

Innovative ZLD desalination process for minerals recovery using solar and geothermal energy

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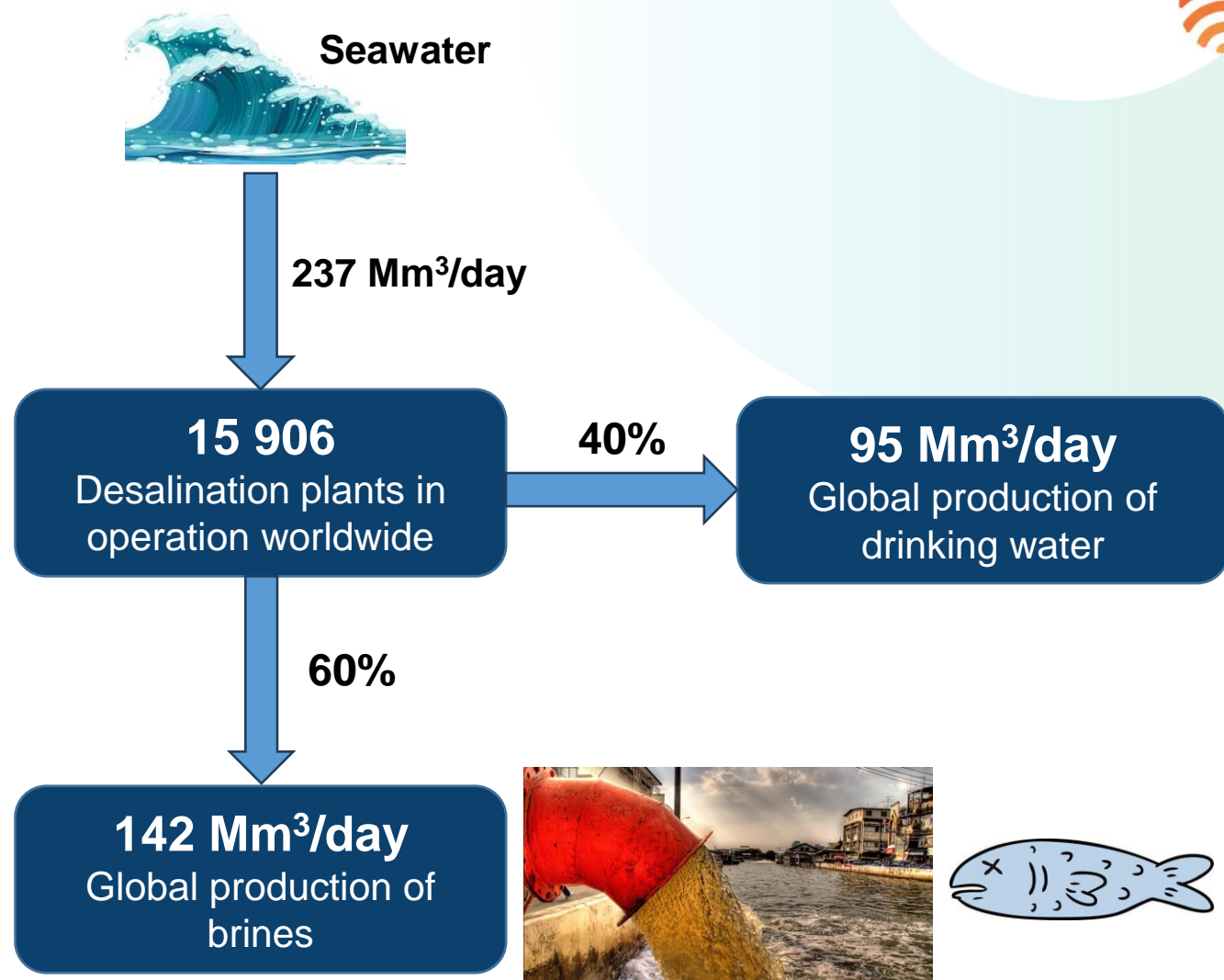
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Introduction

Context

3.6 Billion
people affected by water
scarcity worldwide



Data from [1].

Challenges of desalination

Environmental impacts of brine discharge

- Pollution of natural water bodies (sea, ocean, rivers, aquifers)
- Increased water salinity
- Thermal pollution
- Eutrophication
- Population drops in ecosystems
- Waste of water

Desalination is energy-intensive and costly

- High consumption of fossil fuels is not sustainable and contributes to global warming and Oil & Gas dependency.
- The use of solar thermal energy is interesting in arid countries that suffer from water scarcity.
- But solar-driven desalination is not competitive and too expensive (high investment, intermittence).
- Geothermal energy is interesting in volcanic areas and provides constant power, but it is also expensive.
- The LCOW of solar thermal-driven and geothermal-driven desalination varies between 0.95-4.60 vs. 0.26-1.75 \$/m³ for fossil fuel-driven desalination [1].

➔ But large scale can reduce the LCOW through economy of scale, while ZLD brine mining can increase water recovery and produce valuable crystals that can be sold to improve profitability and sustainability by avoiding brine discharge.

Opportunities for brine mining

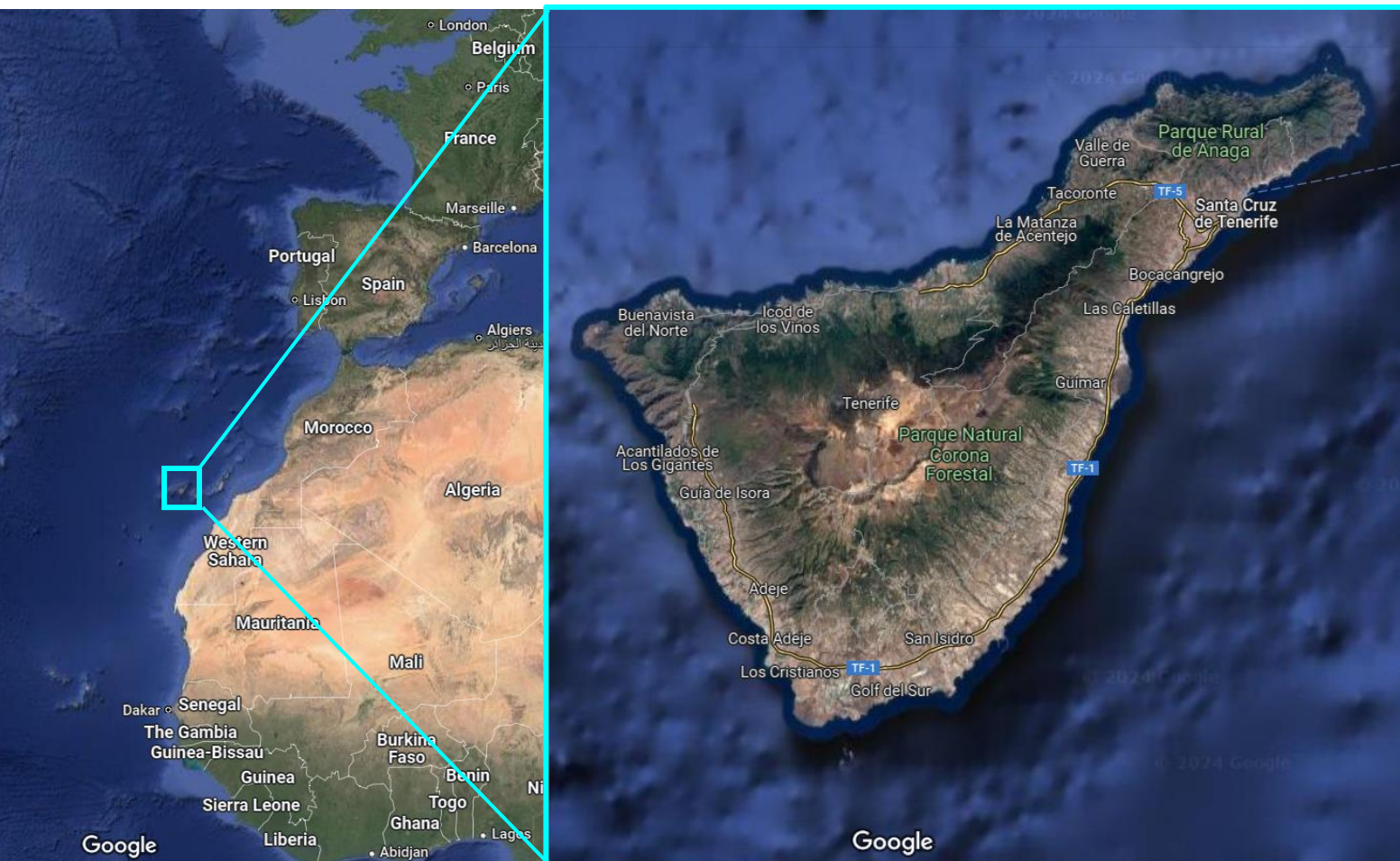
Table 1. Average composition of seawater desalination brine [1].

Ions	Concentration
Na ⁺ (mg/L)	16 200
Cl ⁻ (mg/L)	32 461
Mg ²⁺ (mg/L)	2 350
Ca ²⁺ (mg/L)	702.33
K ⁺ (mg/L)	840.67
Sr ²⁺ (mg/L)	9.70
SiO ₂ (mg/L)	7.36
HCO ₃ ⁻ (mg/L)	119.67
SO ₄ ²⁻ (mg/L)	4 344.33
NO ₃ ⁻ (mg/L)	3.17
F ⁻ (mg/L)	1.77
Li ⁺ (mg/L)	0.29
Cu (mg/L)	0.20
Fe (mg/L)	0.35
Mn (mg/L)	0.07
Zn (mg/L)	0.20
Cr (mg/L)	0.20
TDS (mg/L)	57 041.31
pH	6.7

Table 2. Average product prices.

Parameter	Value
Price of freshwater	2.85 \$/m ³
Price of NaCl	100 \$/tonne
Price of MgCO ₃ 3H ₂ O	800 \$/tonne
Price of CaCO ₃	500 \$/tonne
Price of Li ₂ CO ₃	20 000 \$/tonne

Case study – Tenerife Island



- Remote island with large touristic seaside resorts experiencing water shortages.
- 80% of water demand comes from underground aquifers requiring rainfall.
- But due to droughts, rainfall has decreased by 15-40% within the past years combined with an increase of water evaporation by 10-25% due to global warming.
- This has led authorities to establish water restrictions [2].
- Current desalination capacity of the island: 116 960 m³/day accounting for only 16% of water consumption (water reuse accounts to 4%) [3].
- Large-scale desalination is needed to supply increasing demand.
- But Tenerife has great solar and geothermal energy resources that are practically untapped.



Great candidate for solar- and geothermal-driven desalination.

Innovation

Novel ZLD brine mining process

Seawater desalination brine

Previously developed, modelled and tested a novel ZLD process capable of extracting resources from waste brines:

- 99.8% of water in the form of pure liquid distillate
- 89% of Mg^{2+} in the form of $MgCO_3 \cdot 3H_2O$
- 99% of Ca^{2+} in the form of $CaCO_3$
- 72% of NaCl
- 80% of Li^+ in the form of Li_2CO_3

The process uses innovative thermal energy recovery system that reduces energy consumption to $16.7 \text{ kWh}_e/\text{m}^3$ of produced water.

It uses novel carbon capture technique to reduce carbon emissions.

Liquid distillate

ZLD process

$MgCO_3 \cdot 3H_2O$

$CaCO_3$

NaCl

Li_2CO_3

 **Process to be patented**

Is Brine Mining profitable?

Can it improve the sustainability of desalination?

- Model and simulate a complete sustainable large-scale multi-effect distillation (MED) desalination plant powered by 3 different scenarios:
 - (i) parabolic trough collectors (PTC) without thermal energy storage (TES);
 - (ii) PTC + TES;
 - (iii) low-grade geothermal energy.
- Seawater feed capacity = 100 000 m³/day.
- Calculate the LCOW and payback period with and without the ZLD process.
- Evaluate the techno-economic benefits of brine mining for each scenario.
- Compare results with state-of-the-art and commercial data.

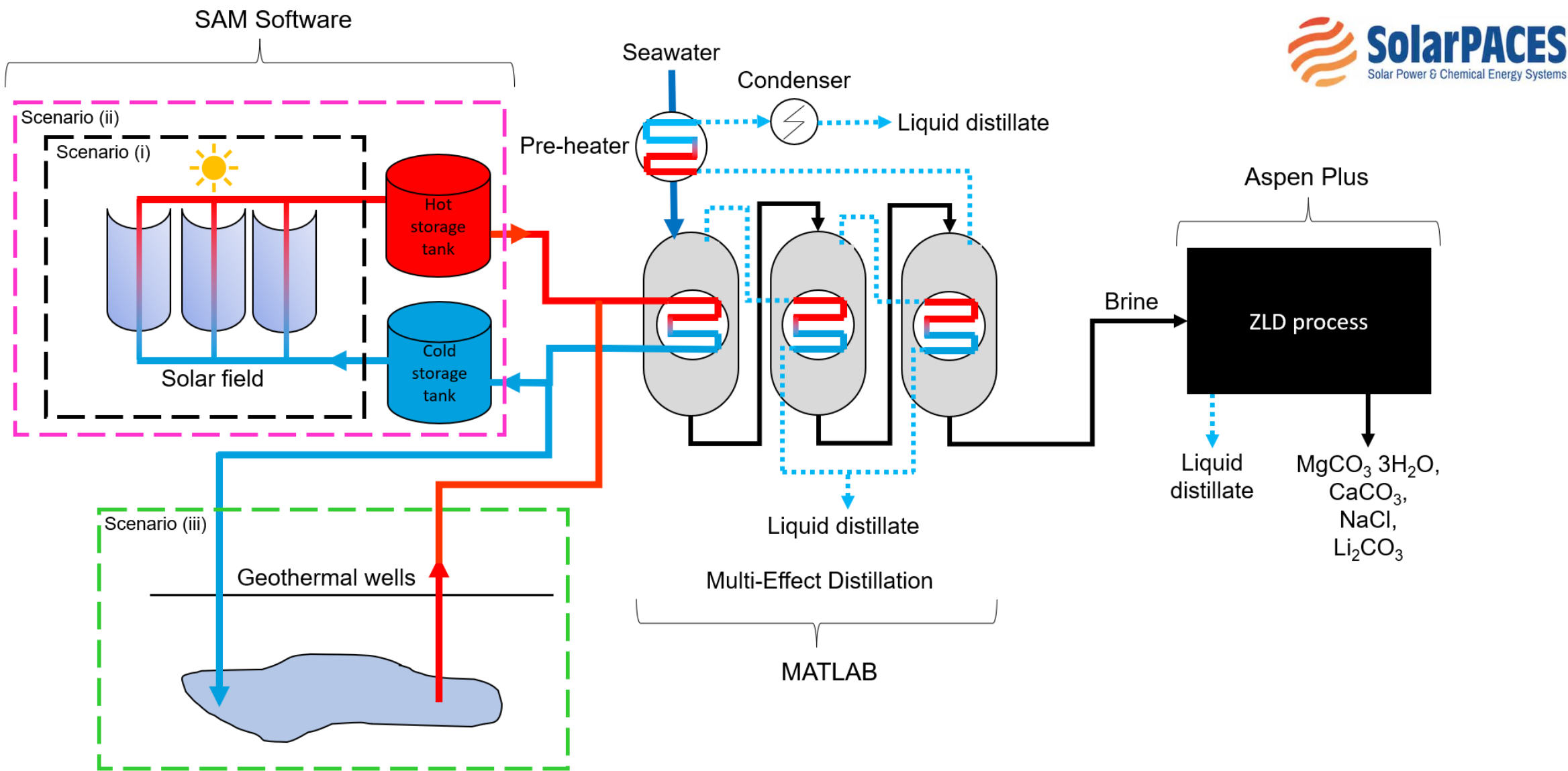


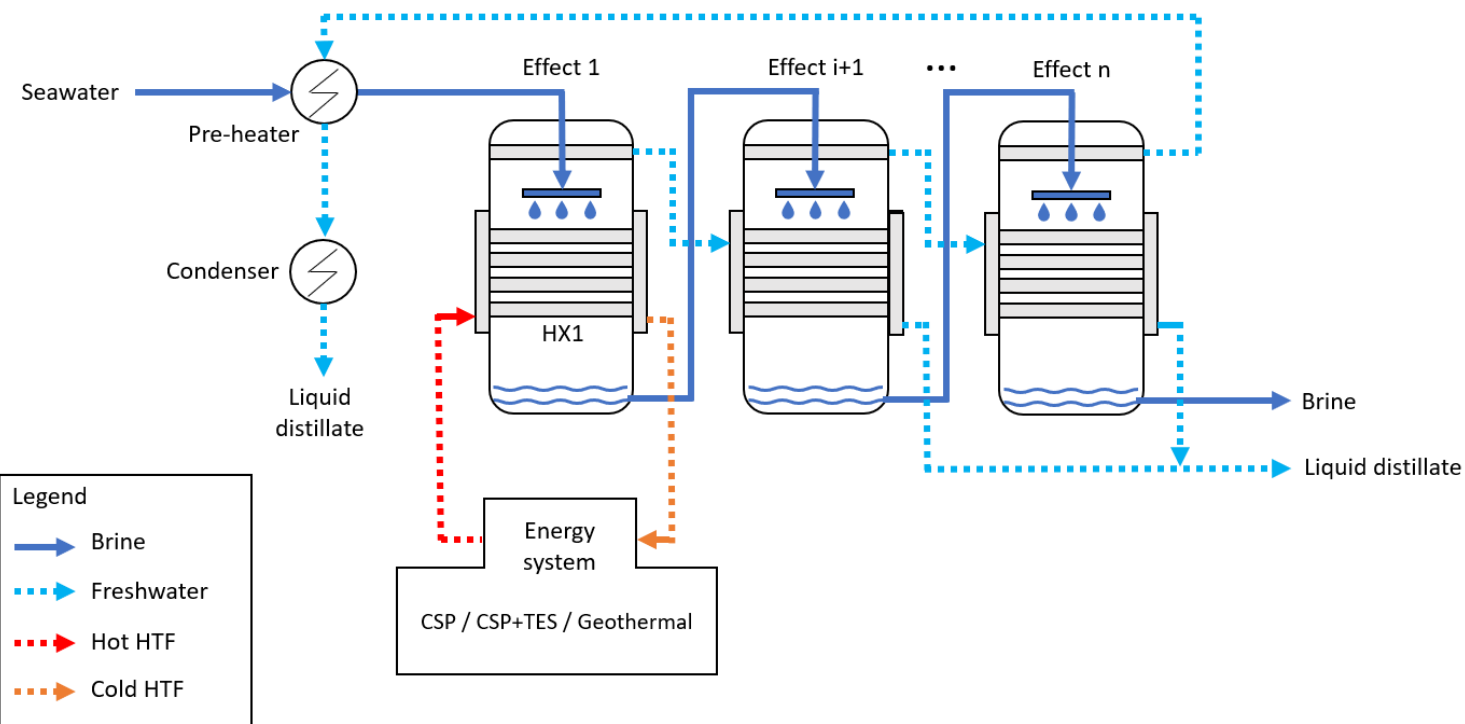
Figure 1. Integrated MED-ZLD model. Scenarios (i), (ii), and (iii) are represented within the black, pink, and green dotted boxes respectively.

Techno-economic modelling

MED modelling

Table 3. Assumptions for the MED system

Parameters	Value
Feed seawater capacity	100 000 m ³ /day
Number of effects	16
Top brine temperature (TBT)	70°C
Temperature difference between effects	3°C
Temperature of last effect	25°C
Feed seawater initial temperature	20°C
Feed seawater initial salinity	35 000 ppm TDS
Distillate salinity	0 ppm TDS
HTF fluid	Pressurised water
HTF hot temperature	90°C
HTF cold temperature	60°C

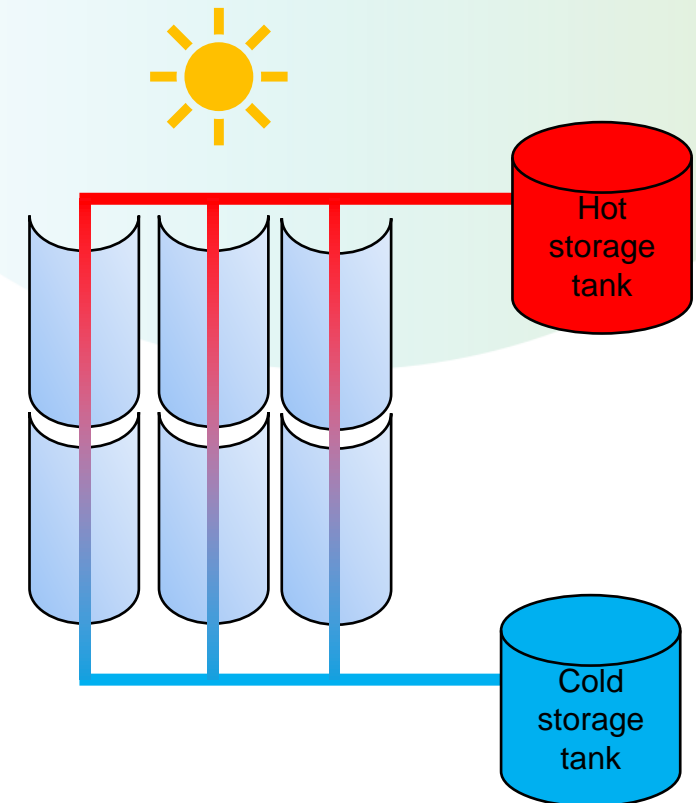


- Heat losses are negligible.
- Vapour leaving each effect is condensed completely.
- Pressure drops are negligible.
- Boiling point elevation and specific heat capacities are functions of temperature and salinity.
- The maximum concentration of the brine coming from the last effect is about 60 000 ppm TDS to avoid scaling. This limits water recovery from the MED plant up to 40%. The MATLAB model is based on [4-6].

PTC solar field modelling

Table 4. Design of the PTC solar fields on SAM software.

Scenario	(i) PTC	(ii) PTC+TES
Thermal power output	179 MW	179 MW
Reflective aperture area of PTC module	817.5 m ²	817.5 m ²
Aperture width of the PTC module	5.75 m	5.75 m
Number of modules per assembly	12	12
Length of the collector assembly	150 m	150 m
HTF	Pressurised water	Pressurised water
Hot HTF temperature	90°C	90°C
Cold HTF temperature	60°C	60°C
Number of assemblies per loop	3	3
Solar multiple	1	4
Hours of storage	0	16h
Total aperture reflective area	232 987.5 m ²	924 592.5 m ²
Number of loops	95	377
TES capacity	0	2 864 MWh _{th}
TES tank volume	0	87 634 m ³
Annual energy output	318 551 616 kWh _{th}	1 124 953 728 kWh _{th}
Capacity factor	20.3%	71.7%



Geothermal system modelling

The Canary Islands have great geothermal potential for both high and low enthalpy due to their volcanic nature.

Assumptions for the design of the geothermal wells:

- Thermal power capacity = 179 MW
- 2 wells are considered: 1 production well and 1 injection well
- Average geothermal gradient $Grad_{geo} = 67^{\circ}\text{C}/\text{km}$ [7]
- Average soil temperature at the surface $T_{surf} = 31^{\circ}\text{C}$
- Heat loss along the well $T_{loss} = 5^{\circ}\text{C}$
- Target temperature of the working fluid $T_{target} = 90^{\circ}\text{C}$

$$T_{target} = T_{surf} + depth_{well} \times Grad_{geo} - T_{loss} \quad [6]$$

➔ Required depth of geothermal wells = 955m.

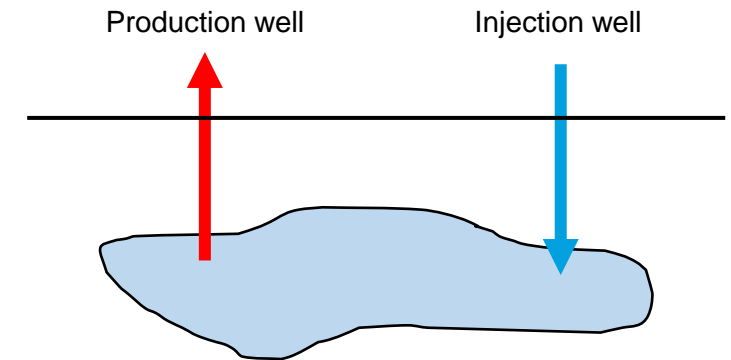


Table 5. Economic assumptions.

Parameter	Value
Plant lifetime	25 years
Interest rate	0.05
Cost of electricity	0.0845 \$/kWh _e
Price of freshwater	2.85 \$/m ³
Price of MgCO ₃ · 3H ₂ O	800 \$/tonne
Price of CaCO ₃	500 \$/tonne
Price of NaCl	100 \$/tonne
Price of Li ₂ CO ₃	20 000 \$/tonne

Results

Performance of the MED plant without ZLD

Table 6. Techno-economic results of the MED plant without ZLD.

Parameter	Scenarios		
	PTC	PTC+TES	Geothermal
Volume of freshwater daily (m ³ /day)	40k	40k	40k
Annual freshwater production (m ³ /year)	3M	10M	14M
Thermal SEC (kWh _{th} /m ³ of produced freshwater)	107.3	107.3	107.3
Electrical SEC (kWh _e /m ³ of produced freshwater)	3.3	3.3	3.3
Cost of renewable energy system (\$)	13M	47M	5M
Cost of TES (\$)	0	32M	0
CAPEX direct (\$)	156M	231M	146M
CAPEX indirect (\$)	16M	23M	15M
CAPEX total (\$)	171M	254M	161M
Electricity cost (\$/year)	822k	3M	4M
OPEX total (\$/year)	6M	11M	11M
Total annual expenses (amortised CAPEX + OPEX) (\$/year)	18M	28M	22M
Water recovery (%)	40%	40%	40%
LCOW (\$/m³)	6.08	2.74	1.54
Revenue (\$/year)	8.5M	30M	41M
Payback (years)	N/A	13.2	5.3

Benefits of the ZLD process

Table 7. Techno-economic results of the MED-ZLD plant.

Parameter	Scenarios		
	PTC	PTC+TES	Geothermal
CAPEX of the ZLD process (\$)	1273M	1273M	1273M
OPEX of the ZLD process (\$/year)	13M	47M	64M
Thermal SEC of the ZLD process (kWh _{th} /m ³ of produced water)	182.9	182.9	182.9
Electrical SEC of the ZLD process (kWh _e /m ³ of produced freshwater)	16.7	16.7	16.7
Water recovery total (%)	99.8%	99.8%	99.8%
Annual freshwater production total (m ³ /year)	7M	25M	35M
MgCO ₃ ·3H ₂ O production (tonne/year)	49k	173k	236k
CaCO ₃ production (tonne/year)	8k	27k	36k
NaCl production (tonne/year)	158k	558k	763k
Li ₂ CO ₃ production (tonne/year)	5	19	26
CAPEX of the total MED-ZLD process (\$)	1444M	1527M	1433M
OPEX of the total MED-ZLD process (\$/year)	19M	57M	74M
Total annual expenses (amortised CAPEX + OPEX) (\$/year)	120M	164M	175M
Production cost of MgCO ₃ ·3H ₂ O total (\$/tonne)	2500	960	750
Production cost of CaCO ₃ total (\$/tonne)	16k	6k	5k
Production cost of NaCl total (\$/tonne)	770	300	230
Production cost of Li ₂ CO ₃ total (\$/tonne)	23M	9M	7M
Thermal SEC total (kWh _{th} /m ³ of produced freshwater)	146.9	146.9	146.9
Electrical SEC total (kWh _e /m ³ of produced freshwater)	10.8	10.8	10.8
LCOW total (\$/m³)	16.97	6.54	5.09
Revenue total (\$/year)	79M	280M	382M
Payback period total (years)	24.0	6.9	4.7

Benefits of the ZLD process

Table 8. CO₂ emissions reduction of the MED-ZLD plant.

Scenario	(i) PTC	(ii) PTC+TES	(iii) Geothermal
CO ₂ emissions reduction (tonne CO ₂ /year)	25 721	90 847	124 170

Table 9. Contribution to revenue by each product from the MED-ZLD plant.

Product	Water	MgCO ₃ 3H ₂ O	CaCO ₃	NaCl	Li ₂ CO ₃
Contribution to revenue total	25.78%	49.37%	4.76%	19.95%	0.14%

Conclusion

Conclusion

Without ZLD	With ZLD
<ul style="list-style-type: none"> Water recovery = 40% 	<ul style="list-style-type: none"> Water recovery = 99.8%
<ul style="list-style-type: none"> LCOW: <ul style="list-style-type: none"> (i) 6.08 \$/m³ (ii) 2.74 \$/m³ (iii) 1.54 \$/m³ 	<ul style="list-style-type: none"> LCOW: <ul style="list-style-type: none"> (i) 16.97 \$/m³ (ii) 6.54 \$/m³ (iii) 5.09 \$/m³
<ul style="list-style-type: none"> Payback period: <ul style="list-style-type: none"> (i) Non-profitable (ii) 13.2 years (iii) 5.3 years 	<ul style="list-style-type: none"> Payback period: <ul style="list-style-type: none"> (i) 24.0 years (ii) 6.9 years (47.7% drop) (iii) 4.7 years (11.3% drop)
	<ul style="list-style-type: none"> Although annual expenses increased: <ul style="list-style-type: none"> (i) by 6.7-times (ii) by 5.8 times (iii) by 8-times <u>Revenue also increased by 9.4-times in all cases</u> CO₂ emissions reduced by 26k-124k tonnes/year <p>➔ Brine mining improves profitability and sustainability</p>

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