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Towards zero liquid discharge desalination

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Demonstration of ultra-high-water recovery and brine concentration in a prototype evaporation unit: Towards zero liquid discharge desalination

Giuseppe Scelfo [a], Alessandro Trezzi [b], Fabrizio Vassallo [a], Andrea Cipollina [a,*], Vittorio Landi [b], Christina Xenogianni [c], Alessandro Tamburini [a], Dimitrios Xevgenos [d,*], Giorgio Micale [a]

[a] Dipartimento di Ingegneria, Università degli Studi di Palermo (UNIPA), Viale delle Scienze, Ed 6, 90128 Palermo, Italy
[b] SWS Sofinter SpA, Milano, Italy
[c] Thermossol Steamboilers SA, Athens, Greece
[d] Technology, Policy & Management Faculty, Delft University of Technology, the Netherlands

ABSTRACT

The availability of water is still one of the most important factors affecting the sustainable growth of a country. Although many countries have free access to an inexhaustible source of water, the sea, this source cannot be used for human purposes as it is. To face this problem, desalination has been proposed for freshwater production but the generation of a waste brine effluent poses some issues of actual sustainability. In this work, the operation results of a Multiple Effect Distillation (MED) demo plant, designed for stable operation at high brine concentrations and operated as a brine concentrator, are presented. To this purpose, the integration with NanoFiltration (NF) has been implemented to minimize scaling risks, by removing bivalent ions from the feed stream. The 2-effects MED pilot unit, with a capacity of 1.7 m³/h, has been installed as part of the treatment chain of the WATER-MINING project, within the premises of the power station of the island of Lampedusa (Sicily, Italy) and is fully powered by waste heat at 70–80 °C from diesel engines. A vapor temperature of 40–50 °C allowed a perfect coupling with the low temperature waste heat source, demonstrating the possibility to produce distilled water with a conductivity between 15 and 25 µs/cm. Among the several operating conditions investigated, a recovery ratio above 80 % has been achieved and an effluent brine conductivity of 240 mS/cm was produced, very close to saturation in NaCl, thus being excellent for food-grade sea salt production in evaporative ponds. For the first time, it has been demonstrated on a pilot scale how a MED unit, supplied with waste heat, can be used efficiently as a brine concentrator, obtaining a brine concentration 8 times higher than the input concentration without any scaling problem.

1. Introduction

Freshwater scarcity is a major problem that poses a significant threat to the socio-economic development of many regions. In fact, the increase in urbanization and industrialization has led to an ever-increasing demand for fresh water, whose availability is decreasing due to desertification. For several decades, more and more efforts have been devoted to the production of fresh water from various sources, including the sea, via desalination technologies. However, extraction of fresh water from the sea, through desalination, also generates a waste brine that, if left untreated, leads to an inexorable loss of resources such as salts, minerals, organic and inorganic substances. Recent studies have shown the potential of capturing the Circular Water Value of brine effluents through circular desalination solutions [1].

Currently, different disposal methods have been adopted in the management of waste saline solutions (brines) such as: i) deep well injection, ii) surface water discharge iii) evaporation ponds, iv) land application and v) sewer disposal. However, these disposal strategies are not always sustainable, due to possible negative effects on the environment and marine ecosystems [2], particularly when the context is linked to small isolated areas or marine ecosystems of great environmental value [3]. For example, Al Shammari [4] and Brika [5], shows cases where, by adopting the technique of surface disposal strategies, there is a radical change in the osmotic balance between marine species and the surrounding environment. This change could lead in the long run to the migration and extinction of some species from the affected basin. Moreover, very often thermal desalination plant rejects

<table>
<tr><td colspan="2">Nomenclature</td></tr>
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P_{el}	Electrical Power [kW$_{el}$]	MD	Membrane Distillation
P_{th}	Thermal Power [kW$_{th}$]	MED	Multiple Effect Distillation
C_{in}	Equivalent molar concentration of sodium chloride in feed brine [mol/L]	MED-AB	Multiple Effect Distillation with Absorption Compressor
		MF-PFR	Multiple Feed Plug Flow reactor
C_{out}	Equivalent molar concentration of sodium chloride in outlet brine [mol/L]	MLD	Minimum Liquid Discharge
		MSF	Multiple Stage Flash
$\dot{V}_{dist}$	Distillate flow rate [m^3/h]	MVC	Mechanical Vapor Compressor
		NCG	Non – Condensable Gases
$\dot{V}_{feed}$	Feed flow rate [m^3/h]	NF	Nano-Filtration
		RO	Reverse Osmosis
Abbreviations		RR	Recovery Ratio
CF	Concentration Factor	SEEC	Specific Electrical Energy Consumption
CPV	Concentrator Photovoltaics	STEC	Specific Thermal Energy Consumption
ED	Electro-Dialysis	TBT	Top Brine Temperature
EDBM	Electro-Dialysis with Bipolar Membrane	TDS	Total Dissolved Salt
EFC	Eutectic Freeze Crystallization	TVC	Thermal vapor compression
HEX	Heat Exchange	WM	Water Mining
HPRO	High Pressure Reverse Osmosis	ZLD	Zero Liquid Discharge

concentrated brine at 30 – 40 °C [6] causing a local variation in basin temperatures with a consequent effect on the growth of marine flora and fauna. As an example, Uddin [7], showed how the increase in salinity and decrease in pH due to carbonate dissolution induces severe stress to the coral communities in the Persian/Arabian Gulf.

Evaporation ponds require very large areas and this leads to an excessive subtraction of fertile land that could be used for the production of food for the local community; injection of deep wells is only possible in regions where the geophysical characteristics of the soil allow safe storage (no possibility in seismic regions, such as Greece [8]) and only for limited quantities of brine [9]. Currently, surface water disposal is adopted in more than 90 % of brine disposal cases but it is possible only if the chemical composition of the brine is suitable for the harmonization with the receiving water bodies [9].

For these reasons, alternative brine management approaches are being considered that are based on waste minimization. The ultimate goal is to maximize the production of fresh water and minimize the production of liquid waste going toward a Minimum Liquid Discharge (MLD) strategy up to, in some cases, a Zero-Liquid Discharge (ZLD).

In a ZLD process, a total recovery of water present in the effluent is achieved through membrane or evaporative processes or hybrid approaches. Having a total recovery of water, the final waste is a solid product, which, in addition to a potential economic interest based on the type of product, allows for easier management and storage.

Recently, MLD processes have been introduced, in which fresh water recovery can reach more than 95 %. This can significantly lower the energy demand of the process, avoiding the final crystallization step, which is very energy intensive and technologically demanding.

In general, MLD and ZLD processes consist of 2 or 3 steps [10]:

1. Preconcentration: with a recovery of fresh water around 40–80 %, mostly implemented by membrane technologies such as: i) Reverse Osmosis (RO), ii) High Pressure Reverse Osmosis HPRO), iii) Electro-Dialysis (ED). All of them are characterized by the lower energy consumption, typically lower than 5 kWh/m^3.
2. Evaporation: a further recovery of fresh water up to 95 % is achieved with thermal technologies such as: i) Multi-Effect Distillation (MED), ii) Multi-Stages Flash (MSF), iii) Mechanical Vapor Compression (MVC). These are characterized by higher specific equivalent electrical energy consumption of up to 125 kWh/m^3. A further possibility, having lower cost but applicable only to small volumes, is the use of evaporative ponds, in which solar energy and wind are used to enhance evaporation and concentrate the brine-

3. Crystallization: typical of ZLD processes, achieving 100 % water recovery/removal, for which thermal or hybrid technologies (Eutectic Freeze Crystallization (EFC), Membrane Distillation (MD), Membrane crystallization) are used, all characterized by very high specific equivalent electrical energy consumption, reaching up to 360 kWh/m^3.

A number of studies reported in the literature have focused on the use of thermal evaporative technologies for the treatment of industrial brines or seawater brine effluents, for the production of a high-quality distillate and/or a further concentrated saline stream, in most cases highlighting the importance of using low-grade thermal energy sources to push the energy sustainability of the process.

On one side, several authors reported theoretical analysis indicating that increasing the number of stages in MED plants results in better thermal efficiency of the process, also guaranteeing high concentration ratios for the saline effluent. For example, Zhao *et al* [11] al analyzed the case of a Chinese refinery discharge brine with a saline concentration of about 6.4 g/l, which had to be concentrated up to 70 g/l, keeping a very high process thermal efficiency. Another example of modelling analysis was presented by Liponi *et al* [12] applied to the case of seawater desalination brine, which pointed out how the use of different MED layouts, t to increasing heat recovery, can affect the performance.

More recently, Chen *et al.* [13] presented a thermodynamic analysis of a MED plant to concentrate brine up to close-to-saturation levels for a ZLD scheme. In this case, the authors showed how to create a ZLD system thanks to the integration of a MED unit with an evaporation/crystallizer chamber for the production of salt via evaporation of water present in the outlet MED brine.

However, theoretical analysis can sometimes mislead the real understanding of the process feasible operating conditions and performance targets, e.g. showing concentration factor values for which the outlet brine from the system is by far above the saturation limit for many salts present in seawater [11].

Looking at the literature of pilot or industrial scale MED plants for saline water treatment, much fewer studies can be found. Ali *et al.* [14] in 2021 focused on the integration of Multiple Effect Distillation with Absorption compressor (MED-AB) to reduce the energy consumption and unit water cost obtaining interesting results in terms of Specific Electric Energy Consumption (SEEC), which values turn out to be 3 times lower than a conventional MED unit. Same authors, shown also a new design of the Multi Effect Distillation (MED) to minimize the thermal losses and footprint of the evaporator [15].

Although MED technology is already mature and commonly implemented at industrial level, all the optimization efforts so far focused on the increase of water recovery and reduction of energy consumption, while little interest had been placed on the increase of the outlet brine concentration. This stream, often intended as waste, can be further concentrated to make it a valuable by-product of the process, also by adapting the operating performance parameters of the MED itself. Xevgenos [16,17] designed a novel MED pilot system (2 effects) with a forward-feed configuration for the treatment of seawater desalination brine. This system was demonstrated at pilot scale (capacity: 2 m^3/day) and achieved high concentration factor obtaining brine with Total Dissolved Salts (TDS) near to 260 g/L, recovery of high-quality water (TDS~50 ppm) [18] as well as integration with solar energy to cover its energy needs. Despite its novelty, this system suffered from scaling, as no pre-treatment was employed. Furthermore, the capacity was limited to enable a robust design for scaling-up. Further advances to this design, integrating composite materials in the heat exchanger have recently been proposed [19]. Within the EU project called ZERO BRINE, this evaporator was tested using nanofiltration as a pre-treatment, demonstrating elimination of scaling of the heat exchanger surface, as well as enabling the recovery of pure products at the downstream treatment. However, the demonstration scale remained as a challenge to enable its market uptake by the industry.

Therefore, MED technology still needs to be optimized and tested at the large demo (pre-industrial) scale in order to better exploit its capability to concentrate brines in integration with other technologies within MLD or ZLD schemes.

The present work focuses on the test of a demo-scale evaporator (a MED unit with 2 effects) for the production of highly concentrated brine and high-quality distillate water. The MED pilot is integrated within a treatment chain with the aim to process seawater for the production of high-quality water (conductivity below 25 μS/cm), minerals (such as magnesium and calcium hydroxide), chemicals (e.g. hydrochloric acid and sodium hydroxide solutions), and food grade salt (sodium chloride). The MED unit, along with the entire treatment chain, were developed within the framework of the EU-founded project "WATER-MINING" [20] and resulted in the demonstration of the operation of the integrated pilot plant at the premises of the local power station of the island of Lampedusa (Italy), where waste heat was available to provide full thermal power to the evaporator prototype unit.

The whole treatment chain consists of the following pilot units: (i) Nano-Filtration, (ii) Multiple Feed Plug Flow reactor (MF-PFR), (iii) Eutectic Freeze Crystallizer (EFC), (iv) Electro-dialysis with Bipolar Membrane (EDBM), (v) Multiple Effect Distillation (MED), (vi) Evaporative ponds. The results from the demonstration of the integrated treatment chain can be found in Morgante *et al* [21].

Seawater enters a Nano-Filtration unit, producing a retentate stream enriched in bivalent cations/anions (such as Magnesium, Calcium and Sulphate) and a permeate stream enriched in monovalent ions, such as sodium chloride. The permeate stream is then conveyed to the MED demo plant, which produces distilled water and a high concentrated brine. On the other side, the retentate stream feeds the MF-PFR unit for selective recovery of magnesium and calcium in the form of hydroxides by chemical precipitation using an alkaline solution [22]. Different studies have been conducted to optimize this stage, investigating how operating conditions can affect crystal nucleation and growth [23], as well as crystal purity, sedimentation and filtration capacity [24]. After separating the hydroxides by means of a settler and a drum filter, the clarified solution (almost Ca^{2+} and Mg^{2+} free) is directed into the EFC to recover sodium sulphate [25], and, then, to the EDBM unit, in order to produce, thanks to the use of renewable energies, an acid and alkaline solutions [26], and a low concentration saline solution that can be recycled to the MED inlet. The high concentration saline solution produced by MED is finally fed into the evaporative ponds in order to produce food-grade salt (sodium chloride > 97 %) and a mixture of salts constituting the sole final solid waste of the process.

This paper presents the activities related to the commissioning and testing of the Multi Effects Distillation demo plant including the results of a first experimental campaign carried out to evaluate the main performance indicators in term of recovery ratio, concentration factor and specific electrical energy consumption.

2. Description of the MED prototype unit

The MED process consists of multiple effects (evaporation chambers), in which evaporation of a part of inlet feed water takes place, on the external surface of a tube bundle, where the feed solution is sprayed via special distribution nozzles. A vapor stream flows inside the tube bundle, providing the evaporation heat to the feed water and condensing inside the tubes. MED unit can be fed using different kind of hot sources, as an example MED unit can be integrated with waste hot water currents such as cooling water from a power plant or even hot water from a photovoltaic system and not only.

The top temperature of the MED is due to the origin of hot sources, this determines the maximum temperature gradient allowed in the unit. Typically, 65 °C is chosen as the upper limit to avoid scaling/fouling problems on the surface of the pipes due to the precipitation of calcium sulphate (CaSO$_4$) and calcium Carbonate (CaCO$_3$). Very often, the hot motive steam has a temperature below 100 °C, thus requiring sub-atmospheric operating pressure, in order to promote the evaporation of the incoming water. In multiple effects evaporation units, the steam generated in the first effect is used as motive steam in the following effect, thus recovering its latent heat and producing additional water. Obviously, because the steam generated from the first effect is at a lower temperature than the hot source, the operative pressure of the second effect has to be lower than the first one. This process can be repeated for a number of effects up to 10–18 in industrial MED plants [27]. A large number of effects would correspond to distributing the driving force between the hot sources and the condenser causing a reduction of ΔT and an increase of the required heat exchange surface. Finally, the steam produced in the last effect is directed into a condenser, where cooling seawater allows to condensate completely the vapor. All the produced condensed streams are collected together producing the final distillate (product water). On the other side, the water remaining in the effect after the evaporation concentrates in salts in exits the plant as a concentrate saline effluent, typically discharged back to the sea or sent to crystallization systems for the production of salt.

The present prototype MED unit can be divided in three sub-sections (see Fig. 1):

- A heat input section, where thermal energy enters the system at the available temperature in order to power the process.
- A heat recovery section, where the energy input is transformed, by means of heat exchange, into produced distilled water and concentrated brine.
- A heat rejection section, where the final condensation takes place and the residual thermal energy flow is finally released into a lower temperature sink.
- Auxiliary systems: vacuum generation and chemicals dosing units.

2.1. Heat input section

This heat input sub-section consists of a closed loop circuit of demineralized water for the production of "primary vapor" (needed to "power" the MED unit) by exploiting the waste heat of diesel engine cooling water. In particular, cooling water exiting from the diesel generator at a temperature between 70 °C and 80 °C, enters a plate heat exchange (HEX) and provides heat to the flowing demi water. Then, the heated demi water is directed into a flash drum, operating under vacuum condition guaranteed by a special restriction orifice plate that causes the vaporization of a part of the demi water in order to produce
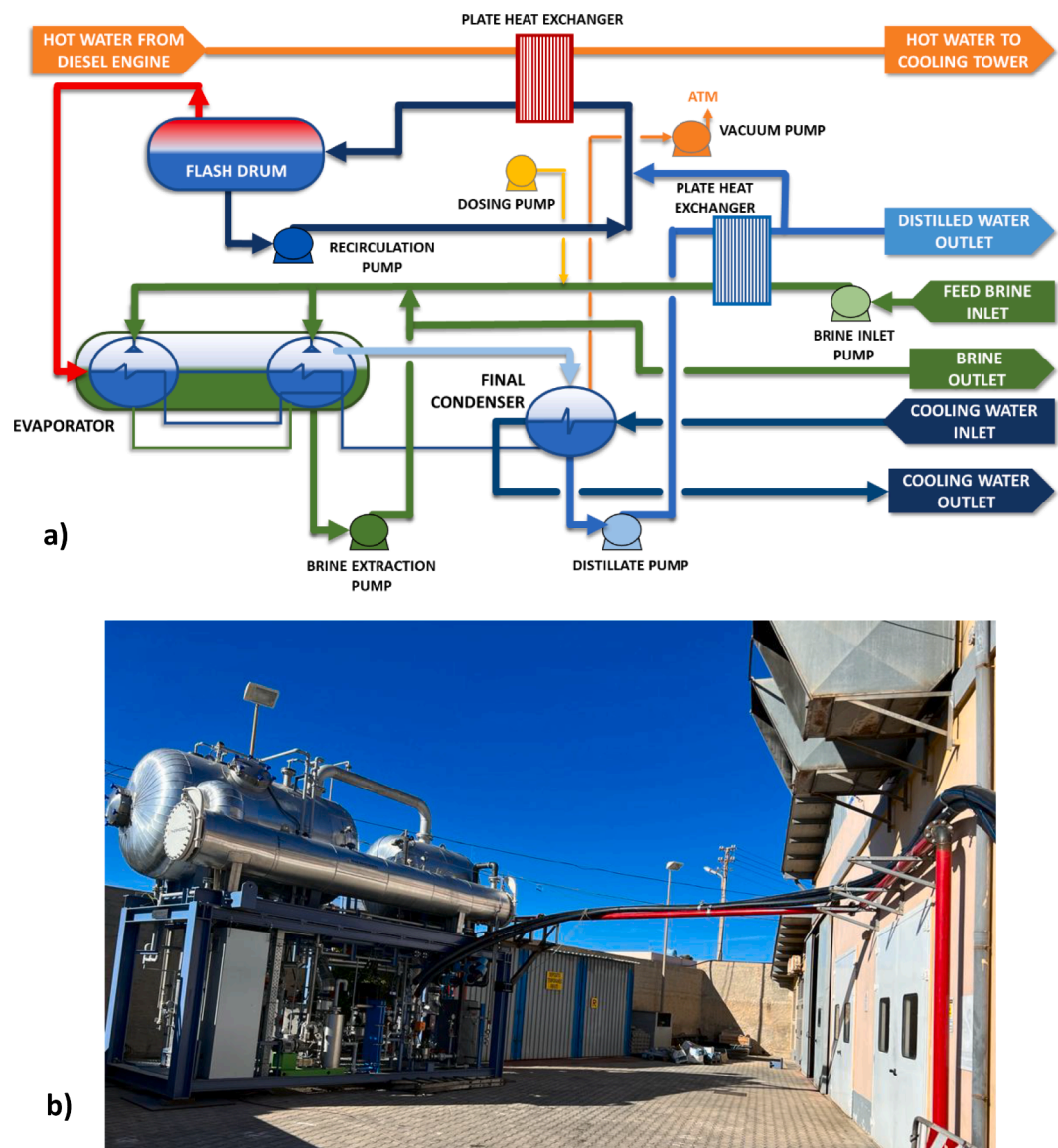
Fig. 1. A) block flow diagram of the med prototype plant representing the main units constituting its 4 sub-sections. b) overview picture of the med pilot with the interconnection pipes conveying hot water from the engine and cooling water for the condenser.
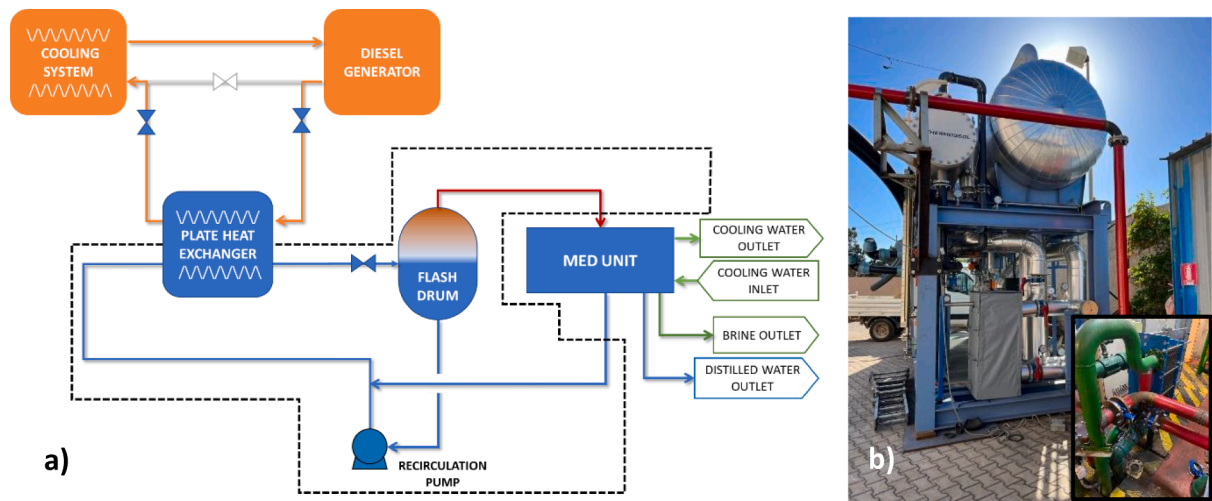

Fig. 2. A) block flow diagram of the heat input section of the med prototype plant. b) picture of the inlet heat exchanger and flash drum (inset showing the connection with the engine cooling circuit for waste heat recovery).

the primary vapor. A scheme of the Heat Input section is shown in Fig. 2.

2.2. Heat recovery section

The generated primary vapor is used as motive steam in the MED unit. As shown in Fig. 3, the core of MED unit is the evaporative chamber or effect. It consists of one horizontal cylindrical vessel, which is divided in two part in order to make the two effects. Each effect of the evaporator is composed by a bundle of Titanium tubes fixed with rubber grommets between the tubes and tubes-plate. The primary vapor flows inside the tubes and therein condensing, while the incoming raw water is sprayed outside the tubes and forms a liquid falling film, part of which evaporates. The vapor produced by evaporation flows through a demister in order to avoid the entrainment of brine droplets within the steam going

inside the following tube bundle to produce additional vapor. The incoming feed water is fed continuously in both effects, while the produced brine of the first effect flows into the second one, flashing due to the pressure drop (thus, further increasing the conductivity) and merging with the concentrated produced in the second effect, before exiting from the prototype plant as final outlet concentrate. In order to optimize the fluid dynamics of the feed distribution system in the tube bundles, a part of the outlet brine is recycled back into the effects, after mixing with make-up feed water.

2.3. Heat Rejection section

The vapor produced in the last effect is sent into a shell-and-tube heat exchange works as the final condenser, where the condensation heat is

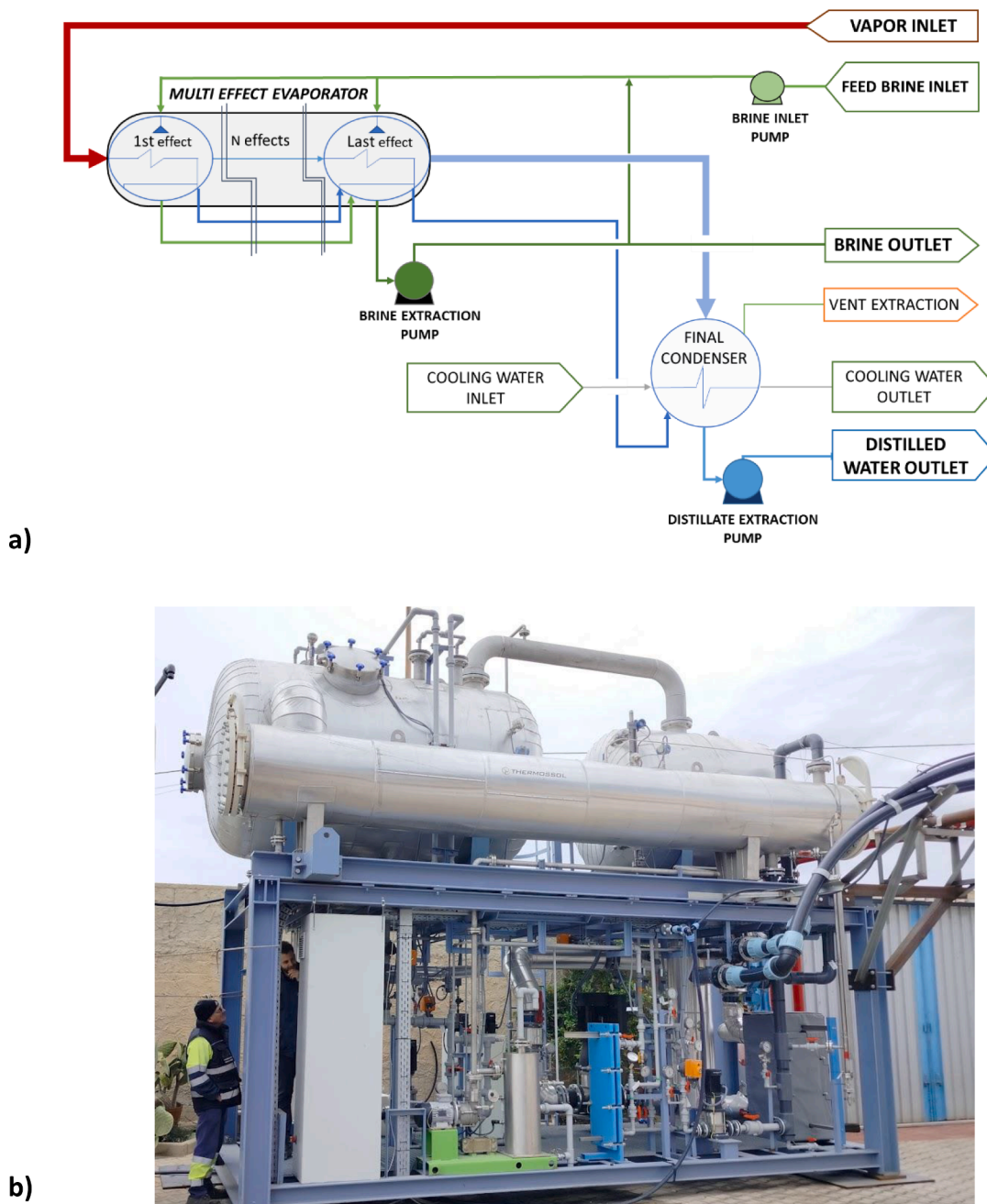**Fig. 3.** A) block flow diagram of the heat recovery & rejection sections of the med prototype plant. b) front picture of the pilot plant showing the 2 effects chamber (back left side), connected via a vapor line to the flash drum vapor generator (back right side) and final condenser of the heat rejection section (front side). on the bottom, positioned on a green platform, the vacuum generation system.

transferred to a cooling water stream (15–25 °C), and mixed with the other condensed streams produced in the two effects, forming the final distillate. The vapor condensed in the shell side of the exchanger was extracted by a pump as distilled water, while the cooling water flows in the tube-side, warmed up by adsorbing the latent heat of condensation, was pumped by an external pump. The non-condensable gases are collected in a specially designed under-cooling section of the Distillate Condenser, from where they are extracted by the vacuum generation system.

2.4. Vacuum Generation, chemicals dosing systems and control system

Since, the MED unit operates under vacuum condition, a vacuum system was turned on at the start-up and keeps the vacuum condition extracting the non-condensable gases (NCG) released from the feed water (dissolved air and CO_2) or entering due to possible air leakages. The vacuum system is connected with the unit through the condenser. The vacuum is generated by means of a liquid ring pump, that operates using water in a closed loop. In order to keep a constant water temperature in the closed loop, a heat plate exchange is used fed by a small amount of cooling water.

A dosing station is used to continuously feed an anti-foam agent solution into the feed with the aim to limit the potential foam formation that would jeopardize the heat transfer.

The MED unit operation is fully automatic and assisted by the on-board control system. Thanks to the installed sensors and transmitters, once activated, the unit control system automatically recognizes the conditions to run / stop pumps, generate vacuum, regulate the inlet and outlet flows.

3. Operational procedures

The procedure for starting the unit involved a few steps. Initially, the brine pump is activated to start the brine flowing through the evaporator and keep the heat transfer surface wetted during the whole operation. Then, the flash drum water recirculation pump is activated, the vent closed and the vacuum generation system also activated. As the necessary vacuum condition is established the hot source is opened to the system, the temperature raised up and the first steam was generated by flash. After that, the brine was fed inside the evaporator and the anti-scalant supply system was activated. The brine recirculation pump continuously run to ensure good wettability of the tube bundle inside the ME evaporator while the evaporation / condensation process started via heat transfer across the tubes. The produced distillate is extracted from the final condenser by a pump. The concentrated brine is also extracted as blowdown side stream from the same recirculation pump, varying with the desired concentration factor. The entire start-up procedure, from cold atmospheric condition to steady vacuum operation, has a total duration of less than one hour.

The pilot unit did not govern the heat input but it just receives the available heat from the diesel engine, thus adapting the operation (and the fresh water generation) to the load of the power plant and without interfering with it.

Once the power plant engine is turned off and the heat input to the MED unit went to zero, the brine feed with anti-scaling supply pumps were turned off. By keeping the water recirculation active in the flash, the vacuum will be broken by venting to the atmosphere through the relevant vent valve. Once atmospheric pressure within the system was reached, the wash water recirculation pump could be turned off, but only the brine recirculation pump was left running for about 1 h to wash the tube bundle until the internal temperature dropped to room temperature.

Following the above procedures for start-up and operation of the demon unit, an experimental campaign was carried out varying the fresh brine flow rate from standard condition (1.65 m³/h) down to a minimum value of 1.25 m³/h.

4. Main performance parameters

The following operating/performance parameters were used in order to assess the prototype operational characteristics:

Concentration Factor (CF), indicating the ratio of equivalent molar concentration of sodium chloride, indicated as "C" in the eq. (1), in the outlet brine (C_{out}) and the inlet brine concentration (C_{in}), according to eq. (1):

$$CF = \frac{C_{out}}{C_{in}} [-] \qquad (1)$$

Specific Electrical Energy Consumption (SEEC) and Specific Thermal Energy Consumption (STEC), expressing, respectively, the electrical ($P_{el}[kW_{el}]$) and thermal energy ($P_{th}[kW_{th}]$) consumption per cubic meter of produced distillate water. They are computed as the ratio between the electrical or thermal power absorbed by the plant and the distillate water flow rate ($\dot{V}_{dist}[m^3/h]$)

$$SEEC = \frac{P_{el}}{\dot{V}_{dist}} \left[\frac{kWh_{el}}{m^3}\right] \qquad (2)$$

$$STEC = \frac{P_{th}}{\dot{V}_{dist}} \left[\frac{kWh_{th}}{m^3}\right] \qquad (3)$$

The SEEC was evaluated according to 3 different scenarios:

- Considering the whole electrical consumption of the unit (steam generation, MED pumps, auxiliary circuits, etc.)
- Considering only the electrical consumption of the MED unit (circulation pumps and vacuum pump), but excluding flash drum and other auxiliary devices.
- Excluding also the electrical consumption of the vacuum system.

In the last scenario only the brine feed and recirculation pump, the distillate brine extraction pump and the anti-scaling dosing pump were taken into account, as these are considered to be scalable for larger size plants, while the vacuum system and other auxiliary systems energy consumption may be misleading, due to the larger impact that these can have in a small size plant as the one here presented.

On the other side, the STEC was estimated starting from the sensible heat released by the hot water to the flash drum recirculating demi water. Considering that this thermal source is very low-grade waste heat, freely available from the power station, the thermal performance of the plant does not have a significant impact on the operational costs. Moreover, the MED unit was not designed to minimize the thermal efficiency of the unit, but, as a brine concentrator, to increase as much as possible the recovery ratio pushing up the outlet brine concentration. Indeed, the thermal "efficiency" of the process is simply guaranteed by the full integration with the waste heat recovery circuit.

Top Brine Temperature (TBT), indicating the boiling temperature (°C) of the first effect. It is affected by the temperature of the waste heat coming from diesel generator and by the pressure levels kept within the effects.

Recovery Ratio (RR), expressing the conversion of inlet feed water into distillate water, is computed as the ratio between the mass flowrate of produced distillate ($\dot{V}_{dist}[m^3/h]$)) and the mass flowrate of the incoming feed ($\dot{V}_{feed}[m^3/h]$)), according to the equation (4):

$$RR = \frac{\dot{V}_{dist}}{\dot{V}_{feed}} [-] \qquad (4)$$

Once all the performance parameters have been defined, their variation was analyzed in a number of operational assets in which the feed flow rate was made varying.

5. Description of the experimental campaign

A first experimental campaign conducted with the pilot plant aimed at assessing the operational stability of the system and the possibility to achieve the highest concentration factor for the full implementation of the ZLD scheme of the Water Mining integrated treatment chain.

The incoming feed brine, as described above, is the permeate produced by the NF. Compared to the seawater, the NF permeate is deprived of a good part of the divalent ions such as Ca^{2+}, Mg^{2+}, SO_4^{2-}, which mostly concentrate in the retentate stream, while it contains mainly monovalent ions such as Na^+ (with some K^+) and Cl^-, as shown in the following Table 1, reporting the composition, in terms of major ion, of seawater and NF permeate.

Such a low hardness and negligible presence of sulphates effectively address and minimize the problem of scaling, due to the precipitation of calcium carbonates and sulphates on the tube bundle. Notably, this makes it virtually possible to apply the MED technology even in the presence of high temperature heat source for higher thermal efficiency systems. Ortega-Delgado *et al* [28] investigated how NF-MED coupling can lead to markedly favorable operating conditions, reaching TBT of 120 °C with corresponding increase in GOR and STEC. Although this is not the case of the present study, where a very low temperature waste heat is freely available.

Moreover, in order to estimate the CF, the concentration of sodium chloride in the feed and in the produced brine was measured. Since the feed stream was the NF permeate, this contains mainly sodium and chloride ion (as reported in Table 1), which allowed using the conductivity of stream (feed or outlet brine) to determine the sodium chloride molar concentration according to standard correlation between conductivity and salt concentration. PhreeQC, a software for thermodynamic simulations in water environmental (laboratory experiments or industrial processes), was used to obtain a link between the electrical conductivity of the solution and the molar concentration of NaCl. Fig. 4, shows correlation obtained with PhreeQC simulation by varying the concentration of sodium chloride in solution.

In Fig. 4, a characteristic point of the present process is indicated. The point represents the molar concentration of the feed (0.482 M), starting by a known value of electrical conductivity (46.4 mS/cm). This concentration was subsequently confirmed by ion chromatograph analysis giving the same result.

The tests conducted aimed at assessing the performance of MED plant, with a specific focus on the possibility to achieve the highest concentration factor of 8, needed in order to feed the almost saturated solution to evaporative ponds, thus achieving the ZLD condition. The main manipulated variable was the feed flow rate, changing from 1.65 down to 1.25 m³/h. All the other operating parameters were kept within the nominal operating range (see Table 2), which strongly depends on the operational asset of the diesel engine providing the waste heat at slightly variable temperature and flow rate.

On the other side, the following values of feed flow rate (Table 3) were investigated in 7 different tests.

All tests were conducted in different days, following a dynamic start-up operation and once reached the steady state, keeping stable operation

Table 1
Ionic composition (limited to main ions) of the feed seawater entering the integrated treatment chain and the NF permeate, being the feed to the present MED demo plant.

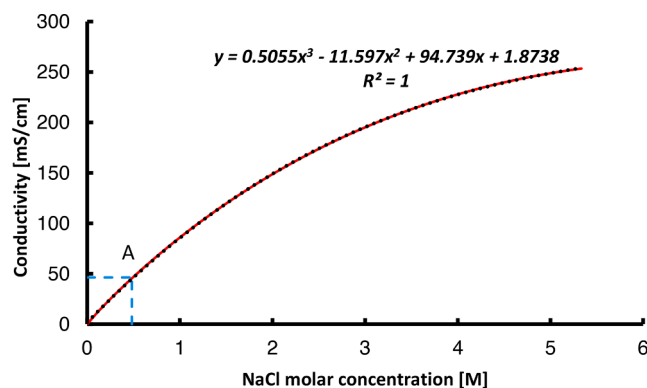| Ions composition [g/L]	NF Feed Composition [g/L]	NF permeate Composition [g/L]
Na^+	11.8	11.3
K^+	0.40	0.35
Mg^{2+}	1.37	0.08
Ca^{2+}	0.43	0.03
Cl^-	20.6	16.7
SO_4^{2-}	2.62	0.12

Fig. 4. Sodium chloride conductivity by varying the molar concentration.

Table 2
Range of variation of operational parameters under nominal conditions.

Operating parameters	Values
Hot source temperature [°C]	75 – 82
Hot source flow rate [m³/h]	20 – 25
Cold utility flowrate [m³/h]	20 – 25
Cold utility temperature [°C]	15 – 25
Pressure inside the condenser [mbar]	50—78
Pressure inside the flash drum [mbar]	100——138
Flow rate of recirculated brine [m³/h]	5.5——7.0

Table 3
Experimental values of feed flow rate in each of the 7 different operating assets investigated in the demo plant.

Test	1	2	3	4	5	6	7
Feed Flow rate [m³/h]	1.65	1.50	1.45	1.40	1.35	1.30	1.25

for a duration variable from 2 to 6 h, depending on the test. An example of the dynamic variation of the main operational variables until the achievement and retention of the stationary condition is reported in Fig. 6.

Some repeatability tests were conducted for some specific conditions, which also allowed to elaborate an experimental error bar, as reported in the result presented in the following section.

6. Results and discussion

The first performance parameters analyzed refer to the concentration of inlet/outlet streams. In particular, outlet conductivity/concentration, concentration factor and feed/distillate flow rate are presented in Fig. 6.

The most interesting achievement regards the increase of outlet brine concentration, which reached a value close to the saturation (conductivity close to 240 mS/cm) when the plant operated at the minimum feed flow rate (see Fig. 6b). In particular, operating at a feed flowrate of 1.65 m³/h, the outlet brine concentration was around 2.25 M, corresponding to 36 % of saturation (in NaCl), while at feed flow rate of 1.25 m³/h the highest value of concentration achieved was 4 M, approaching over 65 % of NaCl saturation. So, as you can see in Fig. 6c, the concentration factor varies along the test starting from a value equal to 4.7 in the test 1 up to 8 in the last test. This high value of concentration factor is considerable considering the feed salinity (28.6 g/L). In fact, there are other studies that shown a high CF but always starting to lower feed salinity (6.4 g/L) [11]. Moreover, the MED unit was able to produce in all conditions a high-grade distillate, with conductivity lower than 25 μS/cm (Fig. 5), thus being perfectly suitable for direct use in all industrial applications related to the power plant functioning.

As expected, the RR follows the trend (see Fig. 6c) of CF. As a matter
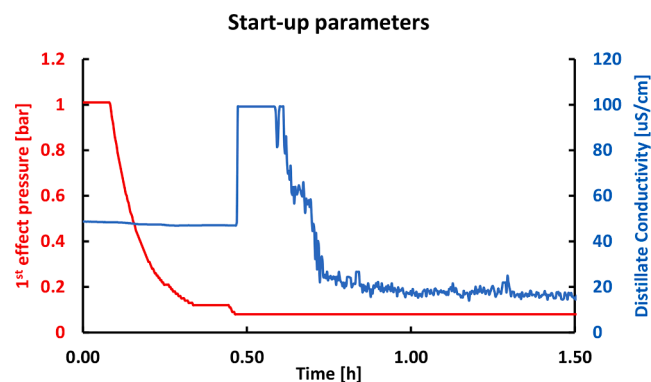
Fig. 5. Example of trend of main operational variables during the start-up and stationary operation of the MED demo plant.

of fact, a high CF corresponds to a large vapor production rate and to a high RR. This is why it proves possible to recover from 78.5 % to 88 % of distilled water. These already high RR values are limited by the ebullioscopy phenomena, which, reaching these high brine concentrations, become predominant. In fact, in the final test, an ebullioscopy rises in saturation temperature of 4.5 °C was estimated. These RR results are even better than those shown in the literature for pilot plant, which difficult reach values of 50 % [14]. These values are perfectly suitable for an optimized industrial scale MED unit, which has recovery values between 85 – 90 % [29].

In the literature it is also possible to find correlations that link the recovery ratio (RR) to TBT [12]. Also, in this case it is possible to note how these values obtained in the experimental campaign are higher than those predicted by the correlation, value close to 80 %.

These results have a double benefit of a considerable increase in water recovery but also in the concentration of brine output that minimizes the footprint of evaporative ponds.

6.1. Analysis of operating temperature and pressure

As mentioned above, the temperature of the first effect was affected by the temperature of the hot source (see Fig. 7 b), which was slightly variable in all tests due to different operational assets of the diesel engine providing the waste heat. On the other side, once the vacuum system and the entire plant reached the stationary operation, the pressure inside the distillation chamber was equal to the vapor pressure of the brine at a given operating temperature of the effect. Therefore, the operative pressure (in the first effect) reported for each test follows a trend very similar to the first effect temperature (Fig. 7 a). Moreover, an average pressure drop equal to 54 mbar is recorded between the final condenser and the flash drum.

Interestingly, the TBT was always in the range 43–50 °C, being thus very low compared to the conventional 60–70 °C [30,31] of industrial MED plants. Finally, as a matter of fact, such low operating temperatures confirm the possibility to operate a MED unit fully powered by a thermal source of very low-grade heat (much below 90 °C), such as cooling liquids from heat engines (as in the present case) or solar thermal collectors. In fact, even the cooling water of concentrator photovoltaics (CPV) systems can reach a temperature well above 70 °C, while being able to provide also the electrical energy needed to power the MED unit [32,33] (as discussed in the next sub-section).

6.2. Specific electrical energy consumption (SEEC) and specific thermal energy consumption (STEC)

SEEC and STEC are among one of the most interesting performance parameters to analyze in industrial plants, as they can determine the
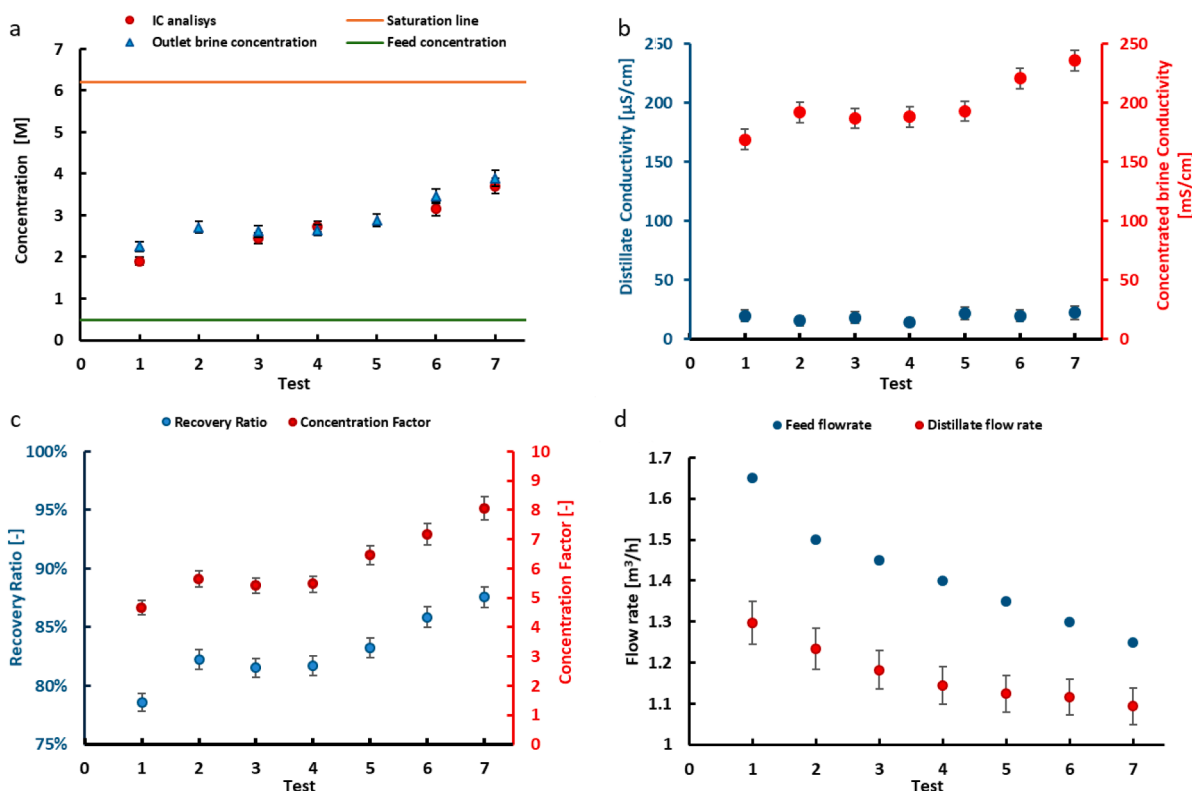

Fig. 6. Measured or calculated performance indicators for each of the experimental run conducted with the demo plant. a) outlet brine concentration (solid lines represent the feed concentration and NaCl saturation line), b) produced distillate and outlet brine conductivity; c) concentration factor achieved and recovery ratio; d) distillate flow rate.
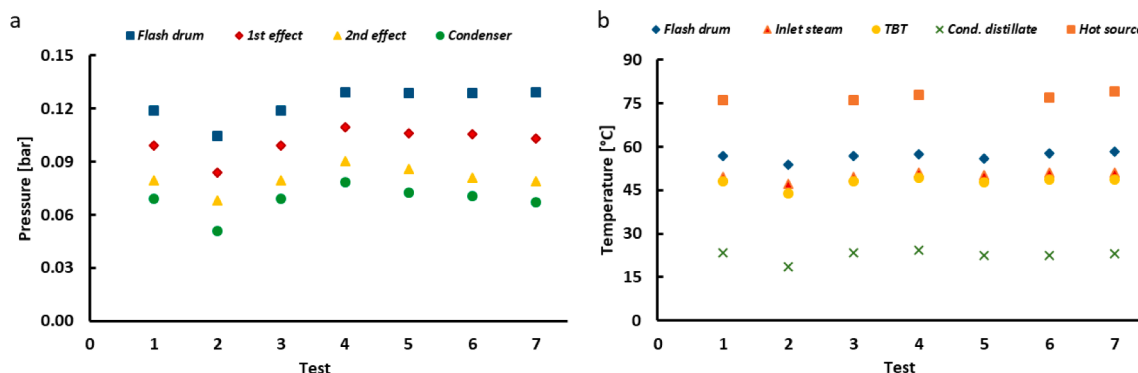
Fig. 7. Observed trends of key pressures (a) and temperatures (b) in the MED plant during each experimental run.

economic feasibility of a process depending on the quality and quantity of available/required energy. Both these parameters have a strong dependence on many plant features, such as the temperature and type of hot source, the number of MED effects, the type and operation of vacuum system, the operational configuration and relevant streams flow rates (e.g. brine recycle). In the present work, the evaluation of SEEC was carried out considering three different electrical contributions, and defining three relative SEEC parameters:

1. Global SEEC: considering all electrical consumption of the unit – $SEEC_{tot}$
2. MED SEEC: considering only the electrical consumption related to the MED – $SEEC_{MED}$
3. Minimal MED SEEC: neglecting the consumption of the vacuum system, which could be dramatically reduced in larger installations compared to the present pilot scale – $SEEC_{min}$

The obtained SEEC trend considering the three different contribution are reported in Fig. 8.

"Global SEEC" refers to the whole electrical power consumption of the MED skid. The power required by the water recirculation pump to extract heat from the hot source accounts for 60 % of overall consumption. This is reason because the maximum obtained SEEC value is around 13 kWh/m^3. However, this value lower than the value found in the literature when using a MED process characterized by a high recovery ratio [14,29,35–37]. This SEEC value, as shown by Prado de Nicolás et al [29], is often between 7.5—21 kWh$_{el}$/m^3.

"MED SEEC" take into account the whole electrical consumption of the MED unit without the vapor generator section, in order to simulate what should be the behavior of the unit in presence of waste steam with the same characteristic of the primary steam generated by the flash. In
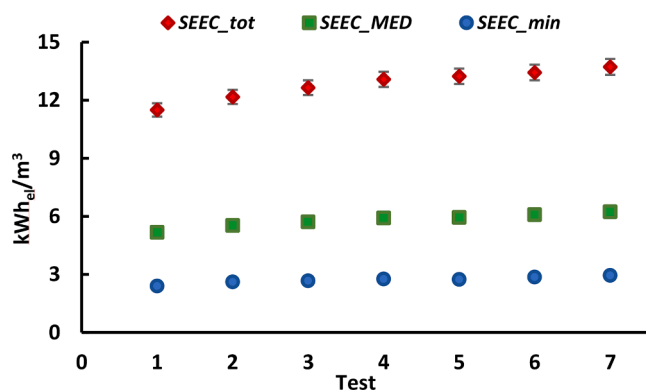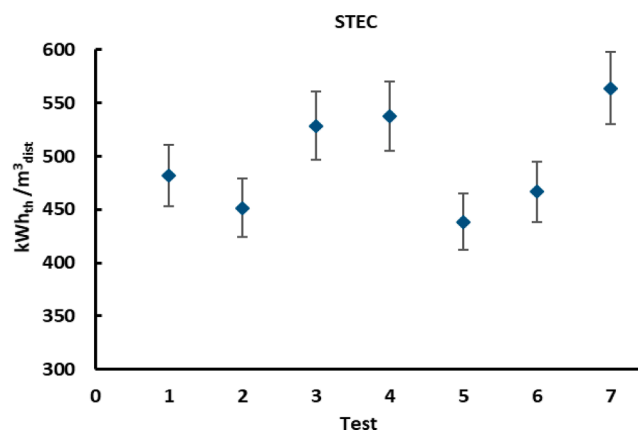

Fig. 9. Calculated STEC required by the MED Unit.

this scenario, the electrical energy consumption was strongly reduced to 5.8 kW/m^3.

The "Minimal MED SEEC" takes into consideration the electrical energy consumption due to, mainly, the feed and recirculation brine pump and distillate extraction pump. In fact, the liquid ring pump is not the only vacuum technology that can be used. For example, ejector – condenser could consume less power respect to the one used in the MED unit. In the latter scenario, the obtained SEEC values remain quite constant on average value of about 2.7 kW/m^3. This value, referring to a pilot plant, is consistent with the value of 2 – 2.5 kW/m^3 found in the literature [37–41] referring to operational and suitably optimized industrial plants.

Even on an industrial scale, the energy consumption of the MED process is higher than the energy consumption of the RO process [41]. In fact, Semiat [42] shown shows how the MED energy demand (electric + thermal) ranges from 15 to 60 kWh$_{el}$/m^3 and this is significantly higher than that of a RO plant which can range from 3 to 6 kWh$_{el}$/m^3. With this demonstration plant, however, it is intended to show how, with other conventional MED plants being equal, a twofold effect can be achieved, i.e., obtaining a distillate of excellent quality and an ultra-concentrated brine in order to approach MLD/ZLD processes.

In general, the SEEC trend is an increasing trend because, keeping the unit's energy consumption constant, the amount of distillate produced decreases. In fact, only the brine feed pump has a small reduction in power required, but this was completely negligible when compared to the consumption of the other pumps installed in the skid. The SEEC data presented, in comparison with other pilot plants, are advantageous. For example, Avramidi et Al. [43] indicates a SEEC of 50 kWh/m^3 for a 2-effect MED with a capacity of 2 m^3/day. Ghenai et Al. [44] shows a SEEC above 60 kWh/m^3 for a 6-effect MED with a capacity of 2.7 m^3/day. From this it is also possible to appreciate how much the scaling factor

Fig. 8. Calculated SEEC values reported in cases of a) total specific energy consumption; b) specific consumption of the MED unit; c) minimum consumption of the MED unit;

affects this parameter.

As said previously, once the MED unit was designed as a brine concentrator using waste heat, this parameter is not crucial for the energy point of view. However, to conclude the energy description of the system, the heat consumption of the unit is also presented.

The fluctuation in the data comes from a fluctuation in the thermal power input from the plant, which varied from test to test. The incoming thermal power values varied from 500 to 650 kW$_{th}$ in a completely random manner depending on the load imposed on the power plant motor. The reported heat consumption is also 10 times higher than the average heat consumption of an industrial MED plant [36]. Furthermore, in this case, the increasing trend of STEC, is more evident because, at an average stable thermal input power, there are gradually decreasing amounts of distillate. The data is however comparable with the consumption of pilot plants (6 effects, 80 m^3/day) powered by fossil fuel, in which STEC of 250 kWh$_{th}$/m^3 were estimated [45].

However, it is reiterated that the MED plant in the case study is a two-effect pilot plant whose focus is not process energy efficiency but the possibility of being able to concentrate brine to near saturation. Once a waste energy current was used for this purpose, the value found is considered acceptable.

7. Conclusions

A 2-effects MED demo plant, suitable for high concentrated saline solution, has been demonstrated as part of an integrated treatment chain for the production of fresh water and minerals from seawater, within the activities of the WATER-MINING project. The plant was installed and operated at the premises of the power station of the island of Lampedusa (Sicily, Italy), thus being fully powered by waste heat (at 70–80 °C) available from the cooling circuits of a diesel engine of the power station. In order to minimize the risk of scaling, the evaporator used as feed solution the permeate of a NF plant treating seawater from a well.

The demo plant nominal capacity was 40 m^3/d of treated brine, targeting very high recovery in order to reach an outlet brine concentration approaching the solution saturation limit.

Among the investigated operating conditions, the effect of changing the feed flowrate on the operational asset of the plant was analyzed. The effect on the Top Brine Temperature and relative stage pressure was small, with temperature ranging between 40 °C and 50 °C and varying mainly due to the variable temperature of the waste heat sources (depending on the variable asset of the diesel engine), thus demonstrating the full suitability for integration with very low temperature waste heat sources.

On the other side, a big influence of feed flow-rate was encountered on the plant recovery ratio and concentration factor, as expected. In particular, a recovery above 80 % has been achieved in most of the operational runs, targeting a recovery close to 90 % when operating with lower feed flow rate (1.25–1.3 m^3/h). In this latter case, an outlet brine conductivity between 220 and 240 mS/cm was achieved, very close to NaCl saturation and perfectly suitable as a feed for subsequent crystallization units or evaporative ponds for food-grade sea salt production. Interestingly, in all cases, the produced distillate flow rate and conductivity were maintained close the nominal values, with the former ranging between 1.15 m^3/h (when operating with the lowest feed flow rate) and 1.3 m^3/h (with the highest feed flow rate) and the latter typically ranging between 15 and 25 μs/cm, significantly below the threshold fixed for internal industrial use in the power station facilities.

In conclusion, this work demonstrates how a well-designed MED unit at such demonstration scale, fully powered by very low-grade waste heat, can be used as a brine concentrator reaching almost saturation levels in the outlet brine, thus being an excellent candidate for integration in the more and more attractive zero-liquid-discharge desalination schemes.

CRediT authorship contribution statement

Giuseppe Scelfo: Writing – original draft, Methodology, Data curation, Investigation, Visualization, Formal analysis. **Alessandro Trezzi:** Conceptualization, Writing – original draft, Methodology, Software, Data curation, Investigation, Visualization, Formal analysis. **Fabrizio Vassallo:** Writing – original draft, Investigation, Formal analysis, Writing – review & editing. **Andrea Cipollina:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Vittorio Landi:** Software, Investigation, Resources. **Christina Xenogianni:** Software, Investigation, Resources. **Alessandro Tamburini:** Methodology, Validation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Dimitrios Xevgenos:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Giorgio Micale:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Some of the authors (Trezzi, Landi and Xenogianni) work for companies developing and constructing MED industrial plants. Of course, all data have been collected and verified through highly accurate procedures and cannot be affected in any manner by any financial interest of these authors, but we think it is appropriate to mention this potential interest.

Data availability

Data will be made available on request.

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