $L\,m^{-2}\,h^{-1}$	Plant pressure / bar	Permeability / $L\,m^{-2}\,h^{-1}\,bar^{-1}$
Pre RO e periment	**93.0**	**30.0**	**34.2**	**1.987**
Post RO E periment J(pre)=J(post)	**98.3**	**30.0**	**55.4**	**0.826**
Post RO E periment p(pre)=p(post)	**97.8**	**15.0**	**35 .0**	**0.943**

Tested with 2 NaCl solution $\Pi = 19.1\ bar$
Permeabilit calculated with transmembrane pressure (= $\Delta p\ - \Delta\Pi$)

Use of RO concentrate as recovered electrolyte in electroplating

Hull cell tests

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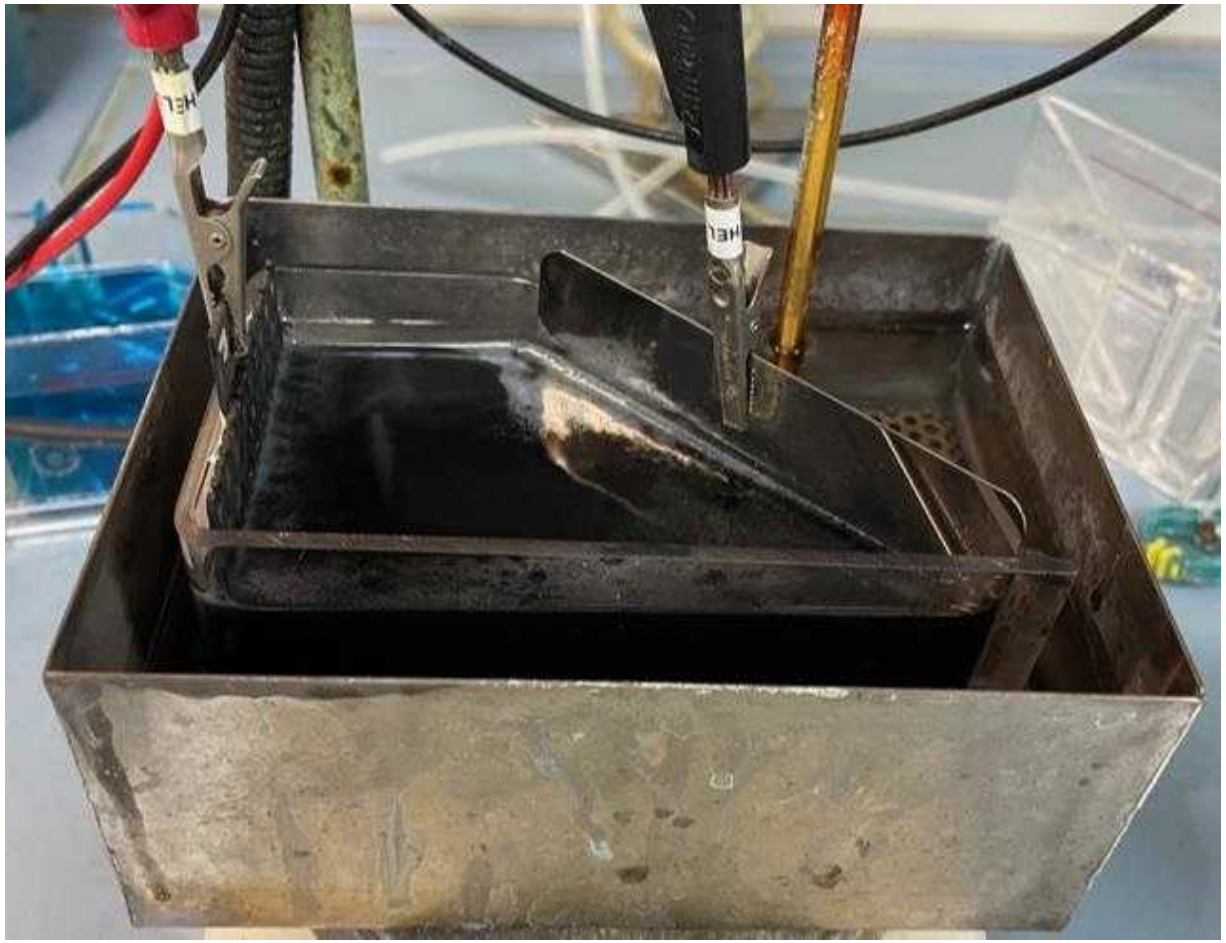
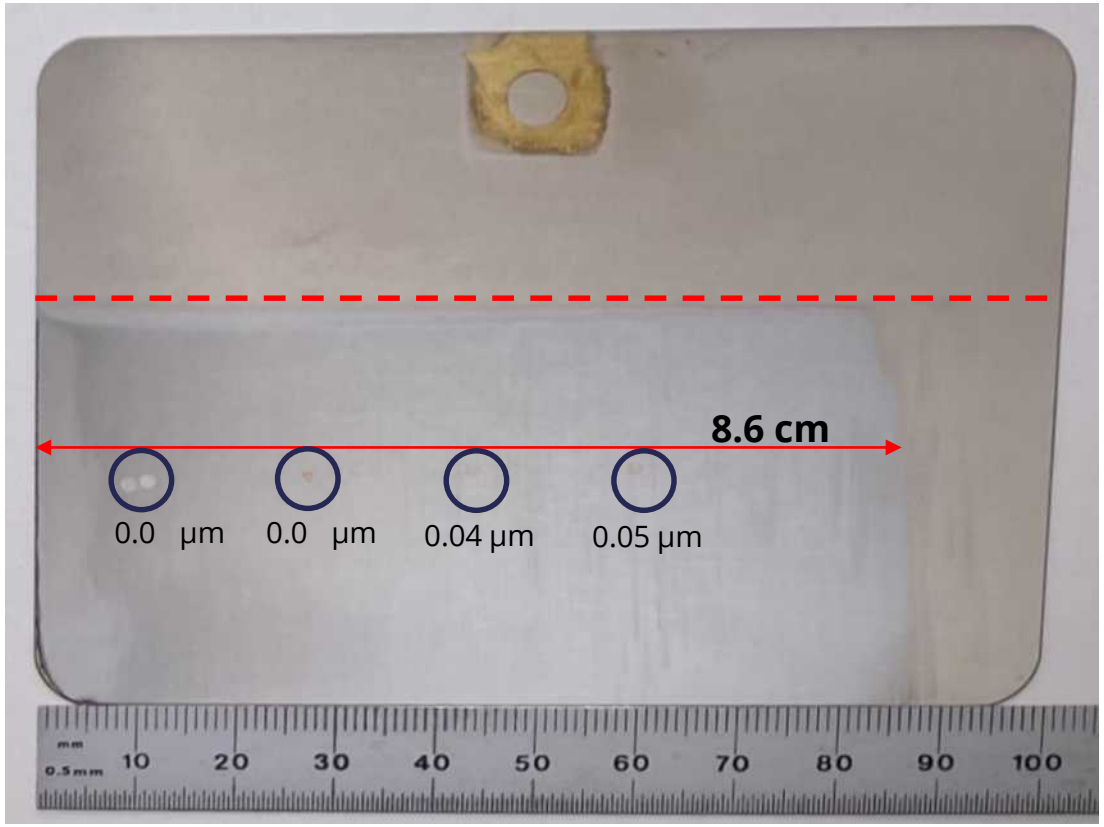
Hull Cell testing – Plating with RO concentrate



Parameter	
Current	5
Plating time	min
Temperature	55 °C
node	r Ta o ide coated titanium
Substrate	Plated on nickel coated brass panel (.5 cm 10 cm)
Volume	250 mL RO concentrate as electrol te

Hull cell test plate analysis

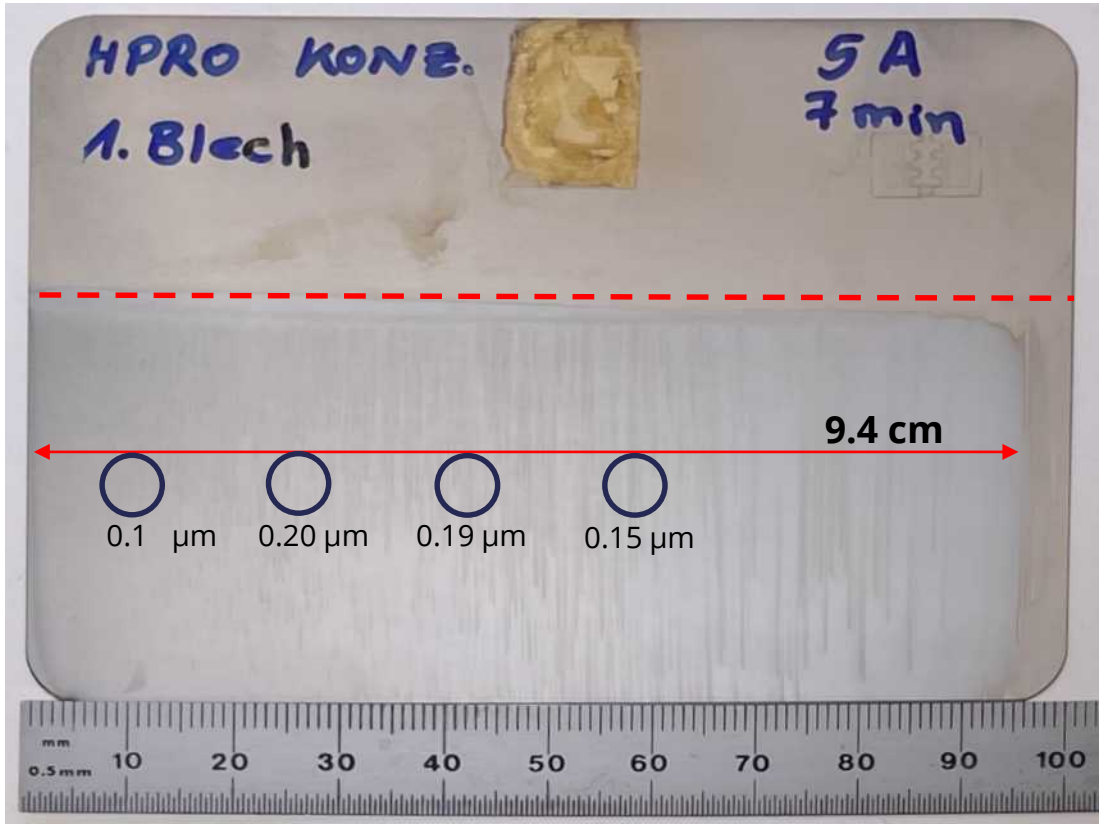
Concentrate initial



High current densit

Low current densit

Concentrate increased conc.



High current densit

Low current densit

Take home message

- Feasibilit of RO treatment for Cr( ) rinse waters
  - Sufficient membrane rejection of Cr( ): 99.95
  - RO 80 bars: sufficient concentrations for concentrate re use achieved
  - Boric acid conc. reached solubilit limit without blocking the membrane

Outlook

- Need for treatment: Permeabilit of membrane decreases significantl
  - Cleaning step (backwashing)

Thanks to

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Universit of pplied Sciences Cologne

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Thank you for your kind attention!

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