ZERO BRINE Final Forum

De Oude Bibilotheek, Delft,
The Netherlands

4 November 2021 (10:00-16:30 CET)

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The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730390.

ZERO BRINE RESEARCH
Special Issue Part I

AFTERNOON SESSION

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Process and R&D Engineer

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Dionysia Diamantidou is a Process and R&D Engineer with experience in water treatment applications. Born in Greece, obtained civil engineering diploma in AUTH and water management MSc in TU Delft, specializing in sanitary engineering.

Mechanisms controlling ion rejection in membrane filtration in presence of saline multi-ionic mixtures

Zero Brine Conference

Date: Thursday 4th of November 2021

LENNTECH
WATER TREATMENT SOLUTIONS

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LENNTECH Water Treatment Solutions

Topics

1. Zero Brine Project: Case Study Description
2. Lab-Scale Research Objectives
3. Material and Methods
4. Results
5. Conclusions

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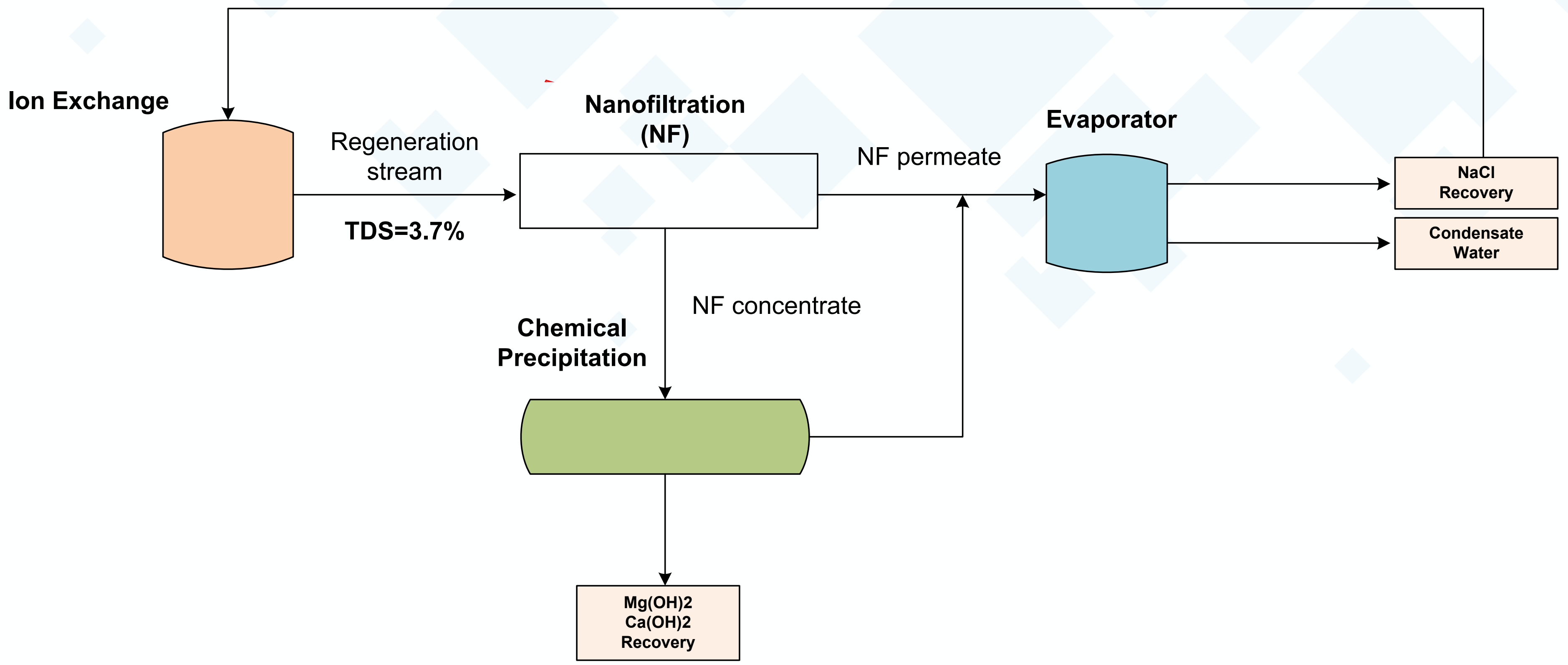
1. Zero Brine Project: Case study description
1.1 Treatment line of the IEX brine



Nanofiltration
- ❑ First step of the treatment of the IEX regeneration stream
- ❑ Separation of monovalent & divalent ions

Objectives of the case study
- ❑ Recovery and reuse of NaCl as IEX regenerant
- ❑ Recovery of $Mg(OH)_2$ and $Ca(OH)_2$
- ❑ Recovery of water

2. Lab-Scale Research Objective

Scientific objective:

- Assess the membrane performance and the mechanisms that control the ion rejection in presence of saline multi-ionic mixtures

Practical objective:

- Select the most suitable nanofiltration membrane that contributes to an optimal separation of monovalent (Na^+, K^+ and Cl) from divalent ions (Mg^{2+} and Ca^{2+}) in the IEX brine and highly rejects the divalent cations

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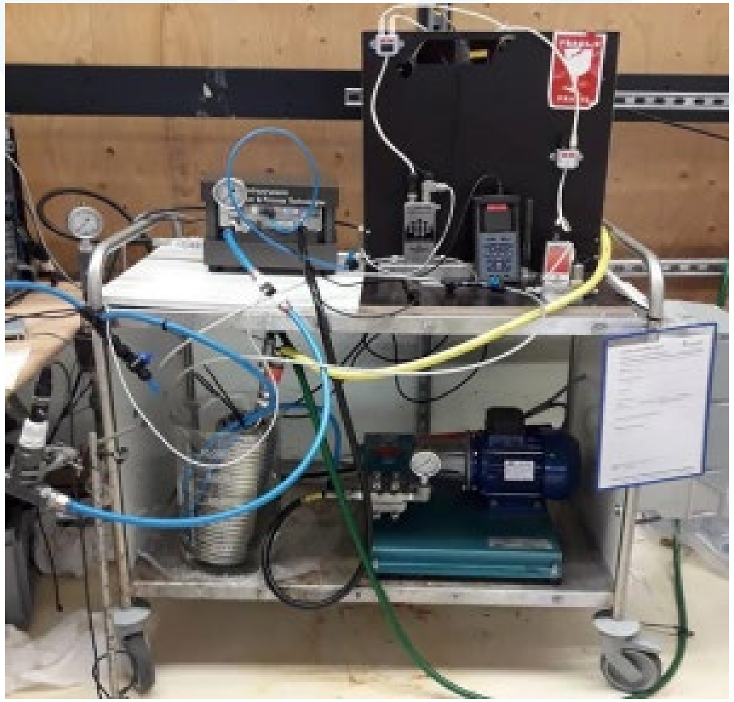
3. Materials and Methods

Equipment:
- Flat sheet cross-flow cell
- Active membrane area: 0.014 m^2



Membranes:
- NF270 and NF90 (Dow)
- NFG and NFW (Synder)
- SR3D (Koch)
- TS80 (Microdyn Nadir)
- RO98pHt (Alfa Laval)
- LFC3 (Hydranautics)

Molecular Weight Cut off (MWCO) experiment:
- Filtering a mixture of polyethylene (PEGs) at a concentration of 0.6 g/L
- MW ranging from 62 to 1000 Da

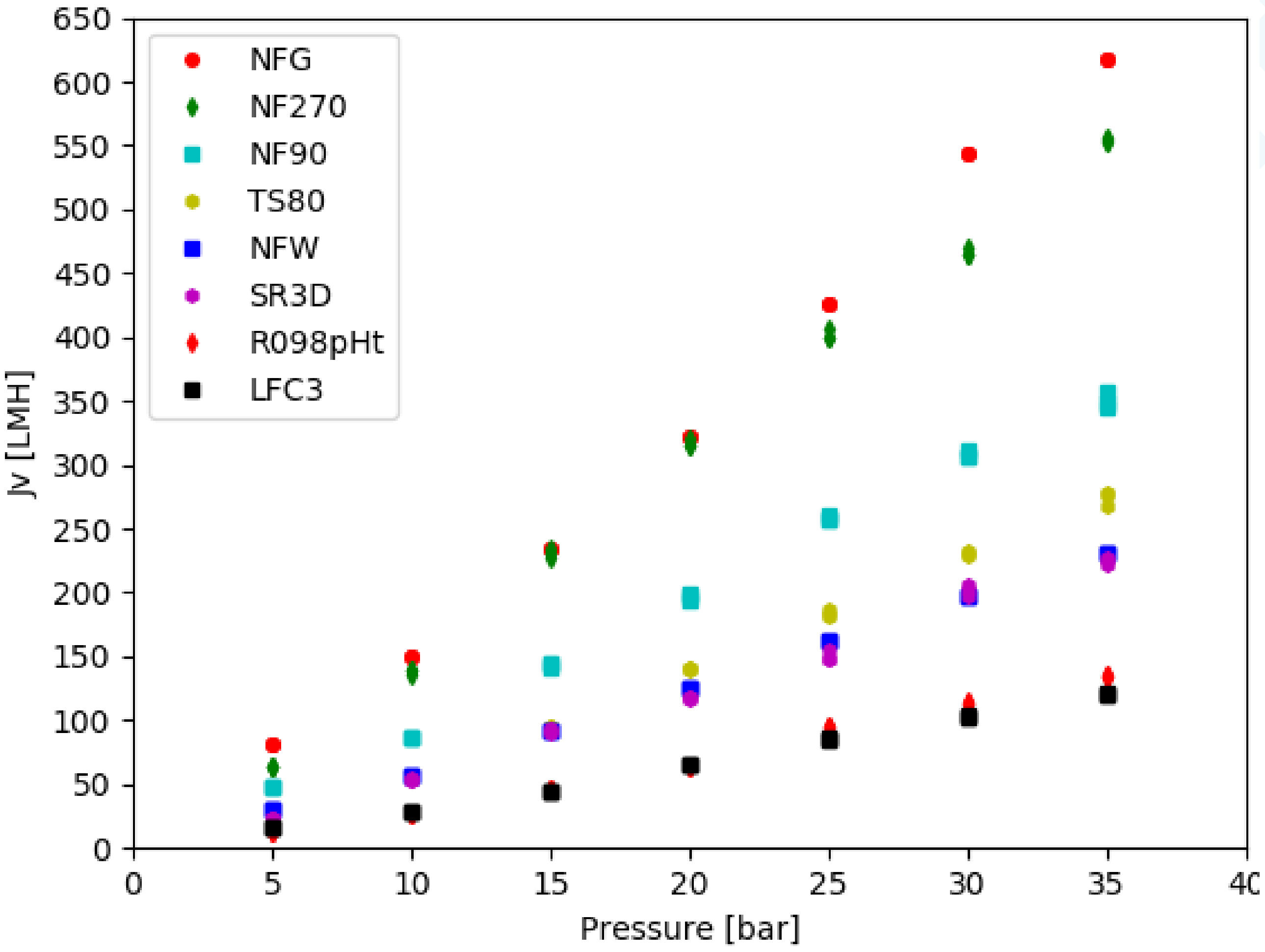
Permeability experiment:
- Filtering demineralized water at different applied pressures

Ion rejection experiment:

- Assess the membrane performance in presence of the multi-ionic mixture:
  - ✓ Test three different fluxes (15, 30, 45 L/m^2/h)
- Compare the membranes and conclude on the best performing membrane
- Keeping the flux constant at 30 L/m^2/h, the feed water was concentrated
- Concentration and properties of the ions:

Solute	Ion concentration (ppm)	MW (g/mol)	r_i (nm)	Hydration free energy (kJ/mol)	$D_{i,oo}$ (x 10^{-9} m^2 s^{-1})
Na^+	3266	23	0.184	365	1.33
Cl^-	23919	35	0.121	340	2.03
K^+	520	39	0.138	295	1.95
Mg^{2+}	1700	24	0.347	1828	0.706
Ca^{2+}	7590	40	0.309	1504	0.792

4. Results: Water Permeability



- RO membranes (RO98pHt, LFC3): lower permeabilities than NF membranes

4. Results: MWCO and water permeability

Membrane Name	MWCO (Da)	Lp (LMH/bar)
NFG	508	16.5
NF270	272	15.0
NFW	242	6.2
SR3D	200*	5.9
TS80	142	6.8
NF90	115	9.7
RO98pHt	–	3.3
LFC3	–	3.2

*According to the manufacturer

- Tight NF membranes (NFW, TS80, NF90, SR3D): lower water permeabilities than loose NF membranes (NFG, NF270)
- NFG and NF270: Similar water permeability but NFG had double the MWCO
- NF90 and TS80: NF90 is tighter but more permeable
  → NF270 and NF90 might be thinner or have bigger porosity

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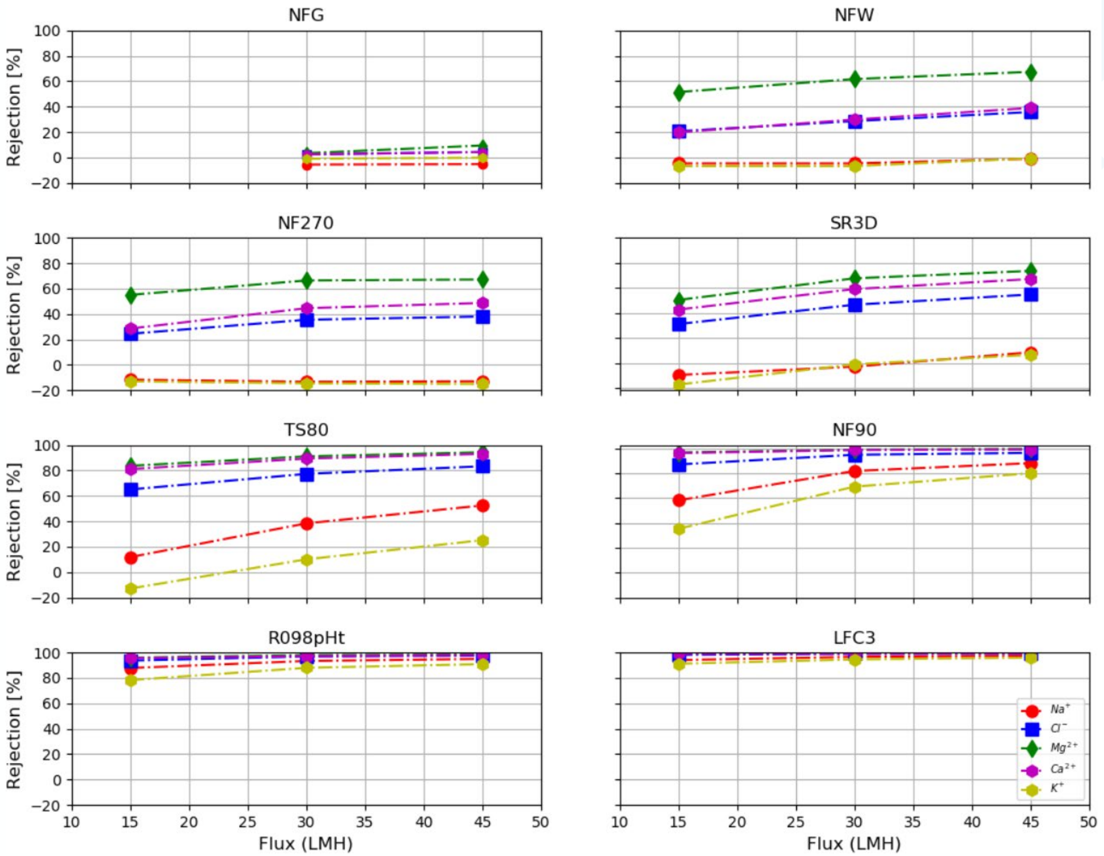
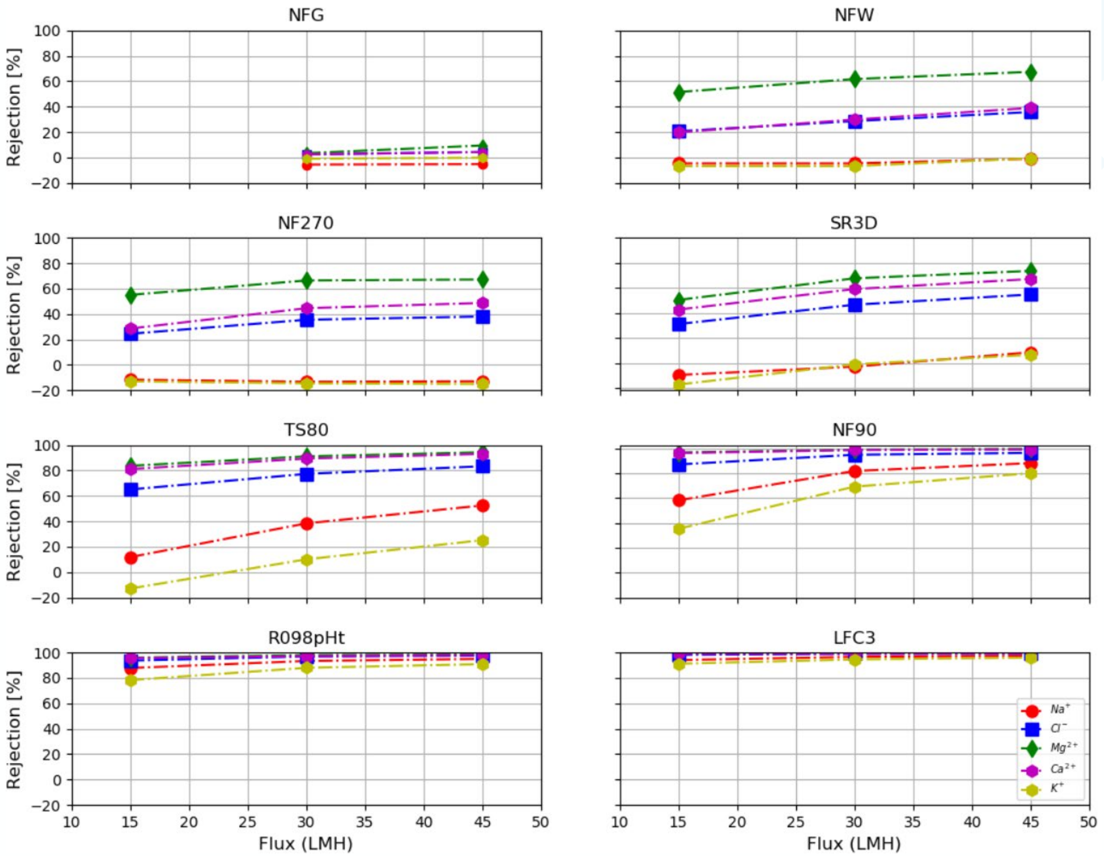
4. Results: Ionic rejections



- Order of the ionic rejections (R): $R_{Mg} > R_{Ca} > R_{Na} > R_K$, due to hydrated radius, hydration free energy and diffusion coefficient of each ion
- Higher fluxes: higher ionic rejections
- Strong dependence of the ionic rejection on membrane MWCO

4. Results: Ionic rejections



- TS80 membrane:
  - efficient ion separation
  - high rejections of divalent cations
  - concentration of Ca^{2+} and Mg^{2+} by almost two times

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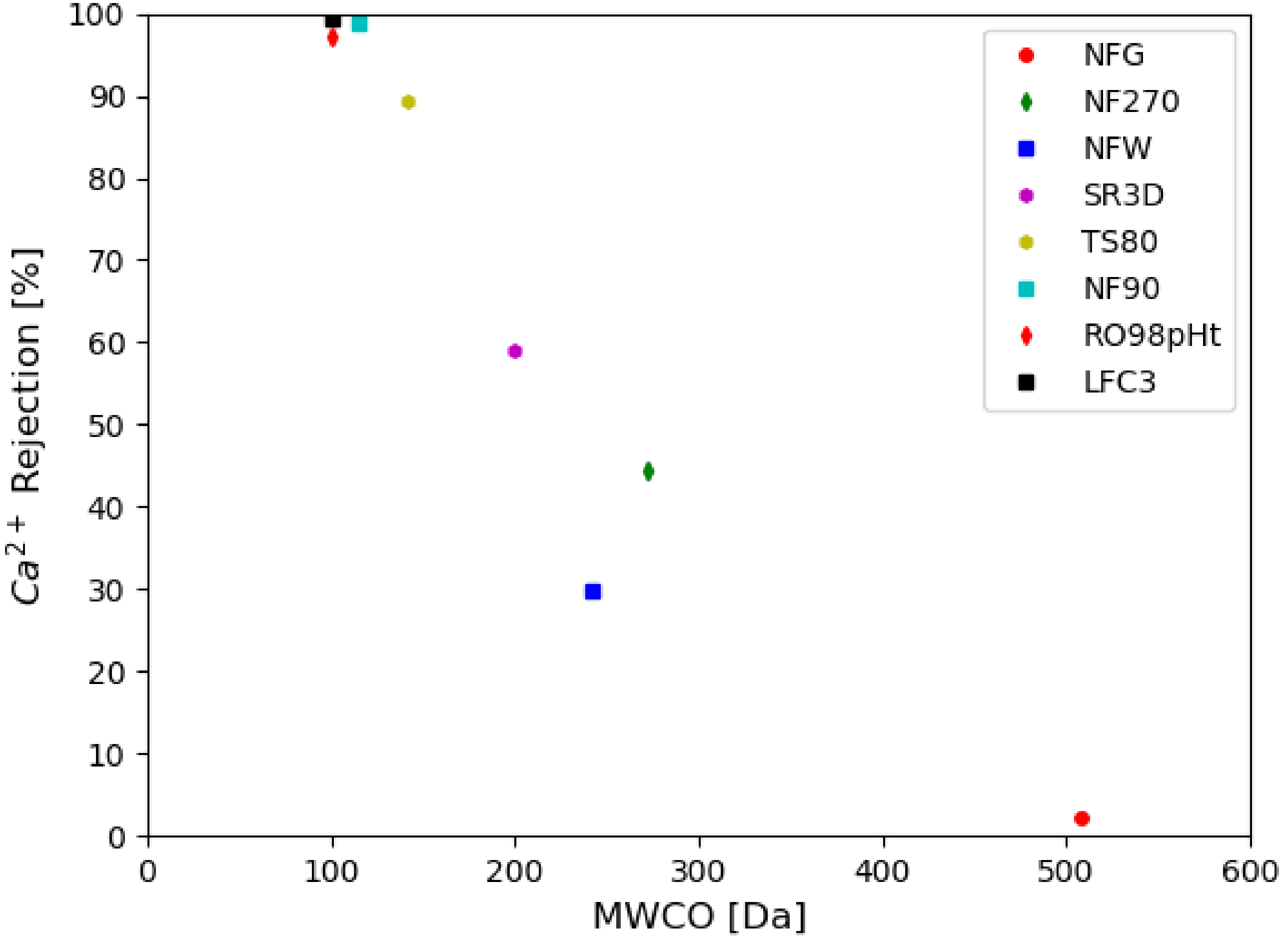
4. Results: Ionic rejections - MWCO



- Ca^{2+} rejection:
  - lower than 10% for a membrane with MWCO higher than 500 Da
  - higher than 95% for a membrane with MWCO lower than 115 Da

5. Scientific Conclusions

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- Ion rejection by membrane filtration correlated with ion properties
- RO and tight NF membranes have lower water permeabilities and higher ion rejections compared to loose NF membranes
- Strong impact of the membrane MWCO on the ion rejection

Mechanisms controlling ion rejection in membrane filtration in presence of saline multi-ionic mixtures

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5. Practical Conclusions

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- TS80 membrane was proven to be most effective: more than 90% rejection of Ca^{2+} and Mg^{2+} and more than 62% permeation of monovalent ions

- Concentration factor of Ca^{2+} and Mg^{2+} ions by almost two times was achieved, allowing for more effective recovery of Ca(OH) and $Mg(OH)_2$.

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D2.3 Bench scale test using equipment from Brine Excellence Center (BEC)

October 2020

Final

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Thank You
For Your Attention

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Nikhil Pawar

PhD candidate

DLR

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Nikhil Pawar completed his Master's at the Technical University of Berlin in Business Engineering (Energy) and is currently a PhD candidate at DLR, Stuttgart with Energy-Water Nexus being his focus area. In the ZERO BRINE project he contributed to the techno-economic modeling of treatment chains on the RCE simulation platform.

Valorization of Coal Mine Effluents – Challenges & Economic Opportunities

Paper Presentation, ZERO BRINE Final Forum, 4th November 2021

Nikhil Pawar[a], Steve Harris[b], Krzysztof Mitko[c], Gijsbert Korevaar[d]

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Agenda

- Motivation
- Pilot plant: Implementation at Site
- Technology Modeling and Simulation
- Results
- Conclusion & Outlook

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730390.

Motivation

- Poland: EU's dominant hard coal producer (~92%) [1]
- **Mine water discharge** containing **chlorides and sulphates** in Polish rivers[2]
- **Circular Economy Approach**: Reduce pollution by pretreatment of effluents, but also **recover valuable minerals** (Mg, Ca, NaCl)
- Polish pilot site: **Economic feasibility** of a **full-scale** implementation

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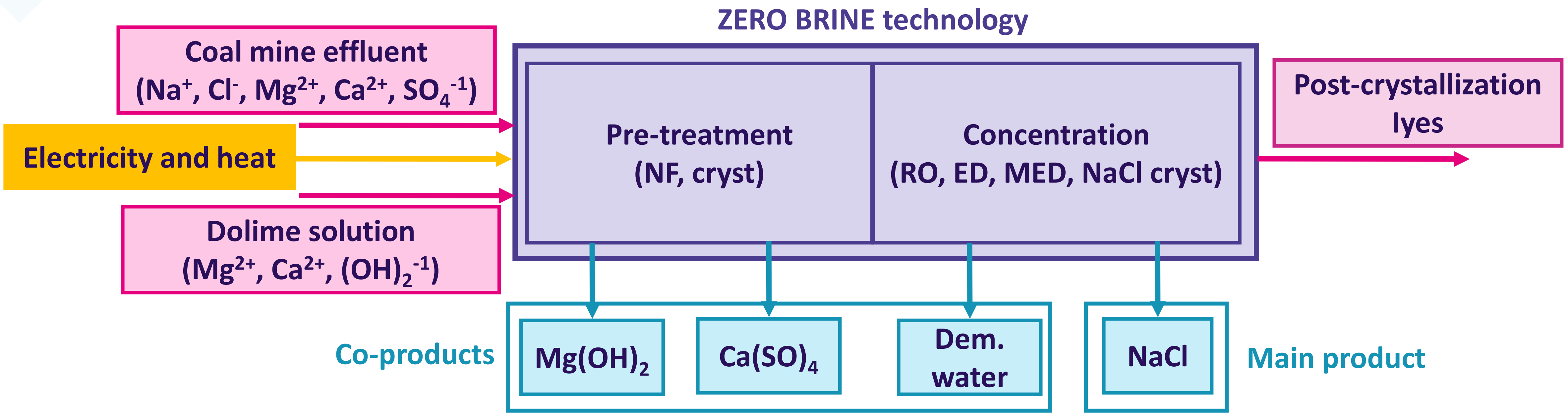
Pilot Plant: Implementation at Site



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Technology Modeling and Simulation (1/2)

- **Technology Tools**: Techno-economic modeling on **Python**
- These Tools are **integrated and simulated** as a treatment chain on DLR‘s open-source integration platform **RCE** (Remote Component Environment)[3]
- **Levelized cost of salt (LSC)** is used as an economic indicator
- Deviation from site:
  - ED is modeled as a single unit instead of two units in a cascade system
  - 100% mineral recovery from the Crystallizers

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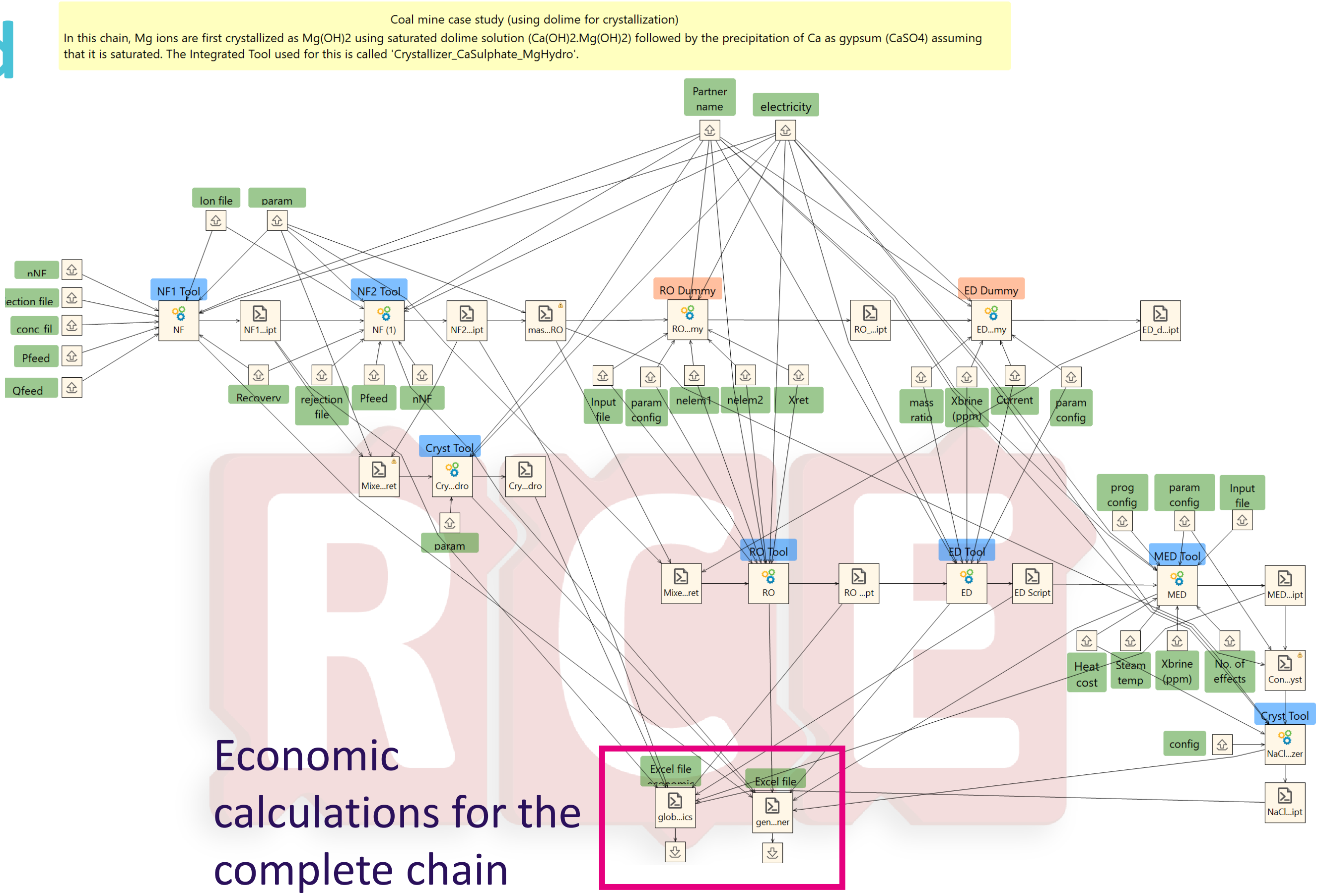
Technology Modeling and Simulation (2/2)

Technology Tools:



Economic calculations for the complete chain

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General Economic Assumptions[4]

Parameter	Value
Electricity cost [USD/kWh$_{el}$]	0.1035
Heat cost [USD/kWh$_{th}$]	0.01
Dolime [USD/ton]	60
$Mg(OH)_2$ [USD/ton]	1200
$CaSO_4$ [USD/ton]	40
Pure water price [USD/m^3]	1
Capacity factor of the plant [-]	0.94
Interest rate [%]	6%

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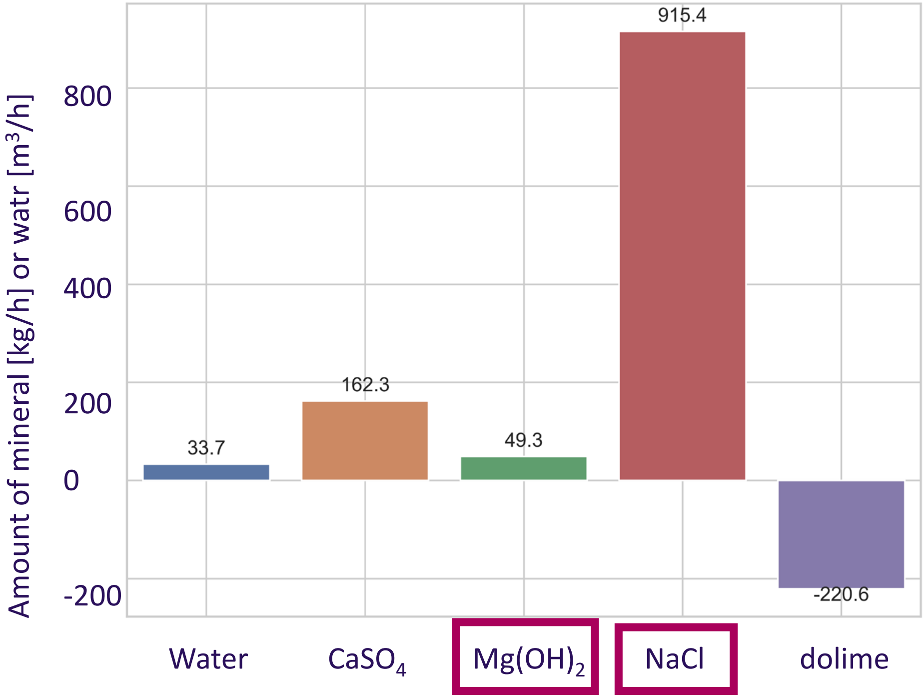
Results: Mineral Recovery

- Recovery: water, $CaSO_4$, $Mg(OH)_2$, NaCl
- Assumption: effluent at $50m^3/h$
- Smallest & largest recovery are $Mg(OH)_2$ & NaCl resp.



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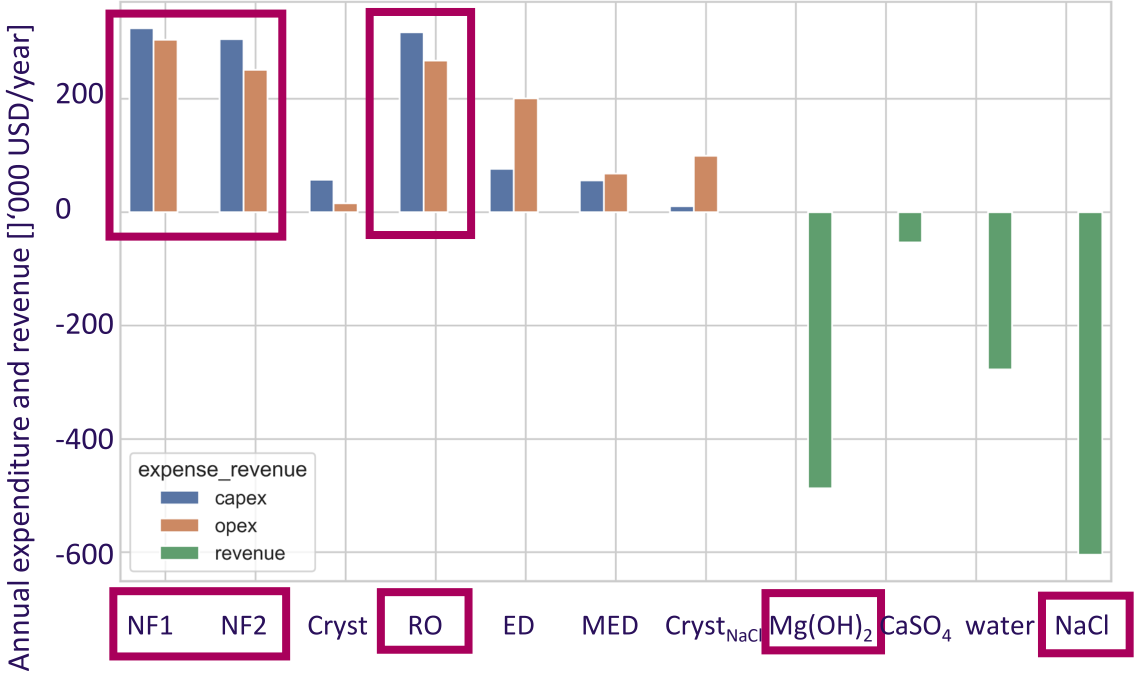
Results: Expenditures & Revenues

- NF and RO have the highest expenses with NF accounting for ~50% of the CAPEX & OPEX
- Total revenue/yr is ~60% of the total expenditure/yr



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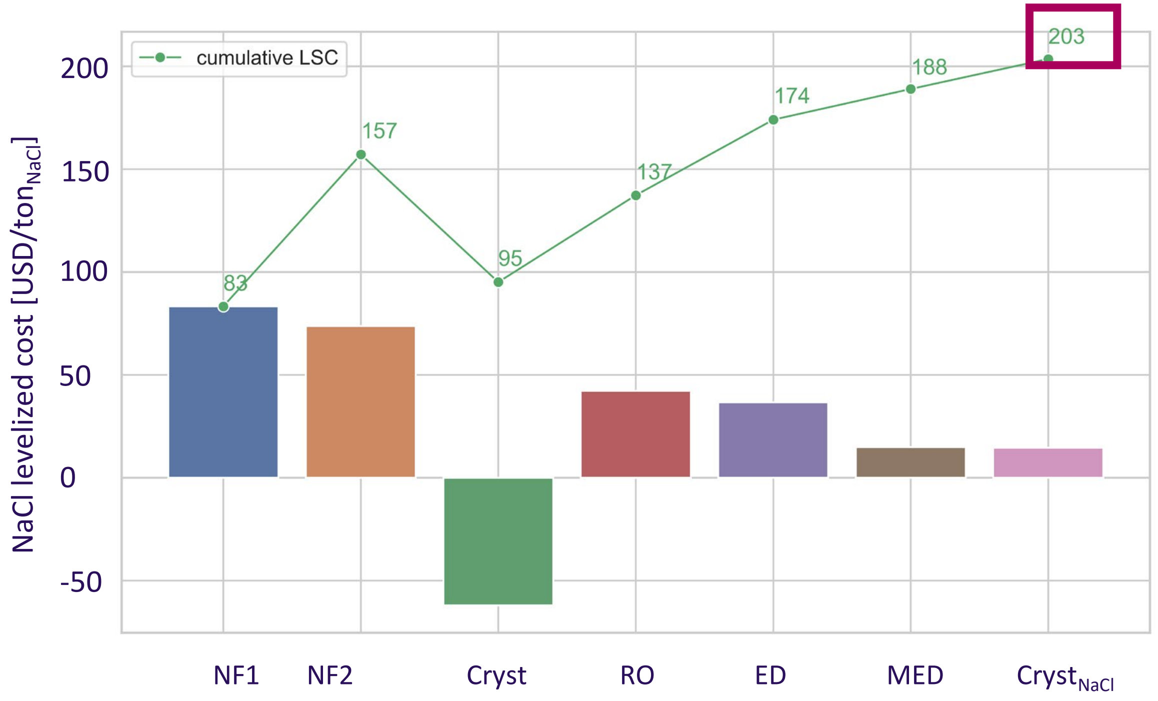
Results: Levelized Cost of Salt (LSC)

- LSC: 203 USD/ tonne NaCl
- Market price: 80 to 150 USD/ tonne NaCl[4]



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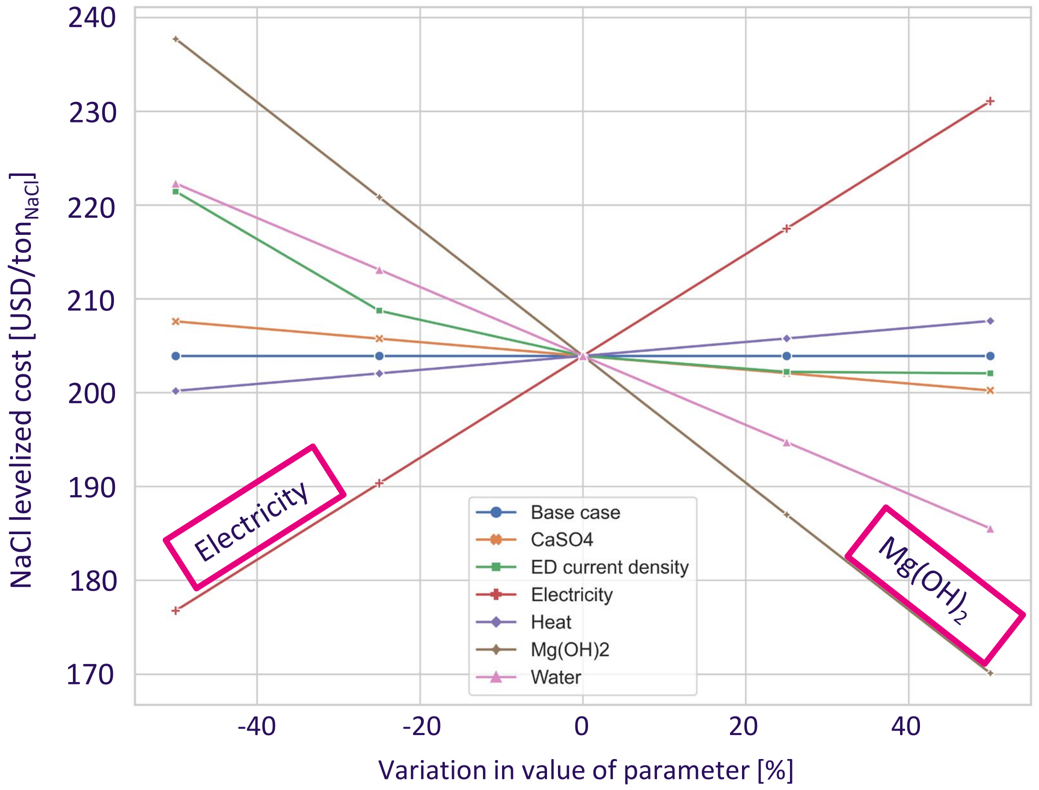
Results: Sensitivity Analysis

- Parameters: prices/costs of $CaSO_4$, $Mg(OH)_2$, water, heat, and electricity
- Variation: -50% to +50%
- LSC: **170 to 180 USD/ tonne$_{NaCl}$**: Reduction in electricity price by 50% or increase in price of $Mg(OH)_2$



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Conclusion & Outlook

- Treatment of coal mine effluent & recovery of minerals is **technically feasibile**
- **Economic feasibility** of the treatment chain **is possible** by improving one or more cost factors
- **Outlook**: To model ED as a cascade system of two units and to account for partial recovery in crystallizers

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References

1. EURACOAL (2020). EURACOAL Annual Report 2019. Brussels, European Association for Coal and Lignite.
2. Turek, M., et al. (2005). "Salt production from coal-mine brine in ED–evaporation–crystallization system." Desalination **184(1-3): 439-446.**
3. (DLR), D. Z. f. L.-u. R. e. V. (2021). "RCE." from https://rcenvironment.de/.
4. Micari, M., et al. (2020). "Techno-economic analysis of integrated processes for the treatment and valorisation of neutral coal mine effluents." Journal of Cleaner Production **270: 122472.**

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Nilay Elginoz

Senior Researcher

IVL

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Dr. Nilay Elginoz is a senior researcher at IVL Swedish Environmental Institute, with her research focused on environmental sustainability assessment of emerging resource recovery systems. Before IVL, she worked as a researcher for KTH Royal Institute of Technology and Istanbul Technical University. She completed her PhD on nature based coastal protection structures and their impact on coastal erosion in 2010.

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Using life cycle assessment at an early stage of design and development of zero discharge brine treatment and recovery

Nilay Elginoz Kanat[a], Christina Papadaskalopoulou[b], Steve Harris[a]
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[b]National Technical University of Athens, Greece

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Aim

- Evaluate the implications of utilising different input data, from two stages of development, on the LCA results.
- Specific objectives
  - (i) Identify the extent of impact on results by comparing results of LCA's using initial design and bench scale data with improved data from pilot scale and simulations.
  - (ii) Assess the resultant consequences for informing the design process and highlight potential pitfalls.
  - (iii) Identify the key challenges in early application of LCA and propose methods to manage.

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Scope

- System boundaries of LCAs cover operation of the treatment and resource recovery units and credits provided by recovered products
- Recovered products were credited by using system expansion method in the LCA model.
  - gypsum
  - deionised water
  - sodium chloride
  - magnesium hydroxide

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Scope

- Out of the system boundaries
  - Construction and operation of the brine generating facilities
  - Construction of the treatment and resource recovery units
- In the system boundaries
  - Chemical and energy consumptions
  - Component replacement for each unit

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Scope

- The International Reference Life Cycle Data System, ILCD 2011 midpoint
  - climate change
  - acidification
  - freshwater eutrophication
  - abiotic resource depletion for mineral, fossil and renewable resources
- Normalization method for Environmental Footprints
- Perturbation analysis

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Coal mine case

- First stage,
  - Experimental data and PH REdox EQuilibrium (PHREEQC) simulations
- Second stage
  - Pilot plant with treatment capacity of 1m^3/h, onsite at the mine
  - Upscaled to a conceptual plant with 50 m^3/h plant capacity

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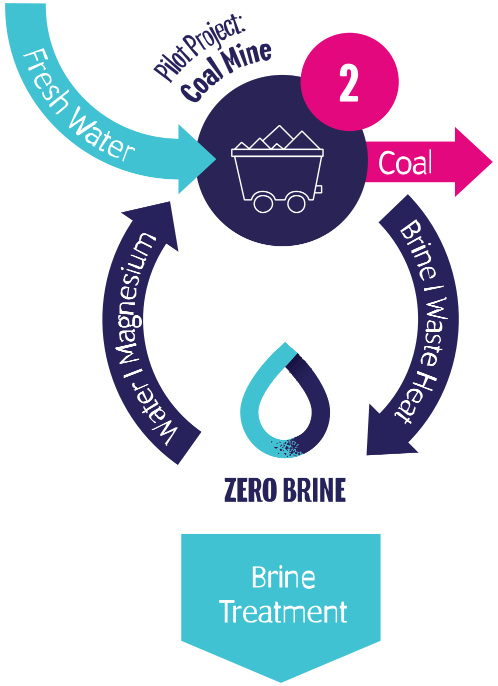

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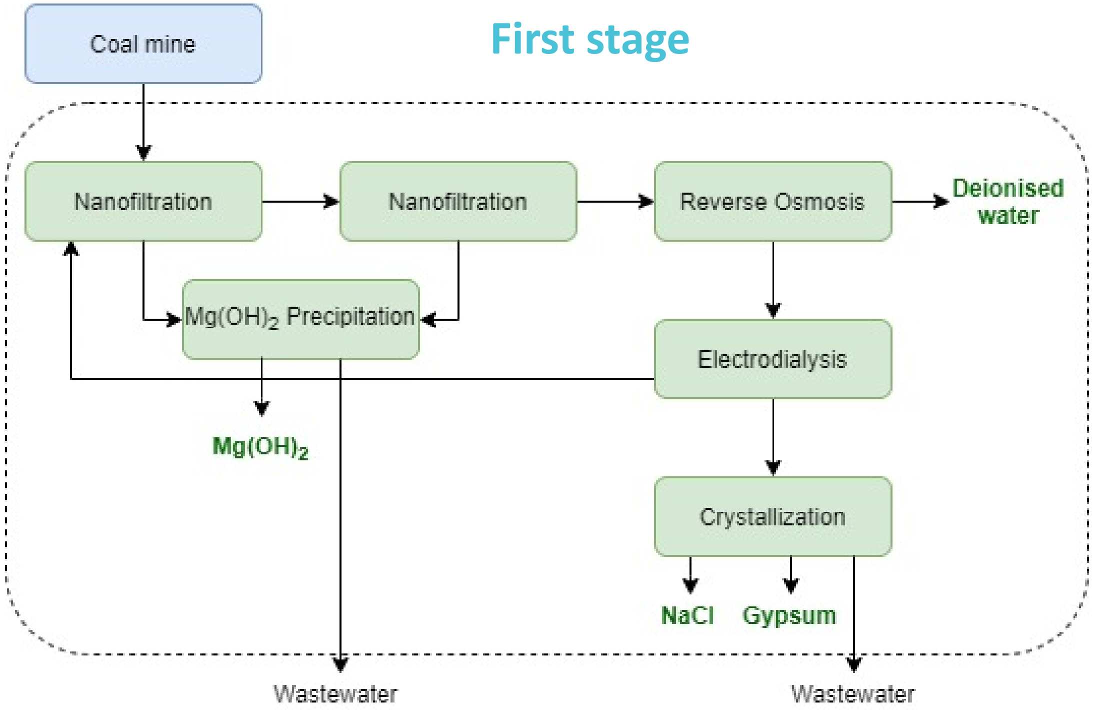
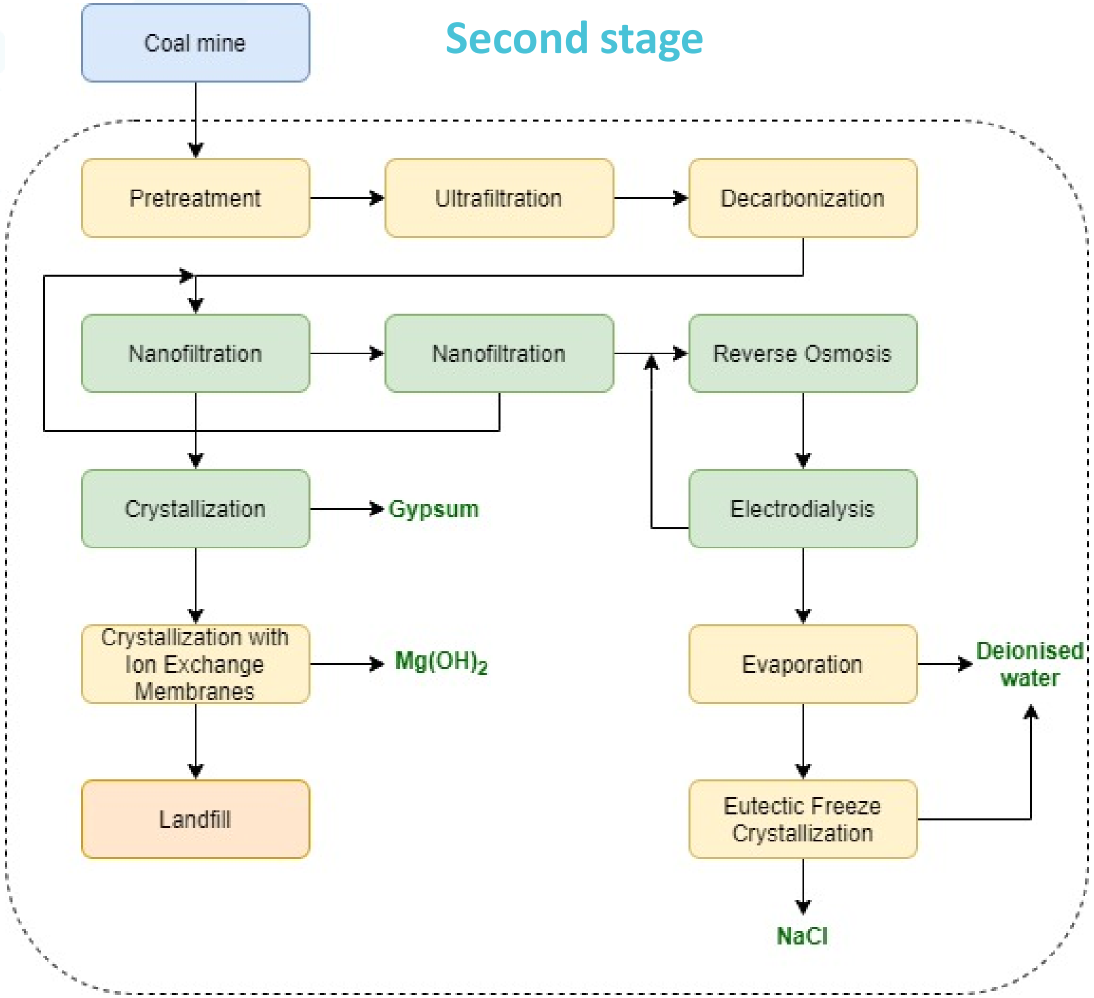
Coal mine case





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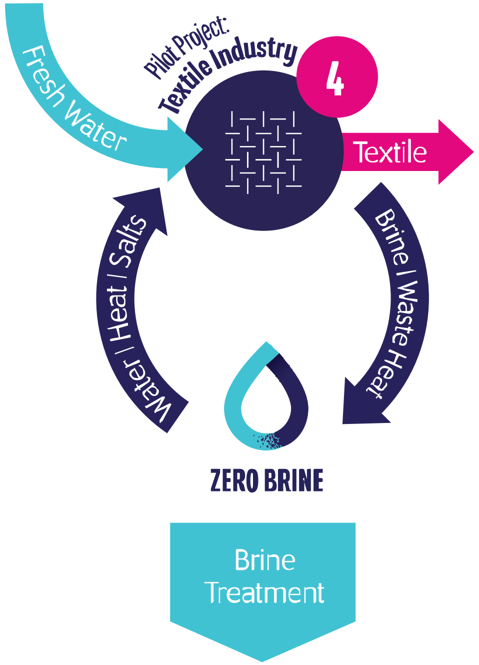
Textile plant case

- First stage,
  - Experimental data of the brine treatment processes and PHREEQC simulations
- Second stage
  - Pilot plant with treatment capacity of $1m^3/h$, onsite at the plant



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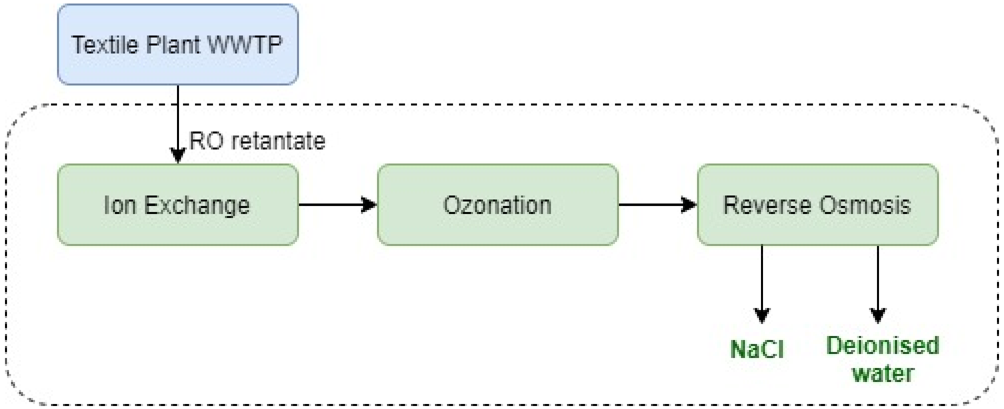
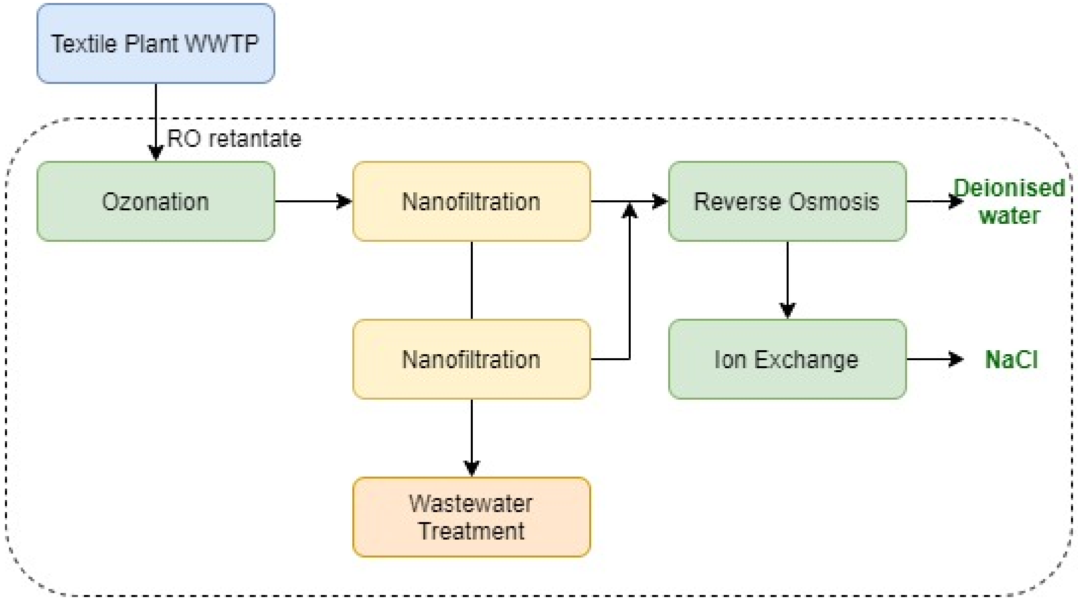
Textile plant case

First stage



Second stage



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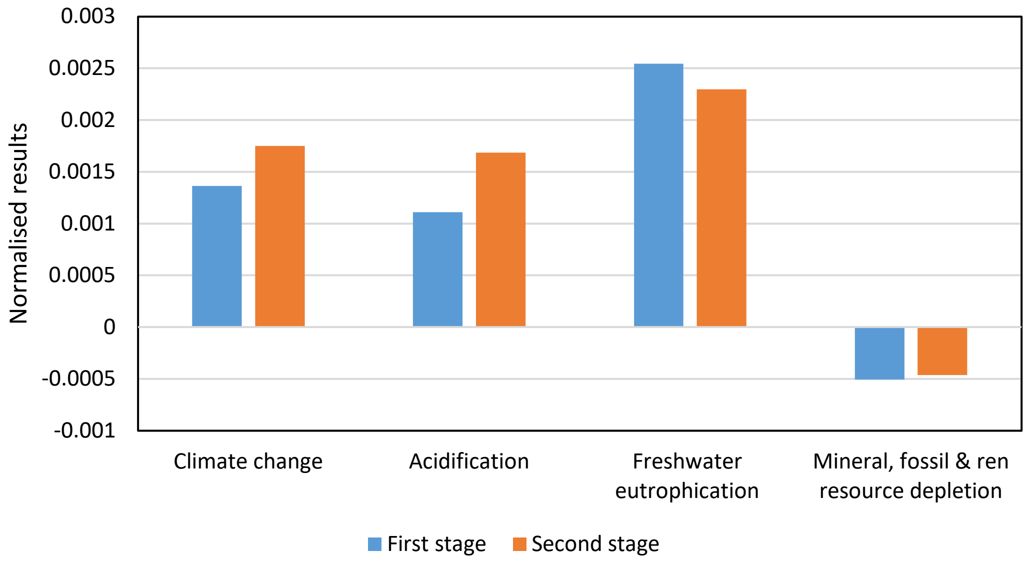
Results: Coal mine case



- Design of the coal mine ZB system changed substantially in the second stage
- Climate change and acidification impacts are 28% and 52% higher
- Freshwater eutrophication is 10% lower in the second stage
- 1% difference in the mineral, fossil and renewable resource depletion

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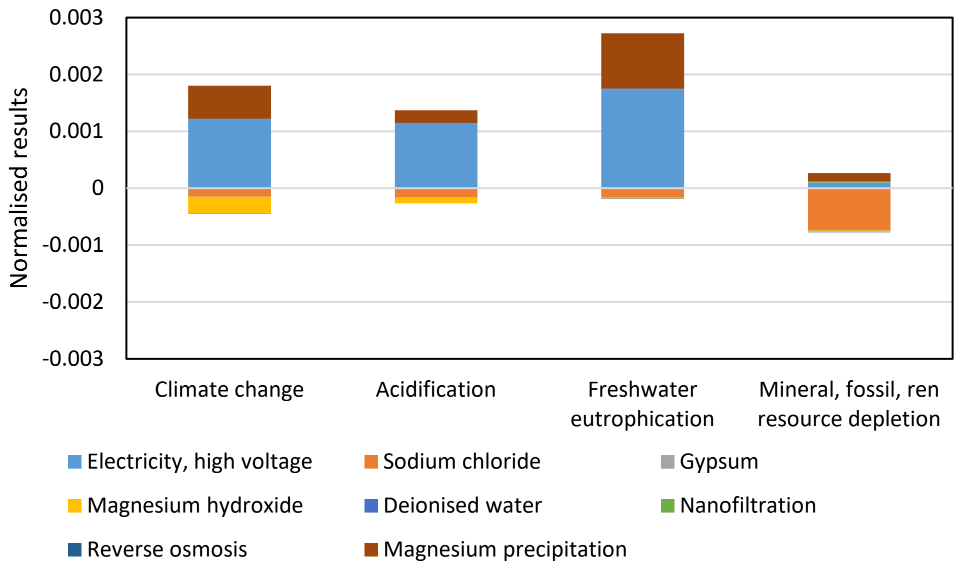
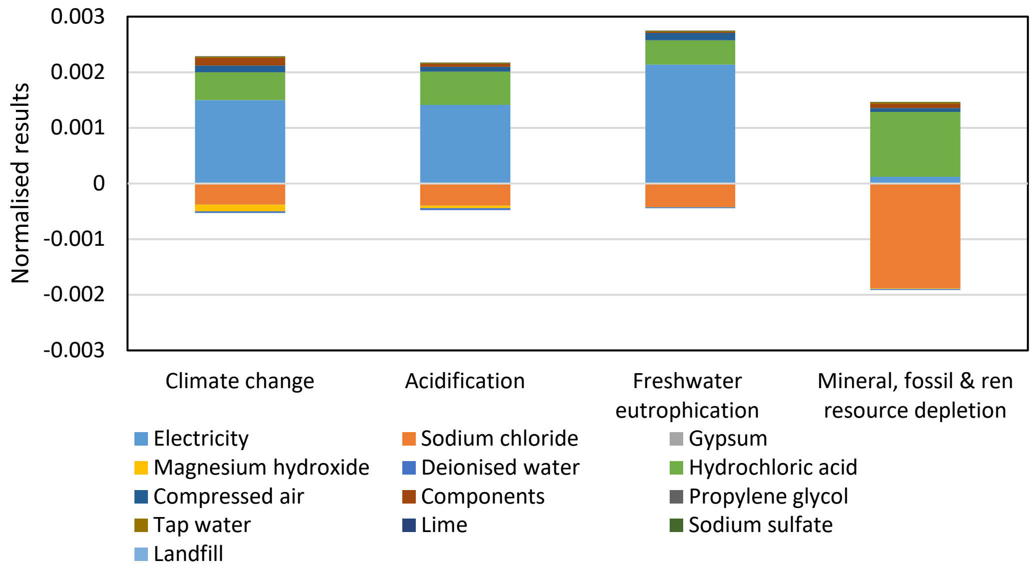
Results: Coal mine case

- Electricity consumption in the treatment steps is the major contributor
- 9kWh and 11 kWh per 1 m^3 brine in the 1st and 2nd stages
- Dolomite production in the magnesium precipitation in the 1st stage
- Hydrochloric acid consumption in the decarbonation stage in the 2nd stage
- Hydrochloric consumption in the 2nd stage and the increase in the electricity consumption is the main reason of the increase in the impacts
- Sodium chloride recovery increase from 6.5 to 16.5 kg
- The increase in deionized water and gypsum recovery doesn`t have a visible impact on the results





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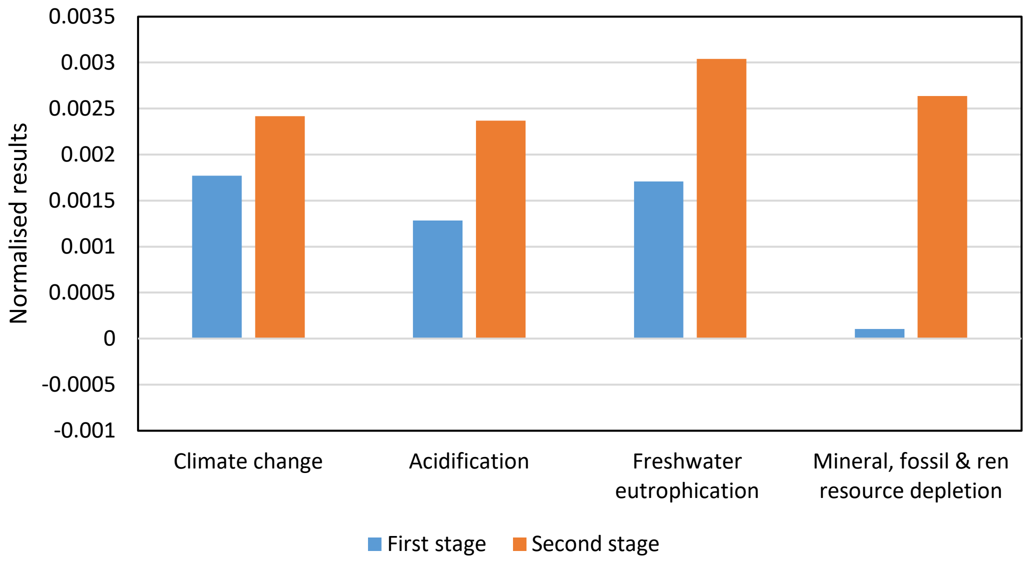
Results: Textile plant case



- 2nd stage configuration cause more burdens in all impact categories
- Climate change 36%
- Acidification 85%
- Freshwater eutrophication 78%
- Resource depletion 25 times higher

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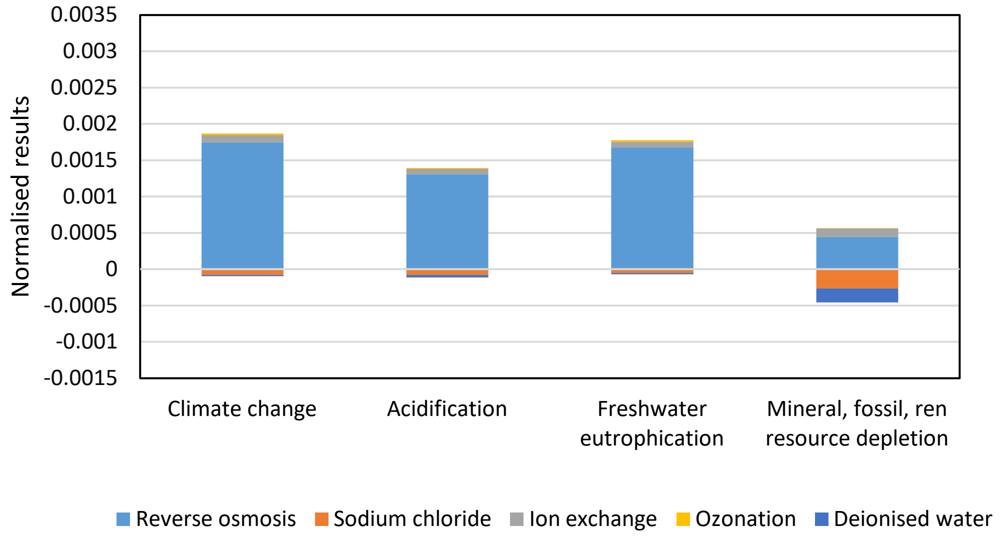
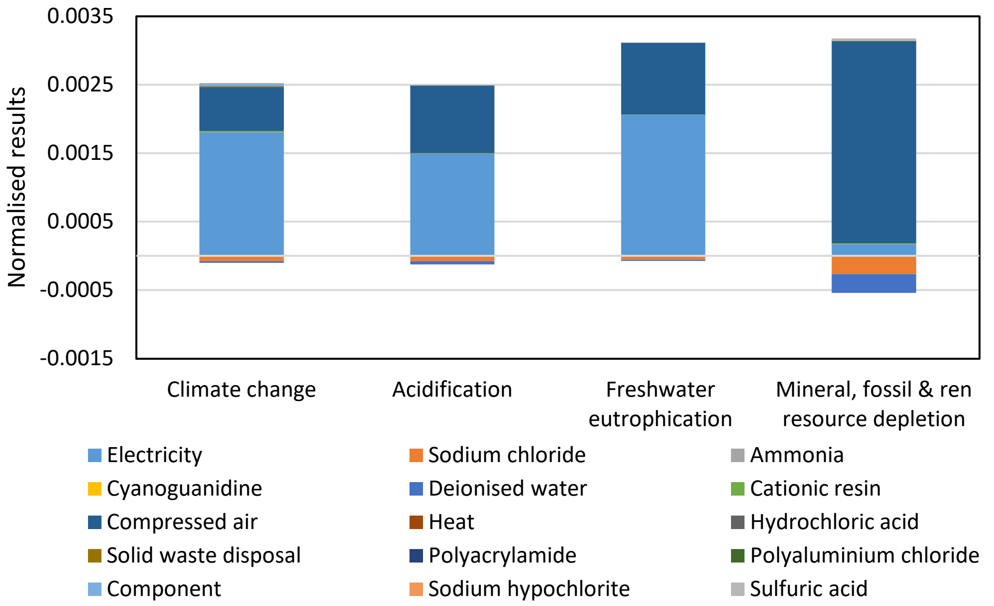
Results: Textile plant case

- Electricity consumption in the treatment steps is the major contributor
- 19 kWh and 22 kWh per 1 m^3 brine in the 1^{st} and 2^{nd} stages
- Compressed air consumption in ozonation unit in the 2^{nd} stage
- Recovered sodium chloride is the same on both stages
- The increase in recovered water from 0.6 to 0.861 m3 in the second stage does not result in any visible improvement on the impacts





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Sensitivity and uncertainty analysis for climate change

Parameter	Sensitivity Ratio			
	Coal mine first stage	Coal mine second stage	Textile plant first stage	Textile plant second stage
Electricity	0.89	0.85	0.88	0.75
Sodium chloride	0.11	0.21	0.04	0.04
Magnesium hydroxide	0.21	0.07	-	-
Deionised water	<0.01	0.02	0.01	0.02
Gypsum	<0.01	<0.01	-	-

- Climate change results are very sensitive to electricity consumption
- +-10% variation of electricity consumption cause 7.5 to 8.9% variation of the results
- Amount of sodium chloride recovery impacts the climate change results less in the textile plant case compared to coal mine case

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Key challenges in early application of LCA

- LCAs investigated in this study were conducted simultaneously with the development of ZB technologies from (TRL) 2-3 to TRL 4-5.
- The results were of limited use for the process design team.
- The main focus, during the pilot stage was solving technical issues and minimizing energy consumption.

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Key challenges in early application of LCA

- Experimental data was combined with simulations and engineering based calculations for scaling up the proposed treatment systems to industrial scale.
- In ZB case studies scaling up was executed in collaboration with technology developers as recommended.
- Data availability issue was overcome by the close collaboration of technology developers, pilot plant implementers and LCA team.
- Background electricity production processes (which determine the mix of coal and other sources) have a crucial impact on the LCA results.

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

LUNCH BREAK

12:45-13:45

ZERO BRINE RESEARCH Special Issue Part II

AFTERNOON SESSION

ZERO BRINE

Amir Haidari
Process Technology & Innovation Manager
Hatenboer-Water

ZERO BRINE
FINAL
FORUM

Amir Haidari was born in Afghanistan and has been living in the Netherlands for more than 20 years. In 2011, he graduated specialized in the topic of zero brine in horticulture. He got his doctoral degree on improvements of reverse osmosis membrane construction. In 2016, he became the coordinator of ZERO BRINE project. After four-years of working on ZERO BRINE, he changed his carrier towards industry. Since 2020, he is the Manager of Process Technology and Innovation at Hatenboer-Water.

High silica concentration in RO concentrate

RO as pretreatment to EFC

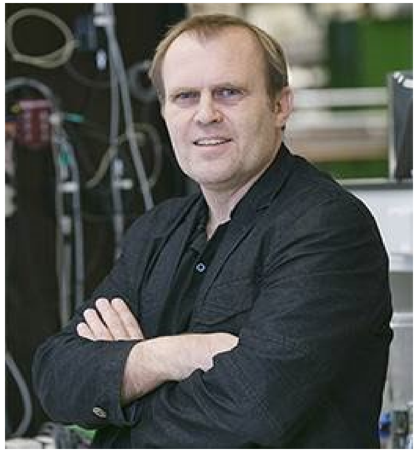
Amir Haidari
amir.haidari@hatenboer-water.com

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

ZERO BRINE

Introduction

- Amir Haidari: manager of R&D at Hatenboer-water
- Bas Heijman: Associate professor at Delft University of Technology
- Geert-Jan Witkamp: Professor, Environmental Science and Engineering at KAUST


The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Introduction

Eutectic Freeze Crystallization (EFC) is one the instrument used during ZEOR BRINE project

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730390.

ZERO BRINE

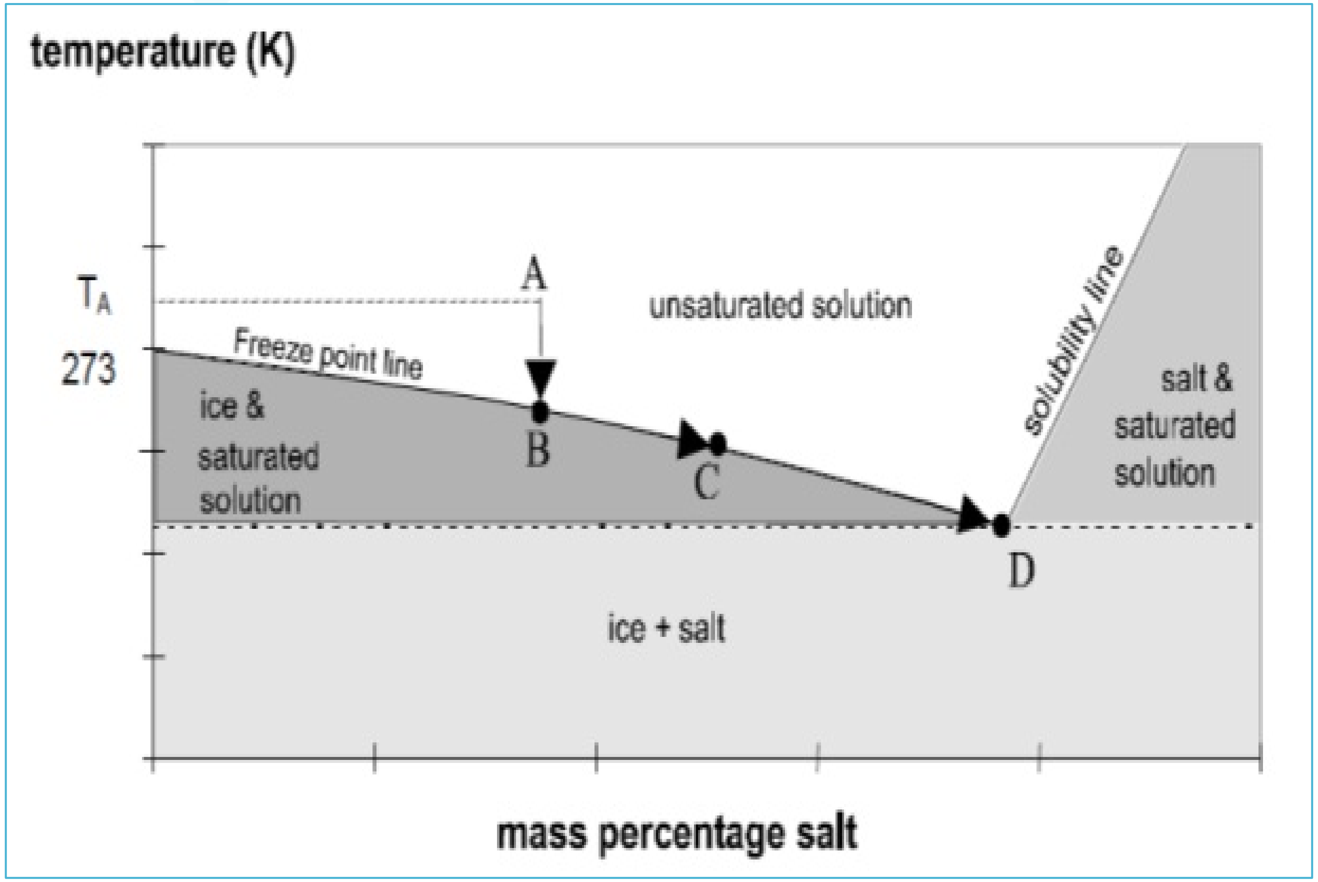
Introduction

A: Solution

B: Formation of ice

C: Increase concentration

D: Saturation solution, start formation of salts (Eutectic point)



The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Introduction

High concentration and RO → Scaling

Calcium, Magnesium, Silica

Recovery of RO is limited to particularly silica

The silica concentration may not exceed 120 mg/L

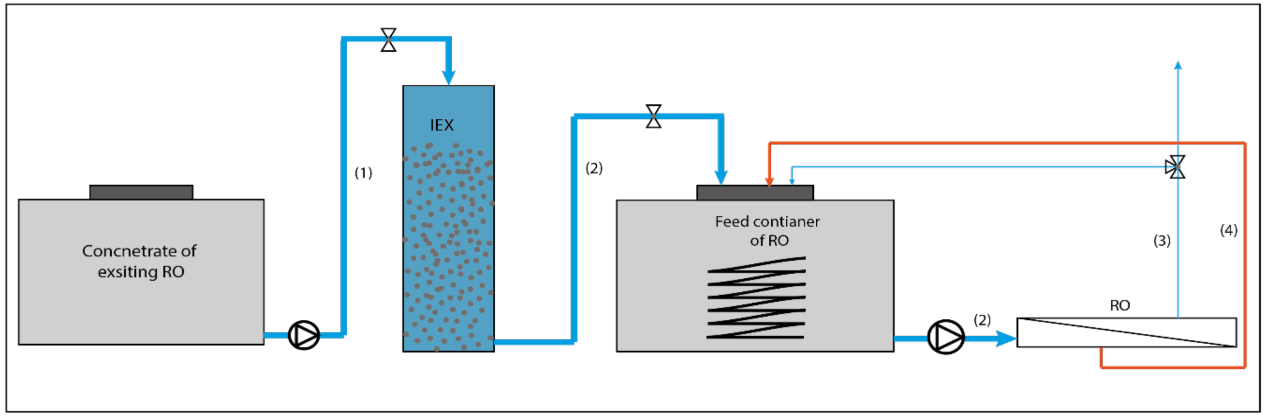
The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Setup

Our feed water: SiO_2 = 45-65 mg/L

When removing the positively charged cation is 120 mg/L SiO_2 valid?

Soften the water → Can 120mg/L be exceeded



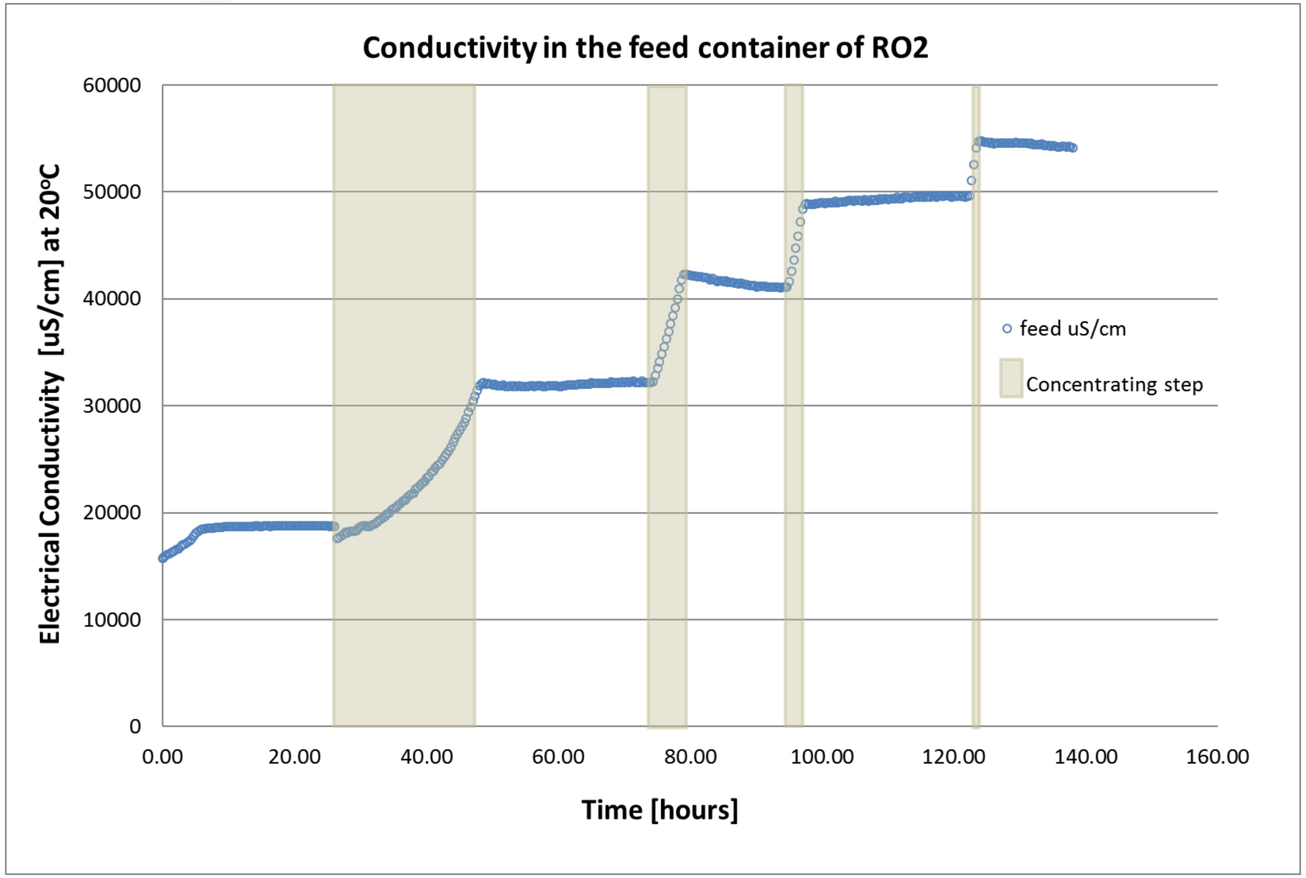
The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Method

During the recirculation of permeate the mass transfer coefficient of the membrane is measured

During discharge of the permeate, the concentration factor is increased

The experiment is repeated three times to ensure the results



The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Method (Experiments)

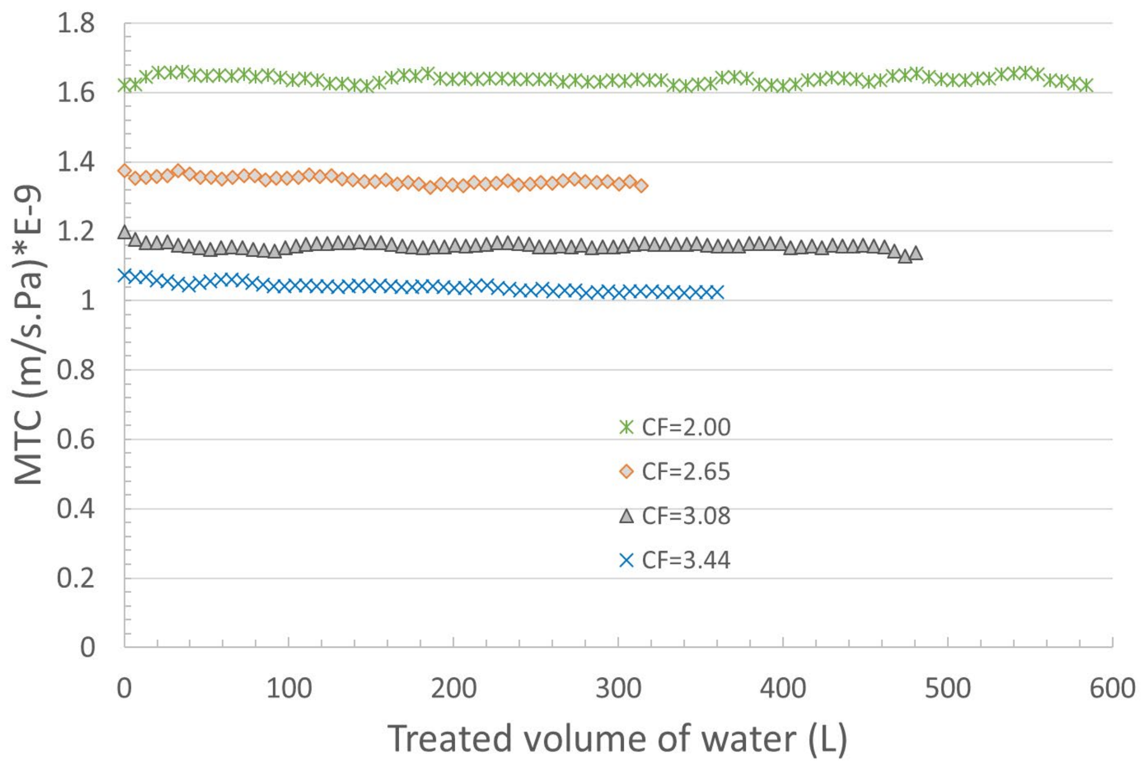
The difference between three experiments was due to concentration difference between calcium and magnesium.

Parameter	Ex 01	Ex 02	Ex 03
Ca^{2+}	0.43	7	50
Mg^{2+}	0.16	29	74

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Results (Experiment 02)

The results from all three experiment were the same up to concentration factor of 3.00



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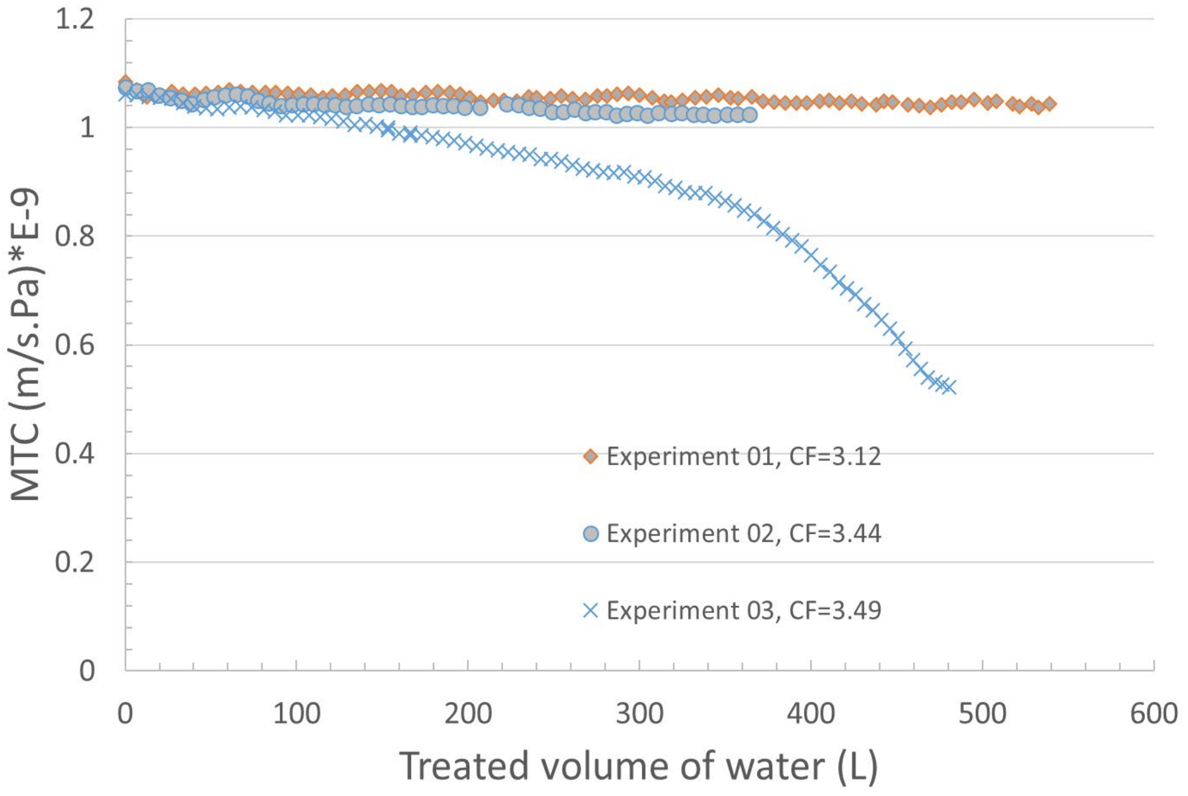
Results (highest concentration factor)

Increase of Ca and Mg results in decrease of Mass Transfer Coefficient



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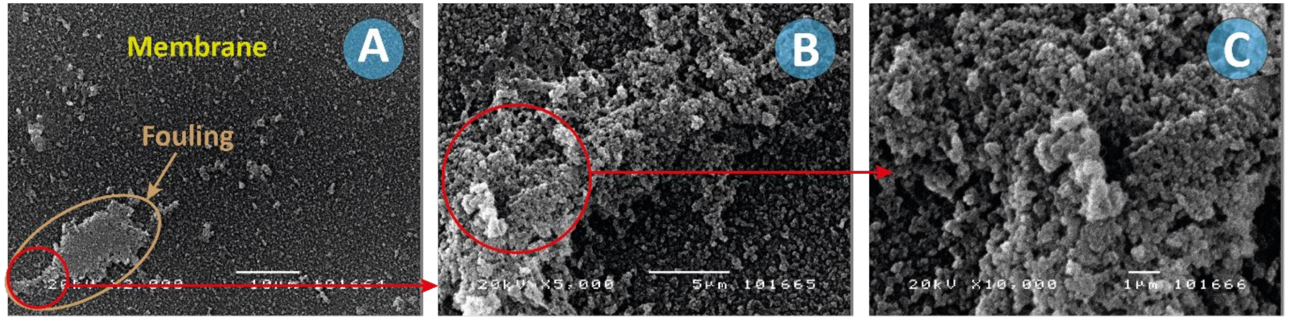
Results (fouling visualization)

Scaling under electron microscope



A = x2000, B = x5000 and C = x10000

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Results: Destruction

Chemical element	Symbol	Amount [µg/cm²]	
		Clean Coupon	Fouled Coupon
iron	Fe	0.41	0.73
Silicon (Silica)	Si	28 (60)	100 (214.29)
Calcium	Ca	1.7	0.061
Magnesium	Mg	0.09	0.12

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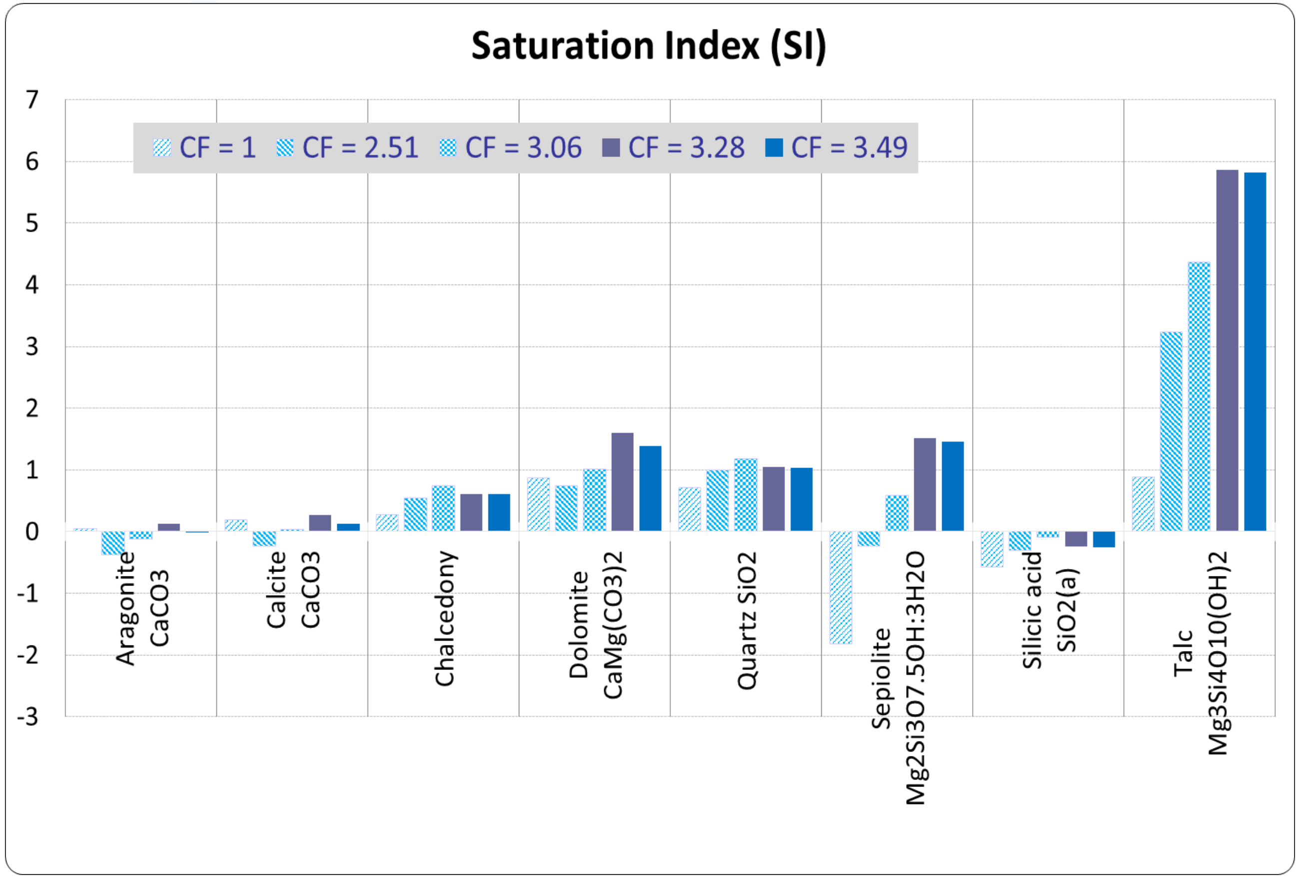
Results (PhreeqC)



The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

ZERO BRINE

Conclusions

In absence of divalent hardening ions, the brine of RO can be thickened to 3.5 times its initial value

In the absence of divalent cations, silica scaling happens a concentration higher than 120 mg/L.

In higher concentration of divalent ions, mostly silica-magnesium polymers are oversaturated

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Frithjof Kuepper
Professor
University of Aberdeen

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Dr. Frithjof Küpper is a Professor (Chair in Marine Biodiversity) at University of Aberdeen since 2011. He has served as Head of the Culture Collection of Algae and Protozoa (CCAP) at the Scottish Association for Marine Science in addition to other postdoc and research positions in the US and Germany. He has 109 ISI-listed, peer-reviewed papers including publications in Nature and PNAS, 5 book chapters, and a long track record in algal halogen research.

Eleni Avramidi
Environmental Engineer & PhD candidate
University of Aberdeen

ZERO BRINE

Benthic biodiversity and environmental gradients of the Port of Rotterdam: A unique estuarine system with strong human impact

Frithjof Kuepper, Professor (Chair in Marine Biodiversity), School of Biological Sciences, University of Aberdeen

Eleni Avramidi, Honorary Research Assistant and PhD candidate, School of Biological Sciences, University of Aberdeen

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Objectives

Assess the **ecological quality status of the Port of Rotterdam** and in particular of **Evides DWP Botlek** in the Brittaniëhaven area and **Evides DWP Maasvlakte** in Hartelkanaal area due to **brine discharge-related activities.**

FOCUS ON

Benthic macroinvertebrates

SUPPLEMENT

Physical and chemical characteristics of seabed and aquatic environment

Ideal bioindicators due to their sensitivity to water quality and inability to escape a disturbance once settled

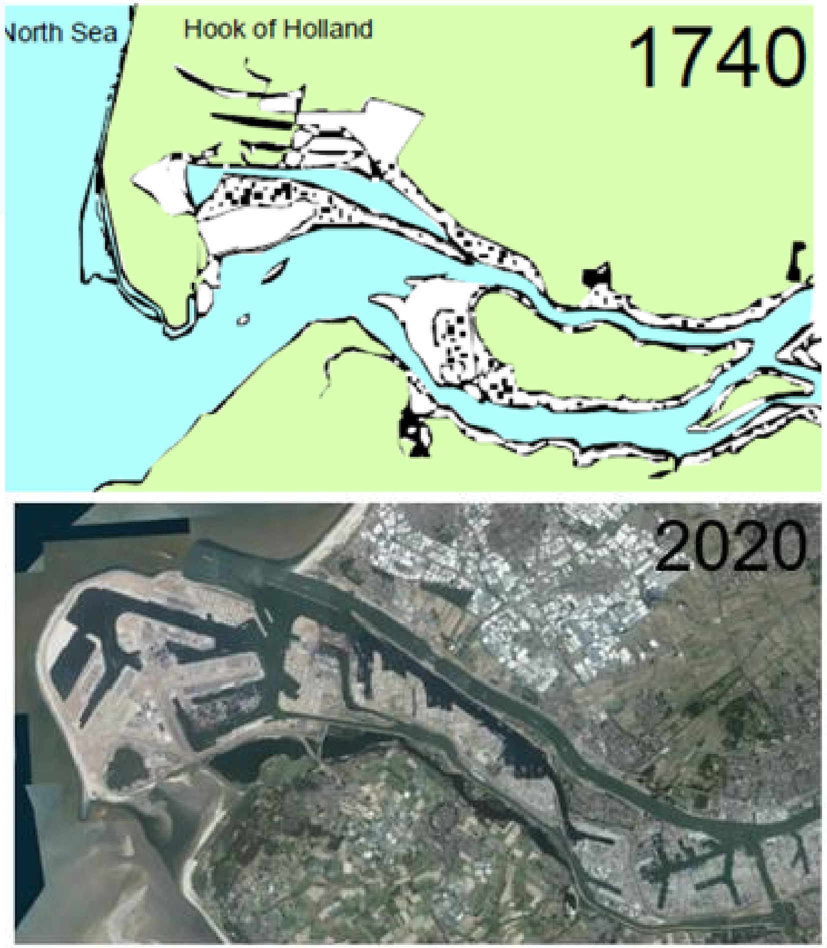
&

Biological quality element in Water Framework Directive 2000/60/EC (**WFD**) and Marine Strategy Framework Directive 2008/56/EC (**MSFD**) for the assessment of the ecological quality status of a water body.

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Port of Rotterdam – Manmade estuarine environment

ZERO BRINE



1960-1970

The pollution of the Port of Rotterdam was severely **degrading the ecosystem**, reducing biodiversity to a low number of pollution-tolerant species (Wolff, 1978).

1978

Rhine Action Programme (RAP) introduced by the International Commission **for the Protection of the Rhine** (ICPR) in 1987, a year after the Sandoz chemical accident (ICPR. International 2021).

2000

European Parliament and the European Council adopted the **WFD** with the purpose to establish a framework **for the protection of European waters.** For artificial water bodies, like the Port of Rotterdam, the WFD stipulates that Member States shall protect and achieve **good ecological potential and good chemical status by 2015, with extensions to 2021 and 2027, respectively.**

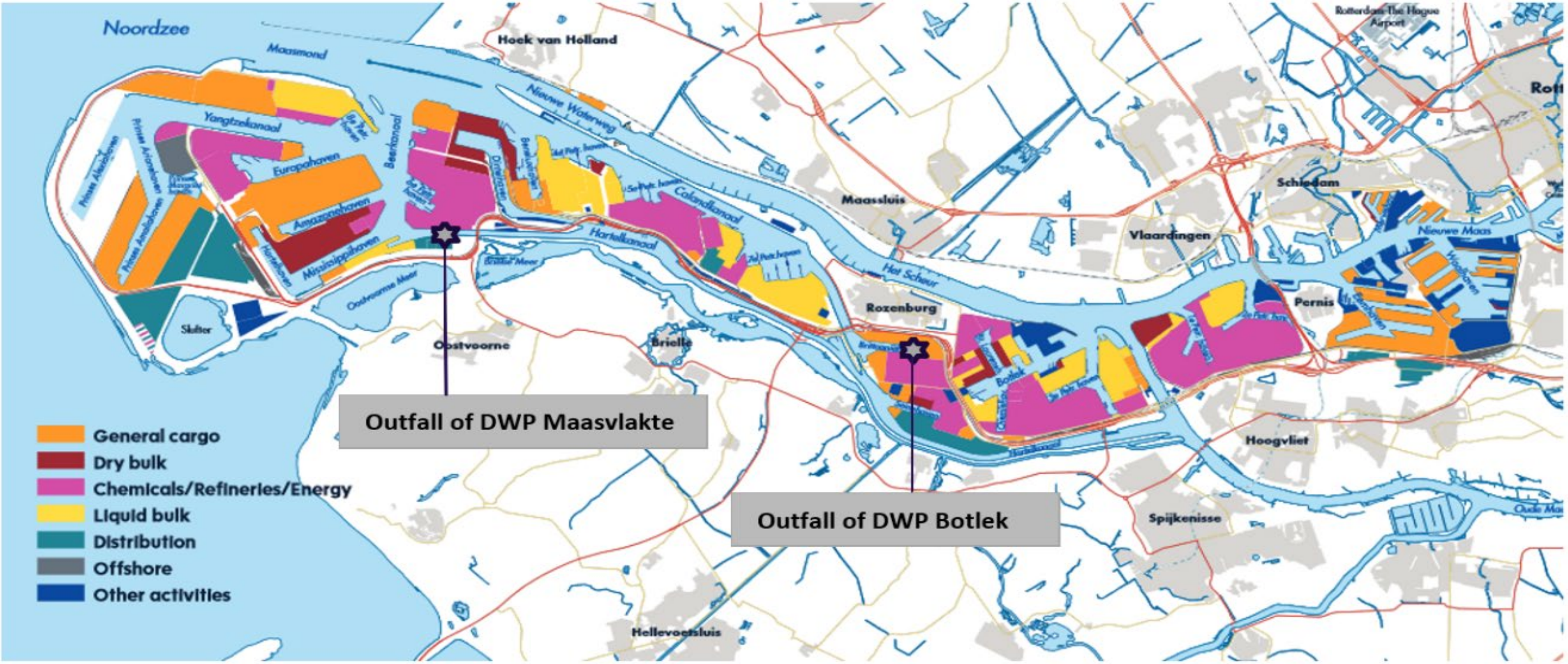
During more recent years, the pollution status of the Rhine and of many of its tributaries has **distinctly improved**

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Port of Rotterdam – Manmade estuarine environment

- Highly industrialized
- Europe’s largest seaport in 2015
- 29,491 seagoing vessels & 85,969 inland vessels in 2019

Distribution of activities in the Port of Rotterdam (Source: P.o.R Authority, 2019)

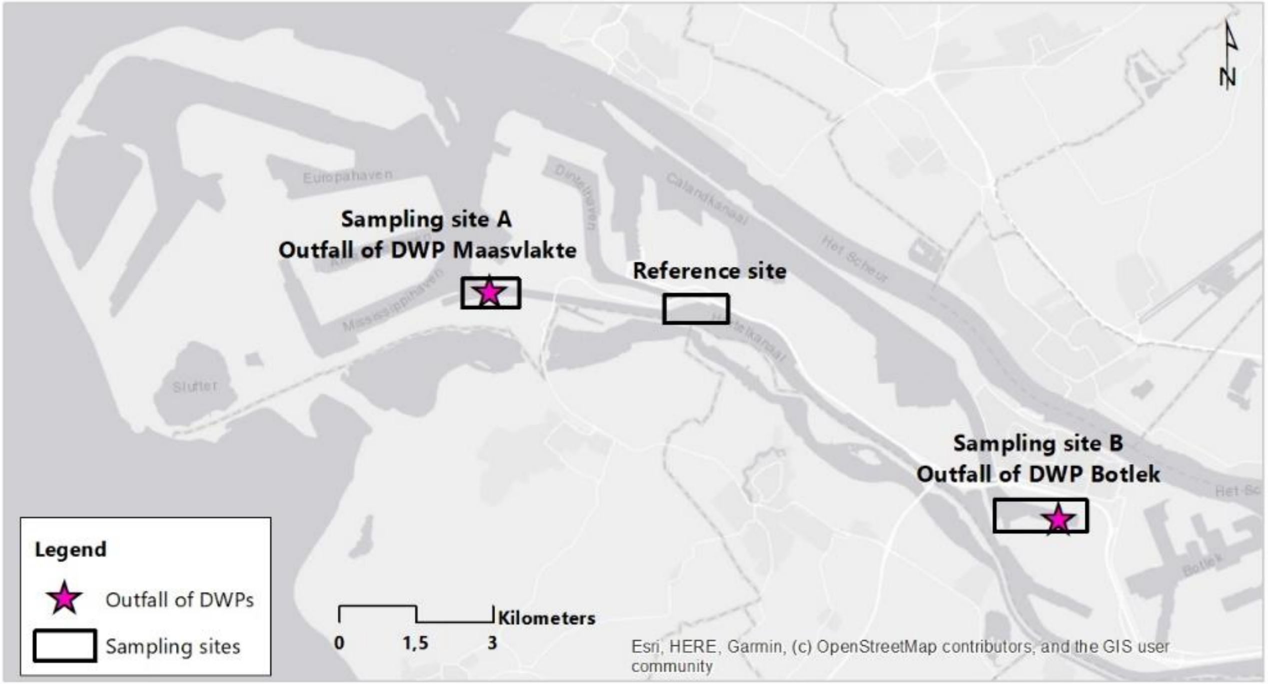


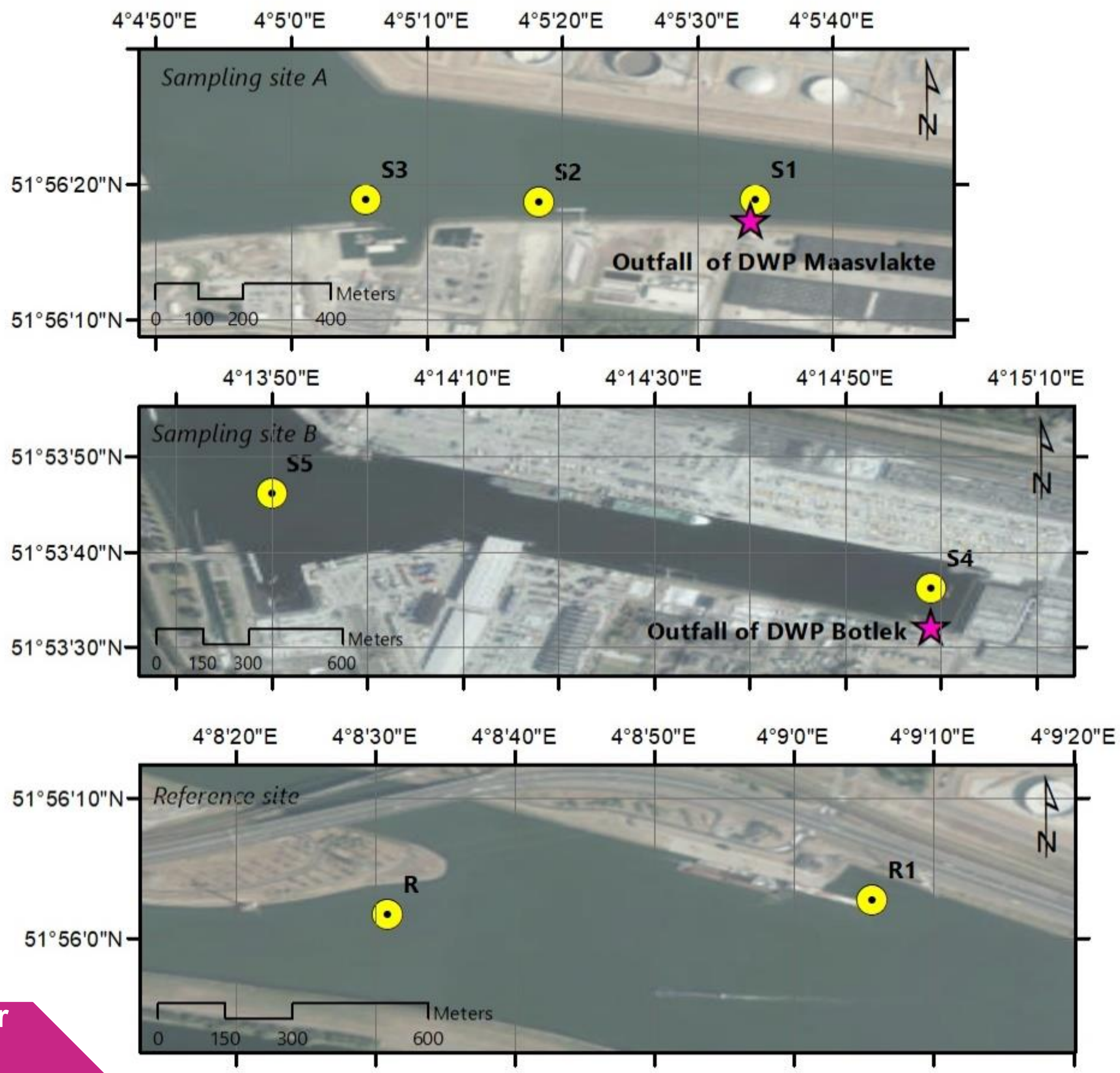
The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 730390.

Methods - Sampling stations

ZERO BRINE

3 sites and **6 stations** were selected and established for the survey.





September 2019 — 1st sampling survey

January 2020 — 2nd sampling survey

April 2021 — 3rd sampling survey

September 2021 — 4th sampling survey

Service layer credits: Source: ESRI, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AeroGRID, IGN, and the GIS User Community.

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Methods - Characteristics of sampling sites

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Sampling site A
Hartelkanaal
DWP Maasvlakte

- Inherently variable salinities,
- Well flushed environment,
- Seabed consists of *Crassostrea gigas* reef,
- Depth around 6-8 meters depending on the tide conditions.

Sampling site B
Brittaniehaven
DWP Botlek

- Dead-end waterway, poorly flushed environment,
- Has no river input and is entirely marine,
- Receives also effluent form Huntsman WWTP and Wilmar oil refinery processing vegetable oils,
- Seabed mainly silt,
- Depth around 10 meters.

Reference site

- Has been selected following the advice of the Port of Rotterdam Authority as the less polluted site in the port,
- Naturally changing salinities,
- Seabed mainly sandy, depth around 9-13 m.

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Methods – Field sampling and laboratory analysis – Benthic macroinvertebrates

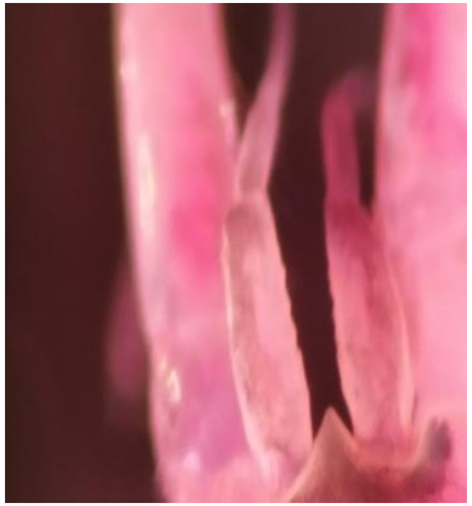
Collection of sediment using a **Van Veen grab**.

3 replicates at each station of 4lt sediment

Sediment samples were **sieved through a 0.5 mm mesh, stained with Rose Bengal and preserved in ethanol.**

In the laboratory, **macrobenthic invertebrates were sorted, identified** to the **lowest taxonomic level possible**, and counted.




The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Methods – Field sampling and laboratory analysis – Water and sediment

Water samples

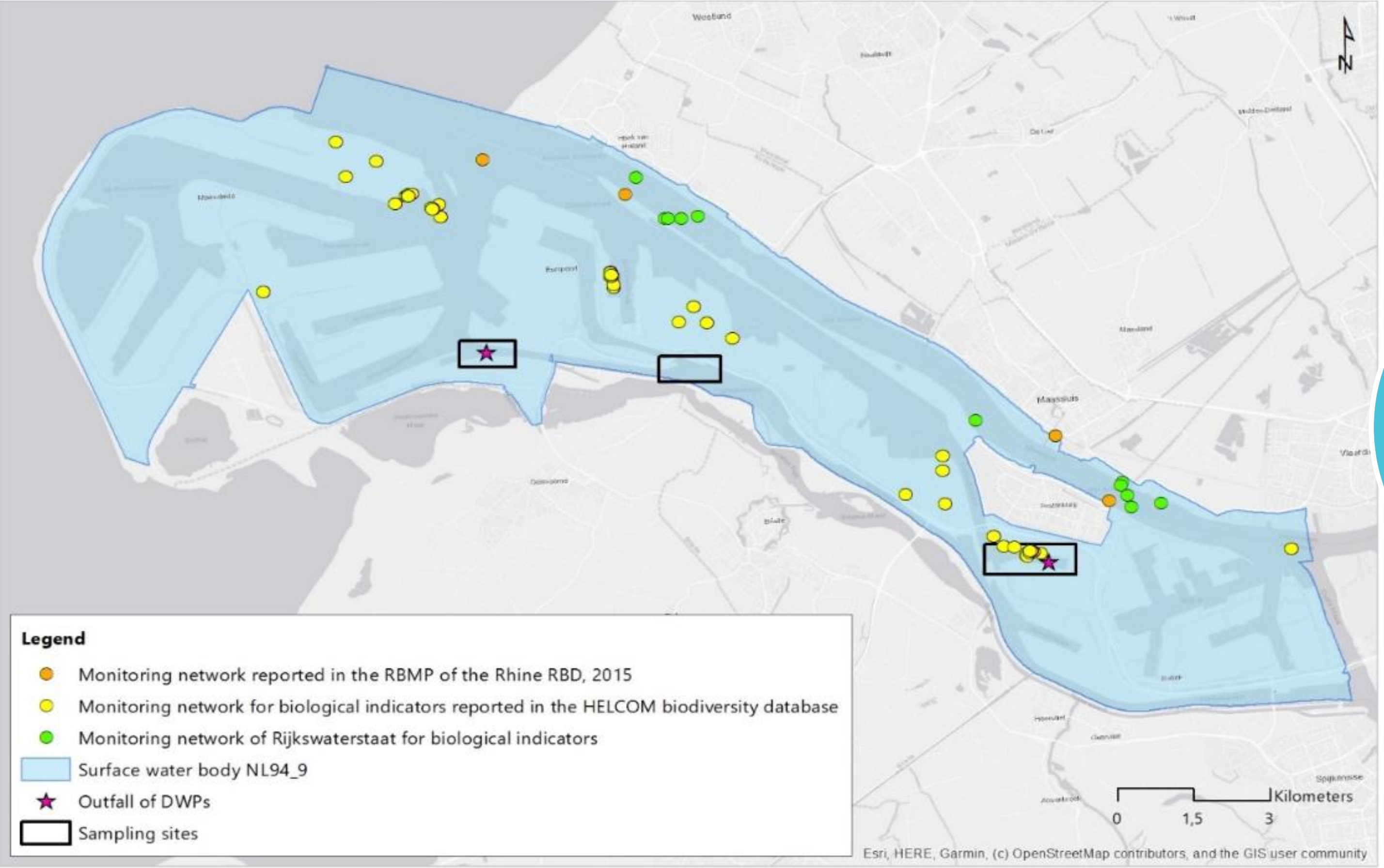
- **Collected from 3 stations out of 6** (S1, S4, and R).
- Collected from a **depth of 1.5 m** from the water surface.
- Analysed for **Ph, EC, TSS, nutrients, a suite of heavy metals, and 16 PAHs.**

Sediment samples

- **Collected from 3 stations out of 6** (S3, S4, and R).
- Collected with a **Van Veen grab**.
- **Granulometric analysis, TOC, Kjeldahl nitrogen, a suite of heavy metals and 16 PAHs content.**

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Methods- Existing monitoring data from Rijkswaterstaat and HELCOM



Existing monitoring data

HELCOM Biodiversity database 2004-2020

Benthic invertebrates, phytoplankton, macrophytes, fish and lamprey, and bacteria.

Rijkswaterstaat 2003-2019

Phytoplankton, diatomeae and macrozoobenthos, water physical and chemical parameters.

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Results – Brine characteristics

DWP effluents (2 streams)

IEX effluent

- **high salinity and density**, **ambient seawater temperature**, **low nutrient content**, **elevated levels of** chloride (Cl), TDS, bicarbonate (HCO^{-}_{3}), sulphate (SO^{3-}_{4}) elevated levels of chromium (Cr), aluminum (Al), copper (Cu), zinc (Zn), barium (Ba) and lead (Pb).

RO effluent

- **high salinity and density, ambient seawater temperature, low nutrient content, elevated levels** of chloride (Cl), TDS, bicarbonate (HCO^{-}_{3}), sulphate (SO^{3-}_{4}), elevated levels of lithium (Li) and boron (B).

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Results – Existing monitoring data from Rijkswaterstaat – Ecological and chemical status reported in RMBP 2015

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Port of Rotterdam (SWB NL 94_9),
Info from the **River Basin Management Plan of Rhine, 2015**

Ecological potential
MODERATE

Phytoplankton, phytobenthos / macrophytes and macrozoobenthos
GOOD

Fish fauna
Moderate

Chemical status
NOT GOOD

The **most significant pressure** is due to **introduced species and diseases** (invasive alien species).

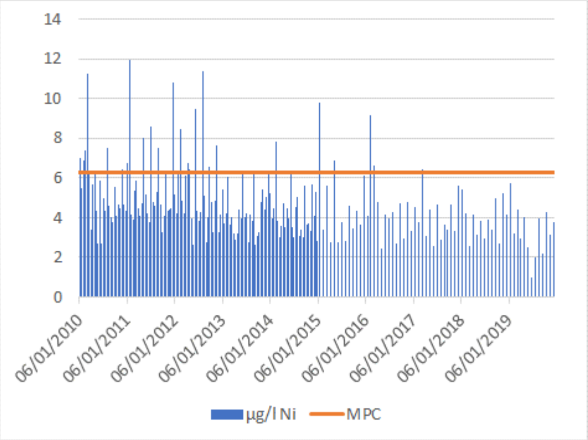
The **most significant impact** is **elevated temperature.**

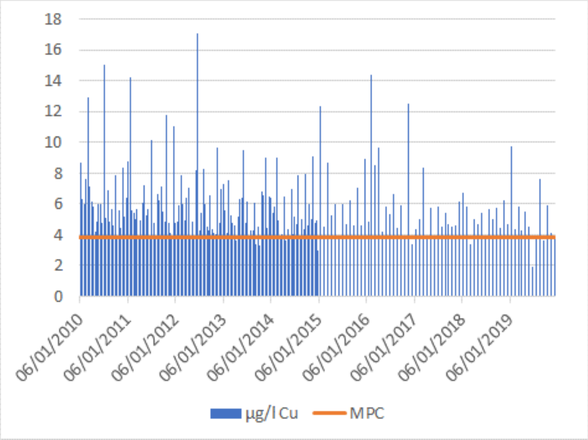
"Good" ecological potential and "good" chemical status **will not** **be achieved in 2021 but it is expected to be achieved beyond 2027.**

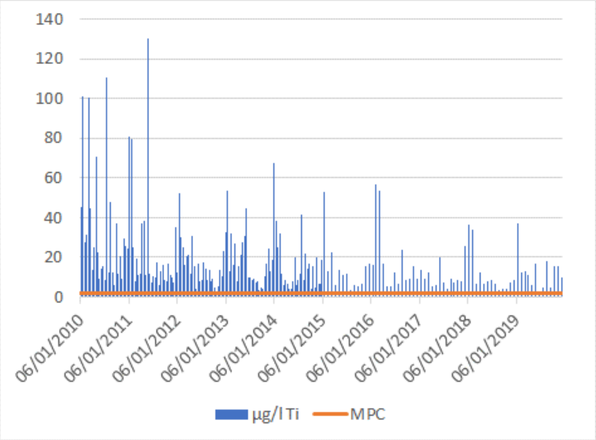
The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Results – Existing monitoring data from Rijkswaterstaat – Water quality (2010-2019)

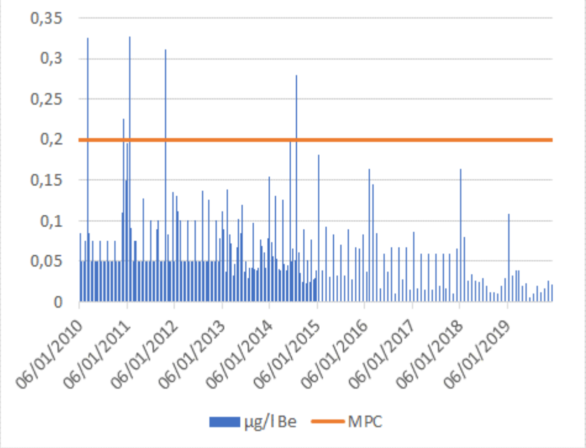
ZERO BRINE

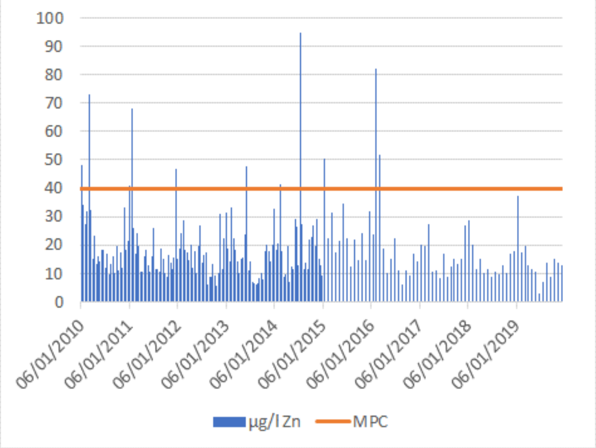


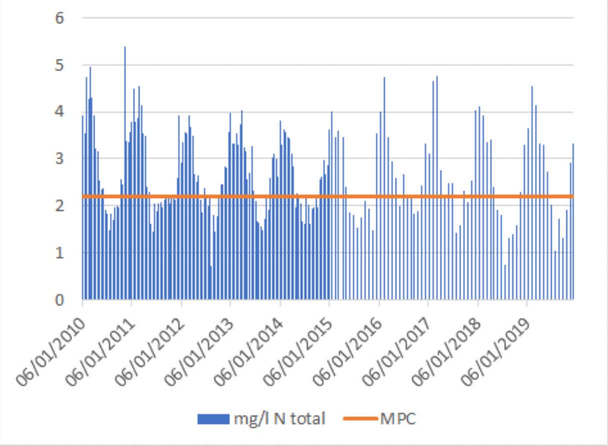


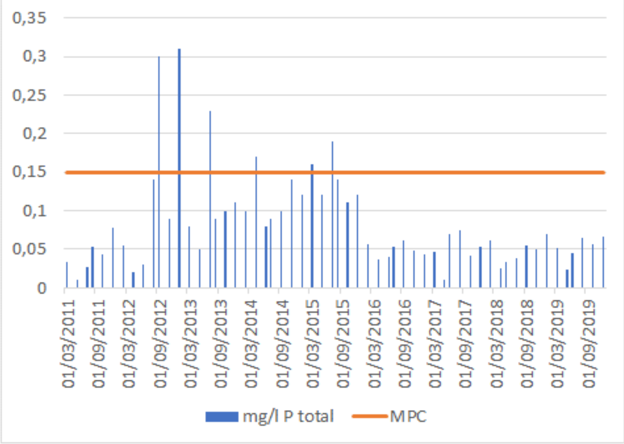


Timeseries of concentrations of metals and P_T, N_T (2010-2019, monitoring stations BEERKNMDN, MAASSS) that have exceeded the Maximum Permissible Concentration (MPC) set in the Staatcourant, The Netherlands, June 2000.









The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Results – Existing monitoring data from Rijkswaterstaat & HELCOM database – Benthic macroinvertebrates (2003-2016 & 2014)

Several non-native species with significant number of individuals have been recorded in the Port of Rotterdam.

Non-native species may have been introduced by shipping and ballast waters and lead to competition with native biota such as in the case of the native *Mytilus edulis* that has been put under competitive pressure by the invasive Pacific oyster, *Crassostrea (Magallana) gigas*.

Port of Rotterdam (SWB NL 94_9)

Benthic macroinvertebrates

Rijkswaterstaat period 2003 – 2016

208 species and 77968 individuals have been recorded.

HELCOM database for the year 2014

82 species and 935 individuals have been recorded.

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Results – Benthic macroinvertebrates communities – Number of species and individuals

ZERO BRINE

Capitella capitata, WoRMS Photogallery

In total, **1761 individuals** were identified belonging to **89 species**.

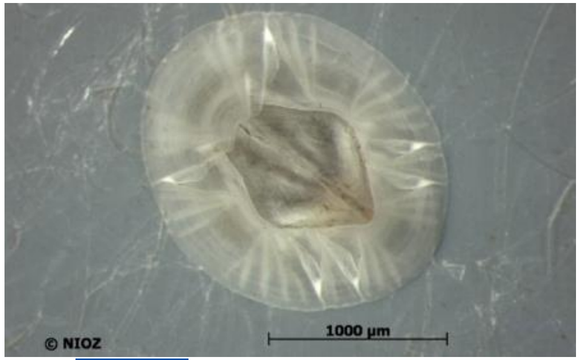
14 species are <u>**non-native**</u> with <u>**1573 individuals**</u> counted.

<u>Most individuals</u> in Hartelkanaal (DWP Maasvlakte):
- **Non-native *Balanidae Amphibalanus*** (small sessile crustacean),
- **Native Capitella capitata** (Class Polychaeta).

<u>Large abundance</u> of the **non-native crustacean *Crassostrea gigas*** at Site 1, just under one of the outfalls – **FULL SCALE REEF**

<u>Most individuals</u> in Brittaniehaven (DWP Botlek):
- **Native *Capitella capitata*** (Class Polychaeta)
- **Native *Streblospio cf shrubsolii*** (Class Polychaeta)
- **Non-native *Theora lubrica*** (Class Bivalvia)

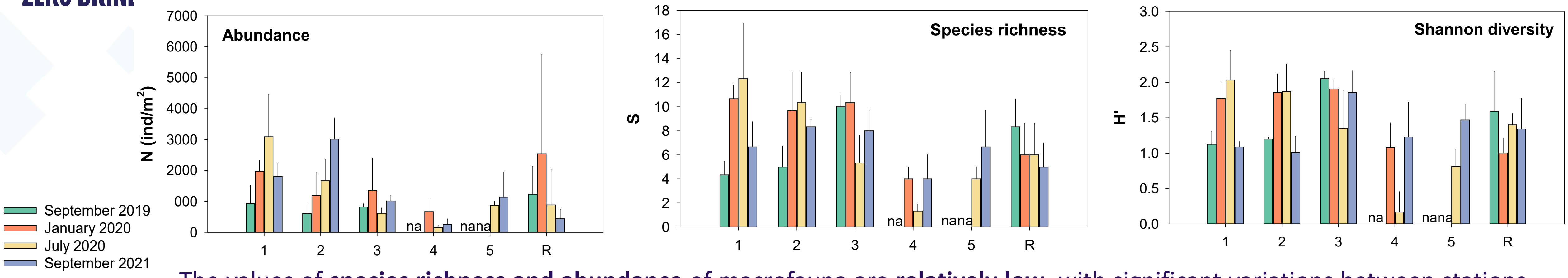
Amphibalanus **(Balanidae) WoRMS Photogallery**



***Crassostrea gigas*,** *Photo credits: Eleni Avramidi*

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Results – Benthic macroinvertebrates communities – Species richness, abundance and diversity



The values of **species richness and abundance** of macrofauna are **relatively low**, with significant variations between stations and sites.

Overall, **the highest species richness and abundance** was recorded at **stations in Hartelkanaal** and was mostly related with sessile animals from hard substrate. In the replicates with the highest numbers, more than half of the individuals belonged to the Family Balanidae (barnacles) or other hard substrate bivalves (mussels), which probably grew on the *Crassostrea gigas* reef or fall off the ships.

Diversity values are **noticeably low**, always below 2 and closer to 1 in many occasions, yet **due to the lack of dominance of few species and the overall disturbance status.**

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Results – Benthic macroinvertebrates communities – Biotic index AMBI

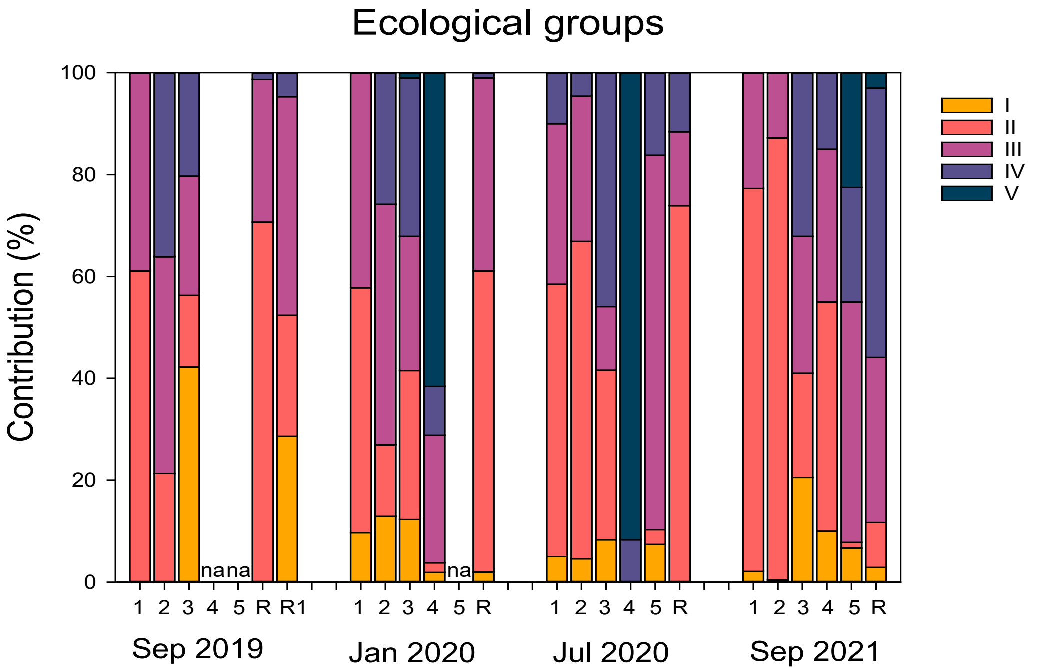


Fig. Contribution of the ***AMBI distinct ecological groups*** *for the stations sampled on each sampling occasion. The* ***contribution of groups IV and V, more tolerant to perturbations, only dominate in a few samples mainly of 4 and 5 sites****. na: no samples available.*

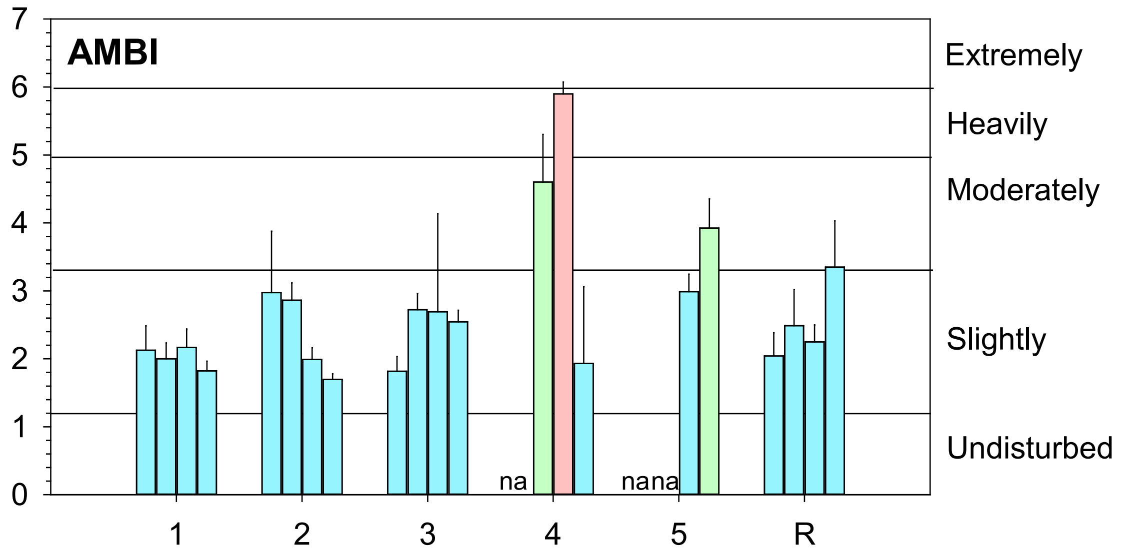


Fig. AMBI index for the sampled stations in the three surveys. The classification of ecological status for the sampling points according to the AMBI index is indicated on the right side.

The results **in the majority of the cases showed a slightly disturbed system** and **stations 4 and 5 were characterised on occasions as moderately or heavily disturbed.**

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Results – Water and sediment quality analysis

<u>TOC and Kjedahl nitrogen</u> values in sediment samples

<u>Higher</u> at Brittaniehaven (S4) in comparison to Hartelkanaal (S1 and R)

Result of the **decomposition of biomass of plant, animal or planktonic origin and / or anthropogenic sources**.

Correlates with the **<u>reduced species richness</u> to this station as an overabundance of organic matter**.

<u>Heavy metals</u> in sediment samples

<u>Higher</u> at Brittaniehaven (S4) in comparison to Hartelkanaal (S1 and R)

Result of **atmospheric deposition of air emissions from industrial processes and discharge of metal containing effluent without adequate treatment**.

Correlates with the **<u>presence of tolerant benthic macroinvertebrates species</u>** in this area.

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Conclusions

This study has established a **baseline understanding of the environmental conditions** in the vicinity of DWPs Botlek and Maasvlakte.

Provides essential **background information for the assessment of environmental benefits** from the implementation of **large scale zero brine technology in the future.**

A remarkable diversity of taxa has been observed, enabling a detailed characterization of biological communities, which constitutes a significant asset considering how little published literature exists about the unique system of the Port of Rotterdam.

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Conclusions

ZERO BRINE

Similar macrobenthic composition, although with a <u>lower</u> abundance and diversity in comparison with nearby environments of the **North Sea**

The invasive species present and the negative biodindicators is comparable to what has been observed in similarly impacted areas previously.

Monitoring periodically the area to detect any potential impact of the desalination plant in the long term.

High distribution of the non-native *Crassostrea gigas* just under the outfalls of DWP Maasvlakte.

Study the reason behind the larger abundances of *C. gigas* at Site 1

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Acknowledgements

- **Dr. Sokratis Papaspyrou**, Associate Professor at Universidad de Cádiz, for his valuable formal analysis of benthic invertebrate results.

- **Sergio Carlos Garcia Gomez**, invertebrate zoologist and analyst of benthic macrofauna species.

- **Port of Rotterdam Authority** for providing access to the Tender and Survey vessel 2, sharing necessary information and data, and providing support during the field work and especially during the survey of July 2020 performed amidst COVID-19 pandemic. Specifically, we would like to thank Chris Schot (Constructions & Dredging Asset Manager), Ed de Boom (Planner Baggerwerk), Robbert Wolf (Nature and environmental advisor), and the crew Peter Mourik, Edwin Smit, Leo de Jong, Daan Koornneef, and Ed Veth.

- **Rijkswaterstaat of the Dutch Ministry of Infrastructure and Water Management** for providing monitoring data of the environmental quality in the Port of Rotterdam.

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Marc Arpad Boncz

Associate Professor

UFMS (Brazil)

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Dr. Marc Arpad Boncz is Associate professor at UFMS (Brazil) with degrees in Chemistry from VU Amsterdam and a PhD in Environmental Technology (WUR).
He works on projects on industrial and domestic wastewater treatment (anaerobic, microalgae) with a special interest in bioenergy and in water and resource conservation.
He worked a post-doc in 2017-2018 at TU Delft, contributing to Zero Brine project.

Physicochemical model for simulating the chemical processes during the crystallization of minerals from spent Ion Exchange Regenerant

Marc Arpad Boncz[1,2], Niels van Linden[1,3], Amir Haidari[1,4], Yundan Wang[1,5] and Henri Spanjers[1]

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3 Lenntech B.V., Distributieweg 3, 2645 EG, Delfgauw, the Netherlands.
4 Hatenboer, Mercuriusweg 8, 3113 AR, Schiedam, the Netherlands.
5 Arcadis Consultancy (Shanghai) Co. Ltd., 11th Floor, Building C, The Place, No.150 Zunyi Road, Changning District, 200051, Shanghai, PR China.

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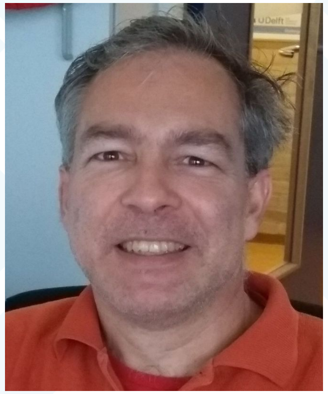

About the author...

- Dr. Marc Arpad Boncz, associate professor, UFMS (Brazil) u

- Chemist (VU Amsterdam), PhD in Environmental Technology (WUR)
  - at UFMS since 2006, professor since 2013
  - projects on industrial and domestic wastewater treatment (anaerobic, microalgae), special interest in bioenergy and in water and resource conservation
  - post-doc in 2017-2018 at TUDelft, contributing to Zero Brine project

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About the Zero Brine project

- Objectives:
  - Closing water cycles and recovery of materials from waste streams

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About the project

- Demineralised water plant in Rotterdam
  - discharges (daily) significant volume of spent IEX regenerant
  - main compound in regenerant is NaCl, significant amounts of Mg^{2+} and Ca^{2+}
  - *hardly any other pollutants*

  - **this should permit recovery of these ions**

- Technologies to be used:
  - nanofiltration, to separate mono and multivalent ions
  - sequential crystallisation
  - evaporation

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About the project

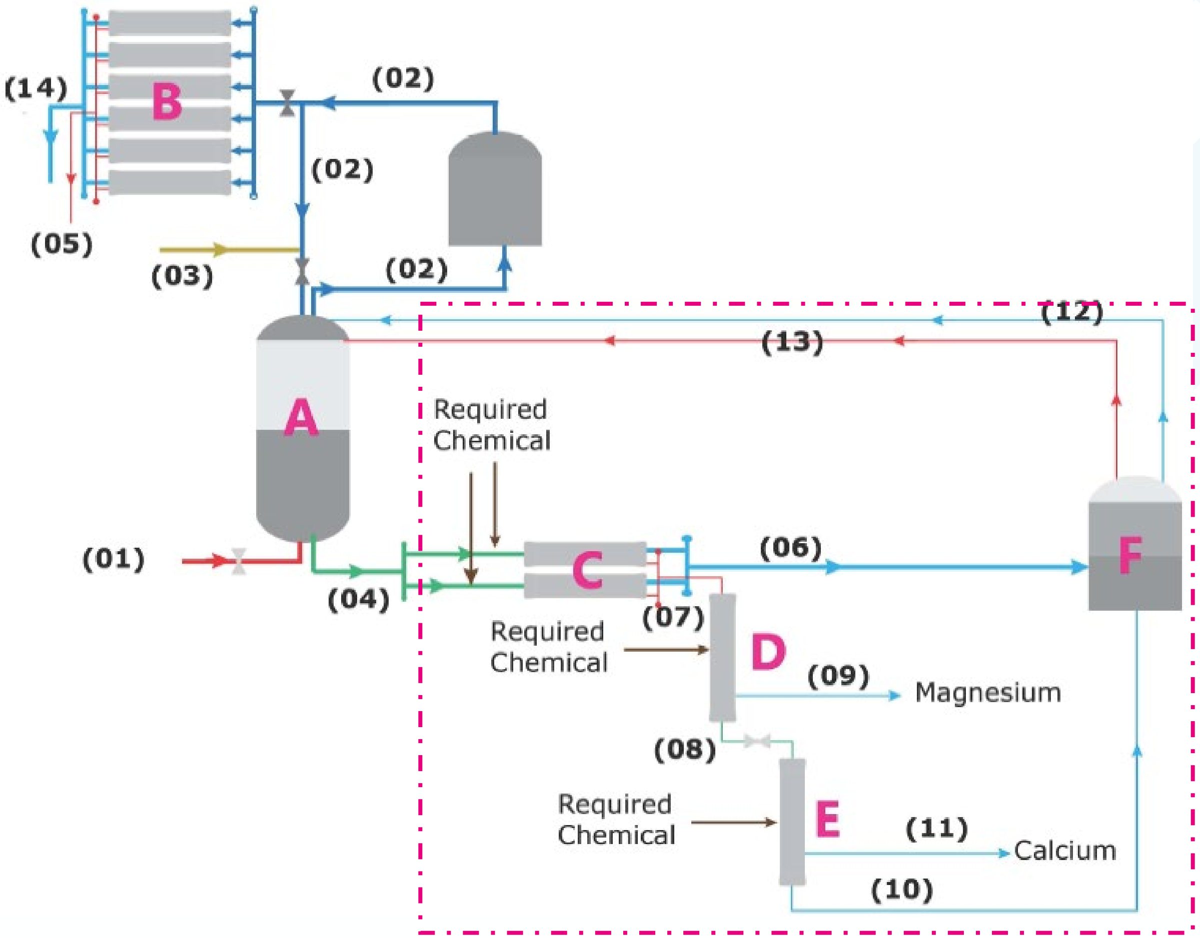
Process overview

processes:

A IEX ion exchange columns (existing)
B RO reverse osmosis units (existing)
C NF nanofiltration unit
D,E CU crystallisation units
F EV evaporator unit

flows:

04 spent IEX regenerant (brine)
06 NF permeate
07 NF concentrate
08 Mg-crystrallisation supernatant
10 Ca crystallisation supernatant
12 distilled water
13 NaCl concentrate



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Objectives of PHREEQC modelling project

- Determine feasability of Mg^{2+} and Ca^{2+} recuperation
- Quantify amount that can be recuperated
- Quantify purity of product
- Study effect of process and flows on results

Methodology

- Analysis of spent IEX regenerant brine
  - metals: ICP-MS
  - anions: IC
  - pH, temp, TSS

- Modelling suggested process
  - Excel: calculating starting situation and analysing simulation results
  - PHREEQC: chemical equilibria and precipitation of minerals; 4 assumptions:
    - neglect elements with concentration < 1 μg/L
    - exclude Co and Mo (not included in PHREEQC's Minteq database)
    - for SO_4^{2-}, PO_4^{3-}: ICP-MS concentrations used rather than (lower) IC results
    - assumed: initially no supersaturation

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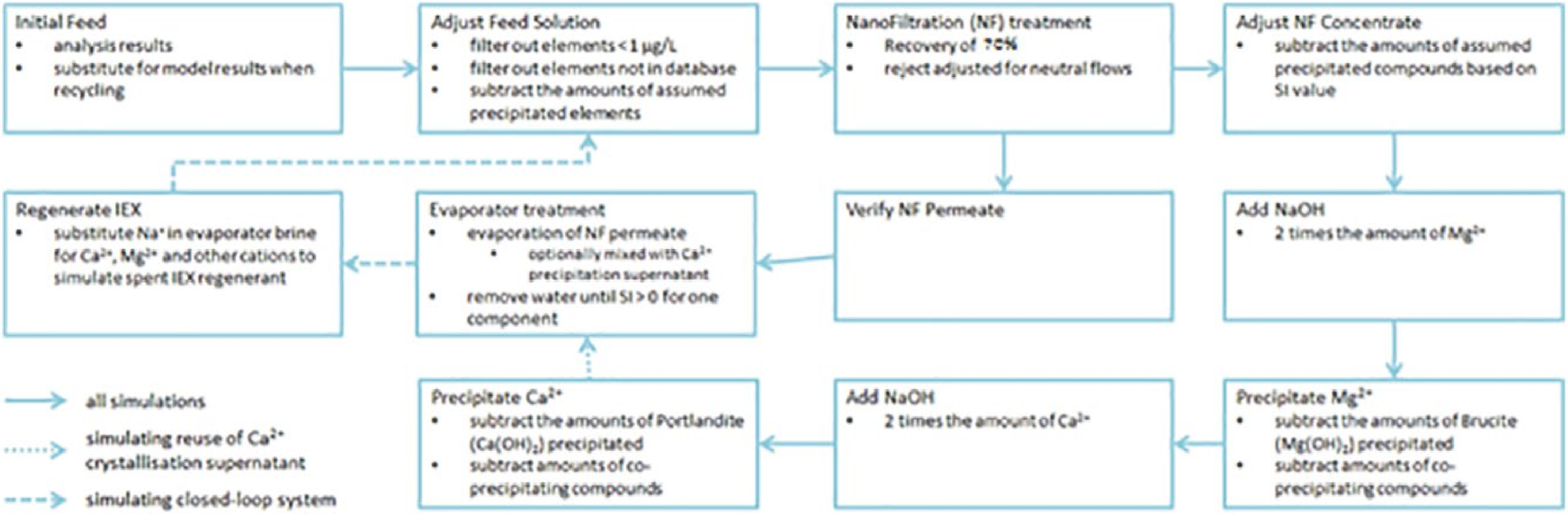
Methodology

- Modeling approach



Results: spent IEX regenerant

- Spent IEX regenerant composition
  - main compound in regenerant is NaCl, significant amounts of Mg^{2+} and Ca^{2+}
    - 98% of cations.
    - Cl- is > 97% of anions
  - hardly any other pollutants
    - TSS as calculated even slightly higher than measured

Cations		MW g/mol	Concentration[1,2] (mM)		Anions		MW g/mol	Concentration[1,2] (mM)	
			sample 1	sample 2				sample 1	sample 2
Calcium	Ca^{2+}	40.1	162.63	206.40	Chloride	Cl^{-}	35.5	528.99	808.78
Iron	Fe^{3+}	55.8	0.005 56	0.420	Fluoride	F^{-}	19.0	.< DL	.< DL
Magnesium	Mg^{2+}	24.3	51.28	55.15	Bromide	Br^{-}	79.9	.< DL	.< DL
Potassium	K^{+}	39.1	6.03	5.12	Nitrite	NO_2^{-}	46.0	.< DL	.< DL
Sodium	Na^{+}	23.0	99.96	349.49	Nitrate	NO_3^{-}	62.0	-.-	-.-
Aluminum	Al^{3+}	27.0	0.000 072	.< DL	Phosphate	PO_4^{3-}	95.0	0.02	0.30
Antimony	Sb^{5+}	121.8	0.000 004	0.000 081	Sulphate	SO_4^{2-}	96.1	1.55	34.10
Barium	Ba^{2+}	137.3	0.025 9	0.036 1	Silicate	SiO_4^{4-}	92.1	0.03	.< DL
Beryllium	Be^{2+}	9.0	.< DL	.< DL	Bicarbonate	HCO_3^{-}	61.0	2.34	2.29
Cadmium	Cd^{2+}	112.4	0.000 002	.< DL					
Cobalt	Co^{2+}	58.9	.< DL	0.000 469					
Copper	Cu^{2+}	63.5	0.000 53	.< DL					
Chromium	Cr^{3+}	52.0	0.000 27	0.001 59					
Lead	Pb^{2+}	207.2	.< DL	0.000 28					
Lithium	Li^{+}	6.9	0.017 1	0.020 2					
Manganese	Mn^{2+}	54.9	0.000 26	0.01					
Molybdenum	Mo^{4+}	95.9	0.000 015	0.000 14					
Nickel	Ni^{2+}	58.7	0.003 5	0.021 3					
Silver	Ag^{+}	107.9	.< DL	0.000 018					
Strontium	Sr^{2+}	87.6	0.342	0.478					
Titanium	Ti^{2+}	47.9	0.000 002	0.001 35					
Thallium	Tl^{3+}	208.4	.< DL	.< DL					
Vanadium	V^{5+}	50.9	0.001 7	0.016 7					
Zinc	Zn^{2+}	65.4	0.001 5	.< DL					
Total Dissolved Solids (TDS)[3]			**29 382** *29 139*	**50 038** *46 176*	**mg/L** *mg/L*		**pH**	**7.26**	**7.10**

1: for simulations, all elements assumed to be present in the form of the ion most abundant in aerated surface water, as listed; 2: .< DL: below detection limit (generally < 1 µg/L), 3:TDS as **sum of all ions** (calculated) and *as measured*.

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Results: nanofiltration

- Some risk of scaling in NF unit
  - but not a good idea to use antiscalants due to recycling

Species		Sample 1		Sample 2	
name	formula	SI	Precip. (M)	SI	Precip. (M)
Anhydrite	$CaSO_4$			0.72	2.38E-02
Aragonite	$CaCO_3$	0.51	3.20E-04		
Barite	$BaSO_4$	1.05	1.02E-05	0.45	
Calcite	$CaCO_3$	0.65			
Dolomite	$CaMg(CO_3)_2$	0.94			
Gypsum	$CaSO_4 \cdot 2H_2O$			0.65	
Hydroxyapatite	$Ca_5(PO_4)_3OH$	10.53	1.44E-07	2.94	6.69E-06
Magnesite	$MgCO_3$				

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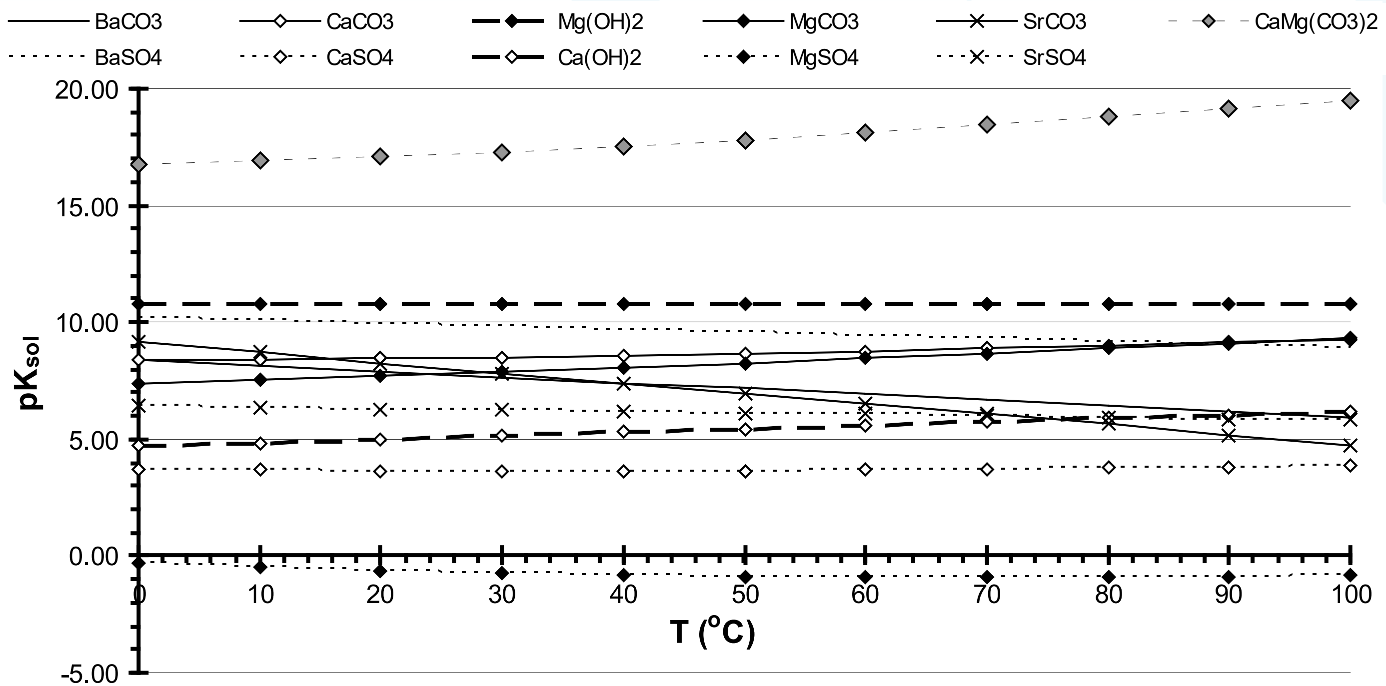
Results: crystallisation

- Salts to be precipitated
  - candidates: hydroxides, carbonates or sulphates
  - best: hydroxides
    - dosing of OH^-
    - stoichiometrically
    - 1st: $Mg(OH)_2$
    - 2nd: $Ca(OH)_2$



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Results: crystallisation

- Recovery of salts

Recovered ions	Sample 1		Sample 2	
	Mg-crystalliser	Ca-crystalliser	Mg-crystalliser	Ca-crystalliser
Mg^{2+} as $Mg(OH)_2$	60.0%	4.98%	70.2%	1.82%
Mg^{2+}, as other minerals				
Ca^{2+} as $Ca(OH)_2$		58.6%		63.4%
Ca^{2+}, as other minerals	0.54%		0.79%	

- Purity of recovered salts

Species		Mg-crystalliser (D)		Ca-crystalliser (E)	
		Sample 1	Sample 2	Sample 1	Sample 2
Barite	$BaSO_4$	0.000 20			
Brucite	$Mg(OH)_2$	6.52	8.75	0.54	0.23
Calcite	$CaCO_3$	0.32	0.56		
Hydroxyapatite	$Ca_5(PO_4)_3OH$	0.000 04	0.000 14		
Portlandite	$Ca(OH)_2$			25.80	32.91
Purity (mass fraction)		95%	94%	98%	99%

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Results: evaporation

- Without recycling crystallisation supernatant
  - 42% evaporated (distilled water)
  - 58% NaCl brine
    - not suitable for IEX regeneration
- Recycling crystallisation supernatant
  - 42 % evaporated (distilled water)
  - 58% NaCl brine
  - slightly more polluted
    - but with less Ca2+ and Mg2+
    - possibility of scaling: mmol/L of barite ($BaSO_4$), brucite ($Mg(OH)_2$) and Calcite ($CaCO_3$)

		NF Perm. + Crys. Eff		NF Perm.	
		Sample 1	Sample 2	Sample 1	Sample 2
pH		12.07	12.12		
Cations [mol/L]					
Sodium	Na	1.47E+00	2.50E+00	4.57E-01	1.31E-01
Calcium	Ca	8.64E-02	7.72E-02	1.34E-01	1.52E-01
Potassium	K	1.60E-02	1.43E-02	6.68E-03	7.88E-03
Strontium	Sr	1.08E-03	1.73E-03	3.56E-04	3.19E-04
Iron	Fe	1.75E-05	1.52E-03	3.13E-04	5.19E-06
Nickle	Ni	1.10E-05	7.71E-05	1.59E-05	3.26E-06
Vanadium	V	5.39E-06	6.05E-05	1.25E-05	1.59E-06
Lithium	Li	4.55E-05	5.63E-05	2.62E-05	2.25E-05
Manganese	Mn		3.61E-05	7.44E-06	
Chromium	Cr	8.51E-07	5.77E-06	1.19E-06	2.51E-07
Barium	Ba	4.82E-06	5.43E-06	1.12E-06	6.03E-06
Tellurium	Tl		4.99E-06	1.03E-06	
Lead	Pb		9.97E-07	2.05E-07	
Magnesium	Mg	8.73E-07	6.70E-07	4.11E-02	4.77E-02
Copper	Cu	1.68E-06			4.98E-07
Zinc	Zn	4.84E-06			1.43E-06
Anions [mol/L]					
Bicarbonate	HCO_3^-	1.65E+00	2.61E+00	4.77E-02	1.52E-03
Sulphate	SO_4^{2-}	5.99E-03	7.85E-03	3.28E-03	5.72E-04
Chloride	Cl^-	1.61E-05	2.24E-05	8.15E-01	5.44E-01
Phosphate	PO_4^{3-}	2.63E-11	2.67E-11	8.32E-07	4.70E-08

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Conclusions

- Recovery of Mg^{2+} and Ca^{2+} possible, but not complete
  - purity of Mg reasonable (≈ 95%), of Ca good (≈ 99%)
- Very strict control of hydroxide dosing is essential
- Complete recycle of water not possible, as this may cause scaling in evaporator and affects IEX regeneration brine quality

Krzysztof Mitko
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Dr. Mitko is an assistant professor at the Silesian University of Technology, Faculty of Chemistry. His research interests include electromembrane processes (electrodialysis, electrodeionization, membrane capacitive deionization); removal of metal ions from the waste waters; seawater, coal mine water and industrial wastewater desalination.

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Pilot studies on circular economy solution for the coal mining sector

Krzysztof Mitko, Marian Turek, Hanna Jaroszek, Ewa Bernacka, Mateusz Sambor, Paweł Skóra, Piotr Dydo

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

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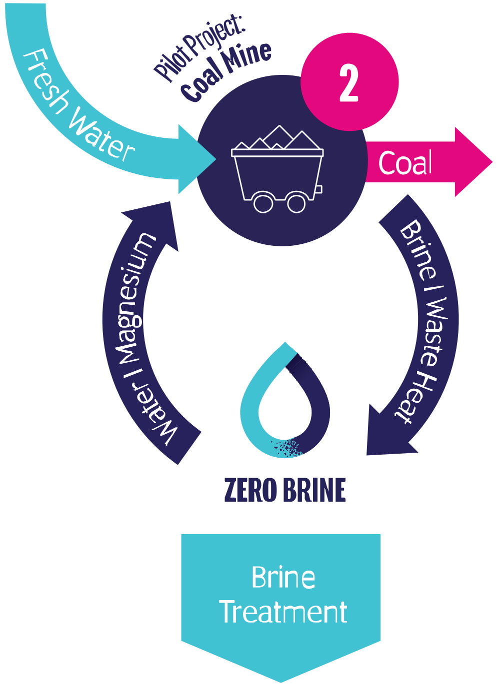
Polish case study

Coal mining generates vast amounts of saline waste water

The amount of discharged salt in Poland alone is ca. 4 million tons per year

The increase in river salinity damages the aquatic life, increases population water pressure and decreases the soil quality



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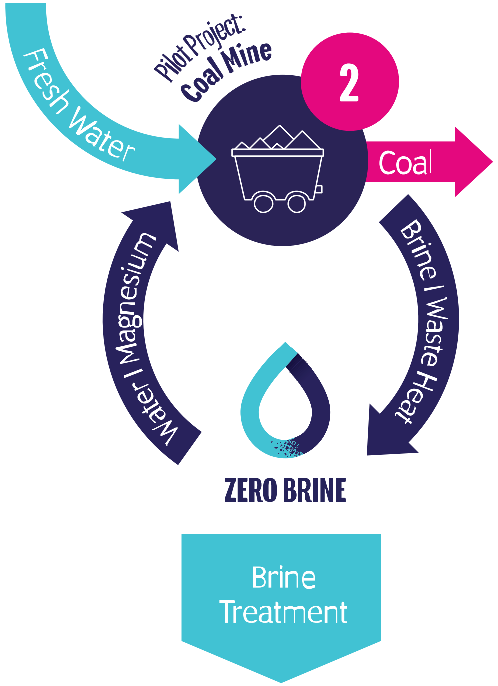
Goals

To demonstrate the principles of circular economy in the coal mining industry

To demonstrate decreased energy consumption compared to reference technolog



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Bolesław Śmiały coal mine water

Cl^- [mg/dm³]	13500	Mg^{2+} [mg/dm³]	263	NO_3^- [mg/dm³]	< 2.5	Li [mg/dm³]	0.4
Na^+ [mg/dm³]	8192	Ca^{2+} [mg/dm³]	248	B [mg/dm³]	2.32	Er [mg/dm³]	0.3
SO_4^{2-} [mg/dm³]	810	K^+ [mg/dm³]	120	Sr [mg/dm³]	1.58	Mn [mg/dm³]	0.1
HCO_3^- [mg/dm³]	301	NH_4^+ [mg/dm³]	< 2.5	Si [mg/dm³]	1.39	Zn [mg/dm³]	0.1

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Plant design

- Pretreatment: 200 µm slot filter, 50 µm bag filter, 25 µm candle filter, carbon filter, 5 µm candle filter
- Ultrafiltration: 8” UF module with membrane of MWCO90 < 0.03 µm
- Decarbonization: weak ion-exchangers with degassing column
- Two-pass nanofiltration, each NF pass consisted of two pressure vessels filled with two modules each (Trisep TS40 membranes)
- Reverse osmosis
- Two-stage electrodialysis: two PC-Cell 1000A electrodialyzers connected in a cascade, each containing 25 pairs of IONSEP K/A membranes separated with 0.35 mm spacers

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Nanofiltration

- nanofiltration can be safely operated at high permeate recovery (80%), without the observable scaling,
- two-pass nanofiltration system has shown very high rejection coefficients with respect two bivalent ions, even above 95%, and relatively low rejection coefficients of univalent ions

		Recovery in first-pass nanofiltration					
		NF2 retentate recycled			NF2 retentate not recycled		
		60%	70%	80%	60%	70%	80%
Rejection [%]	Cl^-	23.5%	6.6%	20.7%	20.5%	9.0%	3.9%
	SO_4^{2-}	98.4%	98.5%	98.1%	98.4%	97.3%	97.3%
	Na^+	20.2%	1.8%	16.5%	16.5%	4.8%	1.4%
	K^+	18.0%	4.0%	12.7%	14.8%	4.1%	6.3%
	Mg^{2+}	95.6%	98.6%	95.9%	95.6%	95.7%	96.0%
	Ca^{2+}	95.7%	89.2%	96.5%	93.9%	92.5%	90.3%

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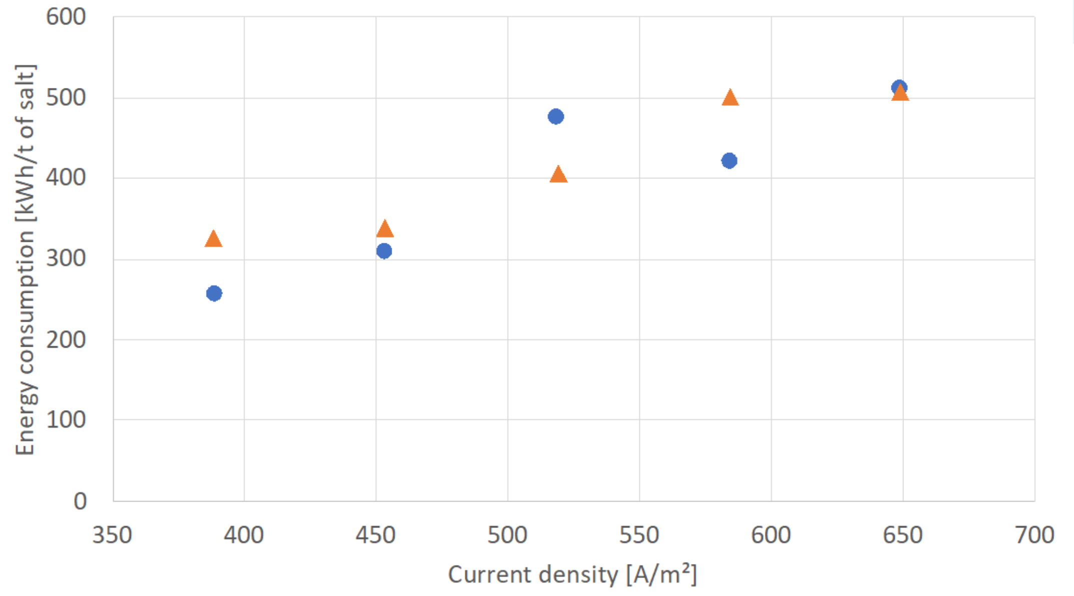
Electrodialysis

- ED working on the reverse osmosis retentate can exhibit relatively low energy consumption
- Additional evaporator might be required

Stream		Reverse osmosis retentate	Concentrate after 1st stage of ED cascade	Concentrate after 2nd stage of ED cascade
Concentration [mg/dm³]	Cl^-	28 517	95 800	111 000
	SO_4^{2-}	102	727	621
	Na^+	18 165	59 600	68 700
	K^+	664	649	1 190
	Mg^{2+}	16	< 50	< 50



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Comparison with reference technology

Technology	Energy consumption [kWh/m³ of treated brine]	Salt recovery [%]	Magnesium hydroxide recovery [%]	Water recovery [%]
“Dębieńsko”	16.7	81.0	0	92.4
“ZERO BRINE” coupled with “Dębieńsko” evaporator	12.9	56.9	96.7	75.7
“ZERO BRINE” coupled with modern evaporator and crystallizer	12.0	56.9	96.6	75.7
“ZERO BRINE” with intermediate gypsum precipitation and modern evaporator	11.2	92.8	94.9	90.6

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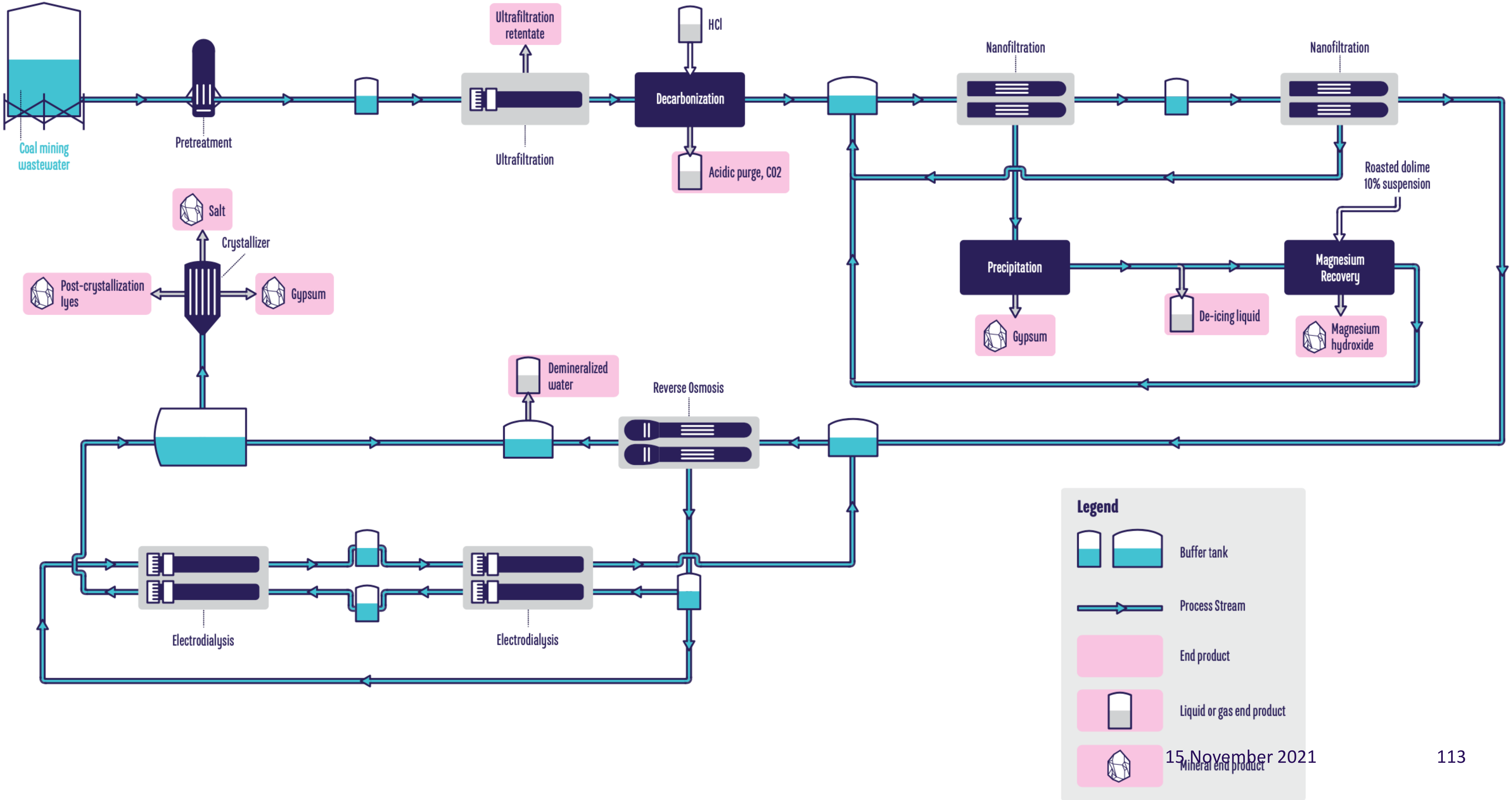
Coal mining wastewater
Pretreatment
Ultrafiltration retentate
Ultrafiltration
HCl
Decarbonization
Acidic purge, CO2
Nanofiltration
Nanofiltration
Roasted dolime 10% suspension
Precipitation
Gypsum
De-icing liquid
Magnesium Recovery
Magnesium hydroxide
Salt
Crystallizer
Post-crystallization lyes
Gypsum
Demineralized water
Reverse Osmosis
Electrodialysis
Electrodialysis
Legend
Buffer tank
Process Stream
End product
Liquid or gas end product
Mineral end product

Conclusions

The results confirm that from the point of view of circular economy, the application of nanofiltration is very desirable

It would not be possible to subsequently recover magnesium hydroxide or gypsum without selective removal of bivalent salts from the feed water

The application of intermediate gypsum pre- cipitation in the two-pass nanofiltration is a necessary step in order to achieve salt recovery higher than the reference “Dębieńsko” technology

The energy consumption of the proposed “ZERO BRINE” technology is substantially lower (33%) than the reference “Dębieńsko” technology

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COFFEE BREAK

14:45-15:00