

# Membrane distillation of industrial cooling tower blowdown water



N.E. Koeman-Stein<sup>a,1</sup>, R.J.M. Creusen<sup>a,\*</sup>, M. Zijlstra<sup>a</sup>, C.K. Groot<sup>b</sup>, W.B.P. van den Broek<sup>c</sup>

<sup>a</sup> TNO Water Treatment, Utrechtseweg 48, Zeist, The Netherlands

<sup>b</sup> Dow Benelux BV, H.H. Dowweg 5, Hoek NM 4542, The Netherlands

<sup>c</sup> Evides IW, Schaarlijk 150, Rotterdam, The Netherlands

## ARTICLE INFO

### Article history:

Received 30 September 2015

Received in revised form

11 March 2016

Accepted 18 March 2016

### Keywords:

Membrane distillation

Cooling tower blowdown

Water recovery

Desalination

## ABSTRACT

The potential of membrane distillation for desalination of cooling tower blowdown water (CTBD) is investigated. Technical feasibility is tested on laboratory and pilot scale using real cooling tower blowdown water from Dow Benelux in Terneuzen (Netherlands). Two types of membranes, polytetrafluorethylene and polyethylene showed good performance regarding distillate quality and fouling behavior. Concentrating CTBD by a factor 4.5 while maintaining a flux of around 2 l/m<sup>2</sup>·h was possible with a water recovery of 78% available for reuse. Higher concentration factors lead to severe decrease in flux which was caused by scaling. Membrane distillation could use the thermal energy that would otherwise be discharged of in a cooling tower and function as a heat exchanger. This reduces the need for cooling capacity and could lead to a total reduction of 37% water intake for make-up water, as well as reduced energy and chemicals demands and greenhouse gas emissions.

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## 1. Introduction

In industry it becomes more important to close water cycles. Closing water cycles and thus (internal) reuse of water relieves water stress on the environment and on other activities such as urban or agricultural water use. Industrial processes often need a considerable amount of fresh water. Among these processes, large water consumers are cooling towers (CT) using 60–70% of the total fresh water demand in industry [1]. In the cooling tower, water evaporates resulting in an increased concentration of salts and other contaminants. This leads to problems such as scaling and corrosion. Hence the concentrated cooling tower water is regularly discharged from the tower. This discharge is called cooling tower blowdown water (CTBD). Make-up water is added to the tower to compensate for the evaporated water and the CTBD. When the blowdown water can be reused, after treatment, this will save the need for about 15% of the make-up water [2]. Electrical conductivity is generally the parameter that is used to determine the rate for blowdown as salts are the main cause for problems in the tower. Treatment of blowdown water should therefore focus on the removal of salts. However, a high concentration of TOC also causes problems due to fouling. Removal of TOC is therefore also

required. Several treatment options can be thought of such as desalination using reverse osmosis (RO), nanofiltration (NF) or electro dialysis (ED). A disadvantage of pressure driven membrane processes is the sensitivity of the membranes towards fouling while electro dialysis minimally removes TOC. Another option is the use of membrane distillation (MD) [3]. Although this is also a membrane process, pressure is low, temperature on the membrane is high and the hydrophobic nature of the membranes may lead to less fouling problems compared to other membrane desalination technologies [4,5]. The advantage of the combination of MD and cooling towers, is the presence of waste heat [6]. Whereas RO and ED use electricity to create a driving force, MD uses (waste) heat as driving force. Membrane distillation is a thermally driven transport of water vapor through non-wetted porous hydrophobic membranes, the driving force is the vapor pressure difference between the two sides of the membrane, which is usually caused by a temperature difference between the two sides of the membrane. Therefore the option of using membrane distillation for the treatment of cooling tower blowdown water is investigated. Desalination by membrane distillation could use the heat that would otherwise be cooled away in a cooling tower. This results in a reduction of required cooling capacity by cooling towers, thus reducing the need for more make-up water intake, costs and GHG emissions [7,8].

Cooling tower blowdown water at Dow Benelux BV in Terneuzen (NL) was used for the experimental evaluation of desalination of CTBD. The main research focuses on whether it is possible to desalinate CTBD water by membrane distillation, and what type of problems that are met. As biocides, biocides, biocides,

\* Corresponding author.

E-mail addresses: [nienke.koeman-stein@kwrwater.nl](mailto:nienke.koeman-stein@kwrwater.nl) (N.E. Koeman-Stein), [raymond.creusen@tno.nl](mailto:raymond.creusen@tno.nl) (R.J.M. Creusen), [martin.zijlstra@tno.nl](mailto:martin.zijlstra@tno.nl) (M. Zijlstra), [ckgroot@dow.com](mailto:ckgroot@dow.com) (C.K. Groot), [w.vandenbroek@evides.nl](mailto:w.vandenbroek@evides.nl) (W.B.P. van den Broek).

<sup>1</sup> Author currently working at: KWR Watercycle Research Institute, Groningenhaven 7, 3433 PE, Nieuwegein, The Netherlands.

corrosion inhibitors and antiscalants are present, it is expected that they may affect the membranes and may cause leakage or wetting of the membranes. The pores of the hydrophobic membrane may become hydrophilic because these components may enter the pores and make them hydrophilic. Furthermore the high TOC concentration may result in fouling. Both short term laboratory experiments and long term pilot scale experiments are performed to identify the general treatability and preferential set points as well as the long term behavior such as fouling impacts. As far as the authors are aware, this is the first time that CTBD from a real industrial site is used for desalination by MD on pilot scale. Experiments were executed to investigate the flux while concentrating the CTBD, to determine maximum recovery, and to test if a constant flux could be maintained over a longer period at a set concentration factor.

Potential water saving when recovering distilled water from CTBD and reusing it as make-up water will be discussed. Also the total concept to integrate membrane distillation with the cooling system of an industrial site is discussed. When this desalination is done by membrane distillation, it does not only produce desalinated water, but also uses heat. This could therefore replace part of the cooling done by the cooling towers and decrease the required capacity from the towers.

## 2. Material and methods

### 2.1. Raw water

Cooling tower blowdown water at Dow Benelux BV in Terneuzen (NL) was used for the experimental evaluation of desalination of CTBD. Two types of cooling tower waters were used: LHC3, which is cooling the exothermal processes from the Dow factories, and Elsta, which is the powerplant that provides Dow with power and steam. Currently, sand filtered surface water is used as the source for make-up water at Dow. The water is relatively high in TOC concentration [9] which is not removed during filtration and mainly consists of humic acids. Cooling tower blowdown water from the Elsta cooling tower near the Dow site in Terneuzen amounts  $1 \times 10^6 \text{ m}^3/\text{yr}$ . The cooling tower is operated as a natural draft counter flow CT. The make-up water for the cooling tower was supplied and monitored by Evides for 7.5 yrs (01–01–2005 to 15–06–2012) before the start of the experiments with an average conductivity was  $676 \mu\text{S}/\text{cm}$ . This water is concentrated in the cooling tower by a factor 5–6.5 reaching a conductivity of  $3500\text{--}4500 \mu\text{S}/\text{cm}$ . CTBD water quality from the Elsta cooling tower was analyzed for main composition (Nov 2012, Sept 2013–Jan 2014). The results are shown in Table 1. Chemicals are added to the cooling tower. These chemicals are:  $\text{H}_2\text{SO}_4$  96% for pH-adjustment, corrosion inhibitor (Nalco, 3DT187), biodispersant (Nalsperse 7348, 4.3 mg/l), corrosion inhibitor (Nalco, 3DT199, 3.2–6.3 mg/l sodium benzotriazole), NaClO. The blowdown is currently discharged to the river directly ( $2 \times 10 \text{ h}$  per day).

The second type of cooling tower blowdown was called LHC3 and the composition of the blowdown is shown in Table 1. The make-up water of this tower is for at least 50% fed by the effluent from the industrial wastewater treatment plant at the Dow premises. The chemicals provided to the cooling tower are different as it is provided by a different supplier.

### 2.2. Laboratory experiments

Laboratory experiments were performed in a direct contact membrane distillation set-up with a membrane area of  $429 \text{ cm}^2$ . Blowdown water from two cooling towers, Elsta and LHC3, were used as raw water. A constant feed temperature and temperature

**Table 1**  
Composition of Elsta and LHC3 cooling tower blowdown (raw water).

		Elsta		LHC3	
		Average (st dev)	Number of data points	Average (st dev)	2 datapoints
EC	$\mu\text{S}/\text{cm}$	3944 (610)	11	4600 (140)	
$\text{Cl}^-$	mg/l	549 (36)	11	487 (12)	
$\text{NO}_3^-$	mg/l	88 (21)	8	93 (43)	
$\text{HCO}_3^{--}$	mg/l	65 (16)	8	46 (22)	
$\text{SO}_4^{2-}$	mg/l	1109 (82)	11	1056 (68)	
$\text{Na}^+$	mg/l	332 (41)	11	408 (8)	
$\text{Ca}^{2+}$	mg/l	437 (45)	11	351 (14)	
$\text{Mg}^{2+}$	mg/l	61 (7)	11	49 (0)	
$\text{K}^+$	mg/l	81 (12)	11	59 (0)	
Dissolved Fe	mg/l	< 0.2	11	< 0.2	
P	mg/l	2 (3)	10	8 (0)	
TOC	mg/l	53 (5)	8		
TSS	mg/l	< 15	11		
Chlorophyll A	mg/l	< 0.2	11		
pH		7.5–8	11	6.5	

\*\* This value is not very accurate as it is highly dependent of pH, and balancing with the gas composition above the liquid.

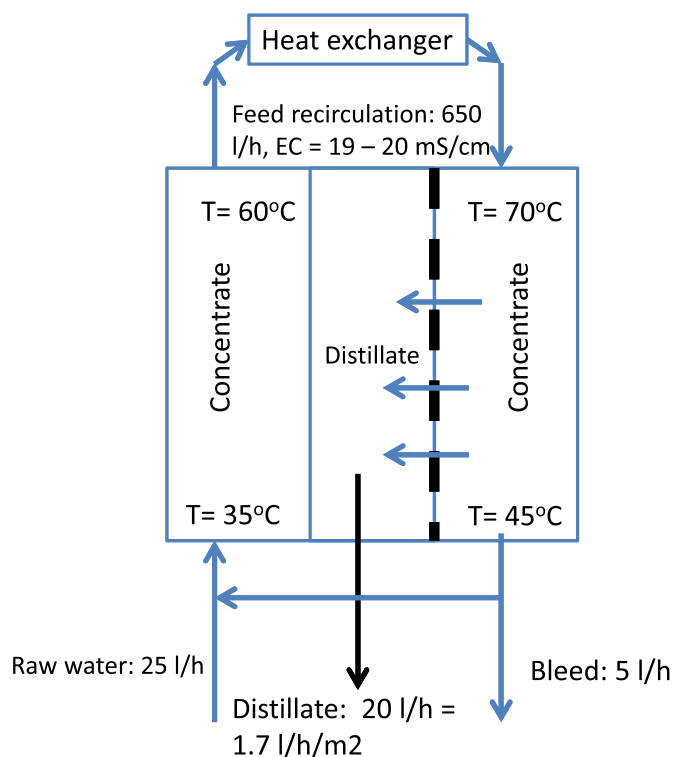
difference were maintained in the set-up using an external heat exchanger. A temperature of  $70 \text{ }^\circ\text{C}$  was maintained. Temperature difference ( $T_{\text{feed}} > T_{\text{distillate}}$ ) was  $10 \text{ }^\circ\text{C}$ . The circulation flow of the feed water was 3–4 l/min. Two different membranes were used: polytetrafluorethylene (PTFE) and polyethylene (PE) membranes. In all experiments no pretreatment was used. Ion concentrations in the feed and distillate were measured using ICP analysis. Electrical conductivity was measured every minute in the feed and distillate, and once in the raw water, as this was a single batch with constant quality.

### 2.3. Pilot experiments set-up

The pilot plant was built by Aquastill. It was built as a liquid gap MD system using external heat exchange (see Fig. 1). In liquid gap MD, water vaporizes on the hot side of the membrane, diffuses through the membrane pores and condenses on the cold side of the membrane producing a liquid gap between the membrane and the cooling plate. The temperature difference was  $10 \text{ }^\circ\text{C}$  at a top temperature of  $70 \text{ }^\circ\text{C}$ . A spiral wound module with membranes of  $7.2 \text{ m}^2$  was used. The pilot experiments were all performed with the Elsta CTBD. Two runs were performed with the raw CTBD without any pretreatment or additives. Two runs were performed using a filter cartridge with an average pore size of  $10 \mu\text{m}$ , as pretreatment to prevent larger particles such as sand to enter the system. The configuration was then changed to a configuration with internal heat exchange (based on the Memstill principle [10]). Two more runs were done. All experiments were performed in a feed-bleed configuration. The pressure drop at the feed side along the membrane was used as an indication for the need of cleaning. Pressure increase does not tell anything about membrane fouling, however it indicates fouling of the channels. Membrane fouling is indicated by a decrease of flux. The set-up however was not automated to measure a flux and therefore it was only possible to use pressure as an indicator for the need for cleaning. Cleaning started when the pressured had increased to 300 mbar and was done with HCl. The pH was lowered to 3 and the cleaning was stopped when the pressure had dropped to below 50 mbar.

### 2.4. Analysis of precipitation

Precipitation was analyzed using light microscopy and scanning



**Fig. 1.** Schematic drawing of MD set-up. The water streams are given with the used terms. The bleed stream is not used when concentrating.

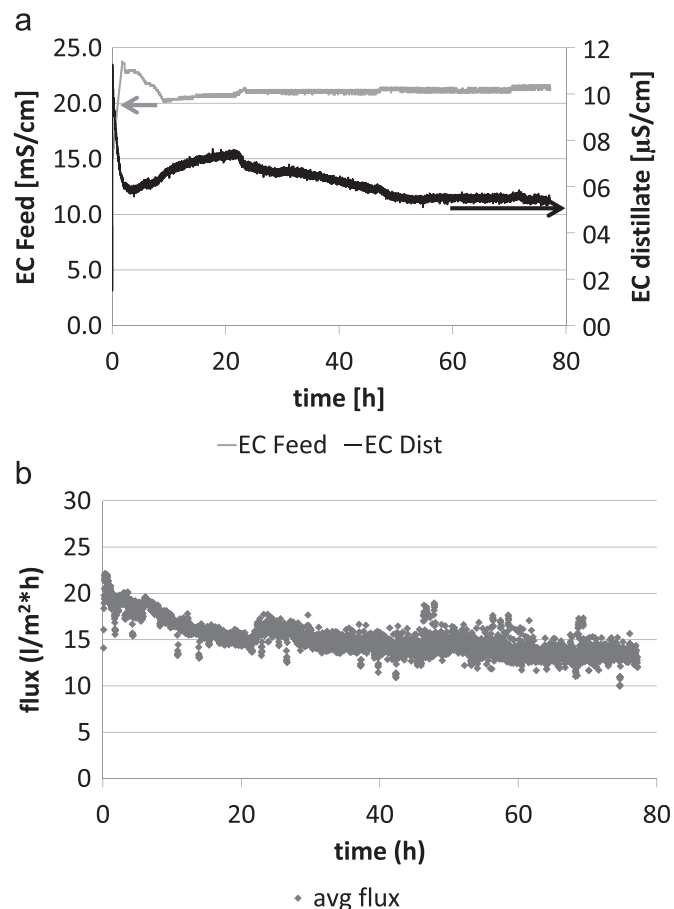
electron microscopy (SEM). A SEM with X-ray diffraction analysis was used for optical observation and elemental analysis.

### 3. Results

#### 3.1. Laboratory experiments – fouling behavior

Laboratory experiments were performed to get insight in the fouling of the PTFE membranes of the MD setup while a constant concentration factor was maintained. It was possible to concentrate LHC3 water from 4.3 up to 22.3 mS/cm (concentration factor 5.2, water recovery of 81%) and keep a constant flux through the membrane at this concentration factor for 25 h. Concentrating further then led to a rapid decrease in flux. Analysis of ions showed that up to a concentration factor of 3.6 of the feed EC, all ion concentrations increased proportionally. However, at higher concentration factors, the concentrations of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  did not increase proportionally but fell behind. This may indicate precipitation of these ions in the system.  $\text{Ca}^{2+}$  concentration increases less fast than sulfate. Therefore it is likely that both  $\text{CaSO}_4$  and  $\text{CaCO}_3$  are precipitating at these high concentration factors. The solubility product (in demineralized water) of  $\text{CaSO}_4$  is also higher than of  $\text{CaCO}_3$  and therefore it is expected that  $\text{CaCO}_3$  is more likely to precipitate. This can be a reason for a decreasing flux. In the used system precipitation is most likely to happen on the heat exchangers as here the temperature is highest in the system, and this was also observed. However, precipitation on the membrane is also possible. It was possible to remove the scaling from the heat exchanger by cleaning with acid. This may indicate  $\text{CaCO}_3$  scaling. As  $\text{CO}_3^{2-}$  concentrations cannot be measured accurately, a balance cannot be made.

Using Elsta water and PTFE membranes, it was possible to concentrate from 4.0 to 21 mS/cm (concentration factor 5.25, see Fig. 2). The flux slowly decreased from 16.6 to 13 l/m<sup>2</sup>·h over a period of 76 h.



**Fig. 2.** A: EC of concentrate (grey, left axis) and of distillate (black, right axis) and 2B: flux of membrane distillation with Elsta water and PTFE membrane,  $T_{\text{feed}} = 70^\circ\text{C}$ ,  $T_{\text{feed}} - T_{\text{distillate}} = 10^\circ\text{C}$ .

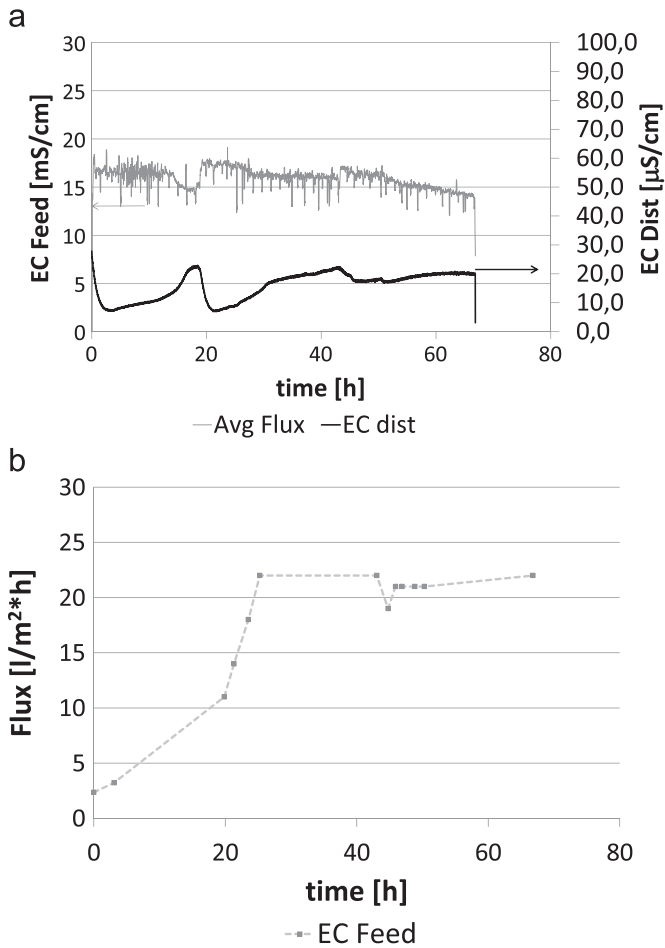
MD experiments were also performed to desalinate Elsta water with a PE membrane (Solupor) at a feed temperature of  $70^\circ\text{C}$  and a temperature difference ( $\Delta T$ ) of  $10^\circ\text{C}$ . It was possible to concentrate the feed from 2.3 to 22 mS/cm (concentration factor 9.6) and keep a flux for 66 h. The flux slowly decreased from 17 to 14 l/m<sup>2</sup>·h as can be seen from Fig. 3. Analysis of the ion concentrations in the feed solution (see Fig. 4), showed that  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  were concentrated slightly less than  $\text{Na}^+$ . Where  $\text{Na}^+$  was concentrated by a factor 7 ( $\text{conc}_{t_0}/\text{conc}_{t_i}$ ) at a conductivity of 22 mS/cm of the feed,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  were concentrated by a factor 6,  $\text{HCO}_3^-$  was concentrated only by a factor 4.  $\text{HCO}_3^-$  is hard to measure as the concentration depends largely on pH, and  $\text{CO}_2$  concentration. This may indicate that these ions form precipitates at higher concentration factors. The solubility of the salts cannot be calculated because of the presence of antiscalants. However the antiscalants will not be able to prevent scaling completely at the high concentrations as seen here.

The conductivity of the permeate was in all experiments below 20  $\mu\text{S}/\text{cm}$ . Membrane distillation can thus be regarded as total desalination as the salt retention is  $>99\%$  and individual ion concentrations in the permeate in most samples were below the detection limit (0.1 mmol/l for  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , 0.05 mmol/l for P and 0.1  $\mu\text{mol}/\text{l}$  for Fe (total  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ),  $\text{Cu}^{2+}$ ,  $\text{B}^{3+}$ , Mo (total:  $\text{Mo}^{+4}$ ,  $\text{Mo}^{+6}$ ),  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ).

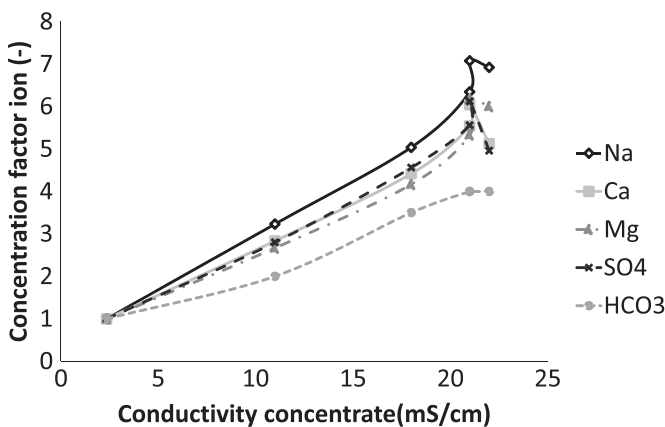
#### 3.2. Pilot experiments

##### 3.2.1. Long term performance of MD with external heat exchange

The average electrical conductivity (EC) of the CTBD was 3.7 mS/cm. A concentration factor of 4.5 was reached, leading to

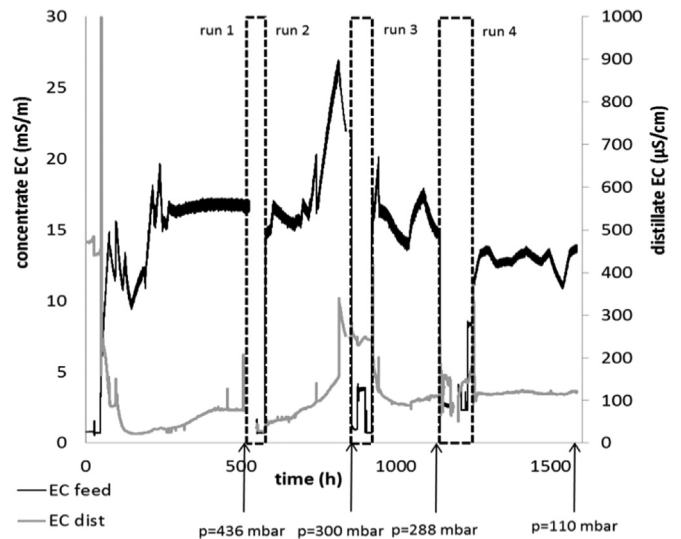


**Fig. 3.** Membrane distillation of Elsta CTBD and Solupor membrane,  $T_{\text{feed}}=70\text{ }^{\circ}\text{C}$ ,  $T_{\text{feed}}-T_{\text{distillate}}=10\text{ }^{\circ}\text{C}$ . 3A: EC of the concentrate solution (grey squares) and EC of distillate (black line, right axis). 3B Flux through the membrane.



**Fig. 4.** Concentration factor of individual ions in the concentrate solution (Elsta CTBD) as a function of the conductivity of the concentrate solution (Solupor membrane,  $T_{\text{feed}}=70\text{ }^{\circ}\text{C}$ ,  $T_{\text{feed}}-T_{\text{distillate}}=10\text{ }^{\circ}\text{C}$ ).

concentrate EC of 17 mS/cm. The distillate EC was 70–120 μS/cm. This is slightly higher than found in the laboratory experiments. However it is still below the set limit of 1 mS/cm. It was possible to keep this distillate EC for over 1500 h (2 months). This indicates that the membrane was not wetted by the CTBD. As can be seen in Fig. 5 the distillate EC increases at the moment that the concentrate EC also increased. This indicates a small hole/leakage in the membrane, but as the low EC was restored after the concentrate EC is lowered, no wetting was observed.



**Fig. 5.** Pilot results: electrical conductivity of concentrate (black, left axis) and distillate (grey, right axis) of membrane distillation of cooling tower blowdown water. The dotted marked periods at  $t=550\text{ h}$ ,  $850\text{ h}$  and  $1150\text{ h}$ , are cleaning periods, using HCl. Pressure difference across the membrane was used as an indication for cleaning. The pressure before the external heat exchanger is given in the graph.  $T_{\text{top}}=70\text{ }^{\circ}\text{C}$ ,  $T_{\text{feed}}-T_{\text{permeate}}=10\text{ }^{\circ}\text{C}$ .

The pressure before the heat exchanger was measured. Fouling could be caused by either scaling or (bio)fouling. After cleaning with acid (pH lowered to pH3 using concentrated HCl) it was possible to restore the pressure and this is an indication that scaling was the major cause for the pressure drop, as opposed to (bio)fouling of the membrane, which would not be removed by acid. Scaling may be a faster process than biofouling but the duration of the experiments (> 2 months) was long enough to show that biofouling was not a (major) cause for pressure drop. Even after two months only acid cleaning was sufficient to restore the pressure and the flux (See Fig. 6).

### 3.2.2. Long term performance of MD with internal heat exchange – energy usage

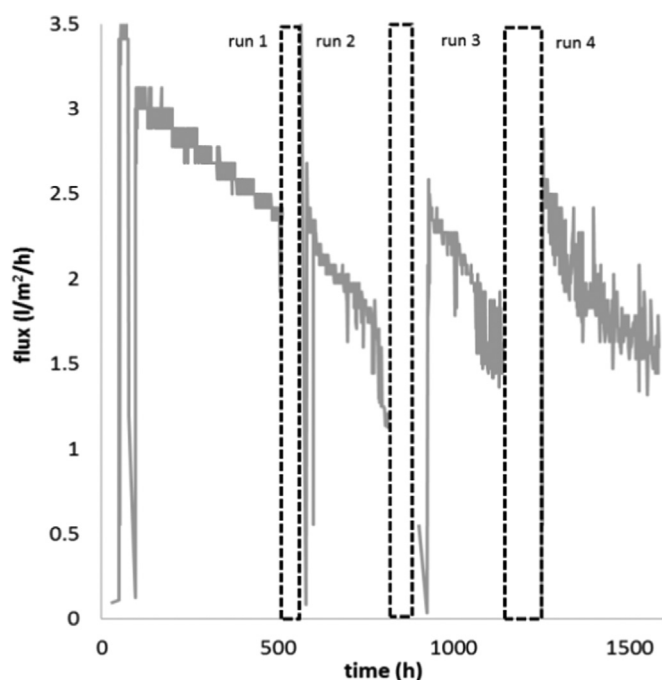
Pilot experiments were done with a membrane configuration with internal heat exchange. The flux was 1.7 l/m<sup>2</sup>\*h at an EC of 15 mS/cm. Increasing the EC to 16 mS/cm however, gave a decrease of flux to 1.5 l/m<sup>2</sup>\*h and increasing the EC even further made the flux decline very rapidly. As with this configuration, heat is exchanged internally, it was possible to calculate the energy efficiency and the performance ratio. The average energy that had to be supplied for a flux of 1.7 l/m<sup>2</sup>\*h through the membrane was 25.8 MJ/h, which is a specific heat of 1500 MJ/m<sup>3</sup> distillate and an energy efficiency, calculated as the latent energy transfer divided by the total energy transfer, of 60%.

This is not a very efficient system. However simulations showed that the design of the modules can significantly decrease the energy demand. When a module with the same surface area would be used, but which has a module length that is doubled, the specific energy requirements decrease drastically by approximately 50%. Optimization of the module design can therefore significantly improve the set-up.

### 3.2.3. Analysis of precipitation

Precipitation in the heat exchanger after the first run was analyzed. The precipitation looked like brown fine grains (Fig. 7A). Addition of acid caused creation of gas bubbles, indicating the formation of CO<sub>2</sub>-gas. However, the gas composition was not analyzed. Scanning electron microscopy (Fig. 7B and C) showed the





**Fig. 6.** Flux through the membrane during the pilot runs. Dotted marks at  $t=550$  h, 850 h and 1150 h indicate cleaning periods.  $T_{\text{top}}=70$  °C,  $T_{\text{feed}}-T_{\text{permeate}}=10$  °C.

presence of many organic components including diatoms (after acid addition). To prevent large organisms like diatoms to enter the system, the cartridge filter (10  $\mu\text{m}$ ) was used in run 3 and further. Elemental analysis of the precipitate was also performed (Table 2). A small amount of S was seen, indicating little  $\text{SO}_4$  precipitation. The atomic ratio (4th column in Table 2) of the precipitate was Ca:C:O circa 1:1.7:4. As  $\text{CaCO}_3$  precipitation has an atomic ratio of Ca:C:O=1:1:3, we see approximately twice as much C. This is probably present as organic components. However, as the pressure is restored after acid cleaning, this organic material does not cause major fouling during the experiments (1600 h).

### 3.3. Water recovery

One of the main objectives of the experiments was water recovery and reuse from CTBD. Using membrane distillation, water is recovered through the distillate. The distillate EC was below 120  $\mu\text{S}/\text{cm}$  in all experiments. Two types of CTBD were tested. On laboratory scale LCH3 could be concentrated by a factor 5.3 using PTFE membrane, giving a water recovery of 81%. Elsta CTBD water could be concentrated by a factor 5.25 using PTFE membrane, giving a water recovery of 81% as well. Concentrating Elsta CTBD water with a PE membrane in the MD module, a concentration factor of 9.6 was reached, giving a water recovery of 90%. A water recovery of  $> 80\%$  of cooling tower blow down water could thus be obtained over a longer period using membrane distillation. In the pilot experiments a concentration factor of 4.5 was reached, giving a water recovery of 78% while maintaining a good flux for a long period (average 12.5 days). For the cooling towers at Dow, where the blowdown is approximately 1  $\text{Mm}^3/\text{year}$ , this would save 800,000  $\text{m}^3/\text{year}$  on make-up water.

## 4. Discussions and conclusions

Both laboratory scale experiments and pilot scale experiments show that membrane distillation is a promising technology for desalination of cooling tower blowdown water from Dow

Terneuzen. When membrane distillation is used the recovered water has a very high quality with an electrical conductivity below 120  $\mu\text{S}/\text{cm}$  and barely any TOC. This water can thus be used for many applications.

### 4.1. Fouling

The main fouling that was observed was scaling at high concentration factors. This could be removed and flux could be restored by cleaning with acid. No pretreatment was used apart from the cartridge filter to prevent large particles such as sand and diatoms to enter the system. No problems were found with bio-fouling. This is a major advantage over other membrane based desalination processes such as RO. Much focus is put on the pretreatment of CTBD water before RO treatment. Even then, chemical cleaning on a regular basis is still required [9,11].

### 4.2. Total concept – integration of MD for water reuse

At this moment in the site of Dow in Terneuzen, the power plant is operated by Elsta, having its own cooling towers. Furthermore Dow has 16 cooling towers that are used to cool the exothermic processes on site of which LHC3 is one. As in the cooling towers water evaporates, make-up water is provided from different sources. The components such as salt concentrate in the tower, and when the electrical conductivity is above 3.6–4  $\text{mS}/\text{cm}$ , water is discharged as blowdown water. When this blowdown water is desalinated it can be reused as make-up water. Assuming a cooling tower evaporates 80% of the make-up water, this represents a certain amount of energy as heat of evaporation. This evaporation will lead to a concentration factor in the cooling tower of salts with a factor 5. The blowdown is being discharged. This is 20% of the make-up water. When this is desalinated by membrane distillation with a recovery of 80%, in total 16% of the make-up waterflow can be recovered for reuse. This is an advantage as stress on the surrounding water bodies is relieved. Moreover, when this desalination is done by membrane distillation, it does not only create desalinated water, but also uses heat, which is partly used in the process and for the most part transferred to the brine. This could therefore replace part of the cooling done by the cooling towers. The current design of the modules with internal heat exchange is in theory very efficient. However, the modules used in the pilot were not so efficient and design could be improved for a full scale installation. For the application of using waste heat an inefficient system is not a disadvantage when seeing it in the concept of replacement of cooling towers. (Table 3).

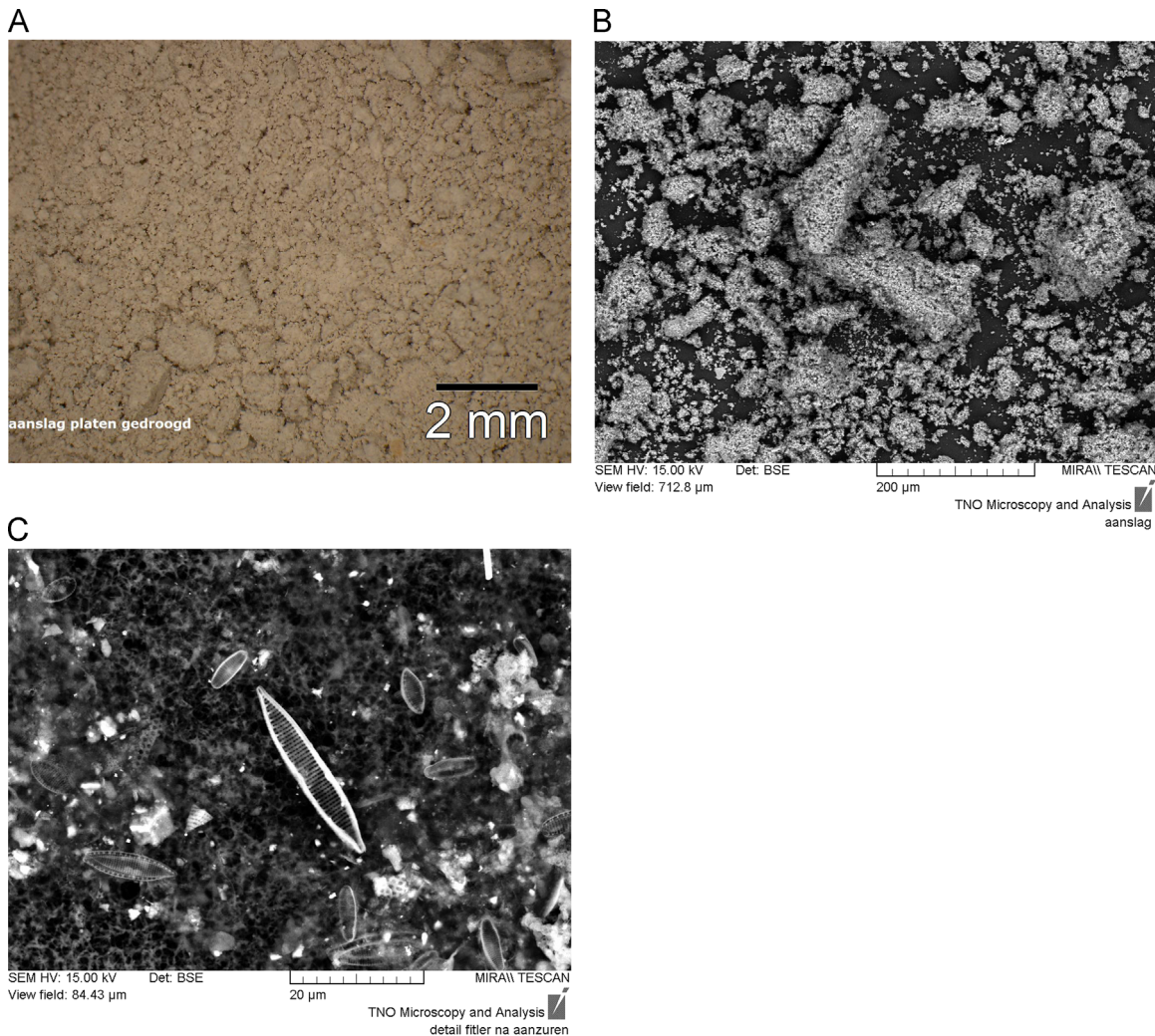
An example: a cooling tower has a temperature difference  $dT_{\text{CT}}$  between the top and bottom of 5 °C. A flow of 100  $\text{m}^3/\text{h}$  make-up water has to be supplied of which 80  $\text{m}^3/\text{h}$  ( $Q_{\text{CT}}$ ) has to be heated up these 5 °C before it evaporates. The total heat ( $E_{\text{CT}}$ ) that has to be supplied is

$$E_{\text{CT}} = Q_{\text{CT}}(dHv + dT_{\text{CT}} \cdot cp)$$

The blow down is 20  $\text{m}^3/\text{h}$  which is recovered for 80%, giving a distillate of 16  $\text{m}^3/\text{h}$ . The total volume in the membrane distillation set up has to be heated up. This is more than just the water that evaporates through the membrane. However most of the energy of evaporation, as well as the energy for heating could be recovered. The energy efficiency (EE) was 60%. The total energy that has to be supplied is

$$E_{\text{MD}} = \frac{E_{\text{evap}}}{EE} = \frac{Q_{\text{distillate}} \cdot dHv}{EE/100}$$

The energy required for desalination of the CTBD is 1/3 of the energy that is cooled away in the cooling tower ( $E_{\text{MD}}/E_{\text{CT}}=0.3302$ ).



**Fig. 7.** Microscopic images of surface deposits in external heat exchanger (run1). A: light microscopy, B SEM analysis of whole sample, C SEM analysis after acidification of sample.

**Table 2**  
Elemental analysis of precipitate in MD pilot.

Spectrum				
Element	Atom number	g/g wt%	## at%	Error (1sigma) wt%
C	6	15.3	24.7	2.14
O	8	44.9	54.5	5.65
Mg	12	1.2	0.9	0.10
Al	13	0.1	0.1	0.03
Si	14	0.3	0.2	0.04
P	15	6.7	4.2	0.30
S	16	1.5	0.9	0.09
Ca	20	28.8	14	0.94
Fe	26	1.2	0.4	0.07
<b>Total</b>		<b>100</b>	<b>100</b>	

This means that the desalination of the CTBD of three cooling towers costs as much thermal energy as would otherwise be discharged by a fourth cooling tower. This means that by replacing this fourth cooling tower also no make-up water has to be supplied, no pumping is required, no chemicals are required, etc. The replacement of 1 cooling tower by membrane distillation of cooling tower blowdown of three other cooling towers thus gives a significant reduction in environmental burden. The total water

**Table 3**  
Values used for calculation of required heat in a cooling tower with 100 m<sup>3</sup>/h make up water and 80% evaporation and membrane distillation of CTBD of this same cooling tower.

Latent heat of evaporation	dHv	2260	MJ/m <sup>3</sup>
Specific heat capacity of water	cp	4.184	MJ/m <sup>3</sup> *K
Evaporated water flow	Q <sub>CT</sub>	80	m <sup>3</sup> /h
Temperature difference in cooling tower	dT <sub>CT</sub>	5	°C
Energy cooled away in CT	E <sub>CT</sub>	182,473	MJ/h
Flow of MD distillate	Q <sub>distillate</sub>	16	m <sup>3</sup> /h
Energy efficiency of MD	EE	60	%
Energy in MD	E <sub>MD</sub>	60,266	MJ/h

that could be saved is (3\*16 m<sup>3</sup>/h recovered CTBD+100 m<sup>3</sup>/h make up water for the fourth tower)=148 m<sup>3</sup>/h. This is a saving of (148/400) **37%** of total water intake of which approximately 1/3rd is due to reuse and 2/3rd is due to reduced cooling capacity. For the cooling towers at Dow, where the blowdown is approximately 1 Mm<sup>3</sup>/year, and the water intake for cooling is approximately 5 Mm<sup>3</sup>/yr, this could save 1.85 Mm<sup>3</sup>/yr.

As heat is not transferred to the vapor phase but is now transferred to the brine phase, this still leaves the industrial site with a lot of heat. However, this heat could be used for other purposes such as desiccant drying [8,12]. When the membrane distillation process would be more efficient, less cooling towers

could be replaced or more heat is transferred to the brine.

#### 4.3. MD as technology for desalination of CTBD

This research was done in the context of the E4Water project, where also nanofiltration [13], electrodialysis and several pre-treatment methods for nanofiltration and reverse osmosis are compared [9]. Membrane distillation as a technology for cooling tower blowdown desalination is very promising. The technology seems much more resistant to fouling than pressure driven desalination technologies such as nanofiltration and reverse osmosis. As waste heat is used as driving force this could lead to a water intake reduction of 37% whereas nanofiltration leads to a reduced water intake of 15% (assuming 75% recovery of the CTBD, which is 20% of the total make up water). The fluxes of membrane distillation are much lower than those for nanofiltration and reverse osmosis. A flux of, on average, 2 l/m<sup>2</sup>\*h could be maintained while nanofiltration fluxes for desalination of CTBD are much higher (12–40 l/m<sup>2</sup>\*h). However the energy required to get the flux by membrane distillation is mostly heat and a small amount of electrical energy is required for pumping, while the flux for nanofiltration and reverse osmosis is completely driven by electrical energy. Typical energy costs for desalination by reverse osmosis is 2–3 kWh/m<sup>3</sup> while the electrical energy required by Memstill is around 0.75 kWh/m<sup>3</sup>. The main advantage for using membrane distillation instead of nanofiltration of reverse osmosis thus comes from the savings in energy, make up water and chemicals.

#### Acknowledgments

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007–2013) under grant agreement no. 280756. The authors are grateful for the support of this research within the E4Water project. We would also like to thank the Applied Environmental Chemistry group of TNO for doing the analysis of the precipitation.

#### References

- [1] J. Wang, D. Qu, M. Tie, H. Ren, X. Peng, Z. Luan, Effect of coagulation pretreatment on membrane distillation process for desalination of recirculating cooling water, *Sep. Purif. Technol.* 64 (1) (2008) 108–115, <http://dx.doi.org/10.1016/j.seppur.2008.07.022>.
- [2] S.J. Altman, R.P. Jensen, M.A. Cappelle, et al., Membrane treatment of side-stream cooling tower water for reduction of water usage, *Desalination* 285 (0) (2012) 177–183, <http://dx.doi.org/10.1016/j.desal.2011.09.052>.
- [3] X. Yu, H. Yang, H. Lei, A. Shapiro, Experimental evaluation on concentrating cooling tower blowdown water by direct contact membrane distillation, *Desalination* 323 (2013) 134–141, <http://dx.doi.org/10.1016/j.desal.2013.01.029>.
- [4] E. Drioli, A. Ali, F. Macedonio, Membrane distillation: recent developments and perspectives, *Desalination* 356 (2015) 56–84, <http://dx.doi.org/10.1016/j.desal.2014.10.028>.
- [5] P. Wang, T.S. Chung, Recent advances in membrane distillation processes: membrane development, configuration design and application exploring, *J. Membr. Sci.* 474 (15) (2015) 39–56.
- [6] J.H. Hanemaaijer, J.V. Medevoort, A.E. Jansen, et al., Memstill membrane distillation – a future desalination technology, *Desalination* 199 (175) (2006) 176.
- [7] N. Kuipers, J.H. Hanemaaijer, H. Brouwer, J.V. Medevoort, A. Jansen, F. Altena, P. V. Vleuten, H. Bak, Simultaneous production of high-quality water and electrical power from aqueous feedstock's and waste heat by high-pressure membrane distillation, *Desalination Water Treat.* 55 (10) (2014) 2766–2776, <http://dx.doi.org/10.1080/19443994.2014.946724>.
- [8] N. Kuipers, R.V. Leerdam, J.V. Medevoort, W.V. Tongeren, B. Verhasselt, L. Verelst, M. Vermeersch, D. Corbisier, Techno-economic assessment of boiler feed water production by membrane distillation with reuse of thermal waste energy from cooling water, *Desalination Water Treat.* 55 (13) (2015) 3506–3518, <http://dx.doi.org/10.1080/19443994.2014.946722>.
- [9] J. Löwenberg, J.A. Baum, Y. Zimmermann, C. Groot, W. van den Broek, T. Wintgens, Comparison of pre-treatment technologies towards improving reverse osmosis desalination of cooling tower blow down, *Desalination* 357 (2015) 140–149, <http://dx.doi.org/10.1016/j.desal.2014.11.018>.
- [10] J.H. Hanemaaijer, Memstill<sup>®</sup>-Low cost membrane distillation technology for seawater desalination, *Desalination* 168 (1–3) (2004) 355, <http://dx.doi.org/10.1016/j.desal.2004.07.019>.
- [11] J. Zhang, L. Chen, H. Zeng, et al., Pilot testing of outside-in MF and UF modules used for cooling tower blowdown pretreatment of power plants, *Desalination* 214 (1–3) (2007) 287–298, <http://dx.doi.org/10.1016/j.desal.2006.12.004>.
- [12] Anthony Y. Ku, Andrew P. Shapiro, The energy–water nexus: water use trends in sustainable energy and opportunities for materials research and development, *MRS Bull.* 37 (2012) 439–447, <http://dx.doi.org/10.1557/mrs.2012.39>.
- [13] C.K. Groot, W.B. van den Broek, J. Loewenberg, N. Koeman-Stein, M. Heidekamp, W. de Schepper, Mild desalination of various raw water streams, *Water Sci. Technol.* 72 (3) (2015) 371–376, <http://dx.doi.org/10.2166/wst.2015.228>.