

Solar driven membrane pervaporation for desalination processes

H.J. Zwijnenberg*, G.H. Koops, M. Wessling

*Membrane Technology Group, EMI-Twente, Faculty of Science and Technology, University of Twente,
P.O. Box 217, 7500 AE Enschede, The Netherlands*

Received 5 January 2004; received in revised form 7 January 2004; accepted 20 October 2004

Available online 22 December 2004

Abstract

We describe details of a solar driven pervaporation process for the production of desalinated water from highly contaminated waters. The membrane material is a polyetheramide-based polymer film of 40 μm thickness. This Solar Dew® membrane is used in a tubular configuration in a direct solar membrane pervaporation process. The feed waters used in this study are untreated seawater and waste water that is simultaneously produced with the mineral oil extraction. In all cases retention of typical ions as sodium, chloride and calcium as well as specific problematic ions (arsenic, boron and fluoride) was higher than data reported for pressure driven membrane processes like NF and RO. The condensate quality was well within WHO limits for drinking water. A reduction of almost five orders of magnitude in conductivity between brine and condensate could be realized, producing condensate with conductivities of 5 $\mu\text{S}/\text{cm}$ or lower. Laboratory experiments show that the measured fluxes are independent of severe fouling and virtually independent of concentration up to 100 g/l total solids.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Direct solar membrane distillation; Pervaporation; Fouling; Seawater; Produced water; Desalination

1. Introduction

A considerable part of the world lacks the supply of sufficient fresh water for irrigation or the production of drinking water. The people in these areas rely on brackish/sea water or sources of highly contaminated water. Future prospects indicate that the water scarcity will increase the coming years [1]. The lack of fresh water coincides often with an abundance of solar energy, as cloudy regions generally receive fresh water as precipitation. It appears obvious to use solar energy for the production of drinking water, especially as the production consumes more energy with increasing salinity or degree of pollution. At the moment commonly used techniques to produce drinking water from brackish or seawater are mainly multistage flash (MSF) or reverse osmosis (RO) [2]. Solar energy, either from solar collectors or photovoltaic cells plays only a minor role for the production of drinking water. Main drawbacks associated with the use of solar en-

ergy are the large surface area needed to collect the necessary sunshine and the resulting high capital investments and land occupation [2,3]. For those areas where land is cheap a direct solar membrane-based process could be interesting. Here, no external energy is needed as the solar radiation heats up the feed and the produced water condensate is of high quality.

One may think of traditional membrane distillation where hydrophobic porous membranes are used. This requires extensive pre-treatment in order to minimize fouling. Akzo (today Membrana) invested significantly in this technology, however abandoned the process due to intrinsic fouling problems. The presence of apolar or surface-active molecules in the feed will absorb onto the hydrophobic membrane materials reducing flux and increasing the chance of wetting the membrane pores. This drastically reduces the selectivity of the process due to leakage of the membrane [4]. In this paper the selectivity of a new type of membrane material and configuration is tested. This paper solely focuses on a new process, using solar thermal energy, similar to air-gap membrane distillation. Contrary to normal membrane distillation the described process uses dense pervaporation type

* Corresponding author. Tel.: +31 53 4892956; fax: +31 53 4894611.

E-mail address: wijnenberg@utwente.nl (H.J. Zwijnenberg).

membranes, hence the process is called solar driven pervaporation. In the designed process (Solar Dew[®]), a hydrophilic non-porous homogeneous membrane material with a thickness of about 40 μm is used. Since dense membranes are used, we hypothesize that wetting induced salt leakage and pore-plugging problems [5,6] are anticipated not to occur, making extensive pre-treatment superfluous. As a result, this would reduce the costs of the total process and open up new feed sources that would otherwise require extensive pre-treatment and operation control equipment [7]. An example of highly contaminated feed water is so called “formation water” produced during the mineral oil extraction (also called “produced water” in the mineral oil extraction industry) which contains high concentrations of hydrocarbons and minerals. In order to produce high quality condensation water from these feeds the membrane process should have a high retention towards hydrocarbons and specific ions, especially boron and sodium chloride that can limit the applicability of the purified water.

The main objective of this study is to characterize the separation performance as well as the sensitivity towards fouling of a new pervaporation membrane in a simulated solar driven process. Therefore, two different media are used, viz. formation water from an Omani oil production plant and seawater from the North Sea. The produced water quality is especially compared to the quality typically obtained by RO.

2. Background

2.1. Process

Membrane distillation is a technology in which a porous membrane is used as barrier between the feed and the distillate. The main advantage of membrane distillation, compared to other membrane processes and traditional distillation, is the high selectivity for salt removal that can be reached in a single step. The selectivity in this process is governed by the partial pressure differences of the feed components. Using a dense membrane like in pervaporation, the membrane has an additional intrinsic selectivity that contributes to the separation process. Both distillation and pervaporation are particularly interesting for those applications where fresh water is unavailable as feed and high demands are set for the permeate quality. Although with membrane distillation membranes care should be taken that the selectivity is not lost due to the presence of surface-active components in the feed.

Using a partial water vapor pressure gradient as a driving force for the transport of water across the membrane, distillation and pervaporation can handle high salt concentrations without losing too much of its driving force. For instance, the partial vapor pressure of a 2 M sodium chloride solution at 75 °C is only 8% lower of that of pure water at the same temperature [8], whereas the osmotic pressure difference between the two solutions is 107 bar at 60 °C [9].

Using solar irradiation to heat up the feed water significantly reduces the external energy demands of the process.

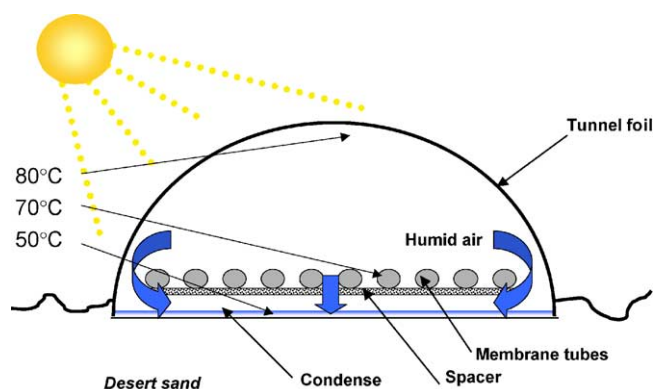


Fig. 1. Cross-section of the single effect solar membrane distillation process unit (Solar Dew[®] process). A tunnel of a transparent foil is constructed in which the black membrane tubes collect the solar radiation. The feed water flowing in the inside of the tubes heats up to about 70 °C and evaporates at the outside of the membrane after which it condenses at the cooler tunnel floor.

In this respect, it does not differ from other solar distillation techniques. However, The use of membranes for direct solar distillation has several advantages like higher evaporation surface area per hold up volume and inclination independent flow. The latter aspect is especially relevant when compared to (open basin) solar stills that require precise leveling of the ground in order to have a constant water depth in the basins [10]. Fig. 1 shows the cross-section of the solar driven pervaporation concept.

The membrane tubes are placed in a transparent tunnel that is closed on all sides to prevent water loss tot the atmosphere and sand. The tubes contain the feed water and act as a solar collector. In order to efficiently collect the solar irradiation the membrane tubes are black and have a black woven support providing mechanical strength. After evaporation of the water through the membrane it condenses at the cooler bottom of the tunnel that lies in the shade of the tubes. In order to keep the evaporation–condensation process going the resulting heat of condensation is conducted to the desert sand that is in direct contact with the waterproof tunnel floor. To prevent direct contact with the condensed water on the tunnel floor the membrane tubes are placed on spacer material.

Using dense membranes might reduce the evaporation of volatile organic components like those that can be expected in water resulting from the mineral oil extraction process. Another advantage is that no crust forming of crystallized salts takes places at the collector surface, which would limit the heat-uptake by increasing the reflection. This is because the salt solution is contained within the black membrane tubes.

2.2. Thermal efficiency and transport phenomena

Using the above concept an average production of about 5 l/(m² day) is obtained in Oman in pilot studies performed by Solar Dew B.V. and Shell [11]. These fluxes are comparable to that of other single effect distillation techniques

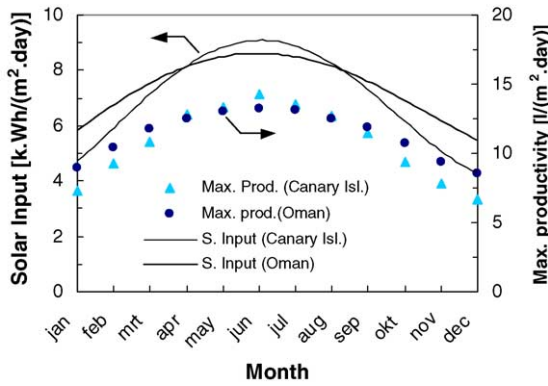


Fig. 2. Solar input (kWh/(m² day)) and maximum productivity (l/(m² day)), normalized on collector surface, of a single effect distiller assuming 100% irradiation conversion for Oman and the Canary Islands through the year. Data adapted from [15].

[12]. However, large differences are reported by Banat et al. [13] and Lu et al. [14]. Banat reported fluxes of 9 l/(m² day), with a thermally insulated solar still and Lu fluxes of approximately 2.6 l/(m² day), using an open salinity gradient solar pond under similar conditions.

Nevertheless, without considering the construction details of the process and experimental set-up, a theoretical productivity can be assumed depending on the daily solar input at a specific location. For Oman and Canary Islands (as a reference) the solar irradiation and theoretical maximum productivity in l/(m² day) for a single effect distillation or pervaporation process is given in Fig. 2 [15]. For the theoretical maximum, a 100% efficiency of the conversion of solar irradiation to distilled water was assumed.

The graph clearly demonstrates that an average of about 10 l/(m² day) could be produced using single effect distillation when the loss of heat to the surroundings is assumed zero. However, in practice, the driving force for distillation and pervaporation is only then sufficiently large when the feed temperature is 60 °C or higher. As a result significant energy leakage to the surrounding via radiation and conduction take place thereby lowering the productivity with about 50% to an average value of about 5 l/(m² day) for a single effect distillation without heat recovery [16,17].

To describe the transport in solar distillation numerous models are developed to calculate the thermal efficiency of a design and to optimize certain aspects. In its basic form the direct solar pervaporation system as used in this study resembles a simple solar still. A simplified transport model as described by Kwatra [18] shows the main parameters affecting the thermal efficiency. The steady-state heat balance over the collector can be given by:

$$\frac{dQ_{irr}}{dt} = \frac{dQ_{loss}}{dt} + \frac{dQ_{evap}}{dt} \quad (1)$$

with Q_{irr} is the heat flow by irradiation, Q_{loss} is the heat loss to the surroundings and Q_{evap} is the heat loss via evaporation.

The ratio between heat loss and produced water depends on the equipment design and the steady-state temperature as can be seen from the following equation:

$$A_c \alpha_c I_e = A'_c \sigma \varepsilon_c [T_c^4 - T_1^4] + A''_c \sigma \varepsilon_c [T_c^4 - T_b^4] + A_m h'_c [T_c - T_b] - A_m k_m H_{ev} [p_m - p_b] \quad (2)$$

with A_c being the collector area (m²) with single and double indices indicating different exposed areas, A_m is the membrane area (m²), α_c is the collector radiation absorptivity, H_{ev} is the heat of evaporation for water (J/kg), ε_c is the collector emissivity, h'_c is the modified convection coefficient (W/(m² K)), I_e is the effective light flux to the collector (W/m²), k_m is the overall mass-transfer coefficient (kg/(m² Pa s)), p_b is the partial pressure at the condenser, i.e. the bottom of the tunnel (Pa), p_m is the partial pressure of the feed (Pa), σ is the Stefan–Boltzman constant (W/(m² K⁴)), T_b is the temperature of the condenser, i.e. the bottom of the tunnel (K), T_c is the temperature of the collector, i.e. the support layer around the membrane tube (K) and T_1 is the temperature of the surrounding (K).

In Eq. (2) the left-hand side ($A_c \alpha_c I_e$) represents the incoming heat flux to the collector by the radiation. The first and second term at the right-hand side represent the heat loss by radiation to the surrounding and bottom of the tunnel. The used surface areas A' and A'' are here given with indices to indicate that only the surface area exposed to the surrounding and tunnel bottom should be used. The third term represents the convective losses to the cooler bottom and the fourth term is the heat loss by evaporation of the water from the tubes. In principle, the heat loss by evaporation equals the productivity of the unit:

$$A_m k_m H_{ev} [p_m - p_b] = J_w H_{ev} \quad (3)$$

with J_w is the productivity (water flux) (kg/s).

Eq. (3) shows that changing either the membrane area, A_m , or mass-transfer coefficient, k_m , the water flux changes under isothermal conditions, i.e. with equal partial pressures. Changing these two parameters in relation (2) shows that the left-hand term is not affected; the same amount of light is collected. Consequently, the sum of the right-hand terms is also constant. This means that a change in membrane area or in mass-transfer coefficient results directly in a change of temperature profile within the tunnel.

The temperature profile determines largely the driving force for water transport varying in time and depending on the irradiation. In this respect direct solar distillation and pervaporation differ largely from many other membrane processes where constant feed pressures or temperatures are used to generate a driving force for transport. This also can be seen directly from Eq. (2); the moment the mass-transfer coefficient is reduced, for instance, by using thicker membranes, an increase in collector temperature results in an accompanying higher partial feed pressure. A similar conclusion was also made by Kwatra [18] who observed a decrease in collector temperature with increasing membrane area.

3. Experimental

3.1. Feed water characterization

Direct solar pervaporation tests were carried out with four different feed qualities, distilled water, seawater from the North Sea, de-oiled formation water from an Oman oil-well and artificial seawater (NaCl solution). The different qualities are described below.

To investigate the retention behavior of several harmful components, three selected components, AsBr_3 , $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, were dissolved in both seawater and formation water in a concentration of about 200–400 ppb. The pH of the feed was not adjusted and remained at its natural value.

Although seawater is not entirely constant in quality over the world, it is a well-defined medium at the specific location of the inlet. Several 25-l containers were taken directly from the North Sea at Scheveningen beach (The Netherlands) during low tide and the seawater was used as such with the exception that floating matter larger than 5 mm was removed in order to prevent plugging of valves. The conductivity and element composition of the seawater was analyzed, see Table 1, and was found to be considerably lower

Table 1

Quantitative element analysis of both feed-waters: FW, formation water from Omani oil field; SW is seawater from the Scheveningen North Sea beach; compared to open sea values the values are about 25% lower

Element	FW ($\mu\text{g/l}$)	SW ($\mu\text{g/l}$)
Al	5	300
As	<0.05	3.1
B	3800	3400
Ba	30	24
Be	<0.2	<0.2
Ca	3.1 mg/l	340 mg/l
Cd	<2	<2
Co	<15	<15
Cr	<5	<5
Cu	<10	11
Fe	<20	740
K	30 mg/l	310 mg/l
Li	200	140
Mg	12 mg/l	1.1 g/l
Mn	<0.6	18
Mo	<5	<5
Na	2.3 g/l	8.3 g/l
Ni	<15	<15
Pb	<30	<30
Sb	<70	<70
Se	<15	<15
Si	75	2.4 mg/l
Sn	<15	<15
Sr	290	6 mg/l
Ti	<5	<5
V	<10	<10
Zn	<15	20
Cl	2.82 g/l	14.2 g/l
Br	15	44
SO_4	240 mg/l	1.92 g/l

than reported data for seawater [15], but normal for the reported data from Scheveningen beach [19] due to the presence of four main rivers less than 100 km south of the sample point.

For formation water, the variances in quality are much larger [20,21] and depend entirely on the geological formation from which the mineral oil is extracted. The formation water was provided by Shell International Exploration and Development and was directly obtained from an oil production plant of Petroleum Development Oman. In the specific oil field of the well of Petroleum Development Oman (PDO) an overall total dissolved solids level of 5–6 g/l, mostly NaCl, is present. This is considerably lower than seawater with about 30 g/l NaCl. The water was characterized with respect to 30 elements, similar to the seawater, as represented in Table 1.

3.2. Set-up desert simulation

In order to measure the influence of feed composition and fouling accurately, a laboratory set-up was built that ensured constant external conditions and was not influenced by outdoor variables like clouds, wind, seasonal sunshine differences, etc. To realize this, a fixed amount of light bulbs with constant on–off cycles and a fixed floor and lab temperature were used to have constant heat input and heat loss throughout the whole experimental program. In this way small changes in flux could be accurately measured and contributed to internal system changes. Care was taken to build a set-up that resembled a short version of the pilot plants in Oman and Gran Canaria as close as possible.

For the direct solar pervaporation process, desert conditions were simulated using a sandbox with 10 infrared light bulbs (Phillips IR250S) above it. The modules and the remainder of the equipment were provided by Solar Dew B.V. and are shown in Fig. 3.

For the indoor (laboratory) set-up, arbitrary setting for day–night cycle, heat input, heat loss via sand, etc. were created. In this respect, they cannot be compared to outdoor

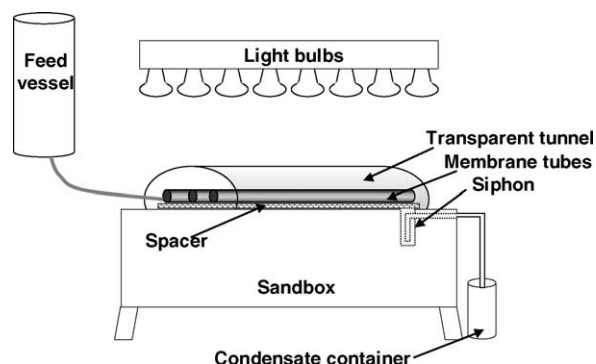


Fig. 3. Overview of experimental set-up. In the tunnel three black membrane tubes are placed that collect the irradiation of the light bulbs. The evaporated water condenses at the inside of the tunnel and mainly at the cooler tunnel floor that rest directly on the sand.

experiments. The values for day/night cycle imitation, amount of light bulbs installed and distance between bulbs and membranes were only chosen in order to realize a steady-state temperature profile in the laboratory set-up that is comparable to the desert pilot and its production per day.

A polyethylene-foil was placed on top of the sand that could be wrapped around a frame to form a tunnel completely enclosing the membrane tubes. The part of the foil in contact with sand actually collects the water that evaporates out of tubes. A spacer net, placed as a support for the black membrane tubes on the tunnel floor, prevents direct contact of the membrane tubes with the foil on the floor of the tunnel. It has a gray porous top-layer that partially reflects the light to prevent heating of the sand below the tubing by the light bulbs and simultaneously allow water vapor to permeate to the condenser below; the tunnel floor.

The membrane tubes consisted of a blown-molded PEA film (polyetheramide-based polymer) of approximately 40 μm thick, with a polyamide/polyethylene non-woven support shell and were connected to distribution caps with clamping rings. They had an inner diameter of 4.1 cm and approximately 0.32 m^2 of membrane area was installed per tunnel. As most polyether amide-based polymers, the membrane material was used as it has a relatively high swelling in water with accompanying high permeability, 50–60 $\text{l}/(\text{m}^2 \text{h})$ at 80 $^\circ\text{C}$ (normalized at a thickness of 1 μm). At high temperature it can be easily blown molded by an extruder at high speed to form endless tubular membranes.

Installed effective solar collector surface was 0.1 m^2 per tunnel. The collector surface is the cross-section of the membrane tubes and therefore π (3.1416) times smaller than the total membrane area, as we will show later. On one side the feed entered the module and on the other side, a blow off valve was installed to remove air and take samples of the feed stream. The later occurred with regular intervals of 2–3 days. The produced distilled water flowed out of the tunnels via a hole in the tunnel bottom into a closed container. Both membrane modules (the experiment was carried out in duplicate) were operated in a continuous fed dead-end mode. As during the process, condensate is produced and samples of the feed are taken, the volume of extracted water is replenished by fresh feed. The overpressure inside the feed tubes was 150 mBar, due to the hydrostatic pressure resulting from the fact that the feed vessel was placed about 1.5 m higher than the membrane tubes in the tunnel.

The temperature of the tunnel ceiling, sand underneath the tunnel floor and water in the tubes was measured. During steady-state, these temperatures varied slightly and were 78–82, 46–51 and 68–70 $^\circ\text{C}$, respectively. Care was taken to get similar temperature profiles and water production in the tunnels as in the desert experiments in Oman. This was carried out by variation of the amount of light bulbs installed and the burning-time during the day. The profile was measured regularly during a preliminary test with distilled water. After this test had run several days, the set-up had a constant temperature profile producing a constant water flux (5 $\text{l}/(\text{m}^2 \text{h day})$).

It was then decided to measure the temperature profile only after changing to a new feed solution.

3.3. Analysis

The flux was measured by collecting the condensate that flowed from the foil on the tunnel floor into a container. The flux is expressed in $\text{l}/(\text{m}^2 \text{day})$. In our case, we have normalized the flux to the solar collector surface area (J_c) to be able to compare the resulting value to solar distillation technologies, in which the collector surface area is often decoupled from the surface area for vapor transport. Generally, in membrane science the flux is normalized to the effective membrane area (J_m). The relation between the two expressions in our case can be derived from:

$$A_c = 2 \times r \times L \quad (4)$$

$$A_m = 2 \times \pi \times r \times L \quad (5)$$

$$J = \frac{M}{\rho \times A \times t} \quad (6)$$

with A_c the cross-section of the tubes (m^2), A_m the outer surface of the tubes, $r \times L$ is the tube radius times tube length (m^2), M is the mass of produced water (kg), ρ is the density of water (kg/l) and t is the production time (day). The flux can be calculated using Eq. (6). Using A_c will then give J_c and using A_m results in J_m . It is clear that in our definition the following relation exist between the two fluxes:

$$J_c = \pi \times J_m \quad (7)$$

In our case we also used a production time of 9 h per day. Converting flux expressed in ($\text{l}/(\text{m}^2 \text{h})$) into ($\text{l}/(\text{m}^2 \text{day})$) is then carried out by multiplying with a factor 9 and not a factor 24. In this paper always a flux normalized on collector surface J_c and 9 h production time per day is used, unless stated otherwise.

Elemental analysis was carried out using atomic adsorption spectroscopy with both axially and radially viewing ICPES (required at high concentrations). Arsenic was measured using HAFS and anion concentrations were determined using titration and ionochrom methods. To monitor the long-term performance, both feed and condensate concentrations were estimated on basis of the electrical conductivity. As the conductivity is a non-linear function of the concentration a correction has to be applied to estimate the concentration of ionic components. The calibration graph for the correction factors was made by diluting the highest concentration feed sample several orders of magnitude with ultra pure water until the condensate conductivity is reached. The conductivity as a function of dilution factor then gives a desired correction factor for every concentration. The used correction function was; $\lambda_{\text{corrected}} = -2.8596 \times 10^{-5} \times \lambda_{\text{measured}}^2 + 8.8024 \times 10^{-3}$

$\times \lambda_{\text{measured}} + 1.3387$ for the range of 6–120 mS/cm. The obtained corrected conductivities can then be used to estimate the retention of the membrane:

$$R = 1 - \frac{C_{\text{condensate}}}{C_{\text{feed}}} \quad (8)$$

or the log removal factor

$$\text{LRF} = -10 \log \left(\frac{C_{\text{condensate}}}{C_{\text{feed}}} \right) \quad (9)$$

All experiments were carried out in duplicate with two tunnels operating next to each other. All membranes were changed upon changing to a different feed. All data are presented as such, without averaging. The concentration of 30 elements, see Table 1, was measured for the samples taken at regular intervals during the experiment, for both modules and for different types of feed. However, these data are mostly not shown, except in some figures, for instance, Figs. 5A and 8A, when it was considered relevant to demonstrate the similarity in behavior between the measured conductivity and element analysis.

4. Results and Discussion

4.1. Seawater and artificial seawater pervaporation

The simulated solar pervaporation of seawater was carried out in semi dead-end mode using the given steady-state temperature profile in the tunnel. The results of the flux measurements of module 1 are presented in Fig. 4A. The flux is normalized using the effective collector surface and a production time of 9 h per day.

An average flux of about 5 l/(m² day) is reached, comparable to the values reported for the pilot trials in Oman and Gran Canaria [11]. In the beginning of the experiment the flux was slightly lower due to a holdup volume at the permeate side. Steady-state was reached after 10 days.

The results of the uncorrected feed conductivity of the same experiment, shown in Fig. 4B, clearly show the increase in concentration during the experiment. The condensate quality increases slightly during the whole experiment going from 6.7 to 3.7 $\mu\text{S}/\text{cm}$ for seawater. In our case the condensate quality was limited by the presence of small amounts of dust and dissolution of components from the construction of the condensate side. Hence, the continuous flushing of the condensate side by produced condensate decreased the conductivity. Optimization of the layout details of the product side in the other experiments resulted in slightly cleaner condensate side with improved product quality. The experiments with artificial seawater show lower concentrations in the condensate. The lowest conductivity found in this experiment was 1.64 $\mu\text{S}/\text{cm}$, as special care was taken to remove dust from the condensate side prior to the start of the experiment. Seawater RO generally produces water with a conductivity of about two orders of magnitude higher.

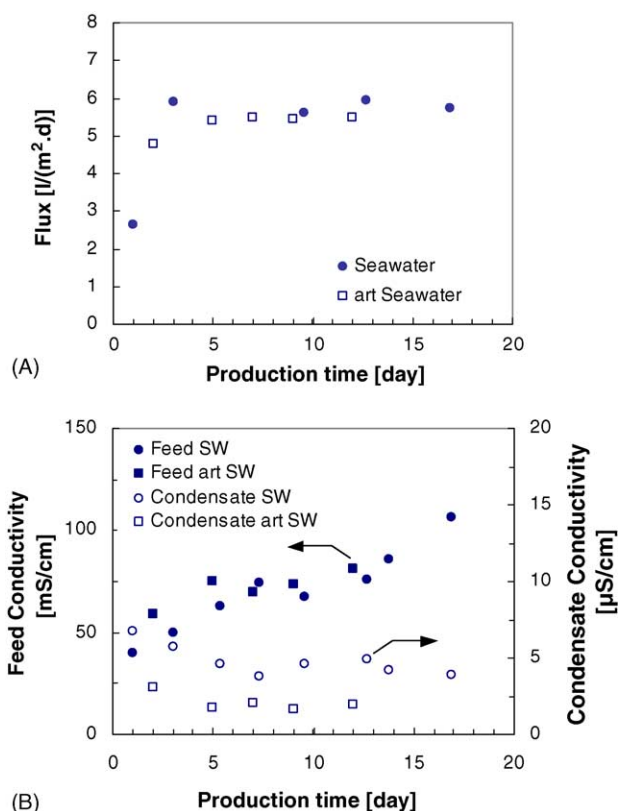


Fig. 4. Solar distillation simulation experiments with seawater from the North Sea shore and artificial seawater in dead-end mode: (A) presents the flux and (B) gives the feed (mS/cm) and condensate conductivity ($\mu\text{S}/\text{cm}$) of the seawater experiment during the concentration experiment.

Correcting the feed conductivity for the non-linearity in concentration allows calculating the concentration factor, i.e. the actual concentration divided by the starting concentration. The concentration factor as a function of time is presented in Fig. 5A. Here, the data of the conductivity are compared to the data from the element analysis of three main ions that did not precipitate. Similar values were found for lithium, bromide, silicium and potassium, however, ions like calcium and sulfate showed an upper limit in feed concentration due to precipitation. It shows that the corrected conductivity is a good indication of the reached concentration.

Combining the feed and condensate concentration data allows the calculation of the retention with Eq. (8) and log removal factor with Eq. (9), see Fig. 5B. The log removal factor was used for similar reasons as in the drinking water industry, i.e. the value of the retention is too high, obscuring the fact that small numerical variations in retention have a large impact on the condensate quality. Overall retention, based on the conductivity, at the end of the experiment was over 99.998%, indicating that the condensate has a 50,000 times lower concentration than the feed.

An overview of the elemental analysis is given in Table 2. It gives the feed and condensate concentration of 30 elements

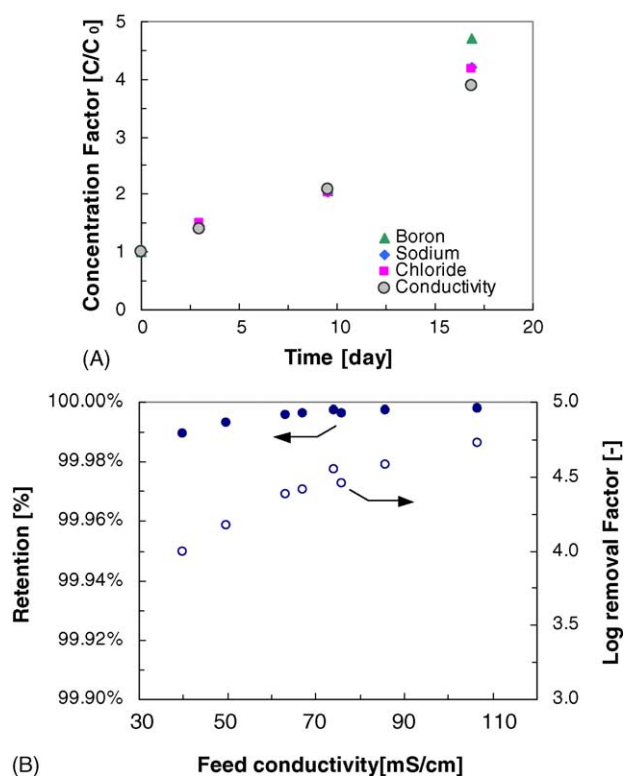


Fig. 5. Solar distillation simulation experiments with seawater from the North Sea in semi dead-end mode: (A) gives the concentration factor of the feed based on the analysis of three elements and on the corrected conductivity and (B) gives the retention and log removal factor (based on corrected conductivity) of module 1 vs. feed conductivity.

at the end of the production time, i.e. when the feed concentration was the highest (data of module 2 are similar).

As no filter was used prior to the sample taking, some sediment was washed out, and concentrations varied strongly for several elements like aluminum, arsenic, calcium, magnesium, silicon and iron. The condensate concentration of arsenic of 0.05 $\mu\text{g/l}$ show that even in the worst case, i.e. the end of the concentration process, the concentration is well within the WHO guideline of 10 $\mu\text{g/l}$. The arsenic removal rates with a measured retention of over 99.7% are much better than for other reported membrane filtration techniques like nanofiltration [22] and ultrafiltration [23]. In this respect, the system gives a performance that can be expected from processes involving an evaporation step of the feed. A similar high performance of the solar pervaporation system was obtained for boron (WHO guidelines of 200 $\mu\text{g/l}$) with improved retentions of over 99.7% being better than RO [24]. Fluoride was left out of Table 2, as the initial feed concentration was not determined, but the end concentration in the feed was 7.8 mg/l, while the condensate concentration was less than 0.1 mg/l. This concentration is well below the guidelines of the WHO (1.5 mg/l) and comparable to RO results [25]. It should be mentioned that in the latter case the condensate concentration of fluoride was below the level of detection.

Table 2

Data from the element analysis of the seawater (brine and condensate) at the end of the concentration process (exp. A)

Element	Feed ($\mu\text{g/l}$)	Condensate ($\mu\text{g/l}$)
Al	950	13
As	21	<0.05
B	14 mg/l	32
Ba	96	3.7
Be	<0.2	<1.5
Ca	1.2 g/l	41
Cd	<2	<0.2
Co	<15	<7
Cr	8	<1
Cu	140	14
Fe	63 mg/l	19
K	1.2 g/l	14
Li	540	<0.2
Mg	4.1 mg/l	31
Mn	550	<0.2
Mo	13	<1
Na	32 g/l	<20
Ni	<15	<2
Pb	40	7
Sb	<70	<10
Se	Interference	<10
Si	10 mg/l	55
Sn	<15	<2.5
Sr	21 mg/l	0.2
Ti	13	<1.2
V	25	<2
Zn	34 mg/l	51
Cl	54.7 g/l	<2
Br	182 mg/l	<0.5
SO ₄	7.9 g/l	<0.5

Values are in $\mu\text{g/l}$, unless stated otherwise. Feed data from multivalent ions can be influenced by their maximum solubility and the inflow of crystallites into the sample. Fluoride is left out, as the initial feed value was not analyzed, end concentration in the condensate was <0.1 $\mu\text{g/l}$.

4.2. Formation water pervaporation

With formation water similar experiments were carried out as with seawater. The flux data are given in Fig. 6A and feed and condensate quality from the same experiment are given Fig. 6B.

As for seawater, the condensate quality of the formation water experiments, given in Fig. 6B, increased during the experiment. Steady-state conditions showed that a condensate conductivity of 4–5 $\mu\text{S/cm}$ could be reached with this system.

The value of about 5 l/(m² day) for the flux is also found in these experiments (Fig. 6A) and corresponds with the (artificial) seawater pervaporation values. In addition, when distilled water is used, also a flux of about 5 l/(m² day) is found in the solar pervaporation simulation set-up. Due to a higher salt concentration in the seawater and formation water, the partial vapor pressure of the feed at a certain temperature is lower. Estimating the maximum difference in driving force then results in a 12% lower value for the seawater experiment than for distilled water [8]. From Fig. 5A it is obvious that this 12% is within the experimental error of the data points.

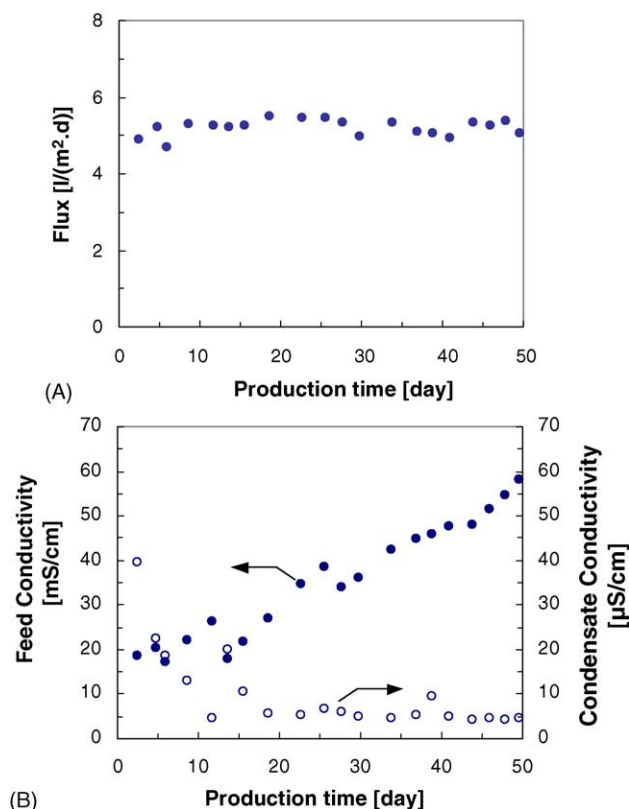


Fig. 6. Solar distillation simulation experiments with formation water in dead-end mode: (A) presents the flux and (B) gives the feed (mS/cm) and condensate (μS/cm) conductivity of the formation water experiment.

A discrepancy is found when this flux value is compared to the intrinsic permeation properties of the membrane. A pervaporation experiment was performed in a simple flat sheet set-up, using the same membrane material, but with recirculation of the feed and using electrical heating. The resulting flux together with the vapor pressure of the feed are shown in Fig. 7.

These tests with distilled water showed at 70 °C a flux J_m of 1.0 l/(m² h) using a 40 μm membrane when the con-

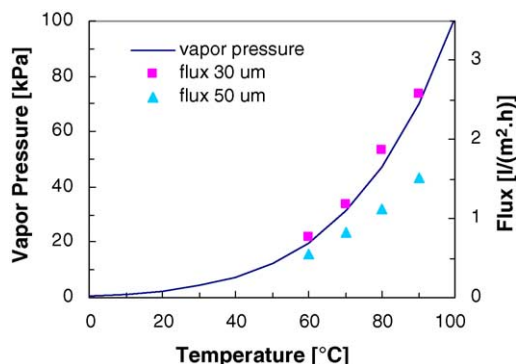


Fig. 7. The vapor pressure of pure water [15], and the membrane flux (J_m) vs. temperature. Membrane flux data are obtained from Solar Dew B.V. and show the water flux for a 30 and 50 μm dense membrane film, condensate side is at room temperature.

densation temperature is 20–25 °C. This value is normalized to membrane area and cannot directly be compared to the production in a tunnel configuration. Therefore, a correction should be made using Eq. (7) and a correction for a production of 9 h per day. The value of a J_c of 5.0 l/(m² day) then compares to a J_m of 0.18 l/(m² h) as it is divided by 3.14 and 24/9. This means that with a feed of 70 °C the tunnel system produces only 18% (0.18/1.0) of that of the flat sheet set-up. Part of this discrepancy is explained by the higher condensation temperature at the bottom of the tunnel (50 °C) whereas the lab temperature was about 20–25 °C. Nevertheless, correcting the flux in the tunnel system for this effect by extrapolation of the partial vapor pressure difference [9], a theoretical J_m of 0.31 l/(m² h) can be obtained in the tunnel assuming a bottom temperature of 20 °C. As a result still a discrepancy of 1.0–0.31 = 0.69 l/(m² h) remains. This remaining discrepancy is an indication that heat/mass-transfer limitations restrict the production rate in the tunnel configuration.

Similar to the seawater experiments the concentration factor for some major elements was calculated and compared with the corrected conductivity, see Fig. 8A. For the correction factor the same calibration curve as for seawater was taken, as the ionic composition is not too different for the major part of the ions.

As the experiment with formation water was carried out for a longer period of time the final concentration factors

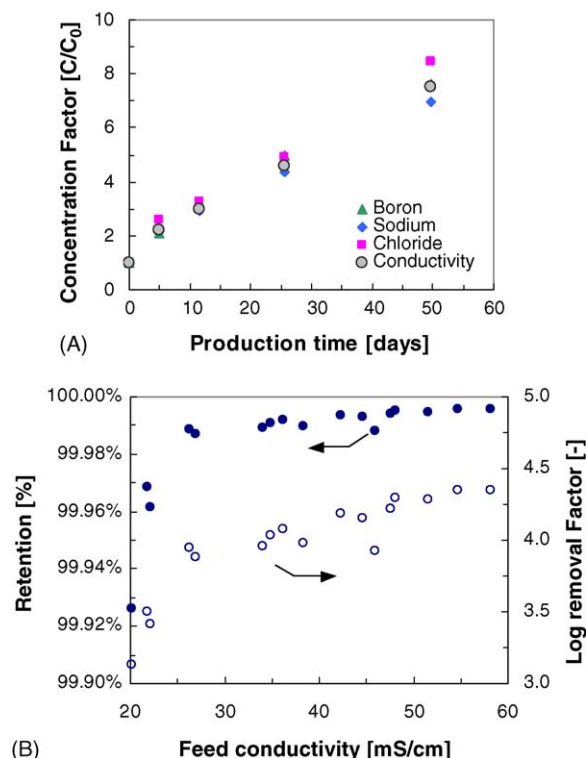


Fig. 8. Solar distillation simulation experiments with formation water from Oman in dead-end mode: (A) gives the concentration factor of the feed based on the analysis of three elements and on the corrected conductivity and (B) gives the retention and log removal factor (based on corrected conductivity).

Table 3
Data from the element analysis of the formation water (brine and condensate) at the end of the concentration process (module 1)

Element	Brine ($\mu\text{g/l}$)	Condensate ($\mu\text{g/l}$)
Al	20	0.7
As	15	<0.05
B	29 mg/l	60
Ba	66	2.2
Be	<0.2	<0.2
Ca	2.6 g/l	23
Cd	<2	<2
Co	<10	<10
Cr	<2	<2
Cu	21	6
Fe	1200	<5
K	0.26 g/l	<100
Li	1.5 mg/l	<5
Mg	76 mg/l	10
Mn	12	<0.5
Mo	30	<5
Na	16 g/l	<200
Ni	<10	<10
Pb	<30	<30
Sb	<50	<50
Se	<30	<30
Si	850	30
Sn	<20	<20
Sr	200	0.2
Ti	<2	<2
V	<5	<5
Zn	300	16
Cl	23.8 g/l	<2
Br	154 mg/l	<0.5
SO ₄	2.4 g/l	<0.5

Values are in $\mu\text{g/l}$, unless stated otherwise. Feed data from multivalent ions can be influenced by their maximum solubility and the inflow of crystallites into the sample.

were higher. Also for this experiment the concentration factor of the three major elements are comparable to the corrected conductivity indicating that the correction factor based on the dilution range of seawater is a good estimate for the actual concentrations. Regarding the retention and log removal factor of the system for formation water similar high values are found that increased with feed concentration. In the case of formation water this increase is only due to an increase of the feed concentration with time and not due to a decrease of the condensate conductivity. Although conductivity values of the condensate were not as low as for seawater, in these experiments they were still over 30,000 times lower compared to the brine at the end of the concentration process. A more extensive overview of 30 elements can be found in Table 3.

4.3. Fouling

The fouling of the system was analyzed after these experiments by visual inspection and scanning electron microscopy of the membrane. The tubes were drained and cut open to inspect the debris and sedimentation that occurred during the concentration process. A picture of the inside of the mem-

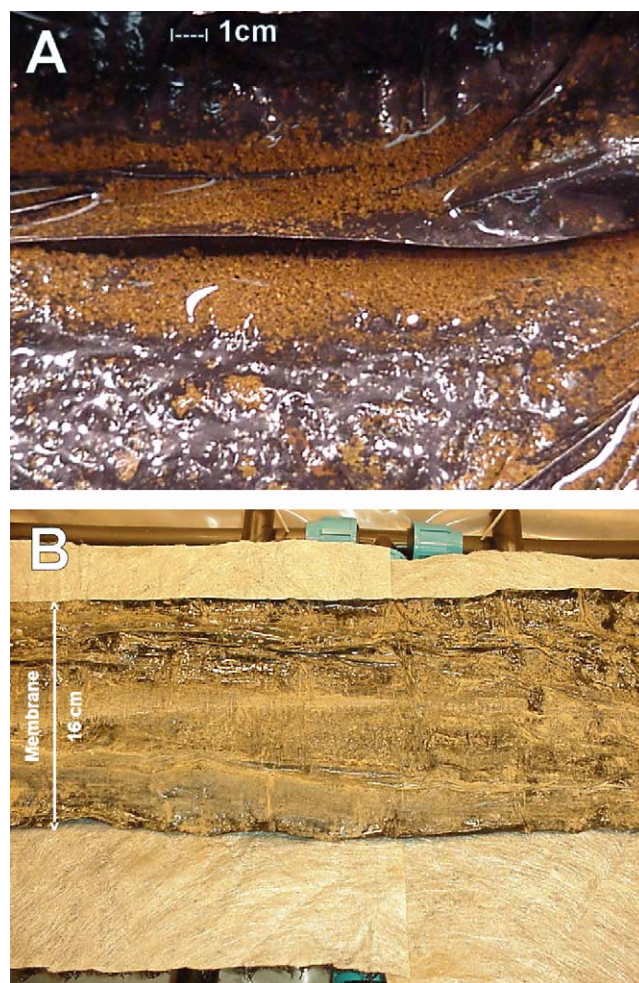


Fig. 9. Inside of a membrane tube that is cut open after use: (A) showing the debris and (B) the dried state of the tube after flushing of the debris with tap water. At the positions of the surface that used to be the topside of the tube, areas with a high concentration of a light yellowish powder are visible.

brane tube after the concentration experiment with formation water can be seen in Fig. 9A and B.

At the end of the experiments the membrane tubes were visually checked for fouling. The outside of the membrane tubes was completely clean, a breakthrough of salt, visible by crystallites, did not occur. Inspection of the inside showed considerable fouling of the membrane. Most of the fouling could be washed away with tap water, the remaining fouling adhered to the membrane. Remarkably, the top of the tube, being the side facing the light bulbs, was dirtier than the bottom. There was also a difference in texture and color of the fouling. At the bottom the fouling consisted more of flakes that were softer and red brown whereas at the top the fouling was yellowish, harder and grainier of texture. A reason for this could lie in the higher temperatures at the top, which result in a stronger evaporation and hence higher concentrations of minerals at the membrane surface.

It was expected that a large part of the fouling consisted of iron oxide. An indication for this was the observation of the

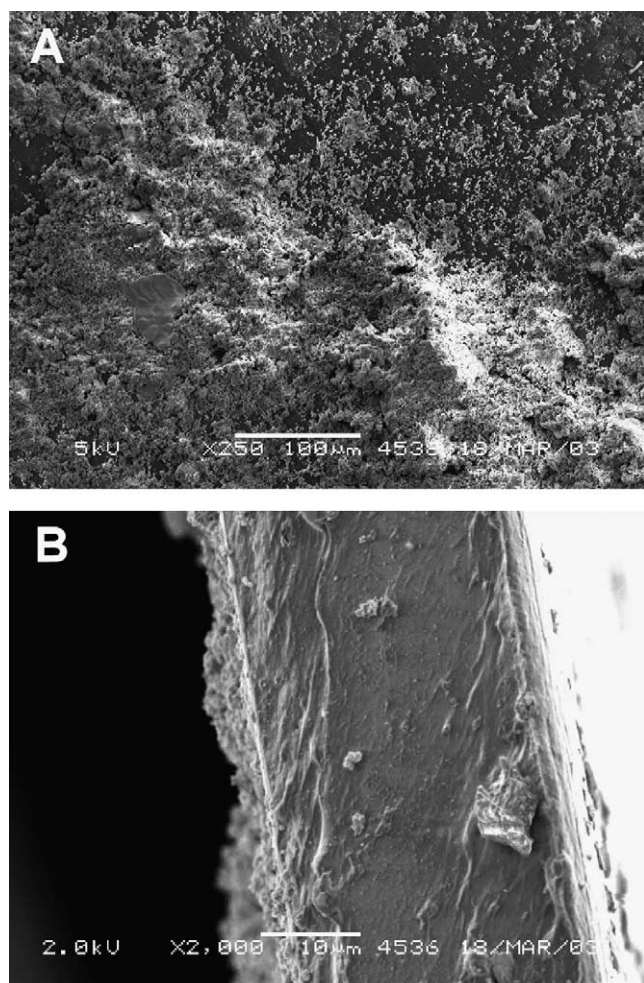


Fig. 10. SEM pictures of a membrane that was used in the seawater concentration experiments: (A) showing the surface and (B) the cross-section. The thickness of the fouling layer is visible at the left-hand side of the cross-section.

connectors of the tubes. These connectors have galvanized iron support rings inside to keep the tube from collapsing when pressure from outside is applied. After the experiments the rings were strongly corroded. The corrosion of the rings also increased the concentration of both zinc and iron in the feed samples to very high values that clearly proof that these elements should be of external origin.

The scanning electron microscope analysis of the fouled membrane, see Fig. 10A and B, showed that considerable fouling had taken place. The layer had a thickness between 2 and 10 μm and showed large variances in density with large grains (0.05–0.2 mm) and small particles of (2–10 μm). The density of the particles was checked with backscatter scanning secondary electron mode revealing that the large particles had a higher density than the other type of fouling.

As the membrane material swells in water at high temperatures, it is known to become permeable towards salts. Therefore, it was investigated if crystallization of salts into the membrane material had occurred due to the concen-

tration process. To check this, SEM pictures were taken from the cross-section of a used membrane both in scanning mode and backscatter mode. From the pictures it was evident that no crystallization had occurred in the membrane material.

When comparing the flux data for all experiments it is clear that the flux seems independent of the production time and therefore independent of concentration. It is expected that within the length of the experiment the fouling increased. This shows that under the applied conditions the flux was not limited by the fouling. However, this does not necessarily mean that the process was not affected by the fouling. Direct solar membrane pervaporation is a dynamic process meaning that solar input, heat loss and evaporation rate are in dynamic equilibrium resulting in a certain steady-state feed water temperature. During the concentration process, a fouling layer increases the transport resistance and the increased concentration lowers the driving force for transport of water through the membrane. This should result in a lower water flux when the process was carried out under strictly isothermal feed conditions. However, the amount of heat input in the system is constant and hardly dependent on the feed temperature. Therefore, the effect of a reduced water flux, which means reduced loss of heat via evaporation, automatically results in an increase of the feed temperature. Consequently, the increased feed temperature enhances the evaporation rate to about the same level as without fouling (or at low concentration). Unfortunately, the temperature profile of the system was not measured continuously during the concentration process and validation of this interpretation remains open in this stage. Therefore, it can only be concluded that the solar membrane pervaporation process as it is operated in these experiments is indifferent to the occurrence of fouling and increase of feed concentration as depicted in this study. Assuming that the above consideration also holds for the outdoor experiments, this would make the operation of the process simple and provide an easy-to-use solution to potable water problems since extensive pre-treatment of the feed water is not necessary.

5. Conclusion

A new membrane process, solar driven pervaporation was used for the production of distilled water from untreated seawater and formation water. The configuration used consisted of direct solar single effect membrane pervaporation unit, using dense tubular membranes made of 40 μm thick modified PEA film. The system was designed to minimize capital cost and pre-treatment cost of high fouling feed streams. In order to test the performance, the retention of 30 elements was tested as a function of time and concentration of the sea and formation water. Retentions over 99.998%, based on calibrated conductivity data, were measured under steady-state conditions. The produced condensate quality was high with a conductivity between 1.6 and 5 $\mu\text{S}/\text{cm}$ and was limited by

the presence of dust at the condensate side. Due to the very high retentions, high levels of boron, arsine or fluoride in the feed water can be reduced to levels far below WHO drinking water standards.

The flux of the system was about $5 \text{ l}/(\text{m}^2 \text{ day})$ when normalized to collector surface and using a day of 9 h. The flux is independent of used feed concentration and was not affected by severe fouling resulting from the concentration process. This can be explained by the fact that the solar process in itself is in dynamic equilibrium in this respect that an increase in transport resistance at the feed side results in an increase of the feed temperature due to a limited evaporation. As a result the transport limitations, as would be expected from increased salinity and fouling, might be mostly compensated by a higher feed temperature and therefore not easily detected via flux measurements.

The studied process allows for the use of feed waters like seawater and formation water without pre-treatment giving constant fluxes in time and producing high quality water in a single step.

Acknowledgements

This contract research was initiated and financed by Solar Dew B.V., membranes, feed and set-up were also provided by Solar Dew B.V., Breda, The Netherlands. The element analysis was carried out by Akzo Nobel Chemicals Research Arnhem (CRA), Arnhem, The Netherlands

Nomenclature

A_c	collector area (m^2) with single and double indices indicating different exposed areas
A_m	membrane area (m^2)
C	concentration (g/l)
h'_c	modified convection coefficient ($\text{W}/(\text{m}^2 \text{ K})$)
H_{ev}	heat of evaporation for water (J/kg)
J_c	water flux normalized on collector area ($\text{l}/(\text{m}^2 \text{ day})$)
J_m	water flux normalized on membrane area ($\text{l}/(\text{m}^2 \text{ day})$)
J_w	productivity (water flux) (kg/s)
I_e	effective light flux to the collector (W/m^2)
k_m	overall mass-transfer coefficient ($\text{kg}/(\text{m}^2 \text{ Pa s})$)
L	tube length (m)
LRF	log removal factor
M	mass of produced water (kg)
p_b	partial pressure at the condenser, i.e. the bottom of the tunnel (Pa)
p_m	partial pressure of the feed (Pa)
Q_{evap}	heat loss via evaporation (J)
Q_{irr}	heat flow by irradiation (J)

Q_{loss}	heat loss to the environment (J)
r	tube radius (m)
R	retention
t	production time (day)
T_b	temperature of the condenser, i.e. the bottom of the tunnel (K)
T_c	temperature of the collector, i.e. the support layer around the membrane tube (K)
T_l	Temperature of the laboratory (K)

Greek letters

α_c	collector radiation absorptivity
ε_c	collector emissivity
λ	conductivity (mS/cm)
π	3.1416
ρ	density of water (kg/l)
σ	Stefan Boltzman constant ($\text{W}/(\text{m}^2 \text{ K}^4)$)

References

- [1] I. Bremere, M. Kennedy, A. Stikker, J. Schippers, How water scarcity will effect the growth in the desalination market in the coming 25 years, *Desalination* 138 (2001) 7–15.
- [2] G. Fiorenza, V.K. Sharma, G. Braccio, Techno-economic evaluation of a solar powered water desalination plant, *Energy Convers. Manage.* 44 (2003) 2217–2240.
- [3] M.F.A. Goosen, S.S. Sablani, W.H. Shayya, C. Paton, H. Al-Hinai, Thermodynamic and economic considerations in solar desalination, *Desalination* 129 (2000) 63–89.
- [4] S. Kimura, S.-I. Nakao, S.-I. Shimatani, Transport phenomena in membrane distillation, *J. Membr. Sci.* 33 (1987) 285–298.
- [5] M. Gryta, M. Tomaszewska, J. Grzechulska, A.W. Morawski, Membrane distillation of NaCl solution containing natural organic matter, *J. Membr. Sci.* 181 (2001) 279–287.
- [6] S.T. Hsu, K.T. Cheng, J.S. Chiou, Seawater desalination by direct contact membrane distillation, *Desalination* 143 (2002) 279–287.
- [7] B. van der Bruggen, C. Vandecasteele, Distillation vs. membrane filtration: overview of process evolutions in seawater desalination, *Desalination* 143 (2002) 207–218.
- [8] B.M. Fabuss, A. Korosi, Vapor pressures of binary aqueous solutions of NaCl, KCl, Na_2SO_4 and MgSO_4 at concentrations and temperatures of interest in desalination processes, *Desalination* 1 (1966) 139–148.
- [9] R.H. Perry, D. Green, in: B.E. Eckes (Ed.), *International Student Edition, Perry's Chemical Engineers' Handbook*, sixth ed., McGraw-Hill Book Co., Singapore, 1984.
- [10] R.L. Hummel, Solar distillation with economies of scale, innovation and optimization, *Desalination* 134 (2001) 159–171.
- [11] P. Verbeek, J. Straccia, H. Zwijnenberg, M. Potter, A. Ter Beek, Solar Dew—the prospect of fresh water in the desert, in: *Proceedings of the 10th Abu Dhabi International Petroleum Exhibition and Conference, Society of Petroleum Engineers, Abu Dhabi, 2002*, SPE78551.
- [12] H. Al-Hinai, M.S. Al-Nassri, B.A. Jubran, Parametric investigation of a double-effect solar still in comparison with a single-effect solar still, *Desalination* 150 (2002) 75–83.
- [13] F. Banat, R. Jumah, M. Garaibeh, Exploitation of solar energy collected by solar stills for desalination by membrane distillation, *Renewable Energy* 25 (2002) 293–305.

- [14] H. Lu, J.C. Walton, A.H.P. Swift, Desalination coupled with salinity-gradient solar ponds, *Desalination* 136 (2001) 13–23.
- [15] D.R. Lide, in: D.R. Lide (Ed.), *Handbook of Chemistry and Physics*, 74th ed., CRC Press, Boca Raton, FL, 1994.
- [16] M. Hermann, J. Koschikowski, M. Rommel, Corrosion-free solar collectors for thermally driven seawater desalination, *Solar Energy* 72 (2002) 415–426.
- [17] P.I. Cooper, The maximum efficiency of single-effect solar stills, *Solar Energy* 15 (1973) 205–214.
- [18] H.S. Kwatra, Performance of a solar still: predicted effect of enhanced evaporation area on yield and evaporation temperature, *Solar Energy* 56 (1996) 261–266.
- [19] Rijkswaterstaat, WaterBase, <http://www.waterbase.nl/>, August 2003.
- [20] T.I.R. Utvik, Chemical characterisation of produced water from four offshore oil production platforms in the North Sea, *Chemosphere* 39 (1999) 2593–2606.
- [21] T. Stromgren, S.E. Sorstrom, L. Schou, I. Kaarstad, T. Aunaas, O.G. Brakstad, O. Johansen, Acute toxic effects of produced water in relation to chemical composition and dispersion, *Mar. Environ. Res.* 40 (1995) 147–169.
- [22] Y. Sato, M. Kang, T. Kamei, Y. Magara, Performance of nanofiltration for arsenic removal, *Water Res.* 36 (2002) 3371–3377.
- [23] P. Brandhuber, G. Amy, Arsenic removal by a charged ultrafiltration membrane—influences of membrane operating conditions and water quality on arsenic rejection, *Desalination* 140 (2001) 1–14.
- [24] M. Taniguchi, M. Kurihara, S. Kimura, Boron reduction performance of reverse osmosis seawater desalination process, *J. Membr. Sci.* 183 (2001) 259–267.
- [25] A. Lhassani, M. Rumeau, D. Benjelloun, M. Pontie, Selective demineralization of water by nanofiltration. Application to the defluorination of brackish water, *Water Res.* 35 (2001) 3260–3264.