Supplementary Information for

Negative Pressure Membrane Distillation for Excellent Gypsum Scaling Resistance and Flux Enhancement

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Section S1: Experimental details for membrane characterization and performance test

S1.1 Pore size measurement

Pore size was conducted with Capillary Flow Porometry (Porolux 1000, POROMETER, Belgium). The membrane was pre-wetted with commercial low surface tension liquid Porefil (surface tension: 16 dyne/cm). After mounting the sample onto the test cell, the measurement was managed with a program consisting of wet-run and dry-run. The wet-run was realized by replacing the wetting liquid within a certain pore size by compressed air at certain pressure until the membrane was dried out (wet-run). Then the air flow rate of the membrane was tested by decreasing the air pressure (dry-run). The bubble point was determined as the pressure at which significant flow of air was detected.

S1.2 Water contact angle and sliding angle

Water contact and sliding angles were measured by a contact angle goniometer (Drop Meter A-100P, MAIST, Ningbo, China) equipped with a high-speed CCD camera. A water droplet of 5 μL was deposited on the membrane surface for contact angle measurements, and each reported value was the average of five measurements.

S1.3 Liquid entry pressure

Liquid entry pressure (LEP) is a measure of the ability of a hydrophobic membrane to resist pore wetting. LEP was measured using a dead-end filtration set-up with deionized water. Pressure on the feed side was increased stepwise while allowing it to stabilize for a couple of minutes after each increment (0.05 bar). The pressure at which the first water droplet gets through the membrane is taken as the LEP.

S1.4 Preparation of CF_4-MP-PVDF membrane

A custom-made PDMS mold was created using a silicon wafer with a micro-pillar

structure as a complimentary structure. It was then utilized in a non-solvent induced phase

separation (NIPS) process to make a micro pillared PVDF membrane (MP-PVDF). Using the

plasma treatment technology, CF4 plasma treatment was used to improve the hydrophobicity

of the MP-PVDF (IoN40, PVA Tepla Co. Ltd). The membrane was pretreated with argon

plasma at 45 W/15 s and CF4 plasma at a glow discharge of 200 W/15 min, to summarize.

CF4-MP-PVDF denoted the name of final membrane.
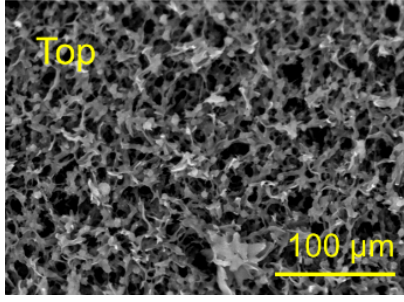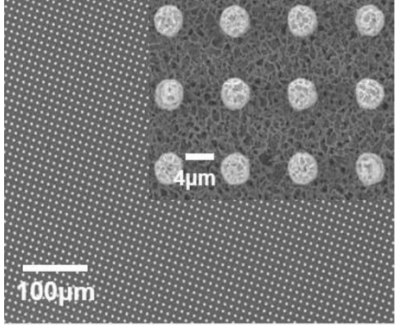
S1.5 Pulse flow membrane distillation

Detailed description of the pulse flow MD experiments can be found in our previous

publication. [1] Briefly, a bench-scale direct contact membrane distillation unit was developed to

assess the scaling behavior of peristaltic pumps with the pulse. In the feed side, the peristaltic

pump revolves at 56 rpm, resulting in a frequency of 2.8 Hz (56 r/min and three pulses per

rotation). The other operation conditions were same with NP-DCMD experiment.

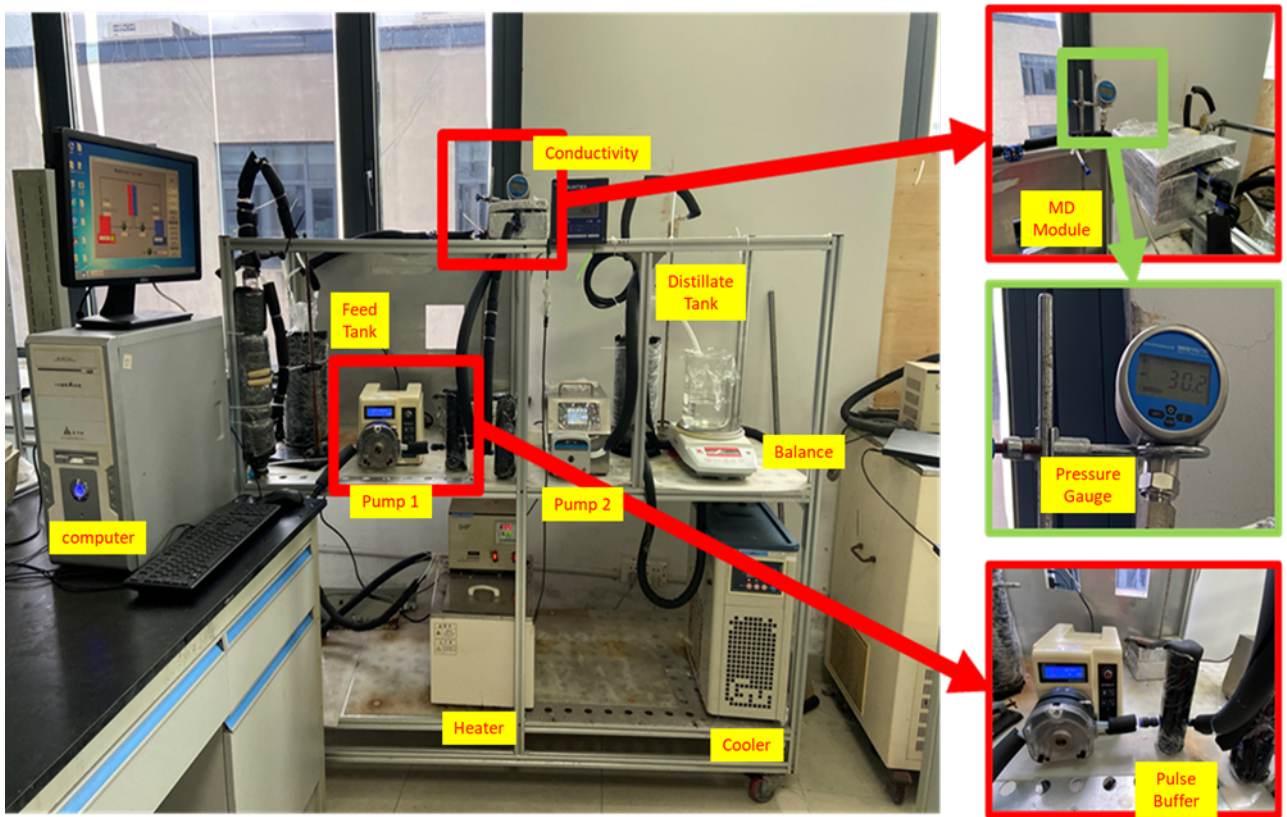**Table S1** Characteristics of the commercial PVDF membrane and CF$_4$-MP-PVDF. *

membrane	Commercial PVDF (GVHP00010)	CF$_4$-MP-PVDF
Thickness (μm)	125	264
Mean flow pore size (μm)	0.22	0.20
Contact angle (°)	110	166.8

Sliding angle (°)		3.0
Porosity (%)	75	79
LEP (bar)	2.4	/
SEM image		

* The results of CF4-MP-PVDF is obtained from our previous work [2].
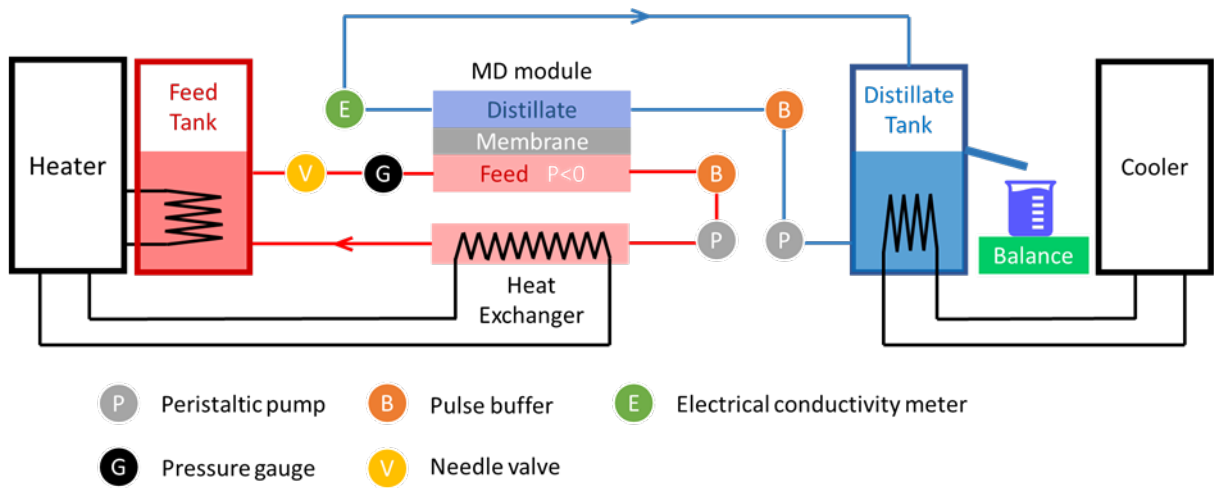
74

75 **Figure S1:** Schematic and photographic image and of the DCMD experimental setup.

76

**Table S2** Pressures outside the MD cell (measured) and in the feed channel (estimated using Bernoulli equation). Diameters of tubing and equivalent diameter of feed channel are 6 and 10.3 mm respectively. Correspondingly, the flow velocities are 0.354 and 0.120 m/s in the tubing and feed channel, respectively. The difference in flow velocities contributes to a pressure difference of ~0.055 kPa (larger in feed channel) based on Bernoulli equation.

Pressure measured in the tubing (kPa)	Calculated pressure in the feed channel (kPa)
1	1.06
-10	-9.94
-20	-19.94
-30	-29.94

85
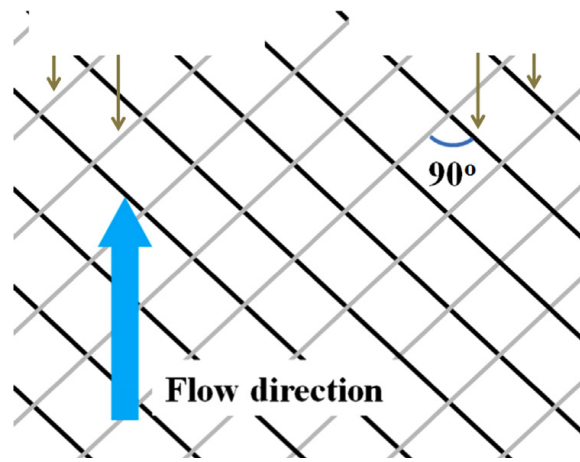
Figure S2. Schematic illustration of the spacer structure. The arrow indicates flow direction. [3]
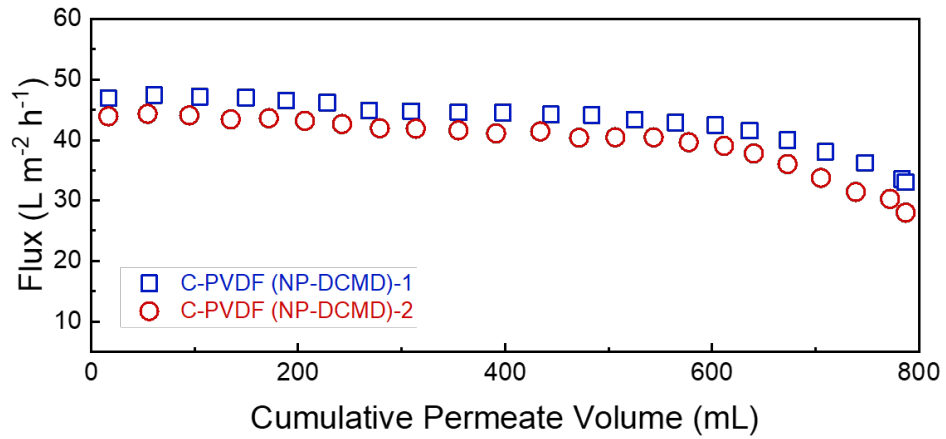
Figure S3. Replicate data of NP-DCMD experiment with a feed solution containing 2000 ppm CaSO$_4$. The feed solution contained 2000 mg L^{-1} CaSO$_4$ solution (saturation index, SI=0.09). The temperatures of the feed solution and distillate were 70 °C and 20 °C, respectively. The same crossflow velocity of 0.17 m/s was used in both the feed and distillate streams. The experiments were stopped when the cumulative distillate volume reached 800 mL because the feed volume became insufficient for flow circulation.

Section S2: Vapor transport in MD

The resistances for the Knudsen flow (R_k) and molecular diffusion (R_{md}) can be estimated using equations 2.1 and 2.2, respectively:[4]

$$R_k = \left[\frac{2}{3} \frac{\varepsilon r}{\tau \delta} \left(\frac{8M}{\pi R T_m} \right)^{0.5} \right]^{-1} \tag{2.1}$$

and

$$R_{md} = \left[\frac{\varepsilon}{\tau \delta} \frac{PD}{P_a} \frac{M}{RT_m} \right]^{-1} \tag{2.2}$$

Where ε, τ and r are the membrane porosity, pore tortuosity and pore radius, respectively, M is the molecular weight of water molecule, R is the ideal gas constant and T_m is the temperature inside the membrane pores, which can be assumed as the average of the temperatures of the membrane surface at feed and distillate sides, P_a and P are the air pressure and the total pressure inside the pore and D is the diffusion coefficient of water vapor molecules. We note that PD is function of temperature. [5] Integrating R_k and R_{md} yields the membrane permeability coefficient, B_m:

$$B_m = \left[\frac{1}{R_k} + \frac{1}{R_{md}} \right]^{-1} \tag{2.3}$$

The water flux J through the membrane can be calculated by multiplying B_m and the driving force for vapor transfer, i.e., the difference of saturated water vapor pressure at the feed-membrane interface, $P_{m,f}$, and that at the distillate-membrane, $P_{m,d}$:

$$J = B_m \left(P_{m,f} - P_{m,d} \right) \tag{2.4}$$
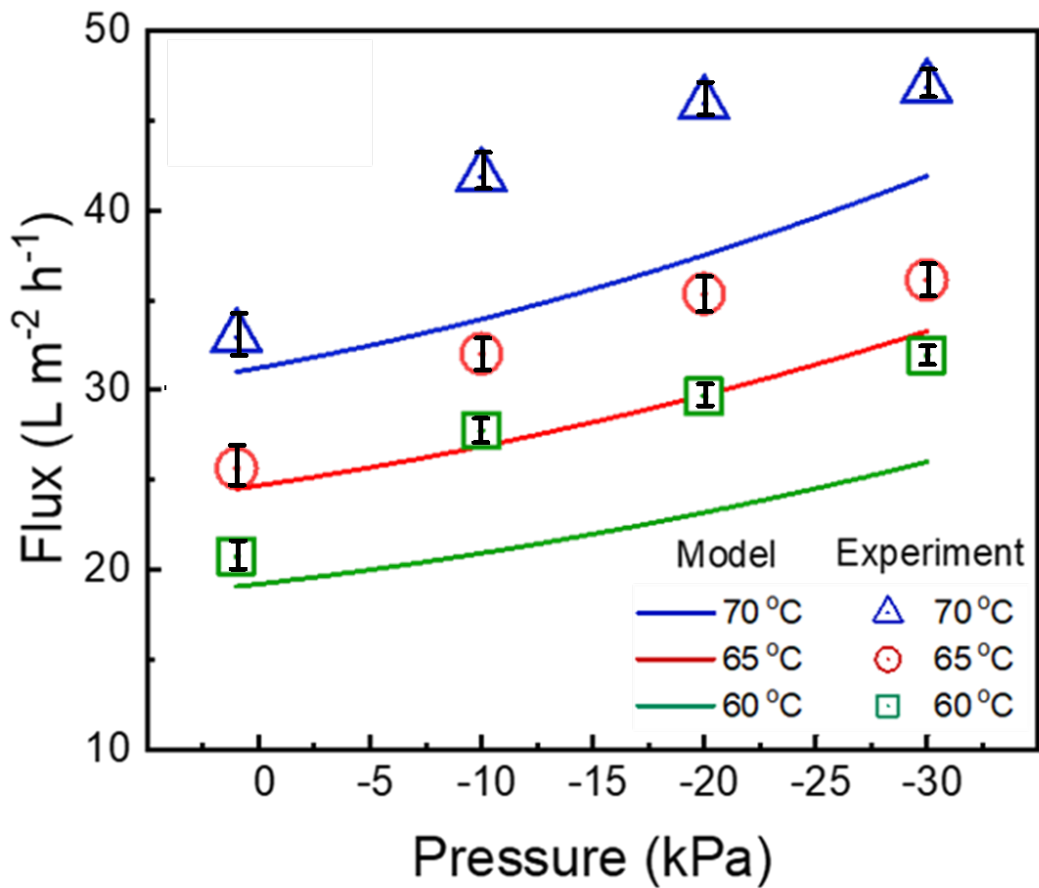
Figure S4. Vapor flux as functions of feed gauge pressure (1.0 kPa to -30 kPa) at different feed temperatures (60, 65 and 70 °C). The symbols represent experimental data whereas the curves represent simulation results based on the Dusty-Gas model. The gauge pressure and temperature of the distillate were fixed at 0.1 kPa and 20 °C, respectively. The experimental results are also reported in Table S3.

124 **Table S3** Mean value (and standard deviation) water flux under different temperature and
125 pressures.

Pressure (kPa)	Temperature (°C)		
	60	65	70
1	20.74 (0.78)	23.86 (1.10)	32.94 (1.17)
-10	27.75 (0.67)	33.61 (0.88)	41.89 (1.00)
-20	29.66 (0.61)	35.46 (0.98)	44.94 (0.91)
-30	31.93 (0.51)	37.51 (0.89)	46.84 (0.76)

126
127

Section S3: Detailed description of heat transfer in MD

At steady state, the overall heat flux from the hot feed to the cold distillate side, q, is given by:

$$q = q_f = q_m = q_d \tag{3.1}$$

where q_f and q_d are the convective heat fluxes through the feed and distillate boundary layers, respectively, and q_m is the heat flux across the membrane.

The convective heat fluxes through the feed and distillate boundary layers are calculated based on the temperature gradient between the bulk (T_b) and membrane surface (T_m) temperatures:

$$q_f = h_f \left(T_{b,f} - T_{m,f} \right) \tag{3.2}$$

And

$$q_d = h_d \left(T_{m,d} - T_{b,d} \right) \tag{3.3}$$

where h is the convective heat transfer coefficient in the boundary layer and the subscript f and d denote the feed and distillate side, respectively. $T_{b,f}$ and $T_{b,d}$ were estimated as the average of the inlet and outlet temperatures on each respective side of the membrane.

The heat flux across the membrane consists of both the conductive heat transfer through the membrane and the heat transferred via the latent heat of evaporation, ΔH_{vap}, as follows:

$$q_m = h_m \left(T_{m,f} - T_{m,d} \right) + J \Delta H_{vap} \tag{3.4}$$

where h_m is the overall conductive heat transfer coefficient of the membrane. The first part on the left side in equation 3.4 represent the conductive heat flux through the membrane (Q_c) while the second part represents the heat transferred via evaporation (Q_v). We note that Q_v is a favorable as it results from vapor flux (i.e., water production), whereas Q_c represents an

150 unfavorable heat transfer that leads to a loss of driving force. The overall conductive heat

151 transfer coefficient, h_m, is calculated from the thermal conductivities of the membrane polymer,

152 k_m, and the trapped air inside the pores, k_g as follows:

153
$$h_m = \frac{k_g \varepsilon + k_m (1-\varepsilon)}{\delta} \tag{3.5}$$

154 where δ is the membrane thickness. The thermal efficiency (η, %) of the DCMD system is

155 the ratio between the heat flux due to vapor transfer and the total heat flux (i.e., the sum of heat

156 fluxes due to both vapor transfer and conductive heat transfer):

157
$$\eta = \frac{Q_v}{Q_c + Q_v} \times 100\% \tag{3.6}$$

158 Under positive feed pressure, the feed stream will have stagnant zones due to the convex

159 liquid-gas interface partially wetting the pores near the surface and a non-slip boundary can be

160 assumed at the membrane surface. However, in NP-DCMD, the liquid-gas interface is concave

161 because the air inside the pores expands when negative feed pressure is applied, thus enhancing

162 the flow hydrodynamics (by eliminating the stagnant zones) and increasing the flow due to

163 slip-boundary condition at the liquid-gas interface (i.e., the feed velocity at the interface is not

164 zero). To account for that, h_f was multiplied with a new factor, φ_1. Moreover, because of the

165 concaved liquid-gas interface, the liquid-solid contact area decreases, and the evaporation area

166 increases, which has an impact on the actual free pore volume within the membrane and,

167 consequently, on h_m (equation 3.5). To account for this, h_m was multiplied by a second factor,

168 φ_2. As a result, equations 3.2 and 3.4 are modified as follows:

169
$$q_f = \varphi_1 h_f \left(T_{b,f} - T_{m,f} \right) \tag{3.7}$$

170 and

171
$$q_m = \varphi_2 h_m \left(T_{m,f} - T_{m,p} \right) + J\Delta H_{vap} \tag{3.8}$$

172   The model calculation process involves combining mass and heat transfer, as detailed in our

173   previous paper. [6] The MATLAB code for the calculations is provided in the following **S4**.

174

Section S4: MATLAB code of mass and heat transfer in NP-DCMD

```
%% NP-DCMD Flux Prediction Program Version 5
% Update Date: 11/10/2021
% Written by Yongjie Liu (Email: liu.yong-jie@outlook.com; 100058656@ku.ac.ae)

%%% The seawater thermophysical performance was obtained from
http://web.mit.edu/seawater/.
%%% Before using this code please download the files from
http://web.mit.edu/seawater/SEAWATER_v3.1.4_20Feb17.zip and decompress all the
files in the same folder of this program.

clear all; close all; clc
%% Input Factor for Negative Feed Pressure DCMD
P_f = 101325+1000 % Pressure in feed channel [Pa]
phi_1 = 1 % Slippery boundary effect [-]
phi_2 = 1 % Optimal heat transfer effect [-]
T_fin = 60+273.15; % Feed Inlet Temperature [K]
T_fout = 59+273.15; % Feed Outlet Temperature [K]
T_din = 20+273.15; % distillate Inlet Temperature [K]
T_dout = 21+273.15; % distillate Outlet Temperature [K]

%% Definitions
% Constants
k_B = 1.381e-23; % Boltzmann constant [J/K]
R = 8.314; % Universal gas constant [Pa m^3/mol K]

% Membrane Parameters
mem_prop = 0.75; % membrane porosity [-]
mem_thick = 125e-6; % membrane thickness [m]
mem_tau = 1.1; % membrane tortuosity [-]
mem_pore = 0.22e-6; % membrane pore diamiter [m]

% Membrane Module
W = 0.02; % Channel Width [m]
L = 0.05; % Channel Length [m]
H = 0.003; % Channel Height [m]
mem_A = L*W; % Effective membrane surface [m^2]
flow_A = H*W; % Area for flow channel [m^2]
d_h = 2*W*H/(W+H); % Hydraulic diameter [m]

% Operation Conditions
    % Temperateure
    T_f = (T_fin+T_fout)/2; % Avarage Feed Temperature [K]
```

```matlab
218        T_d = (T_din+T_dout)/2; % Avarage distillate Temperature [K]
219        T_mf_guess = T_f; T_md_guess=T_d;
220
221        % Flow Conditions
222        V_f = 600/1000000/60; % [mL/min]->[m^3/s] Feed flow rate
223        V_d = 600/1000000/60; % [mL/min]->[m^3/s] distillate flow rate
224        u_f = V_f/flow_A; % [m/s] Velocity of feed stream
225        u_d = V_d/flow_A; % [m/s] Velocity of distillate stream
226
227    % Seawater Parameters
228    uT = 'K'; % Unit of Temperature
229    uS = 'ppm'; % Unit of Saline
230    uP = 'Pa'; % Unit of Pressure
231        % Feed Side
232        T = T_f;
233        S = 0; % Saline Concentration [ppm]
234        P = P_f;
235        Pv_f = SW_Psat(T,uT,S,uS); % Saturation pressure of seawater [N/m^2]
236        rho_f = SW_Density(T,uT,S,uS,P,uP); % Density of seawater [kg/m^3]
237        hfg_f = SW_LatentHeat(T,uT,S,uS); % Latent Heat of vaporization of seawater
238    [J/kg]
239        k_f = SW_ConductivityP(T,uT,S,uS,P,uP); % Thermal conductivity of seawater
240    [W/m-K]
241        mu_f = SW_Viscosity(T,uT,S,uS);          % Dynamic viscosity of seawater [kg/m-
242    s]
243        cp_f = SW_SpcHeat(T,uT,S,uS,P,uP);       % Specific heat of seawater[J/kg-K]
244        % Distillate Side
245        T = T_d;
246        S = 0; % Saline Concentration [ppm]
247        P = 101325+1000;
248        Pv_d = SW_Psat(T,uT,S,uS); % Saturation (vapor) pressure of seawater [N/m^2]
249        rho_d = SW_Density(T,uT,S,uS,P,uP); % Density of seawater [kg/m^3]
250        hfg_d = SW_LatentHeat(T,uT,S,uS); % Latent Heat of vaporization of seawater
251    [J/kg]
252        k_d = SW_ConductivityP(T,uT,S,uS,P,uP); % Thermal conductivity of seawater
253    [W/m-K]
254        mu_d = SW_Viscosity(T,uT,S,uS); % Dynamic viscosity of seawater [kg/m-s]
255        cp_d = SW_SpcHeat(T,uT,S,uS,P,uP); % Specific heat of seawater[J/kg-K]
256
257    %% Loop iteration to calculate
258    eer=1;i=1;
259    while abs(eer)>10^-7
260        % Membrane Thermal Conductivity
261            T_m =(T_mf_guess+T_md_guess)/2; % Avarage Membrane Temperature [K]
```

```matlab
262          k_pvdf_m=5.77e-4*T_m+0.914e-2; % Thermal Conductivity of PVDF [J/m^2-s-K]
263          k_g=1.36e-3+3.885e-5*T_m+1.66e-3*T_m^0.5; % Thermal Conductivity of Gas
264  [J/m^2-s-K]
265          k_m=(1-mem_prop)*k_pvdf_m+mem_prop*k_g; % Thermal Conductivity of Membrane
266  [J/m^2-s-K]
267
268      % Reynolds, Prandtl and Nusselt Numbers
269          % Feed Side
270          Re_f = rho_f*u_f*d_h/mu_f; % Re in Feed [-]
271          Pr_f = cp_f*mu_f/k_f; % Pr in Feed [-]
272          if Re_f > 2300 % Nu in Feed [-]
273              Nu_f = 1.62*(Re_f*Pr_f*d_h/L)^(1/3);
274          else
275              Nu_f = 0.023*Re_f^0.8*Pr_f^(1/3);
276          end
277
278          % Distillate Side
279          Re_d = rho_d*u_d*d_h/mu_d; % Re in Feed [-]
280          Pr_d = cp_d*mu_d/k_d; % Pr in Feed [-]
281          if Re_d > 2300   % Nu in Feed [-]
282              Nu_d = 1.62*(Re_d*Pr_d*d_h/L)^(1/3);
283          else
284              Nu_d = 0.023*Re_d^0.8*Pr_d^(1/3);
285          end
286
287      % Heat Transfer Coefficients
288      h_f=Nu_f*k_f/d_h; % Heat Transfer Coeffecient in Feed [J/m^2-s]
289      h_d=Nu_d*k_d/d_h; % Heat Transfer Coeffecient in distillate[J/m^2-s]
290      h_m=k_m/mem_thick; % Heat Transfer Coeffecient for membrane[J/m^2-s]
291
292
293      % MD mass transfer coefficient
294      CD_a= 364e-12; % Colloined Distance of Air [m]
295      CD_w= 265e-12; %Colloined Distance of Water Vapor [m]
296      M_w = 18e-3; % Molecule Weight of Water [kg/mol]
297      M_a = 28e-3; % Molecule Weight of Air [kg/mol]
298      P_m = P_f; % Pressure in the Membrane [Pa]
299      Pv_mf = SW_Psat(T_mf_guess,uT,S,uS); % Feed Latent Heat of vaporization of
300  seawater [J/kg]
301      Pv_md = SW_Psat(T_md_guess,uT,S,uS); % Distillate Latent Heat of vaporization
302  of seawater [J/kg]
303      P_a = P_m-(Pv_mf+Pv_md)/2; % Average Air Pressure in Membrane [Pa]
304      lamda=k_B*T_m/(P_m*pi*(CD_a+CD_w)^2)*(1+M_w/M_a)^0.5; % Molecular Free Path
305  [m]
```

```matlab
306        Kn=lamda/mem_pore; % Kn
307        Bm_kd=mem_prop*mem_pore/(3*mem_tau*mem_thick)...
308            *(8*M_w/pi/R/T_m)^0.5; % Bm_Knudsen Diffusion[s/m]
309        PD=1.9e-5*T_m^2.072; % PD
310        Bm_mo=mem_prop*PD*M_w/(mem_tau*mem_thick*P_a*R*T_m); % Bm_Molecule
311   Diffusion[s/m]
312        Bm_T=1/(1/Bm_kd+1/Bm_mo);  % Bm_kd+mo [s/m]
313        if Kn>1 % Confirm to use which Bm
314            Bm=Bm_kd;
315        else
316            if 0.01<Kn<1
317                Bm=Bm_T;
318            else Kn<0.01
319                Bm=Bm_mo;
320            end
321        end
322       J = Bm*(Pv_mf-Pv_md); % Water Flux [kg/m^2-s]
323
324        % Temperature on Membrane Surface
325        hfg_m = SW_LatentHeat(T_m,uT,S,uS); % Latent Heat of vaporization of seawater
326   T_m [J/kg]
327        Q_d=h_d*(T_md_guess-T_d); % Distillate Heat Flux [J/m^2]
328        Q_mm=phi_2*h_m*(T_mf_guess-T_md_guess); % Membrane material heat flux [J/m^2]
329        Q_w=J*hfg_m; % Water evaporation heat [J/m^2]
330        Q_m=Q_mm+Q_w; % Membrane Heat Flux [J/m^2]
331        eer=Q_d-Q_m; % Error for Q_d and Q_m
332        if eer < 0  % Majorized Iterative Method
333            T_mf=T_mf_guess;
334            T_md=T_md_guess;
335            T_mf_guess=T_mf_guess-i;
336            T_md_guess=phi_1*h_f*(T_f-T_mf_guess)/h_d+T_d;
337         else
338            T_mf=T_mf_guess;
339            T_md=T_md_guess;
340            T_mf_guess=T_mf_guess+i;
341            T_md_guess=phi_1*h_f*(T_f-T_mf_guess)/h_d+T_d;
342            i=i/10
343         end
344
345   end
346
347
```

Reference:

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