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Sol2H2O

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UNIVERSIDADE DE ÉVORA
Università degli Studi di Palermo
itc INSTITUTO TECNOLÓGICO DE CANARIAS
Ciemat PSA

Fast Track School #2

Beyond State of the Art in Solar-driven Water production & Treatment technologies and brine treatment processes

POZO IZQUIERDO, GRAN CANARIA, 25.-26.09.2024

Sol2H2O

GUILLERMO ZARAGOZA (CIEMAT-PSA)

Beyond SoA of Membrane Distillation

POZO IZQUIERDO, GRAN CANARIA, 25.-26.09.2024

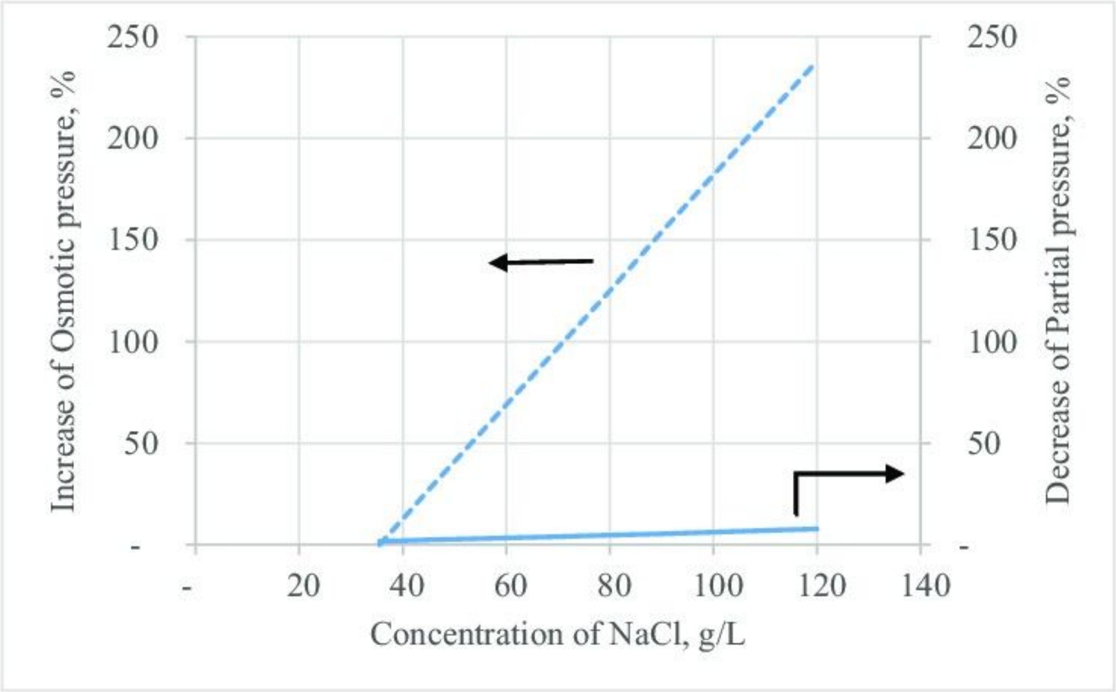
Beyond SoA of Membrane Distillation

- V-AGMD for brine concentration
    - Batch operation vs. semi-batch
    - Comparison with OARO
    - Other configurations: V-MEMD
    - Use of GO for membrane improvements
- Coupling with solar energy
- Other MD applications:
    - Coupling with heat pumps
    - Regeneration of liquid desiccants
    - Industrial wastewater treatment
    - Green H_2 generation

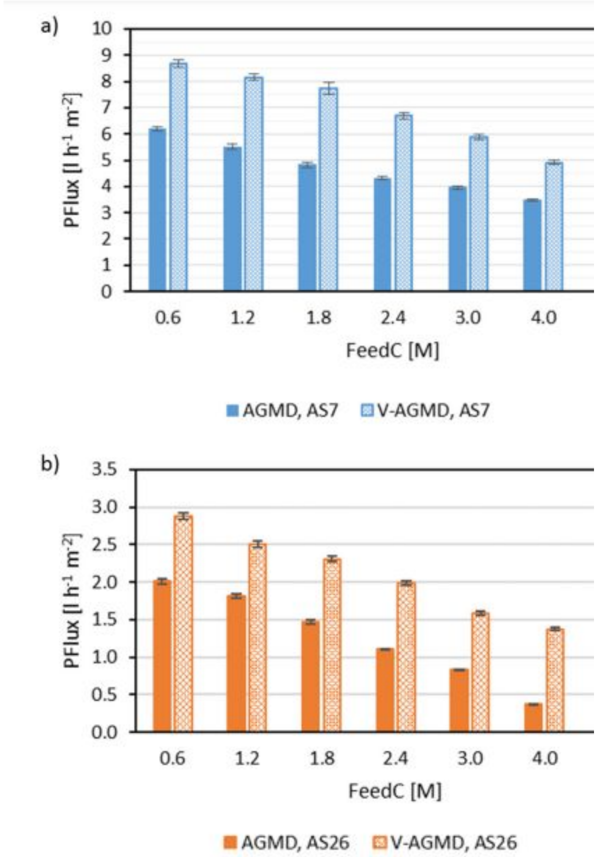
INDEX

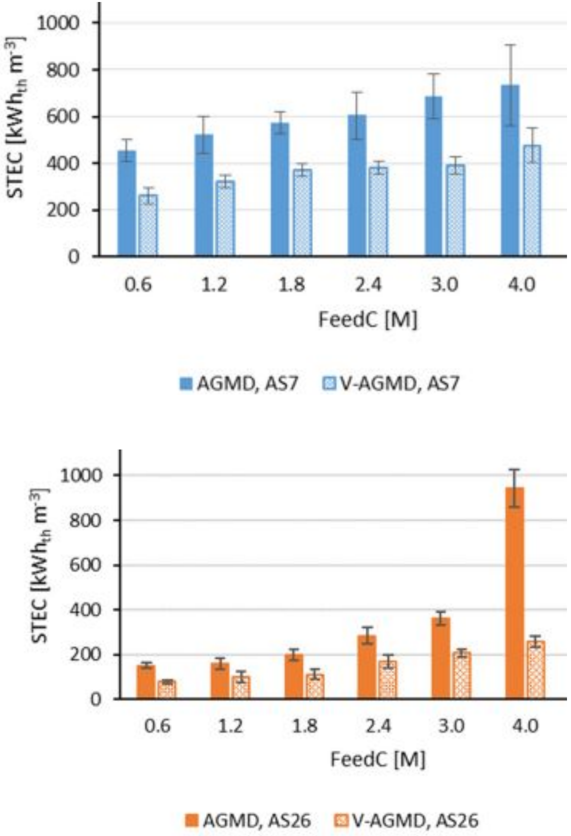
BRINE CONCENTRATION

Clear advantage of thermal desalination systems to treat high salinity feeds compared to RO



V-AGMD FOR BRINE CONCENTRATION



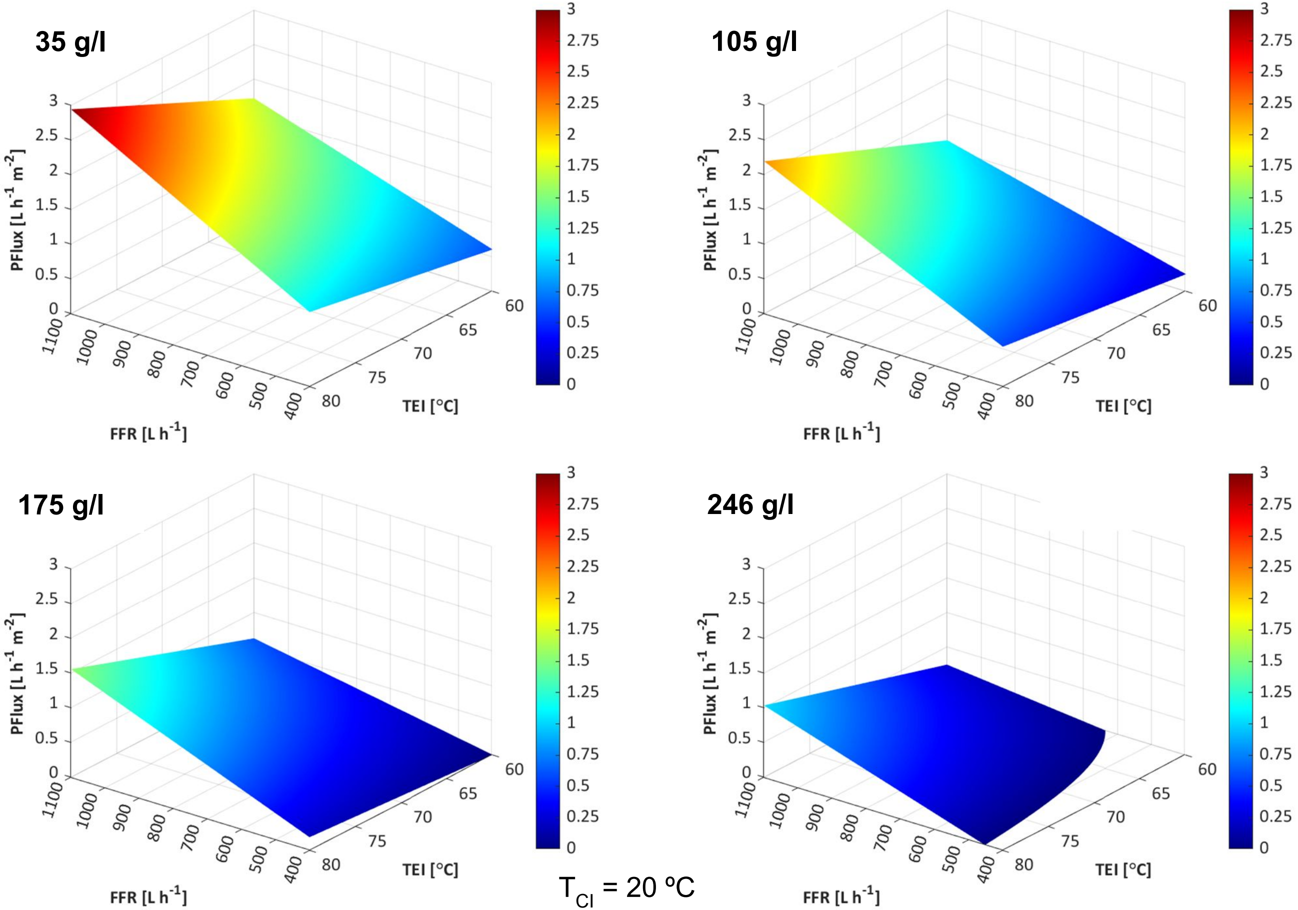


AS7 — $7\ m^2$ (6 envelopes)
1.5 m long channels

AS26 — $26\ m^2$ (12 envelopes)
2.7 m long channels

Andrés-Mañas et al., Desalination, vol. 475, 114202, (2020)

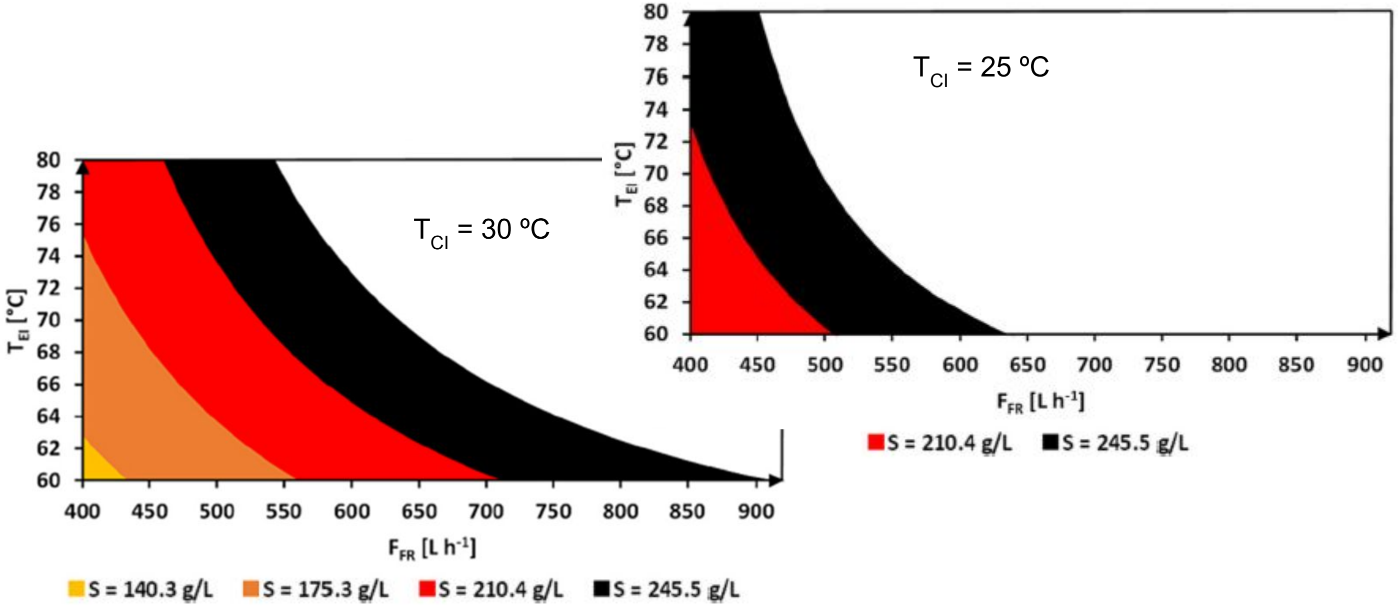
AS26 MODULE IN V-AGMD AT HIGH SALINITY



T_{CI} = 20 ºC

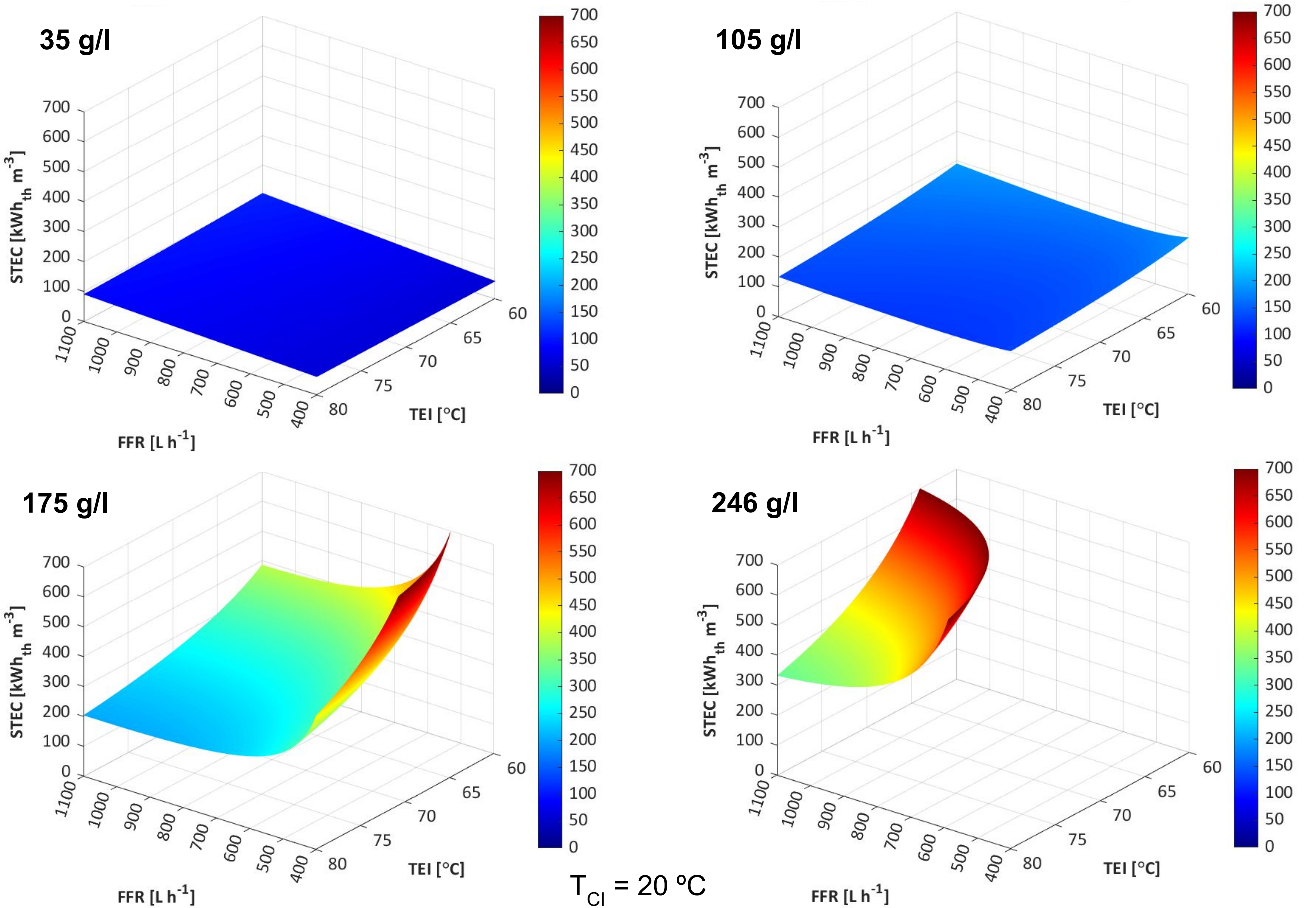
AS26 MODULE IN V-AGMD AT HIGH SALINITY

Range of operating conditions with no permeate production as a result of high salinity reducing the driving force of the MD process



Andrés-Mañas et al., Desalination 553, 116449 (2023)

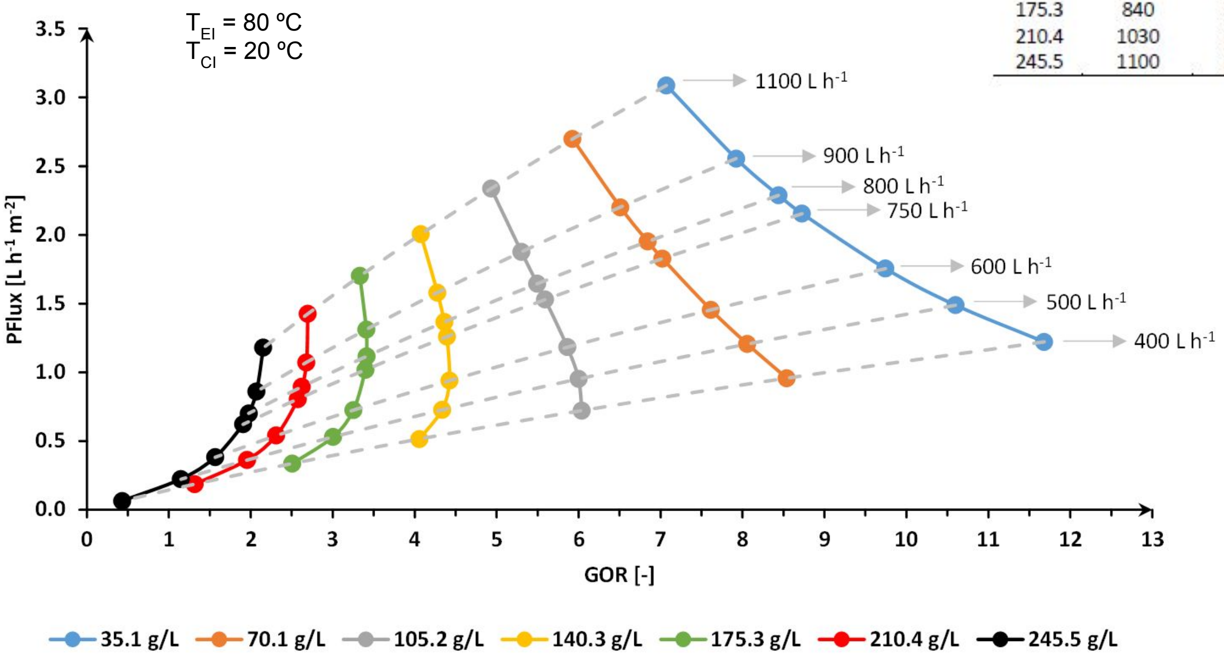
AS26 MODULE IN V-AGMD AT HIGH SALINITY



AS26 MODULE IN V-AGMD AT HIGH SALINITY

The trade-off between productivity and thermal efficiency is mitigated for high salinity feeds

S [g L⁻¹]	FFR [L h⁻¹]	GOR [-]	STEC [kWh$_{th}$ m⁻³]
35.1	400	11.7	56
70.1	400	8.5	79
105.2	421	6.0	112
140.3	639	4.4	153
175.3	840	3.4	198
210.4	1030	2.7	251
245.5	1100	2.2	314



Andrés-Mañas et al., Desalination 553, 116449 (2023)

BATCH V-AGMD FOR BRINE CONCENTRATION

Operation in recirculation (batch mode) for higher feed concentration

seawater as coolant
(large flow rate)

from solar
thermal field

BATCH V-AGMD FOR BRINE CONCENTRATION

Stationary conditions:

- Evaporation channel inlet temperature (TEI): 70ºC and 80ºC
- Cooling channel inlet temperature (TCI): 20ºC
- Feed flow rate (FFR): 1100 L/h

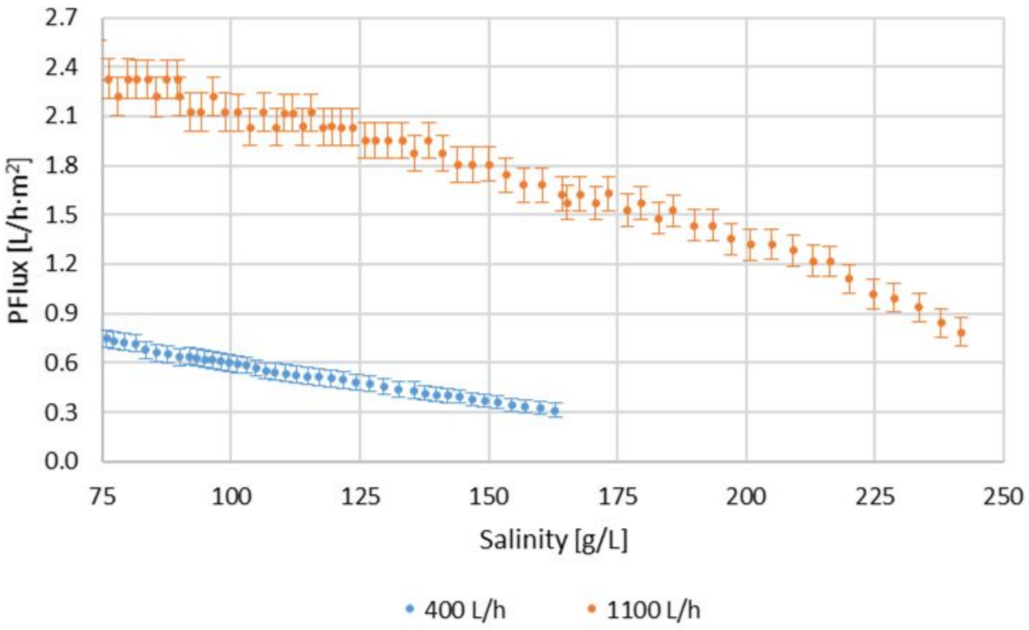
Non-stationary conditions: Feed salinity (initial: 75 g/L)

Along time:

- Permeate Flux (PFlux) decreases
- STEC increases

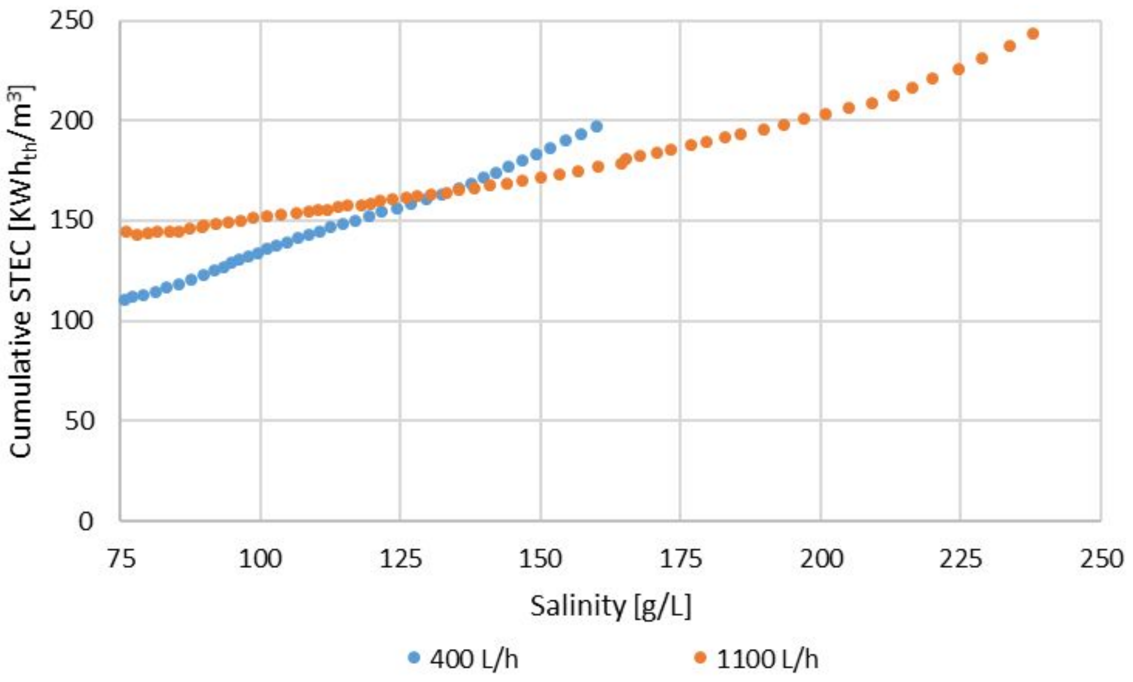
BATCH V-AGMD FOR BRINE CONCENTRATION

Selection of stationary Feed flow rate



BATCH V-AGMD FOR BRINE CONCENTRATION

Selection of stationary Feed flow rate



136 g/L (157 kWh_{th}/m^3)

To reach 163 g/L:

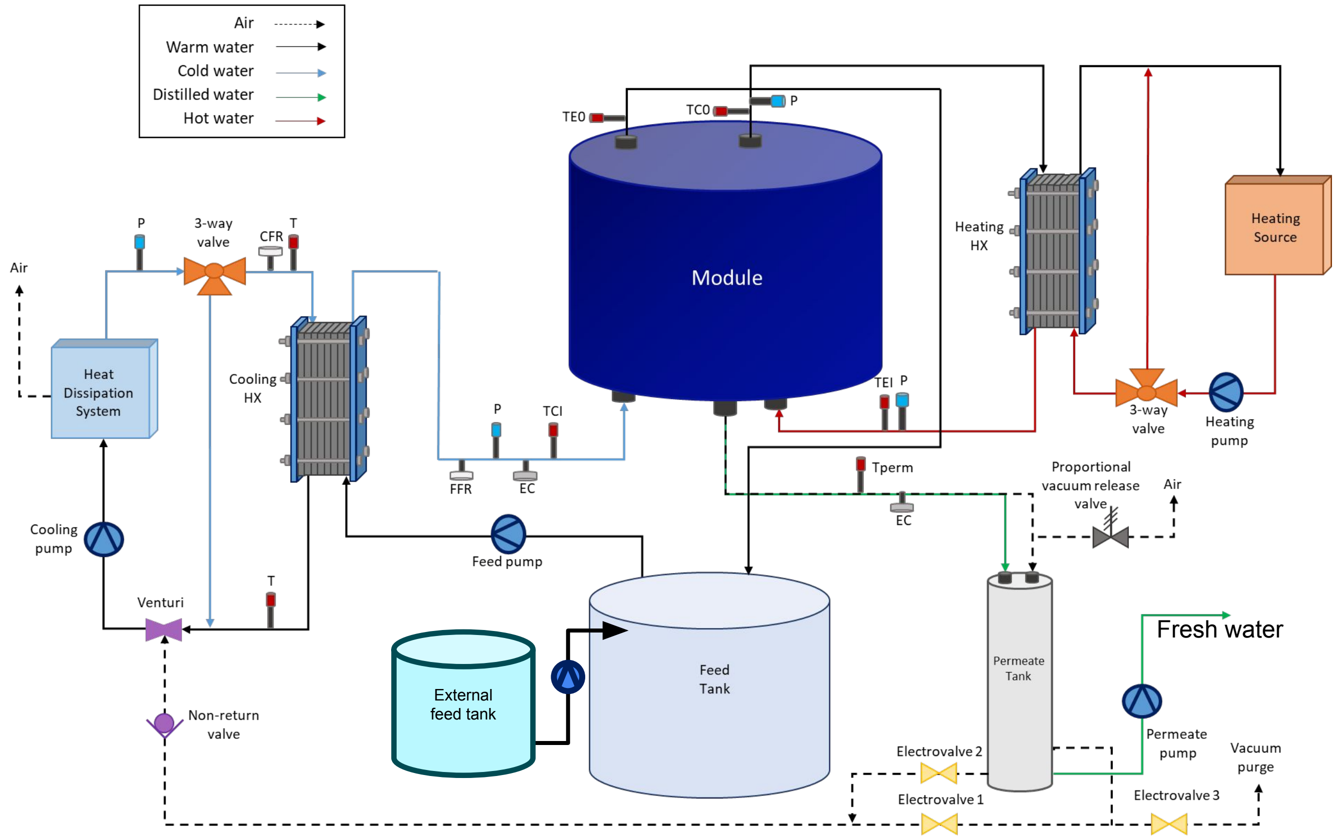
STEC = 197 kWh_{th}/m^3

STEC = 177 kWh_{th}/m^3

Time = 7.15 hours

Time = 1.44 hours

BATCH V-AGMD FOR BRINE CONCENTRATION



Batch operation:

Feed volumen decreases

 Salinity increases faster

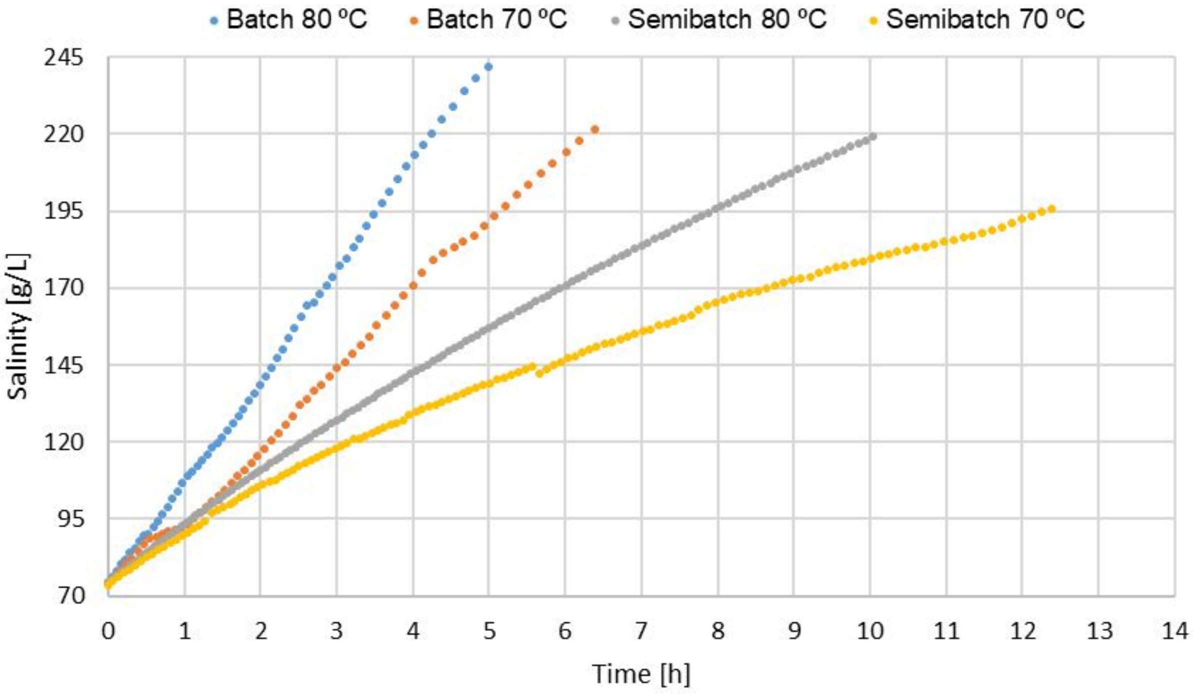
Semi-batch operation:

Feed volume is constant

 Salinity increases slower

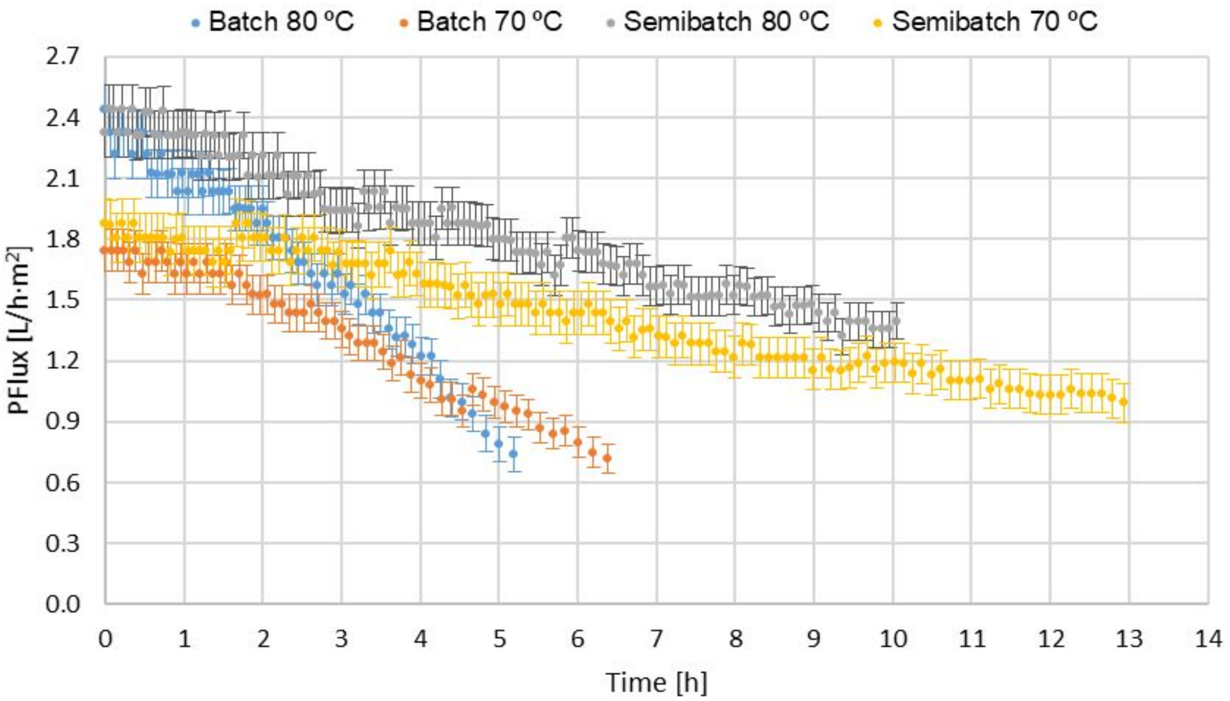
COMPARISON OF BATCH AND SEMI-BATCH V-AGMD OPERATION

→ faster increase of feed salinity with time in batch operation than in semi-batch



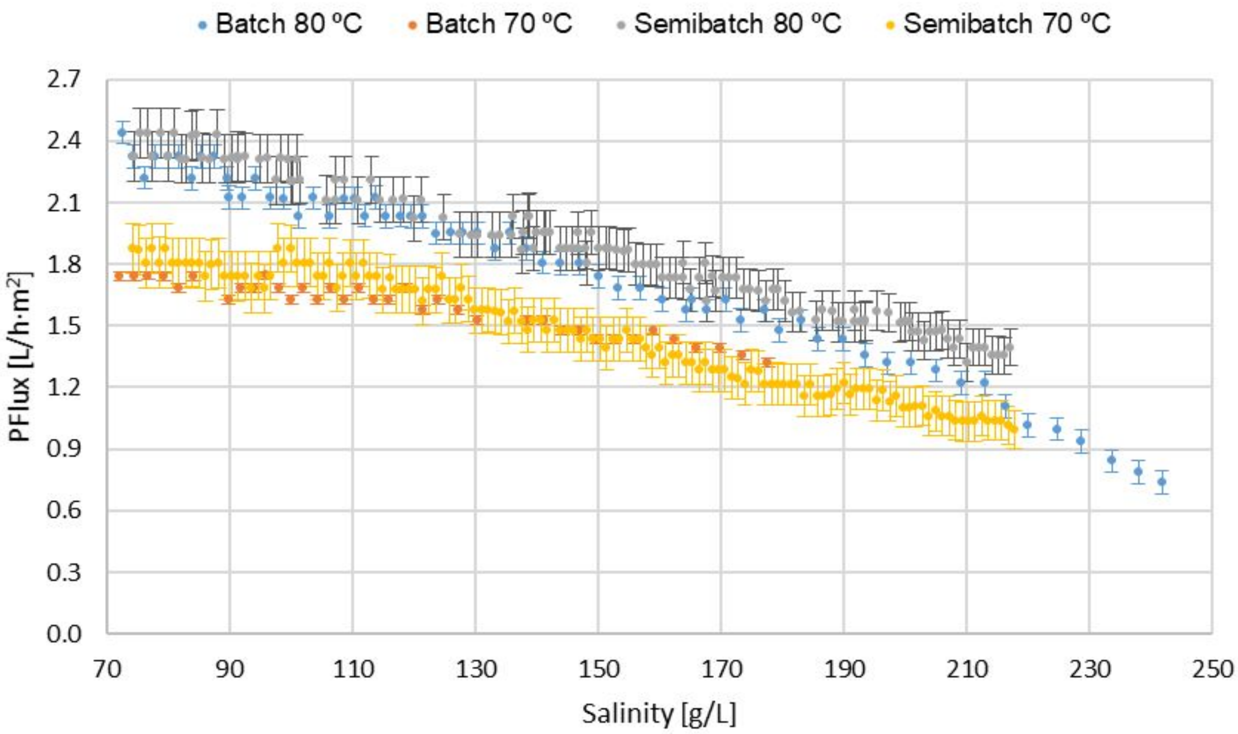
COMPARISON OF BATCH AND SEMI-BATCH V-AGMD OPERATION

→ faster decrease of PFlux with time in batch operation than in semi-batch



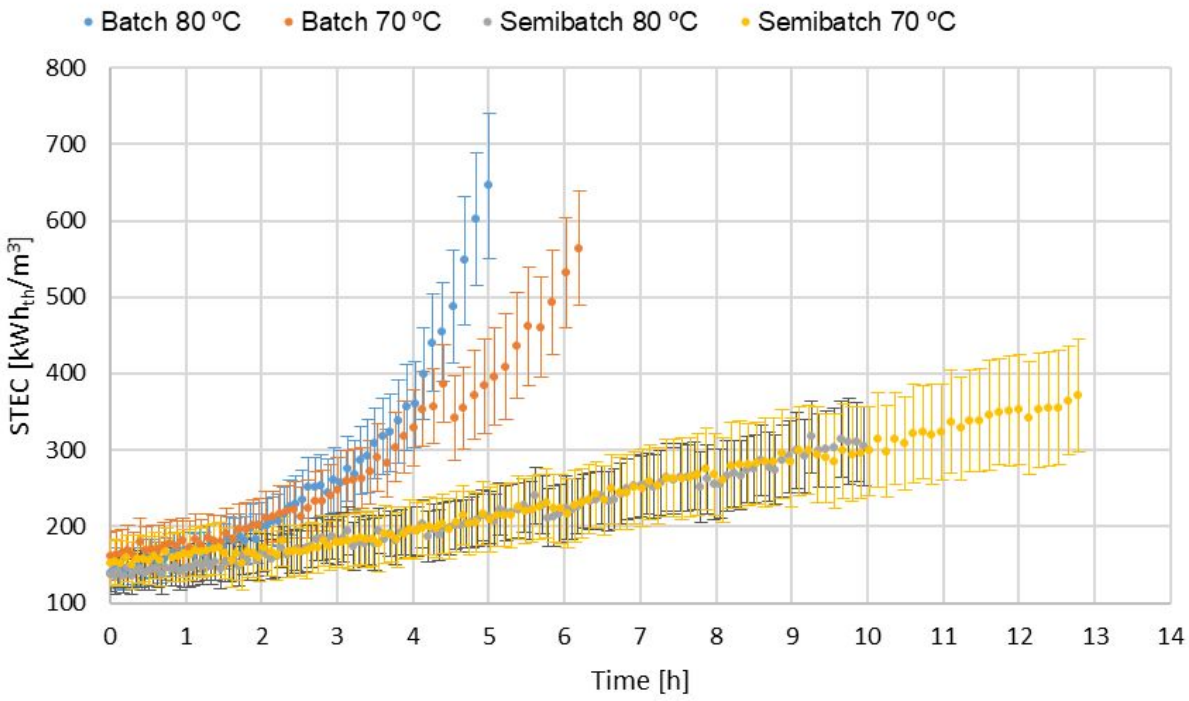
COMPARISON OF BATCH AND SEMI-BATCH V-AGMD OPERATION

→ similar decrease of PFlux with salinity in batch and semi-batch operation



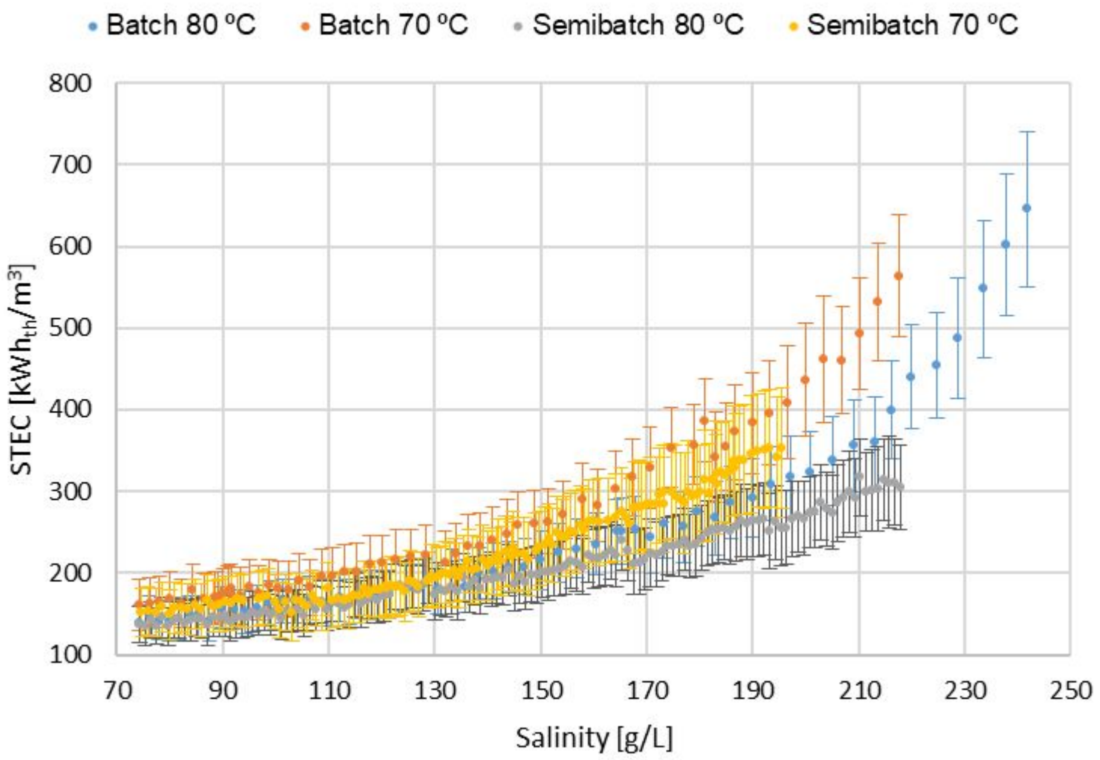
COMPARISON OF BATCH AND SEMI-BATCH V-AGMD OPERATION

→ faster increase of STEC with time in batch operation than in semi-batch



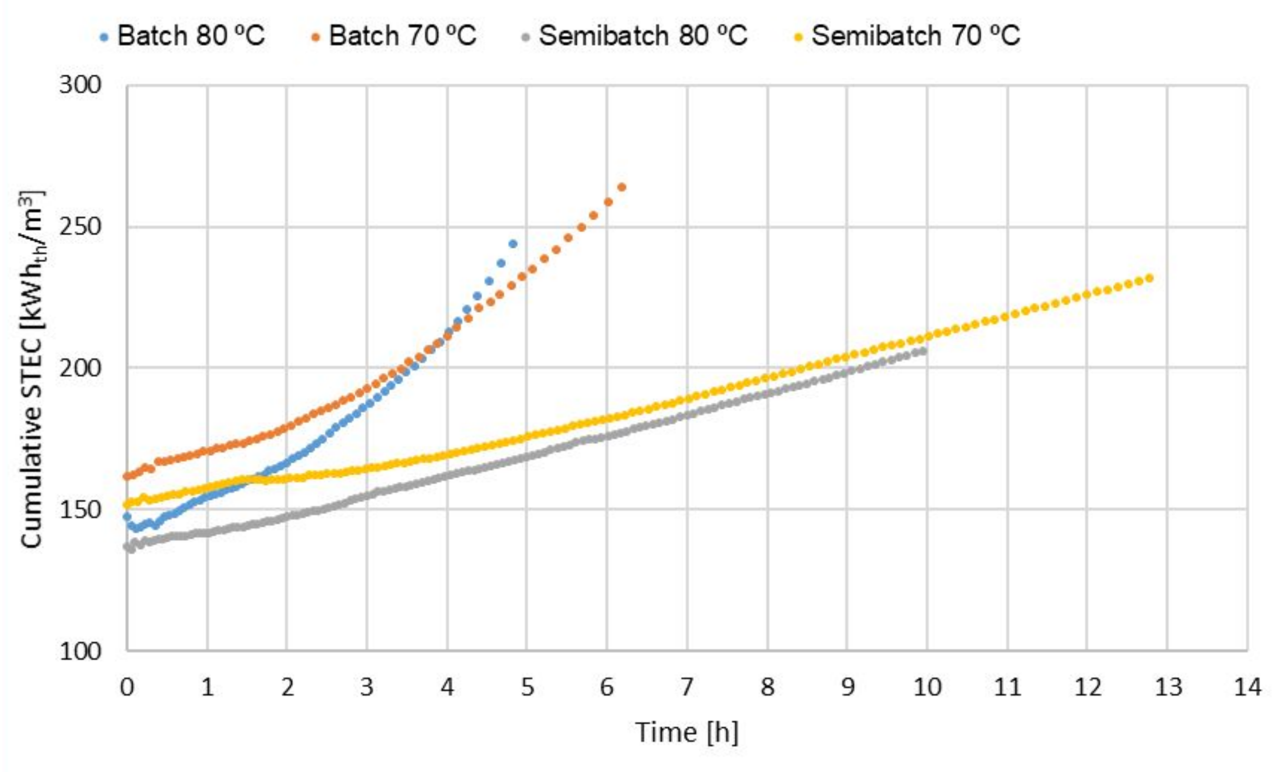
COMPARISON OF BATCH AND SEMI-BATCH V-AGMD OPERATION

→ similar increase of STEC with salinity in batch and semi-batch operation



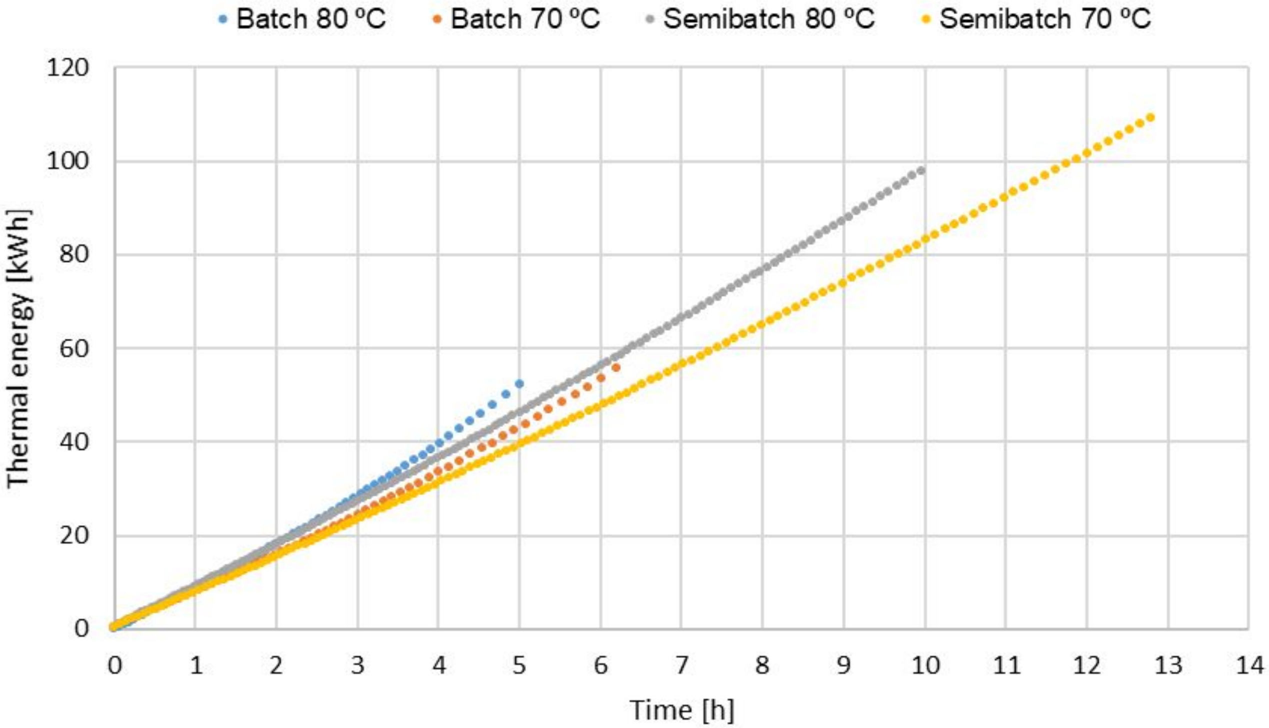
COMPARISON OF BATCH AND SEMI-BATCH V-AGMD OPERATION

→ faster increase of total STEC with time in batch than in semi-batch operation



COMPARISON OF BATCH AND SEMI-BATCH V-AGMD OPERATION

→ faster increase of total STEC with time in batch than in semi-batch operation (compensated by more production in semi-batch)



COMPARISON OF BATCH AND SEMI-BATCH V-AGMD OPERATION

Results for reaching a final salinity of 196 g/L

Experiment	Time [h]	STEC [kWh_{th}/m^3]	Production [L]
Batch 80 ^oC	3.7	198	176
Semibatch 80 ^oC	8.0	190	401
Batch 70 ^oC	5.2	235	187
Semibatch 70 ^oC	12.9	232	472

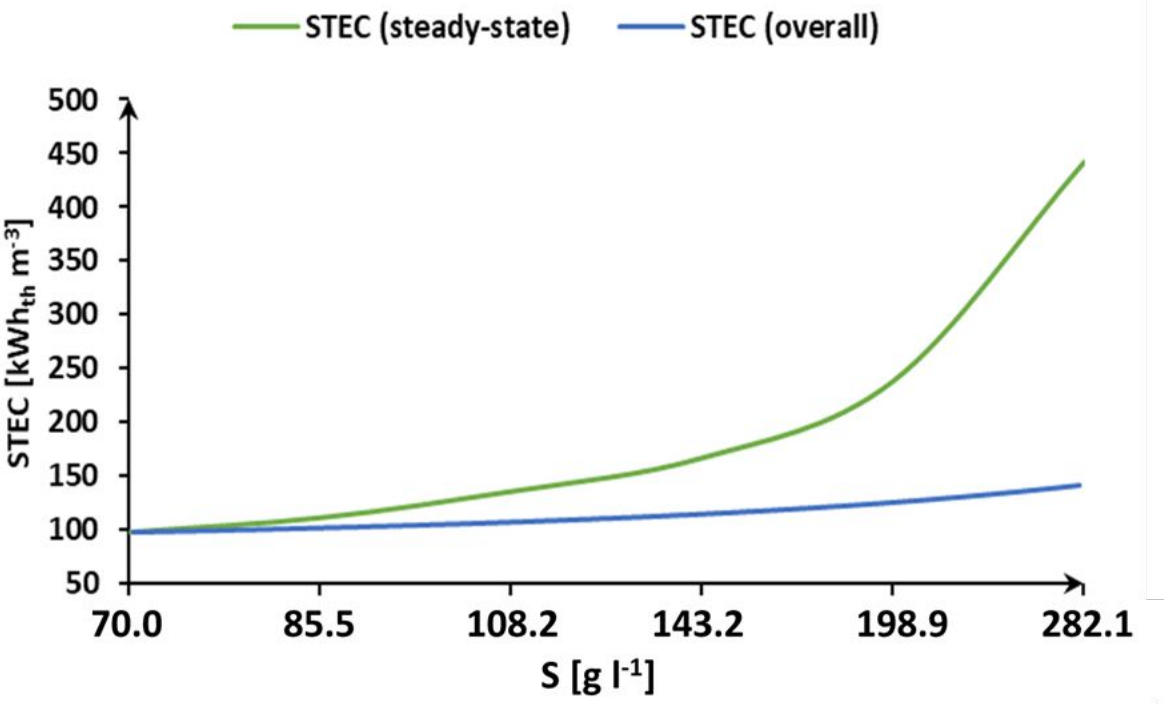
COMPARISON OF BATCH AND SEMI-BATCH V-AGMD OPERATION

<u>Results for production of 211 L of permeate</u>

Experiment	Time [h]	STEC [kWh_{th}/m^3]	Final salinity [g/L]
Batch 80 °C	4.6	211	220
Semibatch 80 °C	3.8	160	140
Batch 70 °C	6.4	263	222
Semibatch 70 °C	4.8	173	133

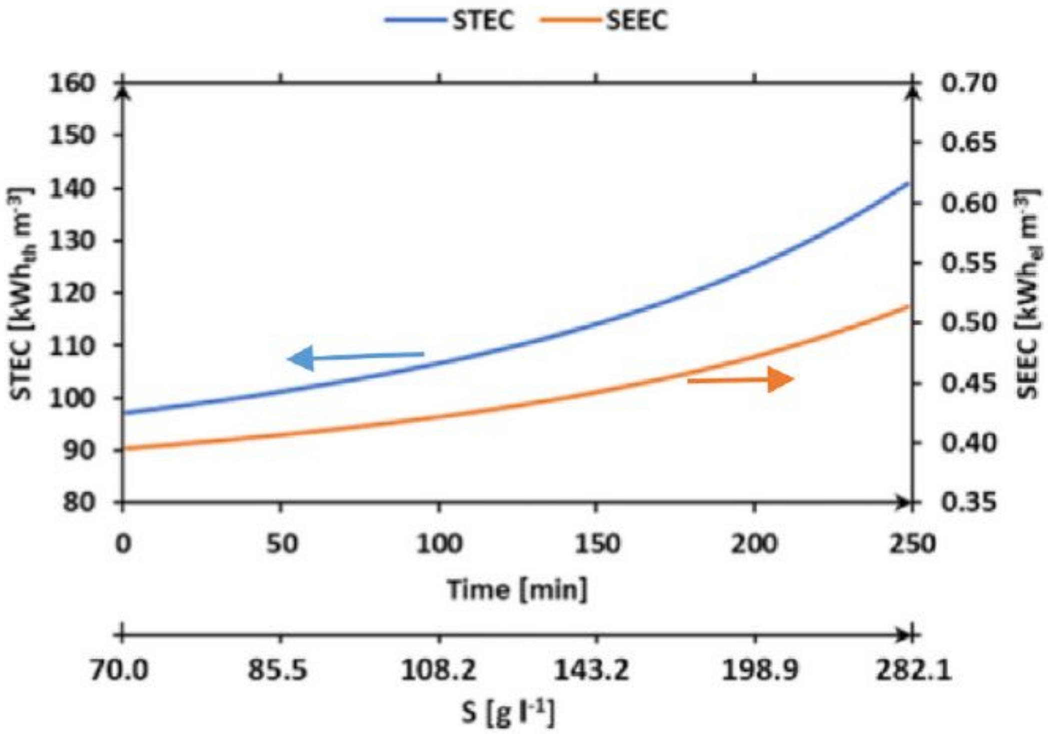
V-AGMD FOR BRINE CONCENTRATION

V-AGMD operation in batch (feed recirculation) for brine concentration



V-AGMD FOR BRINE CONCENTRATION

V-AGMD operation in batch (feed recirculation) for brine concentration

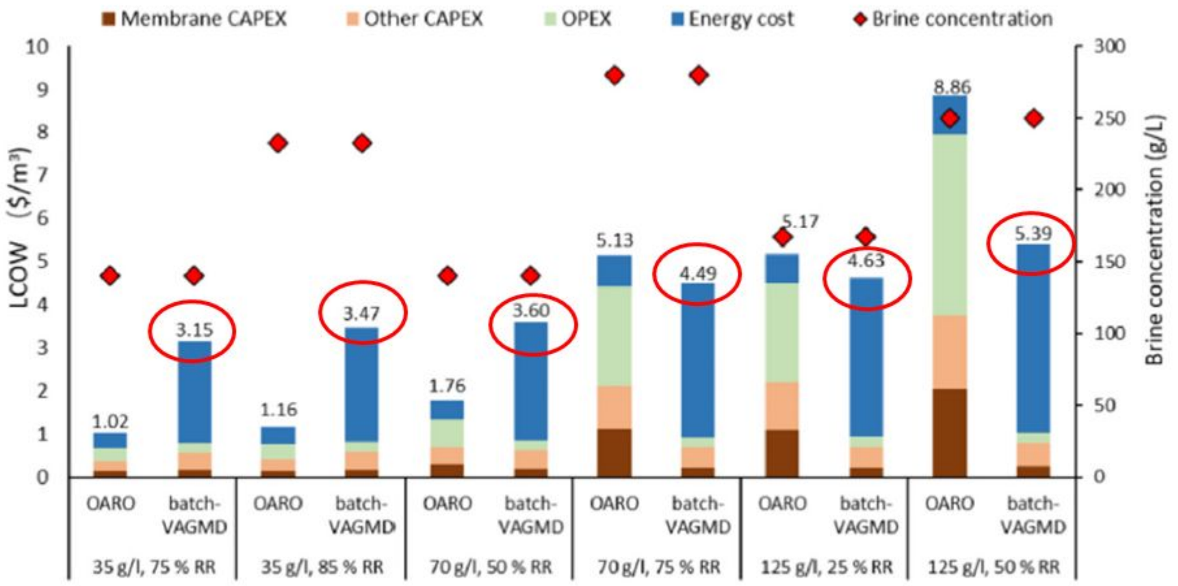


Zhang et al. Desalination 532 (2022) 115737

V-AGMD FOR BRINE CONCENTRATION

V-AGMD operation in batch (feed recirculation) for brine concentration

Comparison with OARO



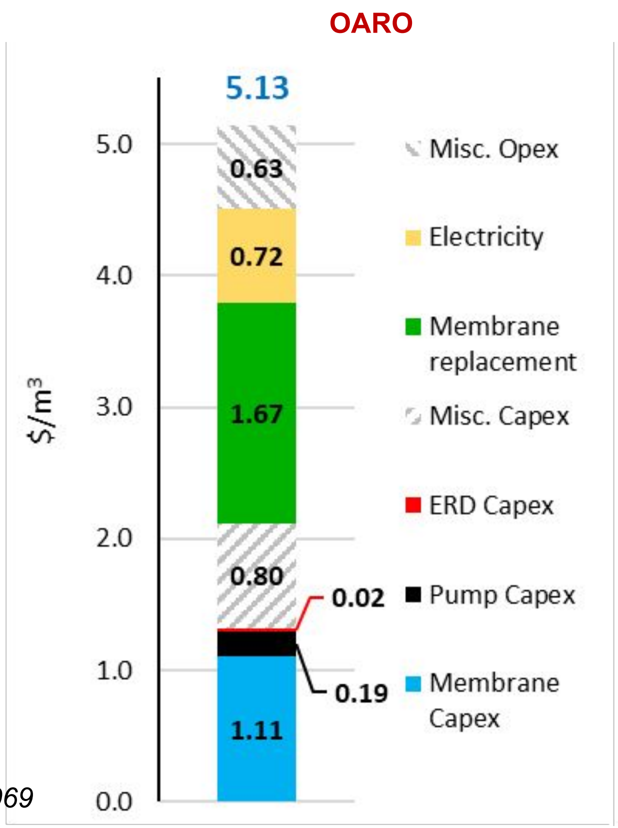
(AS26 module with LCOE: 0.07 USD kWh_e^{-1} and LCOH: 0.025 USD kWh_{th}^{-1})

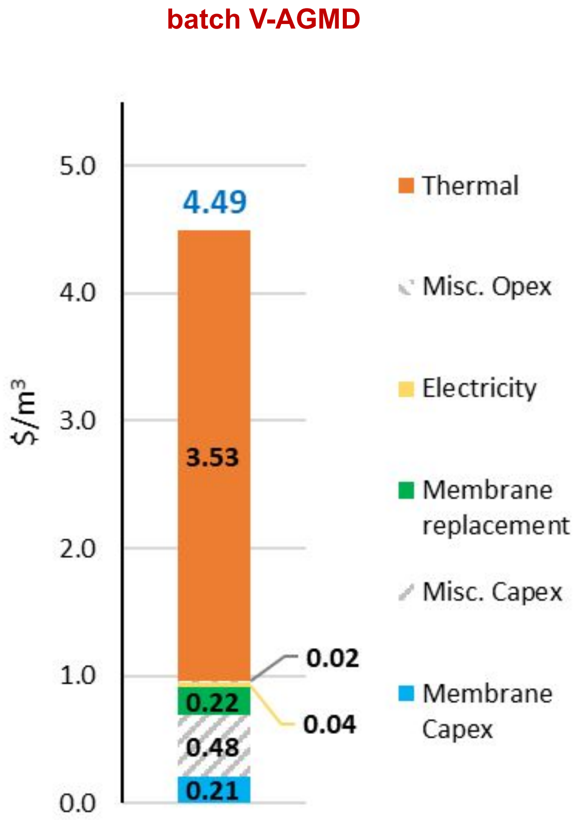
Zhang et al. Desalination 532 (2022) 115737

V-AGMD FOR BRINE CONCENTRATION

<u>OARO vs. batch V-AGMD cost comparison</u>

Feed: 70 g/l; 75% RR



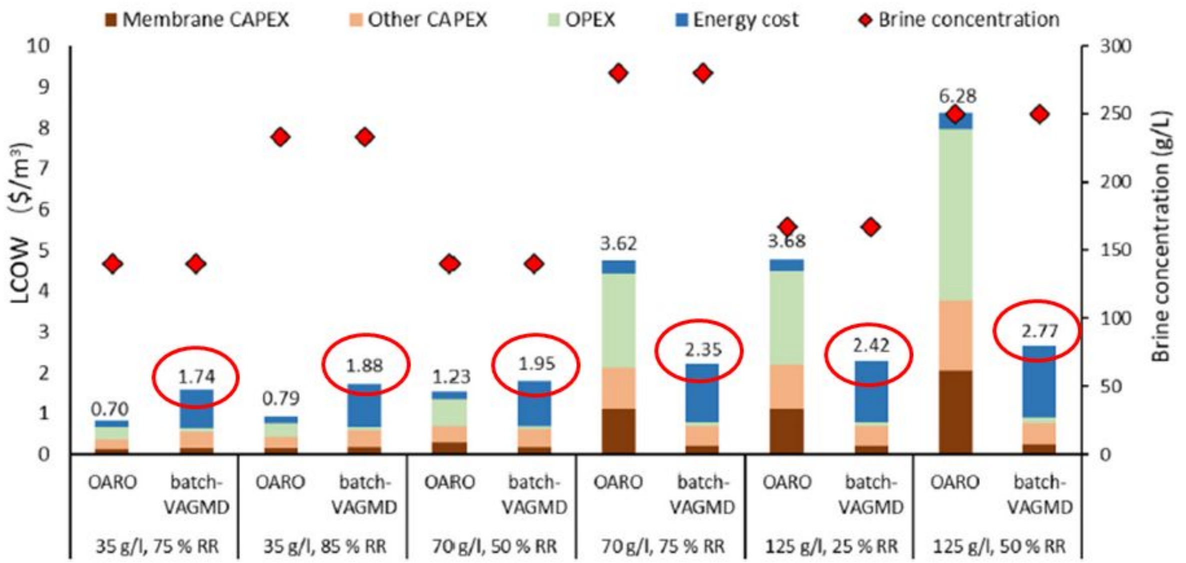


Atia et al., Desalination. 509 (2021) 115069

V-AGMD FOR BRINE CONCENTRATION

V-AGMD operation in batch (feed recirculation) for brine concentration

Comparison with OARO (low energy prices)



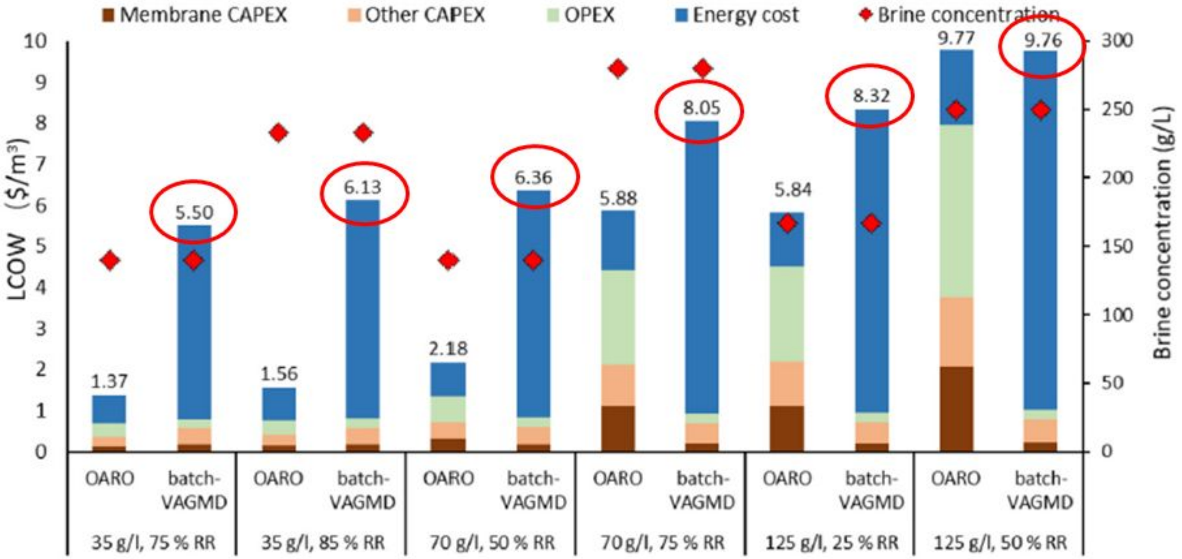
(AS26 module with LCOE: 0.03 USD kWh_e^{-1} and LCOH: 0.01 USD kWh_{th}^{-1})

Zhang et al. Desalination 532 (2022) 115737

V-AGMD FOR BRINE CONCENTRATION

V-AGMD operation in batch (feed recirculation) for brine concentration

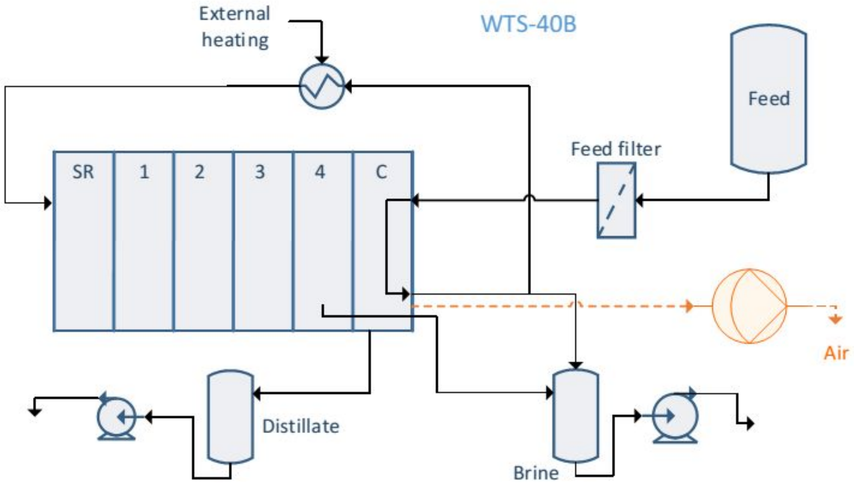
Comparison with OARO (high energy prices)



(AS26 module with LCOE: 0.14 USD kWh_e^{-1} and LCOH: 0.05 USD kWh_{th}^{-1})

Zhang et al. Desalination 532 (2022) 115737

V-MEMD FOR BRINE CONCENTRATION

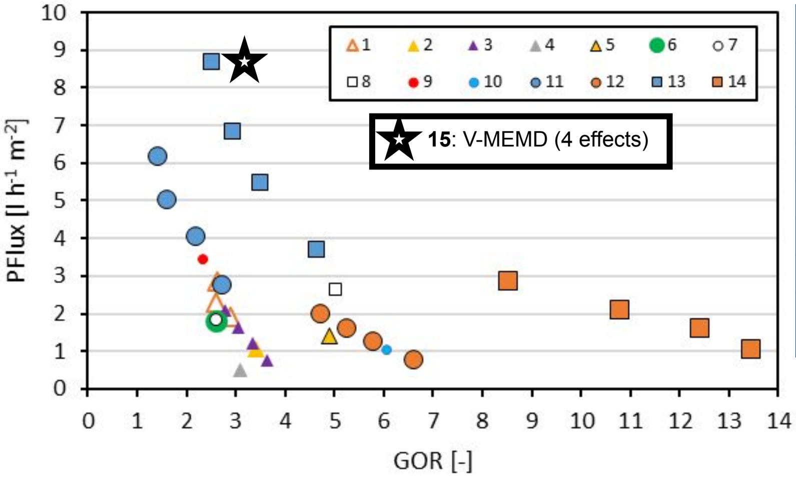


Membrane area: 6.40 m^2
Number of effects: 4

AQUAVER, WTS-40B

V-MEMD FOR BRINE CONCENTRATION

Feed salinity: 35 g/l



1, 2 and 3: PGMD, single envelope	
4: PGMD, single envelope, demonstration plants outdoors	
5: PGMD, single envelope, deaerated feed	
6: AGMD, single envelope, overpressured gap	
7 and 8: AGMD and V-AGMD, single envelope	
9 and 10: AGMD, multi envelope, AS7 and AS24	
11 and 12: AGMD, multi envelope, AS7 and AS26	
13 and 14: V-AGMD, multi envelope, AS7 and AS26	

15: Andrés-Mañas et al., Desalination 443 (2018) 110–21

→ multi-effect configurations achieve better conversion (recovery ratio) but heat efficiency requires many effects

V-MEMD
6.4 m^2 membrane area
4 effects

memsys
module

AQUAVER, WTS-40B

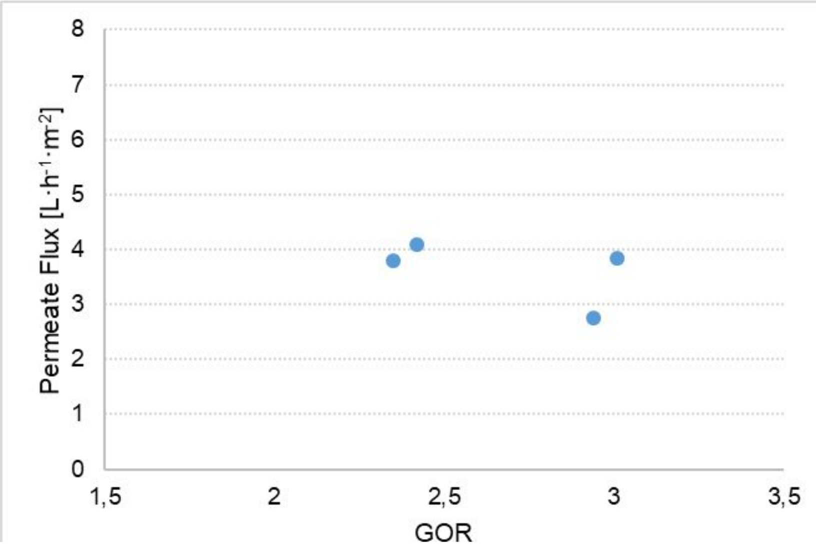
BEYOND VACUUM MULTI-EFFECT MD

Intelwatt project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958454.

EU project Intelwatt: intelligent Water Treatment Technologies for water preservation combined with simultaneous energy production and material recovery in energy intensive industries.

→ Application to the treatment of high salinity brines from a mine effluent: combination of RED and MD using solar energy as heat source.

Use of improved vacuum multi-effect MD.



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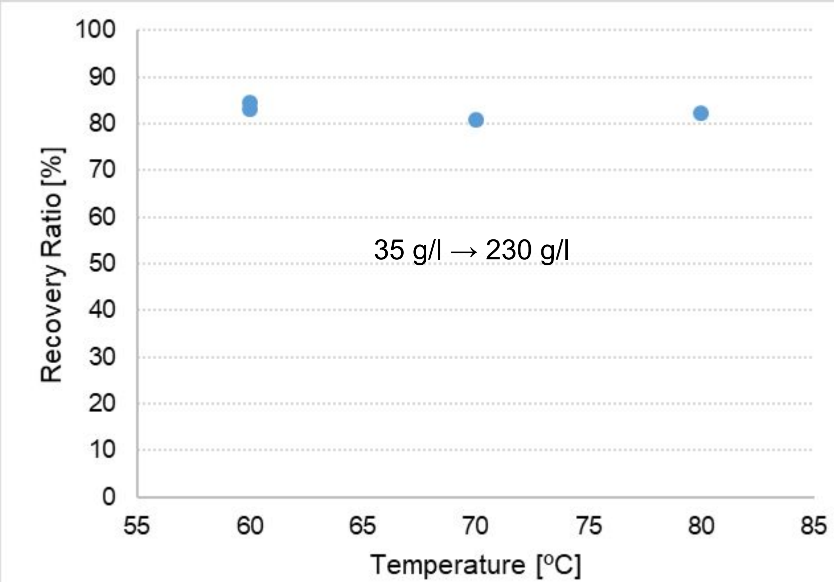

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→ Application to the treatment of high salinity brines from a mine effluent: combination of RED and MD using solar energy as heat source.

Use of innovative membranes (PVDF coated with GO).

→ more resistant to fouling

MEMBRANE IMPROVEMENTS FOR BRINE CONCENTRATION

Fouling performance

A = 77 cm^2, TEI = 75 °C, FFR = 60 L/h, TCI = 20 °C, AGMD

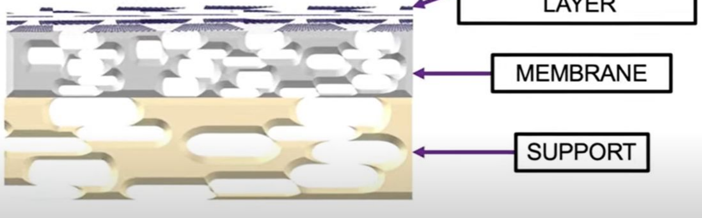
Membrane material	Durapore PVDF
	PDA/PVDF
	GO-PDA/PVDF

Feed solution	**35 g/L NaCl**
	150 mg/L humic acid
	200 mg/L paraffin oil

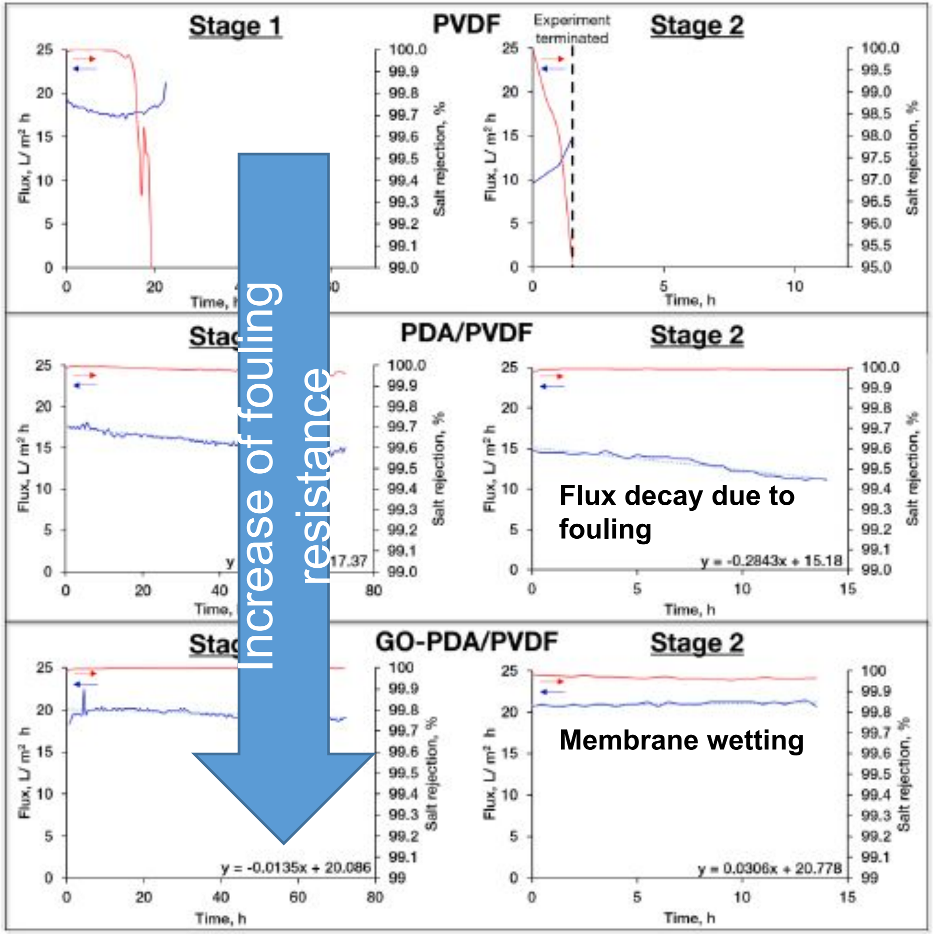
UPSCALING POLYMERIC MEMBRANES MODIFIED WITH GRAPHENE OXIDE

MANCHESTER 1824

The University of Manchester



with hot



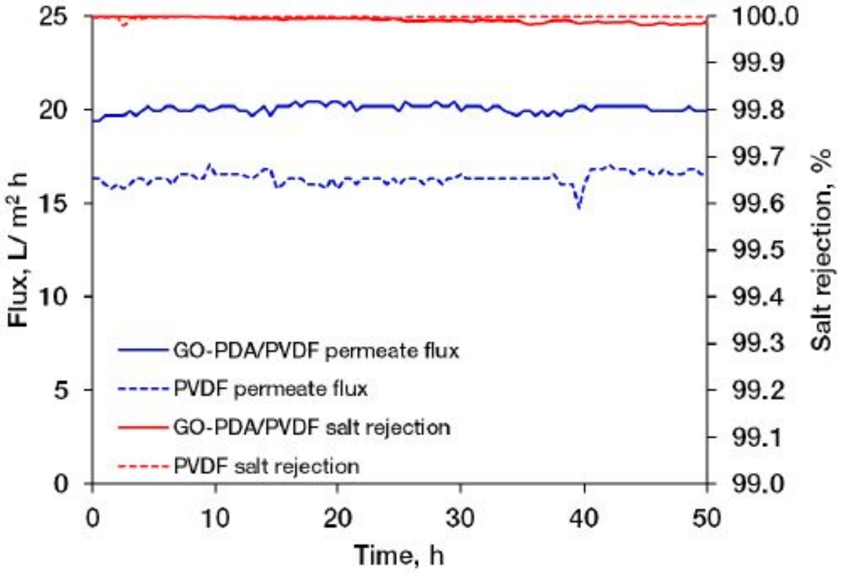
MEMBRANE IMPROVEMENTS FOR BRINE CONCENTRATION

Fouling performance

A = 77 cm^2, TEI = 75 °C, FFR = 60 L/h, TCI = 20 °C, AGMD

Membrane material	Durapore PVDF
	PDA/PVDF
	GO-PDA/PVDF
Feed solution	**Real Seawater**
	150 mg/L humic acid
	200 mg/L paraffin oil

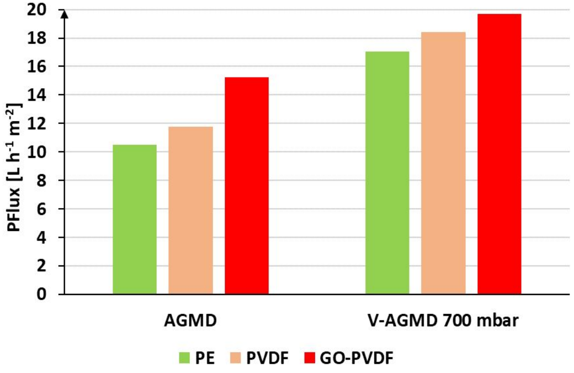
- No evidence of membrane deterioration after 50 h of seawater treatment.
- Although the quality of permeate was the same with unmodified and modified membranes, permeate production was higher with modified membranes.

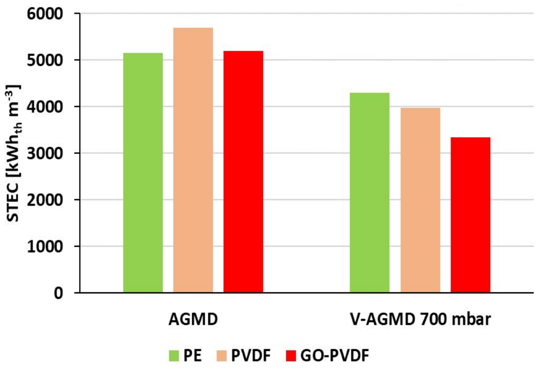


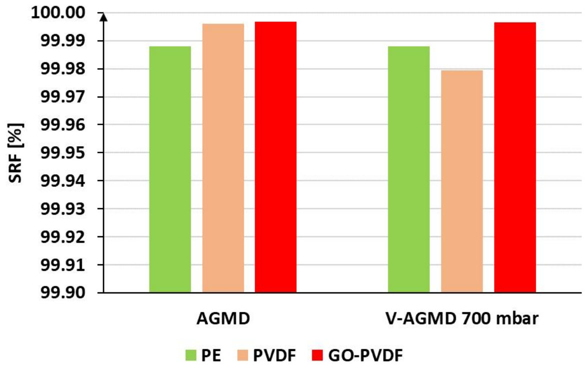
EFFECT OF GRAPHENE OXIDE ON MD MEMBRANES

Capacity / Energy performance

A = 375 cm^2, TEI = 80 °C, FFR = 50 L/h, TCI = 25 °C, AGMD and V-AGMD (700 mbar), 35 g/L NaCl





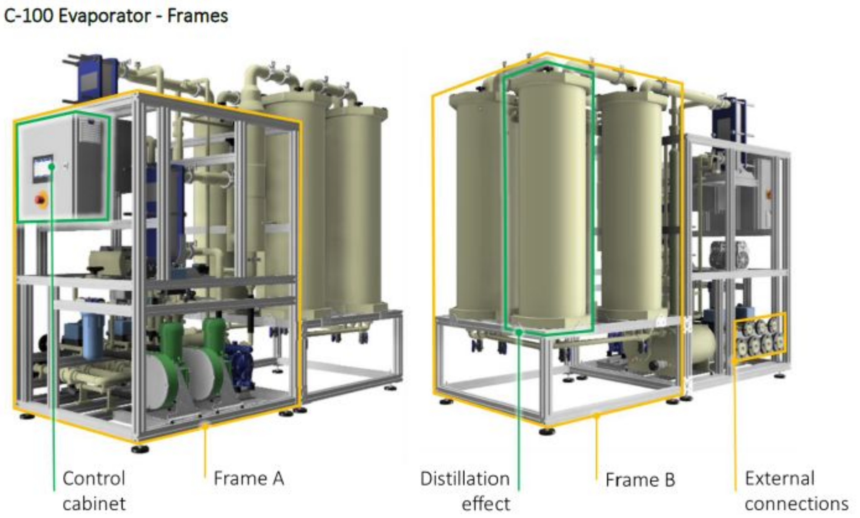


- **Promising results in terms of performance**
  - ❑ Upscaled from 28 to 375 cm^2.
  - ❑ 25% higher PFlux than PE membrane.
  - ❑ 25% improved STEC with vacuum.
  - ❑ Permeate quality not affected by vacuum.

BEYOND VACUUM MULTI-EFFECT MD

A novel multi-effect evaporator (4-effects) based on disposable cartridges instead of membranes

→ for treating high fouling solutions (very concentrated brine)



MD FROM PILOT-SCALE TO INDUSTRIAL SIZE

Building racks of modules in parallel and clustering them in a similar fashion as RO plants

33 m^3/day (Arabian Gulf seawater)

12 m^3/day (Maldives seawater)

60 m^3/day plant built in Ghantoot (UAE) with memsys modules to treat RO brine (decommissioned)

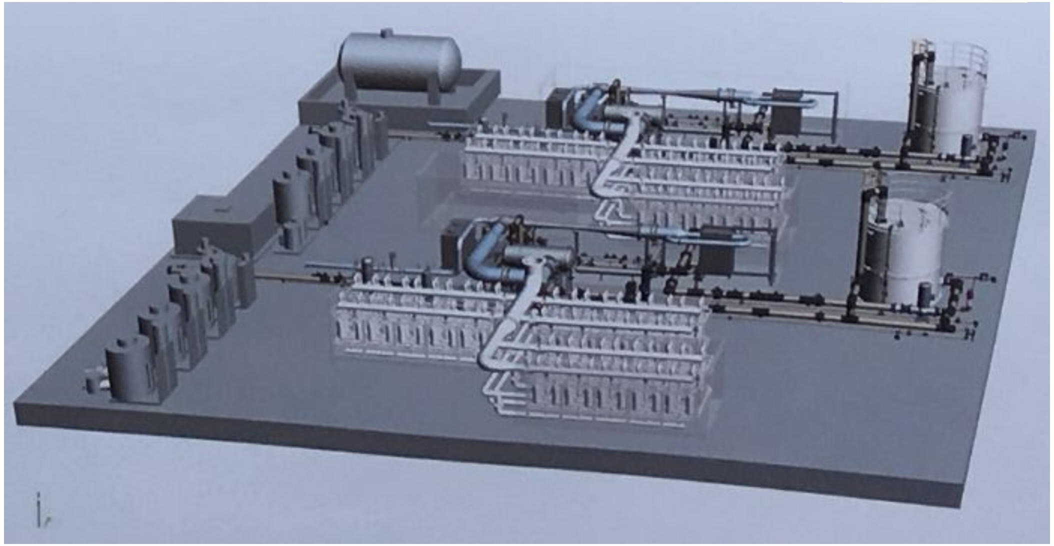
MD FROM PILOT-SCALE TO INDUSTRIAL SIZE

Global MVP research program (2013-2018), South Korea

Econity HF modules (10 m^2 total membrane area)

VMD configuration with thermal vapour compression for heat efficiency (no internal heat recovery)

GMVP



Two VMD units with total water production capacity of 400 m^3/d.

Unit 1: 120 modules (Av. Pflux: 7 $l/h.m^2$)

Unit 2: 104 modules (Av. Pflux: 8 $l/h.m^2$)

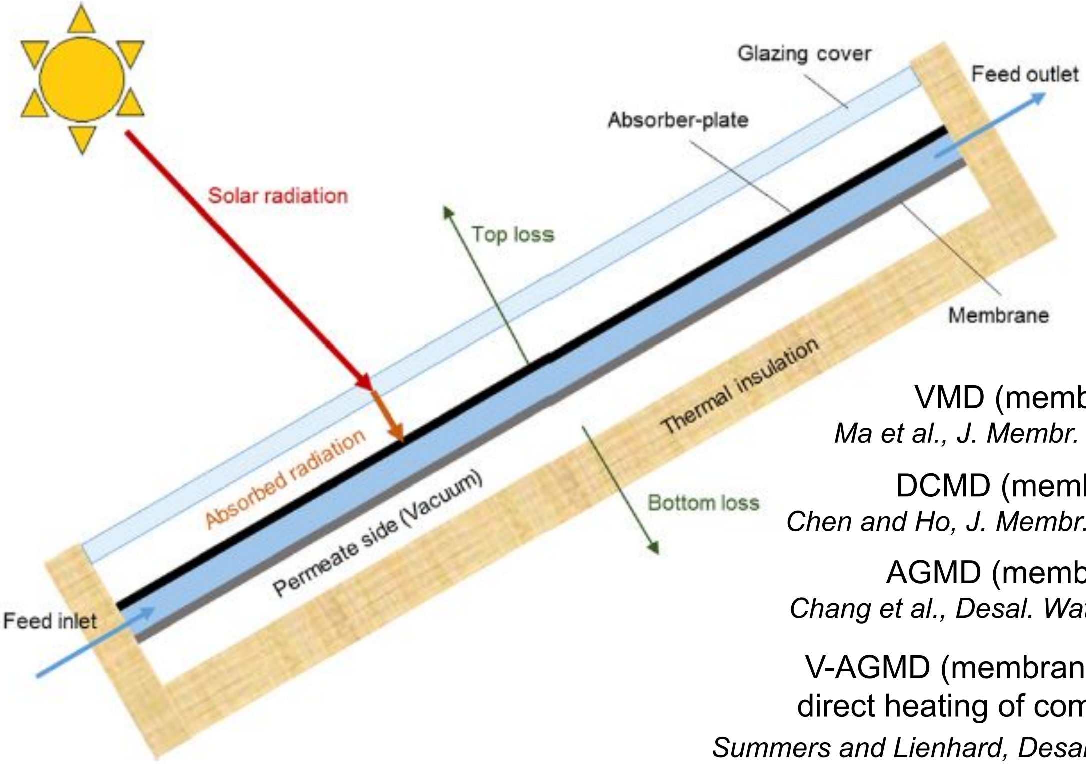
COUPLING MD WITH DIRECT SOLAR HEAT

Advantages:

No additional investment in collectors

Thermal losses reduced

COUPLING MD WITH DIRECT SOLAR HEAT



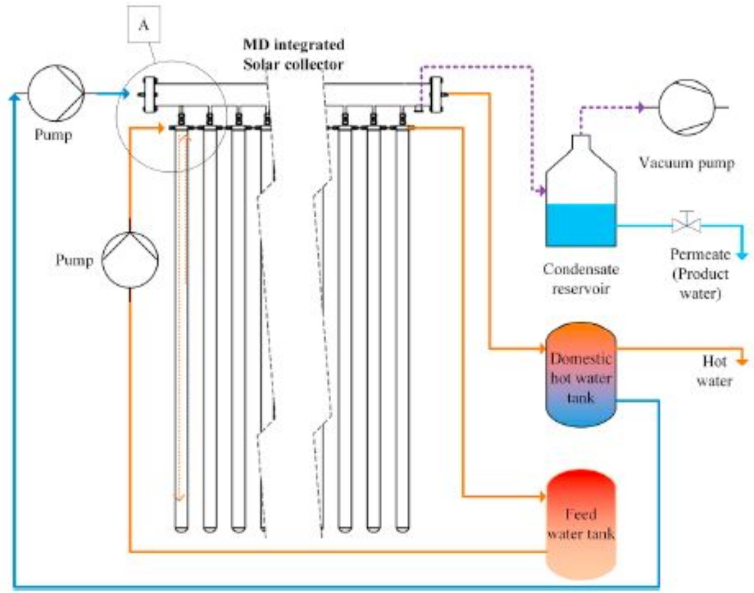
VMD (membrane ≤ 0.35 m^2)
Ma et al., J. Membr. Sci. 564 (2018) 617–633

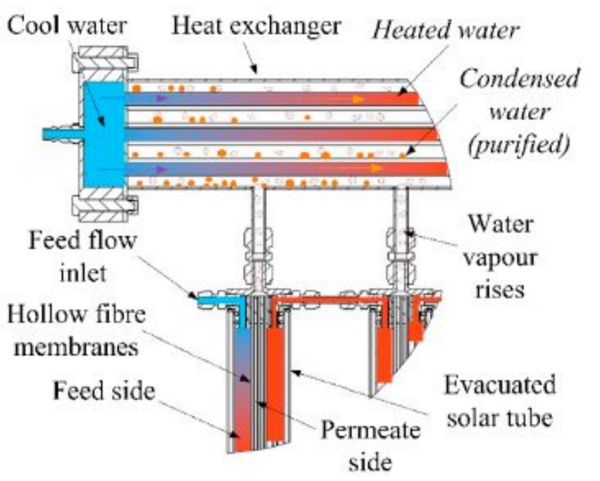
DCMD (membrane 0.06 m^2)
Chen and Ho, J. Membr. Sci. 358 (2010) 122–130

AGMD (membrane 0.05 m^2)
Chang et al., Desal. Wat. Treat. (2011) 251–258

V-AGMD (membrane area < 0.53 m^2)
direct heating of composite membrane
Summers and Lienhard, Desalination 330 (2013) 100–111

COUPLING MD WITH DIRECT SOLAR HEAT

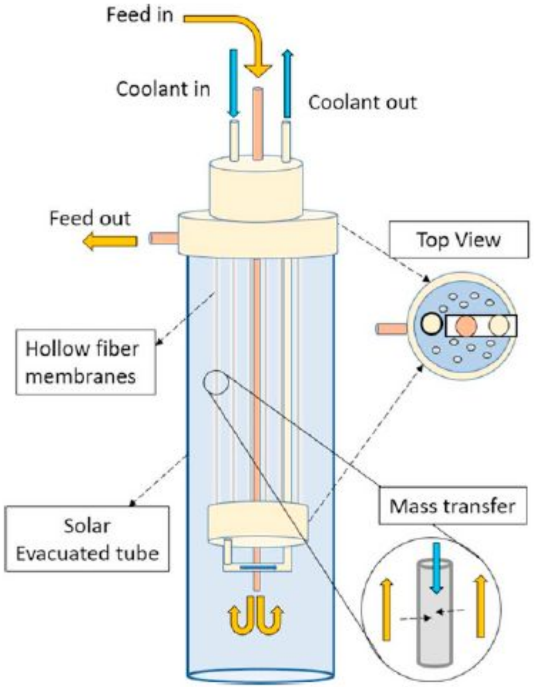




Li et al., App. En. 237 (2019) 534–548

VMD: production of 0.13 l/h.m^2 of collector area

COUPLING MD WITH DIRECT SOLAR HEAT



DCMD: production of 0.37 l/h.m^2 of collector area

Bamasag, et al. Desal. 487 (2020) 114497

COUPLING MD WITH DIRECT SOLAR HEAT

Advantages:

No additional investment in collectors

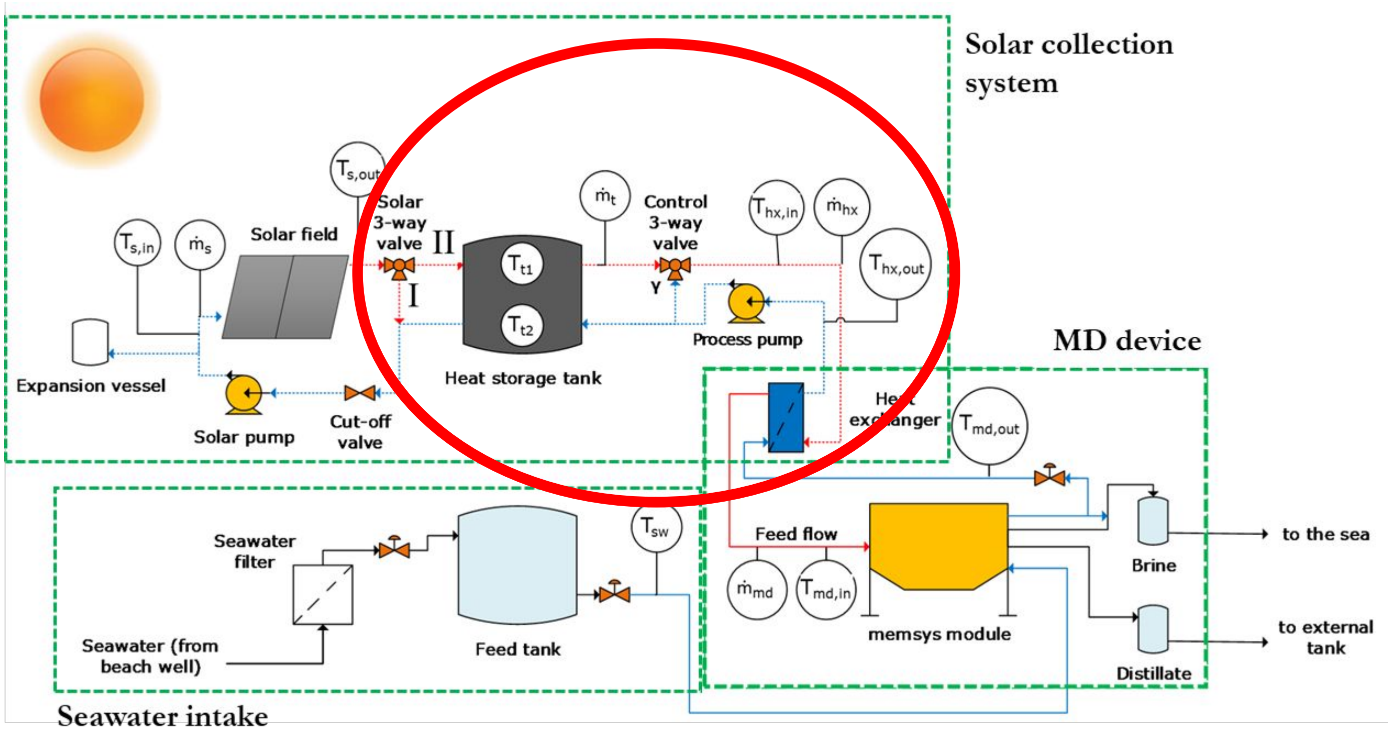
Thermal losses reduced

Limitations:

Solar collection area is restricted to that of the membrane

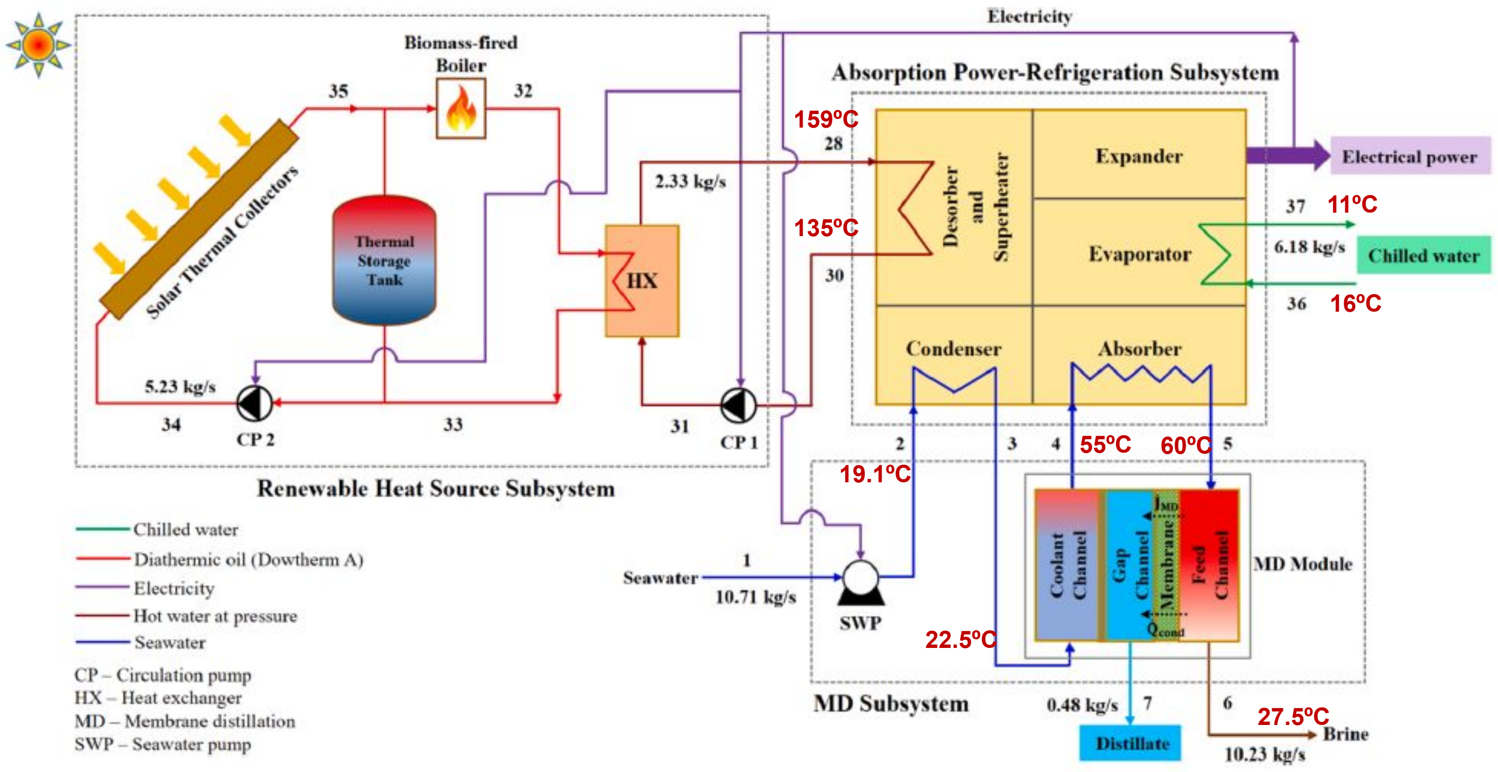
Feed flow rate must be lowered to increase the temperature rise;
as flow rate increases, the temperature rise in the feed becomes difficult and no evaporation takes place
→ temperature polarization limits the efficiency

COUPLING OF MD WITH SOLAR COLLECTORS



COUPLING MD WITH HEAT PUMPS FOR POLYGENERATION

Simulation for Almería (Spain)



D.S. Ayou et al. Applied Thermal Engineering 182 (2021) 116112

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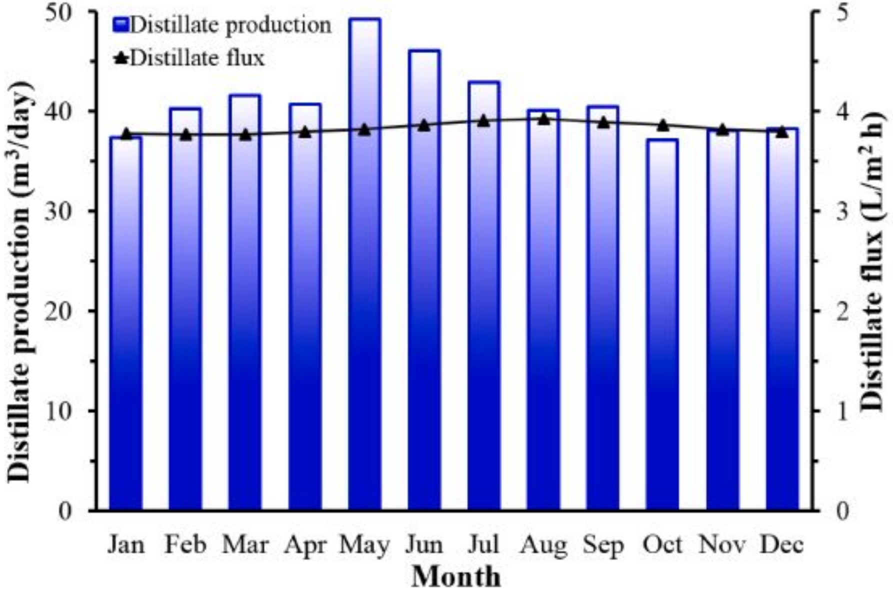
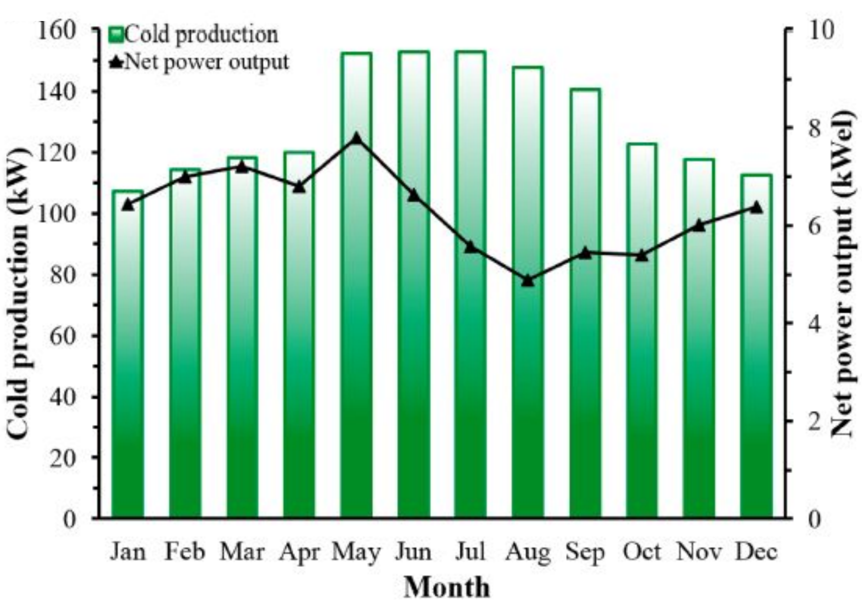


41.4 m^3/day of desalinated water



130 kW cooling capacity and 6.4 kW net electrical power

primary energy resource utilization efficiency = 44.2%; exergy efficiency = 6.9%

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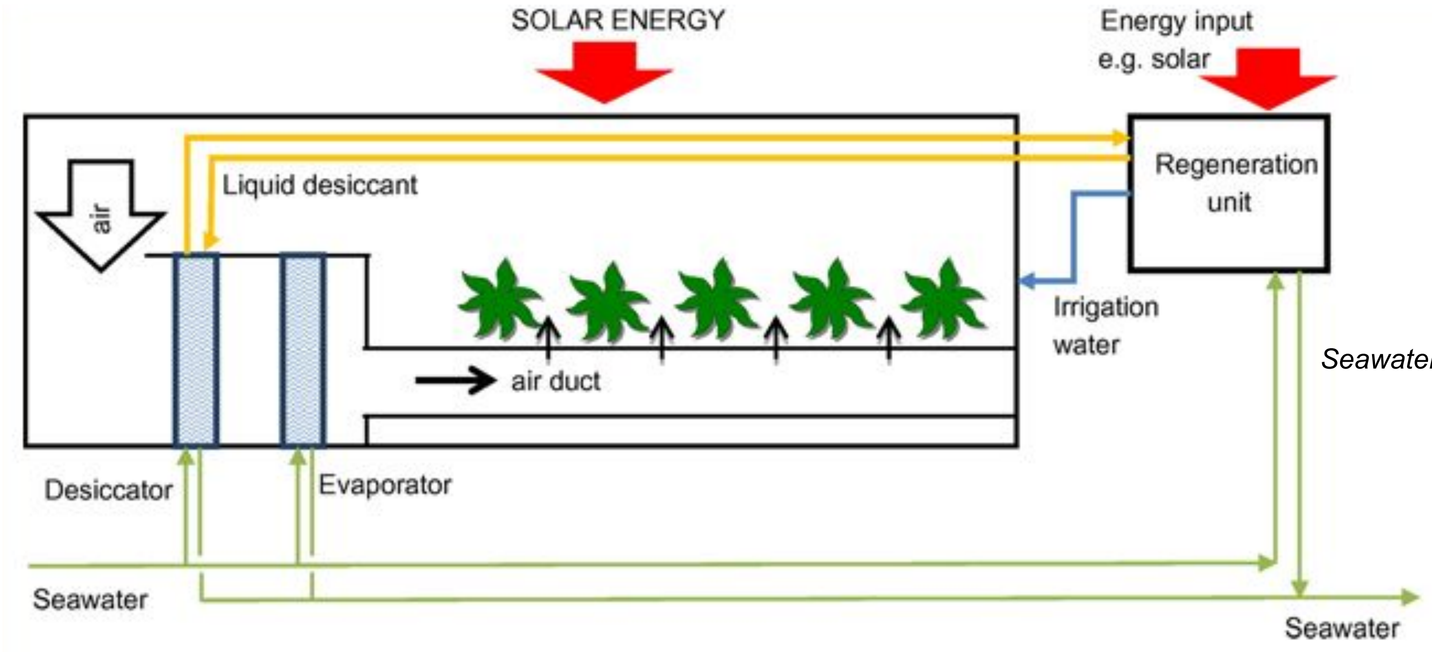
SOLAR ADSORPTION COOLING

Chemical adsorption has been proposed for solar cooling using saline solutions regenerated by thermal desalination technologies

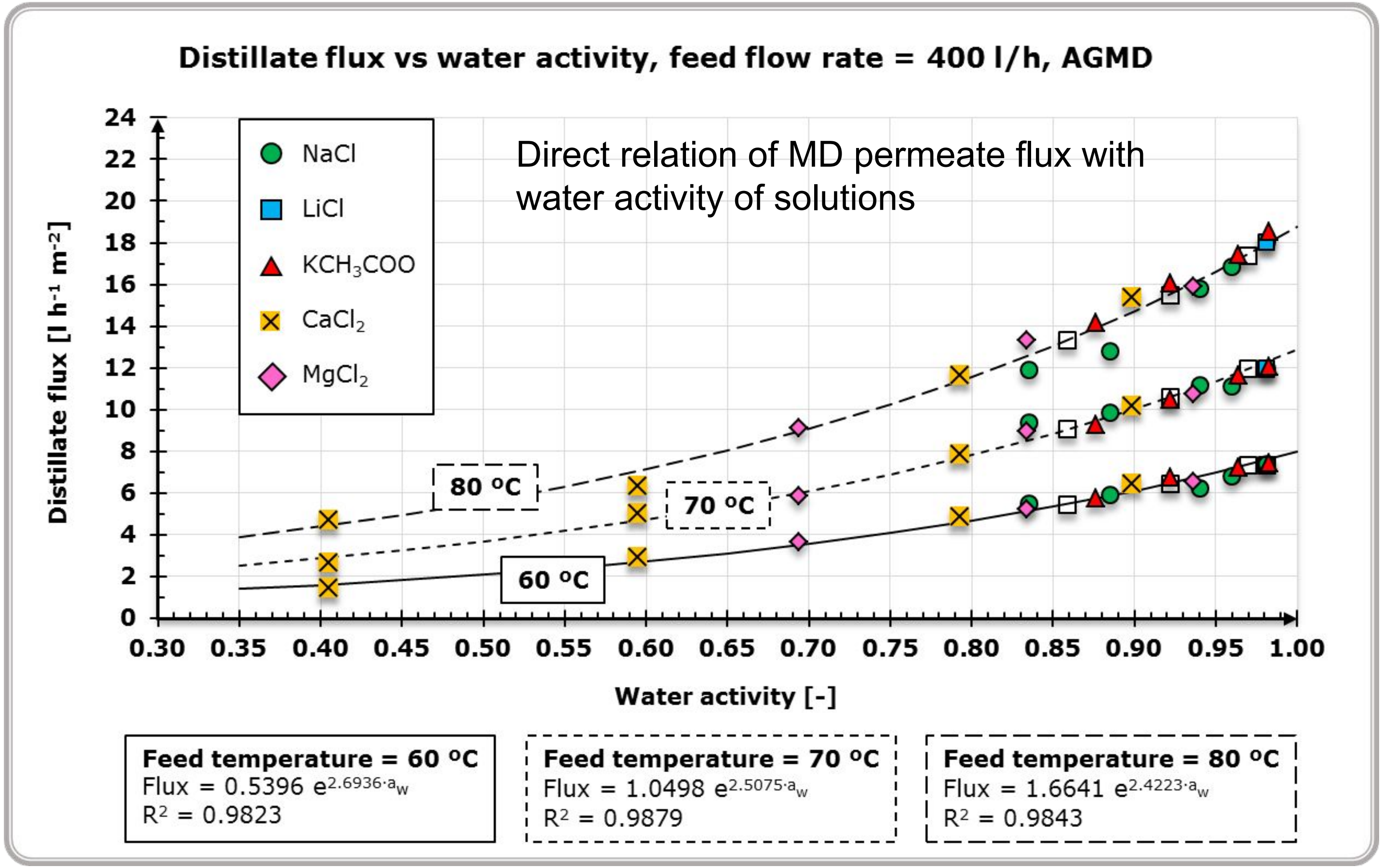
USE OF LIQUID DESICCANTS FOR COOLING

Use of liquid desiccants regenerated by solar energy to support evaporative cooling systems



Seawater Greenhouse©

COUPLING MD WITH LIQUID DESICCANTS

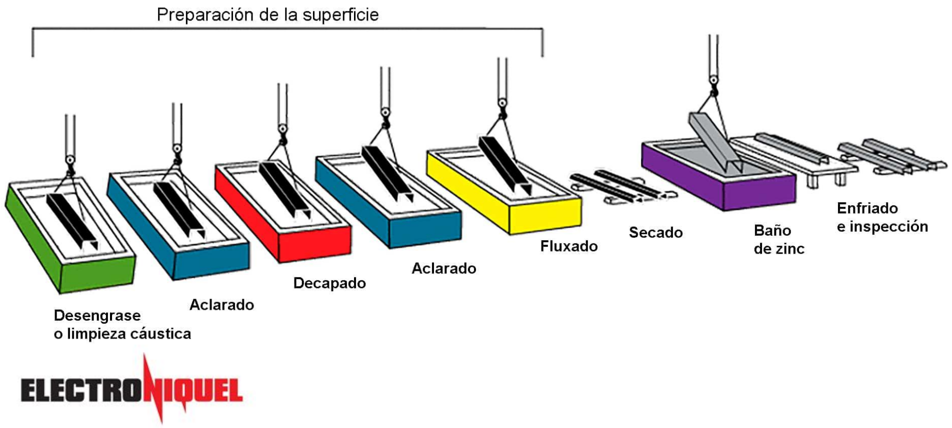


COUPLING MD WITH LIQUID DESICCANTS

The best solutes for liquid desiccant systems have low water activity and therefore require more specific thermal energy for solution regeneration with MD

Salt	Feed temperature [ºC]	Feed concentration [mol l⁻¹]	Water activity [-]
NaCl ●	60, 70, and 80	0.6	0.9810
		1.2	0.9601
		1.7	0.9405
		3.0	0.8852
		4.0	0.8352
LiCl ■	60, 70, and 80	0.7	0.9812
		1.0	0.9702
		2.0	0.9222
		3.0	0.8590
CH_3COOK ▲	60, 70, and 80	0.5	0.9824
		1.0	0.9636
		2.0	0.9224
		3.0	0.8764
$CaCl_2$ ✕	60, 70, and 80	1.5	0.8988
		2.4	0.7930
		3.7	0.5946
		5.0	0.4053
$MgCl_2$ ◆	60, 70, and 80	1.0	0.9359
		2.0	0.8338
		3.0	0.6937

MD FOR REGENERATION OF INDUSTRIAL SOLUTIONS



- **Pickling bath: H_2SO_4 10-38%**

Exhausted: if $[Fe^{2+}] > 80$ g/L

- **Passivation bath: Cl_2CrHO 5 g/L Cr^{3+}**

Exhausted: if $[Fe^{2+}] > 200$ mg/L and $[Zn^{2+}] > 3000$ mg/L

- **Cu-electrolitic bath: $CuSO_4 \cdot 5H_2O$**

Exhausted: if $CuSO_4.5H_2O$ >350 g/l

Neutralization

Water□ Sewerage

Sludge □ External management.

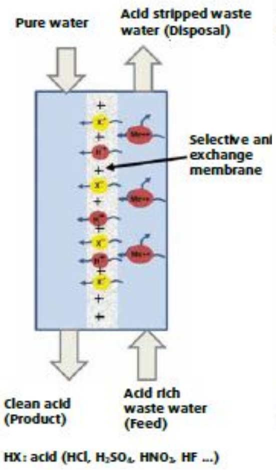
No reutilization of the baths

MD FOR REGENERATION OF INDUSTRIAL SOLUTIONS

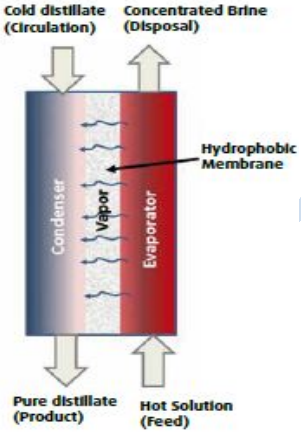
H2020 723729

To develop 4 pilot plants to regenerate industrial solutions from galvanizing industry to:

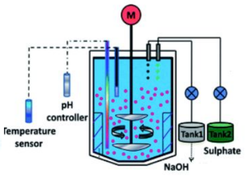
- To reduce the use of water.
- To reduce the production of wastewater
- To recover valuable compounds.
- To guarantee optimal operating conditions.



Diffusion Dialysis



Membrane Distillation

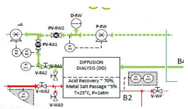


Precipitation

Experim ents

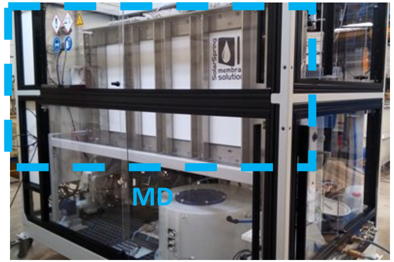
Constru ction

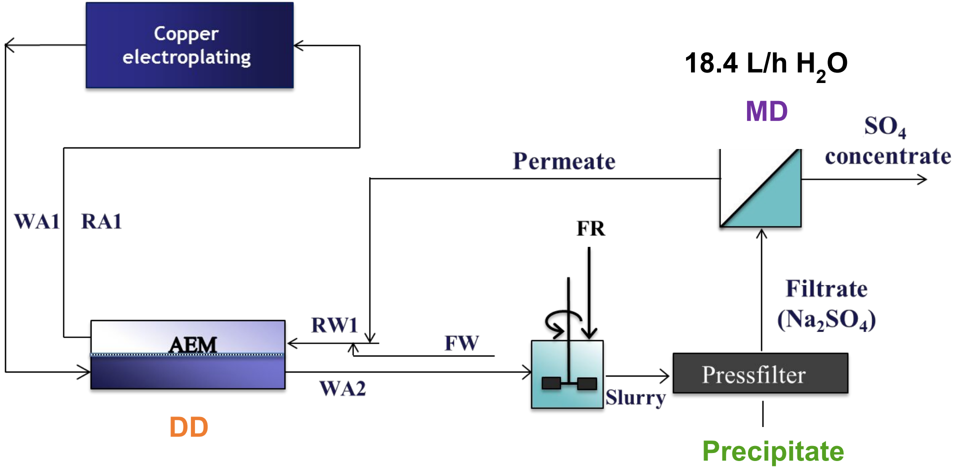
Operatio n



$$r_{H_2SO_4} = 6.8 \cdot 10^{-6} \cdot Cr_{H_2SO_4}^{-1} + 2.2 \cdot 10$$
$$P_{CuSO_4} = 2.4 \cdot 10^{-7} \cdot Cr_{CuSO_4} + 1.8 \cdot 10^{-7}$$
$$P = 1.9 \cdot 10^{-8} \cdot Cr_{H_2SO_4}^{-1} + 8.8 \cdot 10^{-8}$$

MD FOR REGENERATION OF INDUSTRIAL SOLUTIONS





70 % H_2SO_4

20 % Cu^{2+}

84 % Cu^{2+} (pH = 7)

Sale = 50% Cost

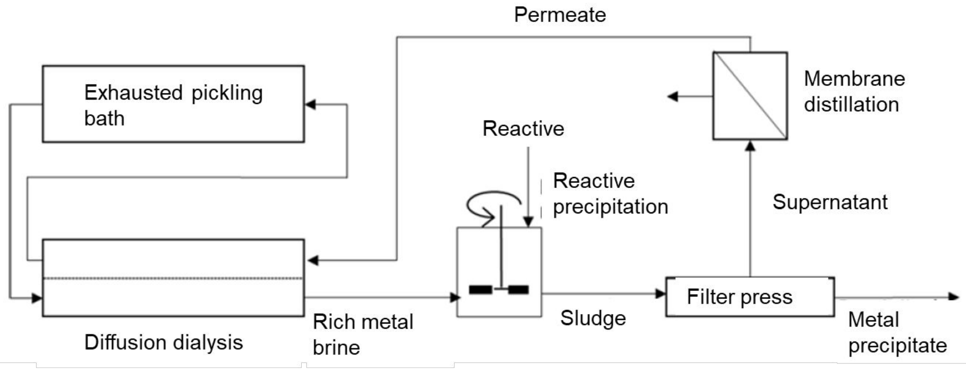
A. Ruiz-Aguirre et al, Separation and Purification Technology, 266 (2021) 118215.

R. Gueccia et al, Membranes, 10-6 (2020) 129-145.

MD FOR REGENERATION OF INDUSTRIAL SOLUTIONS

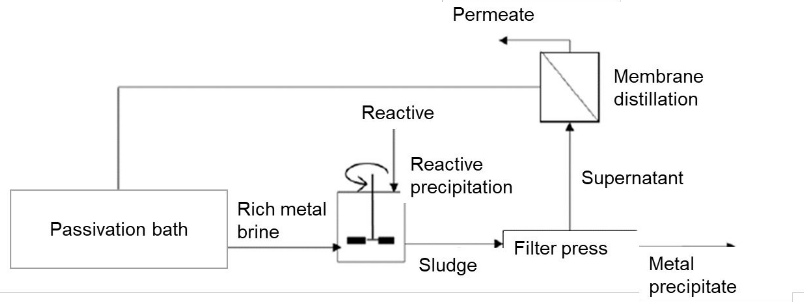
IDE/2020/000398 (IDEPA 2020). → Regeneration of pickling and passivation baths from zinc electroplating line.

Pickling



Recovery of H_2SO_4 above 70% and rejection of Fe^{2+} higher than 80%

Passivation



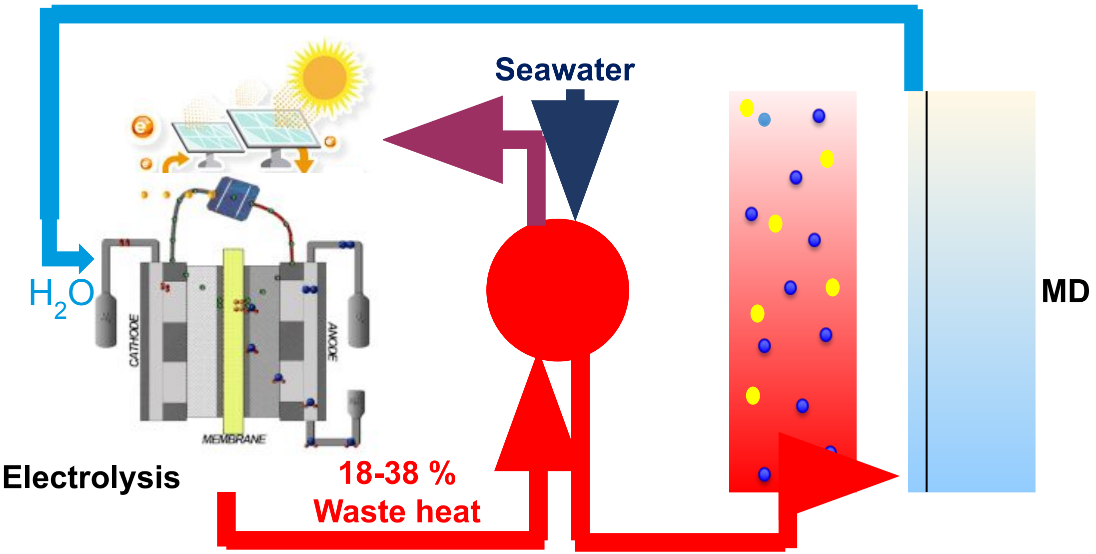
Challenge □

- Selective precipitation.
- Recovery of anticorrosive properties.

Regeneration of 80% of passivation solution.

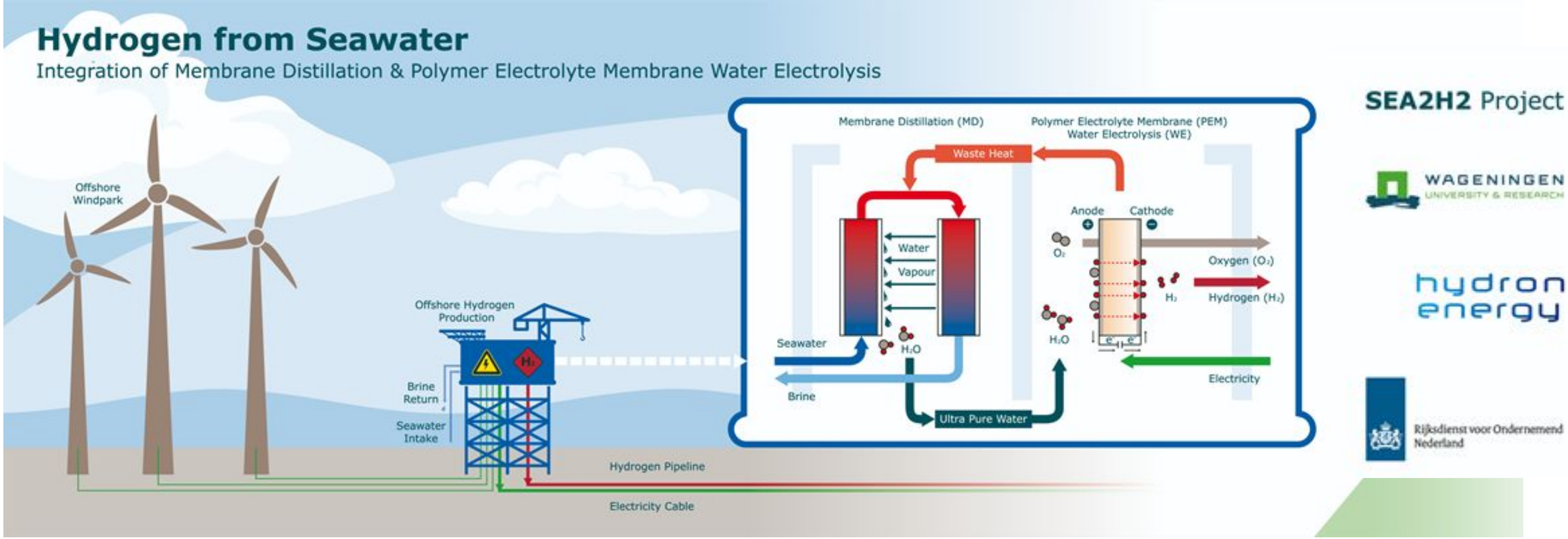
MD FOR RENEWABLE H2 GENERATION

Production of water with MD for generation of renewable H_2 by electrolysis



1. Cooling system of electrolysis is not needed
2. Pure water is produced with MD at zero energy cost waste heat
3. H_2 generation not dependent on the availability of freshwater (abundant saltwater)

MD FOR RENEWABLE H2 GENERATION



Objective: lower cost of green hydrogen production from current level of 4 – 10 €/kg-H_2 towards 2 €/kg-H_2 in 2050

MD FOR RENEWABLE H2 GENERATION

SEA2H2 Project

hydron energy

WAGENINGEN
UNIVERSITY & RESEARCH

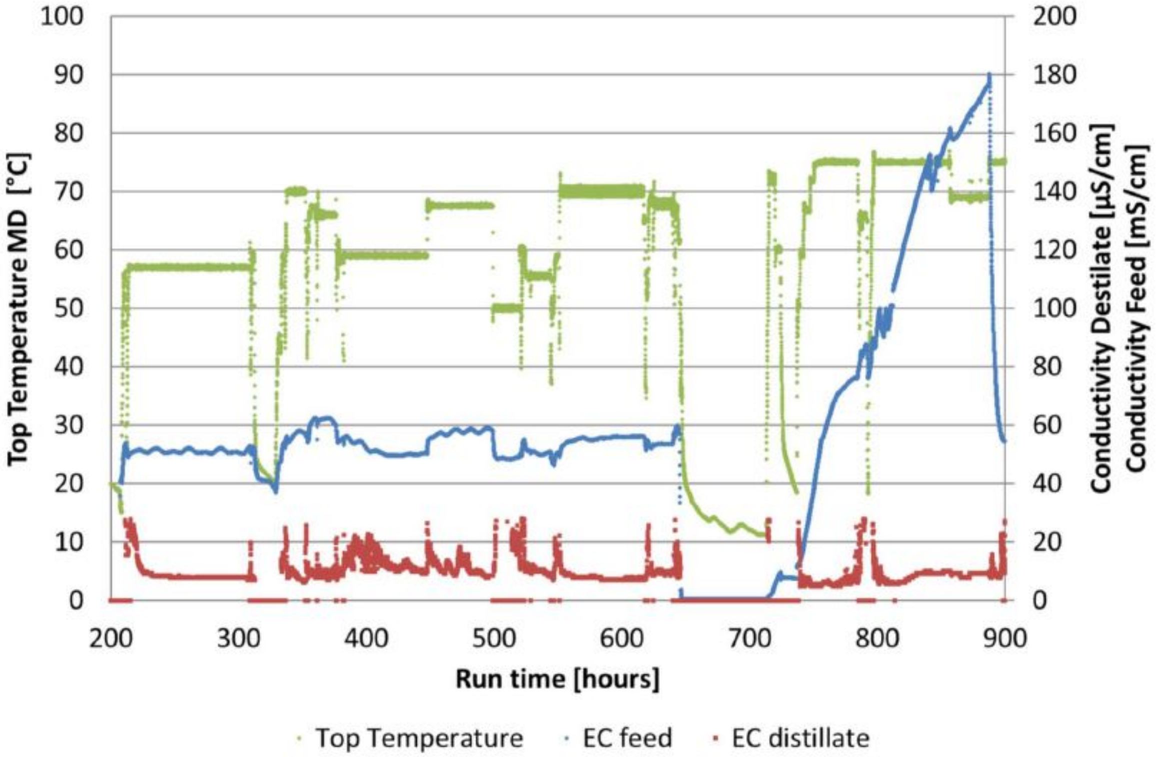
Rijksdienst voor Ondernemend Nederland

pre-pilot plant in the Netherlands:

1 kg/h (Hydron's 50 kW PEMWE stack)

Ultra pure water production capacity ~10 kg/h

MD FOR RENEWABLE H2 GENERATION

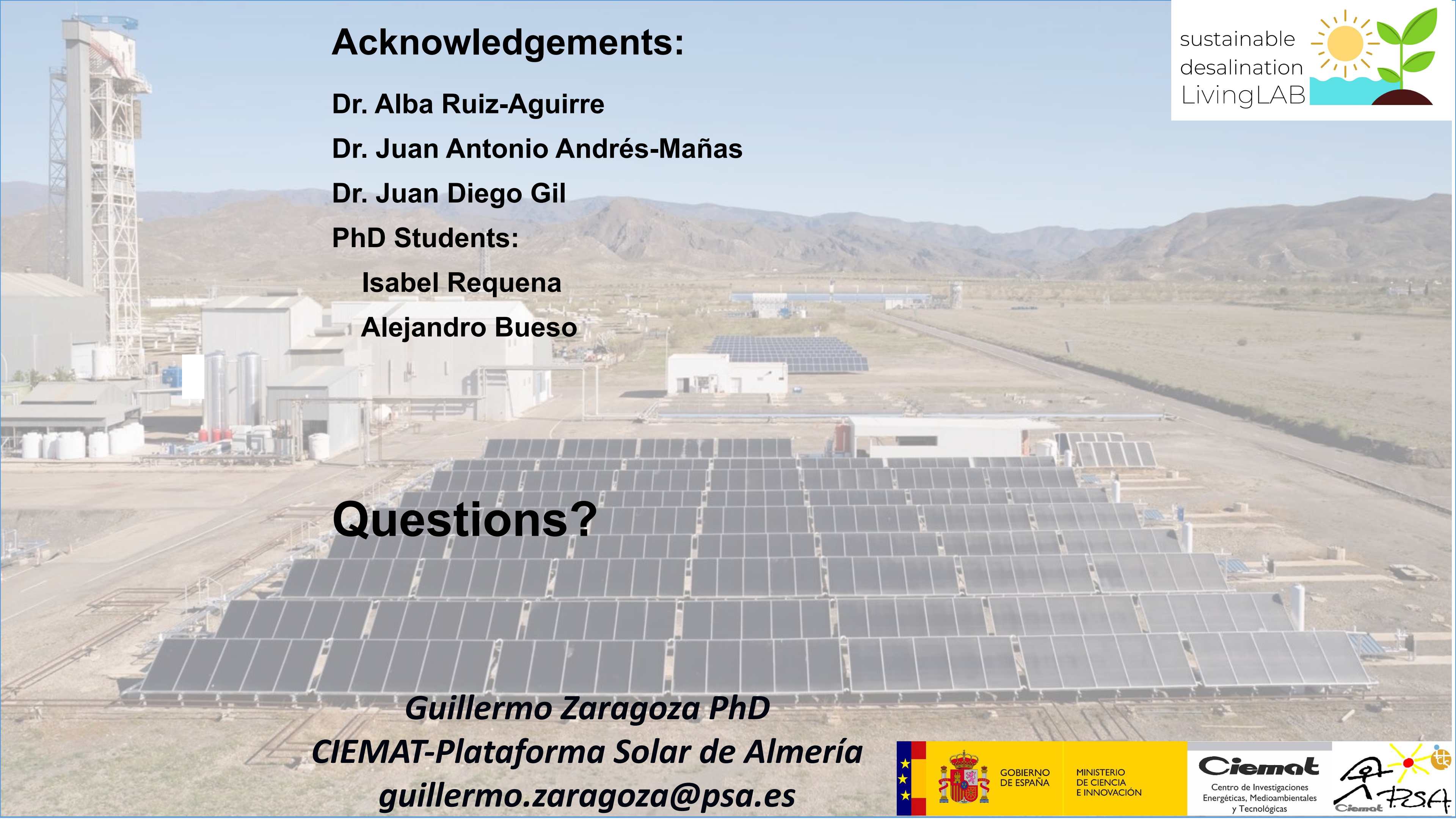


SEA2H2 Project

WAGENINGEN UNIVERSITY & RESEARCH

hydron energy

Rijksdienst voor Ondernemend Nederland



sustainable desalination LivingLAB

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