Supplementary Information

Elucidating the Role of Salinity in Regulating Gypsum Scaling in Reverse Osmosis and Nanofiltration

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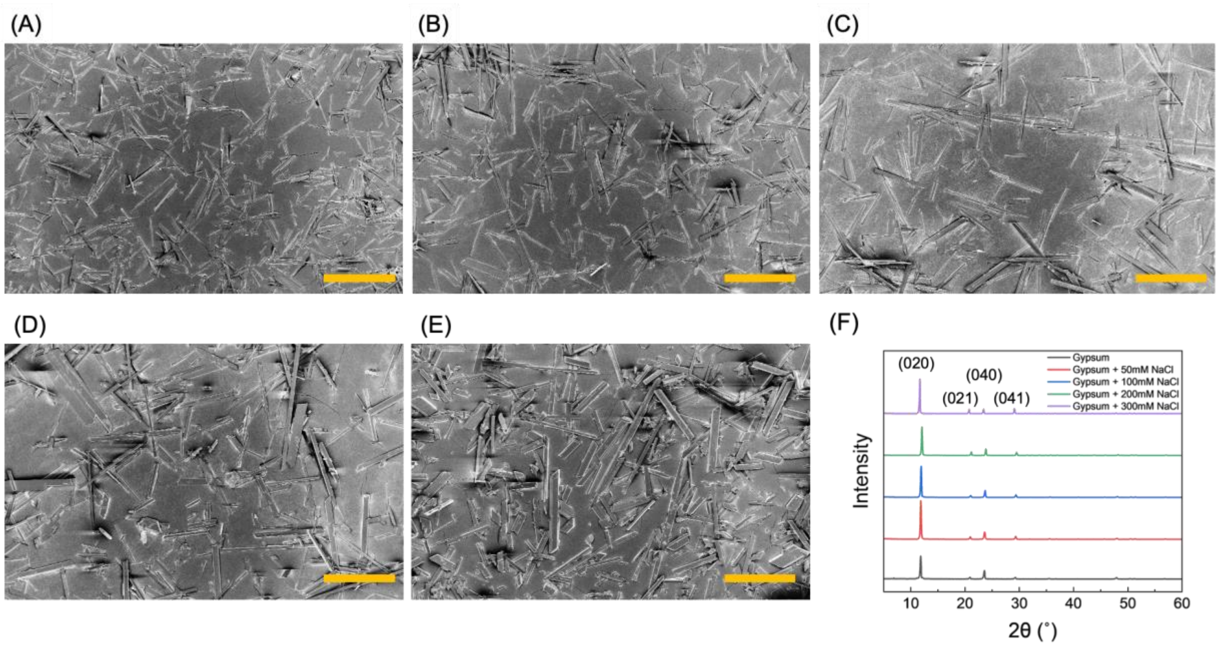

Figure S1. Morphology and crystallinity of gypsum scales formed under static bulk conditions at varying background NaCl concentrations. SEM images of gypsum scale formed under static conditions with 42 mM gypsum and varying NaCl concentrations: (A) 0 mM, (B) 50 mM, (C) 100 mM, (D) 200 mM, and (E) 300 mM. The yellow scale bar represents 200 µm. (F) XRD spectra of the scales.

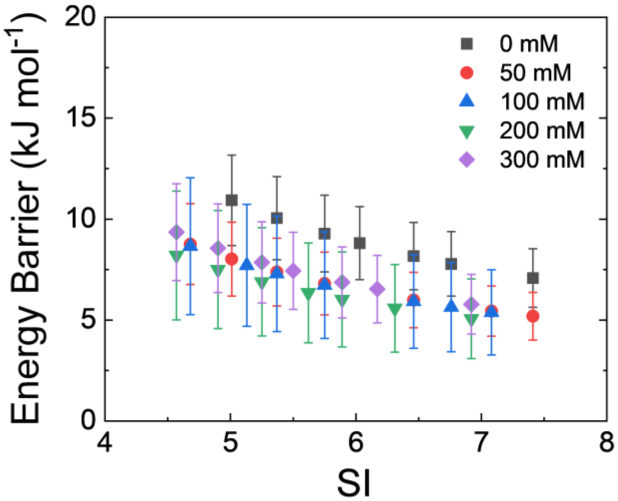

Figure S2. Estimated free-energy barrier for gypsum nucleation (ΔG^*, kJ mol^{-1}) as a function of saturation index ($SI = IAP/K_{sp}$) under different background NaCl concentrations (0, 50, 100, 200, and 300 mM).

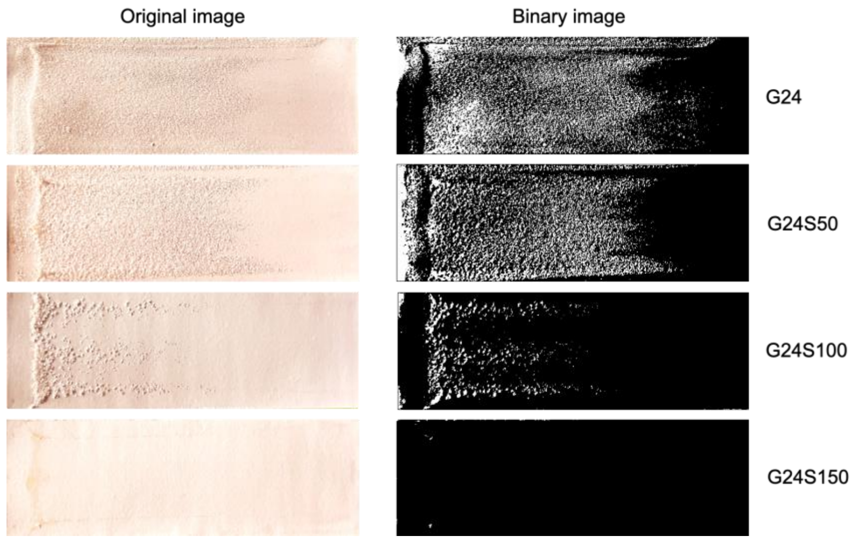

Figure S3. Photographs of membrane coupons (original and corresponding binary images) after 1,400 min of gypsum scaling tests, illustrating the spatial distribution of scale across the membrane surface.

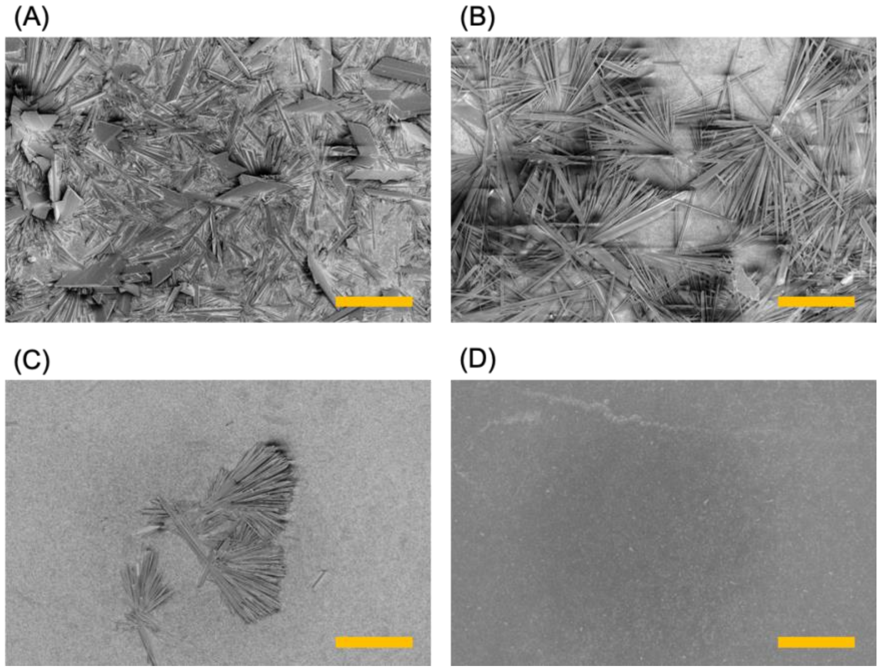

Figure S4. SEM images of membrane surfaces after dynamic gypsum scaling test with varying background NaCl concentrations: (A) 0 mM, (B) 50 mM, (C) 100 mM, and (D) 150 mM. The yellow scale bar represents 200 μm. The images were taken using the same membrane coupons used in the scaling experiments presented in Figure 3 of the main manuscript.

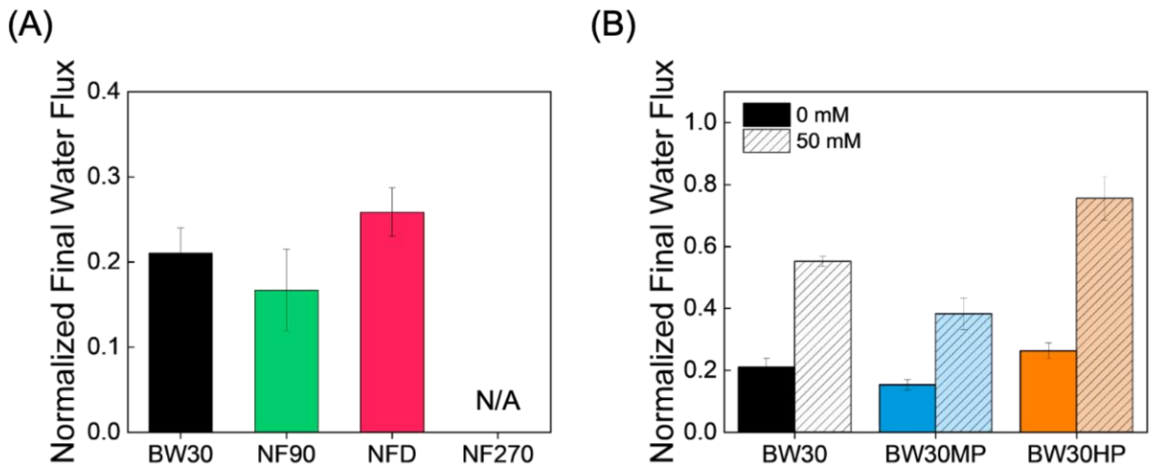

Figure S5. Normalized final flux after 1,400 min of gypsum scaling for (A) commercial membranes and (B) BW30 and modified membranes. Error bars represent standard deviation (n = 3).

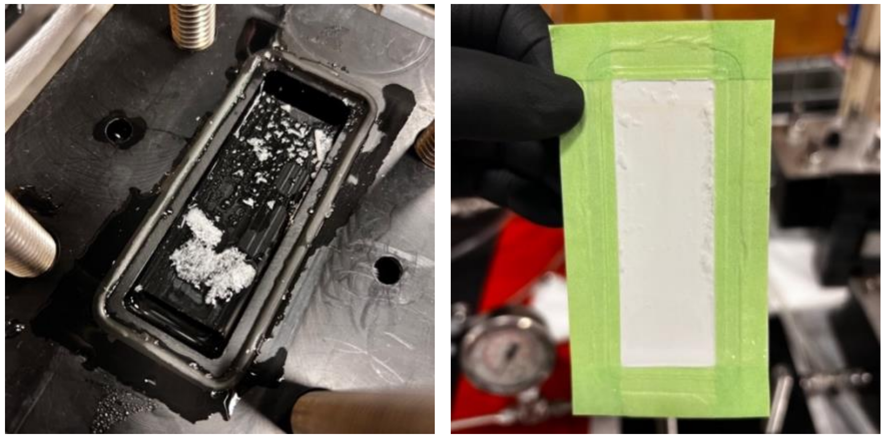

Figure S6. Photographs of the flow cell and NF270 membrane after the scaling experiment.

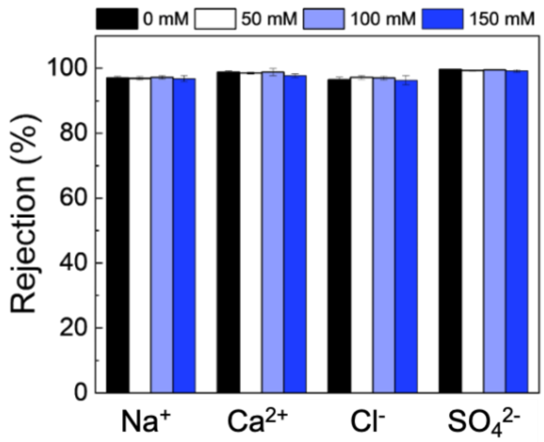

Figure S7. Ion rejection by BW30 membranes tested with 24 mM of gypsum scalant ions (i.e., Ca^{2+} and SO_4^{2-}) with feed salinity levels of 0, 50, 100, and 150 mM NaCl.

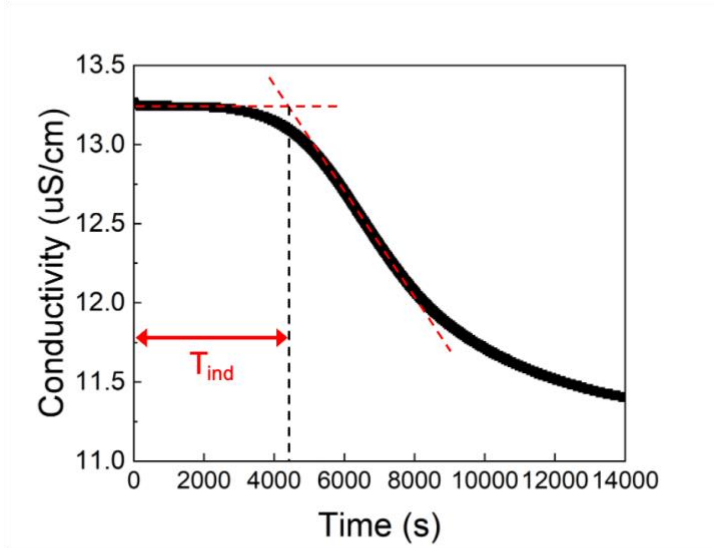

Figure S8. Representative conductivity–time profile for the solution containing 42 mM gypsum scalants in the absence of background NaCl, illustrating the determination of induction time (T_{ind}) from the intersection between the initial stable baseline and the extrapolated linear decline.

Table S1. The water permeability coefficient and salt rejection of the commercial and modified membranes. Salt rejection is measured with the feedwater containing 24 mM of $CaCl_2$ and 24 mM of Na_2SO_4.

	Water permeability coefficient ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)	Salt rejection (%)
NF90	3.4±0.2	95.5±0.2
NFD	6.9±0.2	51.6±1.6
NF270	10.7±1.3	47.5±0.4
BW30	2.8±0.3	97.1±0.4
BW30MP	5.1±0.5	89.8±0.3
BW30HP	12.8±0.6	43.7±1.1

Table S2. Saturation index in the bulk solution (feedwater) and calculated saturation index at the membrane surface.

	Saturation index in bulk (SI_b)	Saturation index at membrane surface (SI_m)
NF90	1.41	2.93 ± 0.04
NFD		2.97 ± 0.04
NF270		3.04 ± 0.04
BW30		2.91 ± 0.04

Table S3. Compositions of model solutions used to evaluate the effect of salinity on gypsum nucleation under static conditions.

$CaCl_2 \cdot 2H_2O$ (mM)	**Na_2SO_4** (mM)	**NaCl** (mM)	**SI**
42	42	0	2.69
42	42	50	2.40
42	42	100	2.14
42	42	200	1.82
42	42	300	1.55

Table S4. Compositions of model solutions with varied salinities and gypsum precursor concentrations, which were used to generate a broad range of saturation index (SI) values for calculating the nucleation energy barrier and kinetic pre-factor.

$CaCl_2 \cdot 2H_2O$ (mM)	**Na_2SO_4** (mM)	**NaCl** (mM)	**SI**
110	110	0	7.41
100	100	0	6.76
95	95	0	6.46
90	90	0	6.03
85	85	0	5.75
80	80	0	5.37
75	75	0	5.01
70	70	0	4.68
60	60	0	3.98
50	50	0	3.24
42	42	0	2.69
115	115	50	7.41
110	110	50	7.08
100	100	50	6.46
90	90	50	5.75
85	85	50	5.37
80	80	50	5.01
75	75	50	4.68
70	70	50	4.37
60	60	50	3.63
52	52	50	3.09
45	45	50	2.57
115	115	100	7.08
110	110	100	6.76
105	105	100	6.46
95	95	100	5.75
90	90	100	5.37
85	85	100	5.13
80	80	100	4.68
70	70	100	4.07
60	60	100	3.31
55	55	100	3.02
48	48	100	2.51
120	120	200	6.92
110	110	200	6.31
105	105	200	5.89
100	100	200	5.62
95	95	200	5.25
90	90	200	4.90
85	85	200	4.57

80	80	200	4.27
70	70	200	3.55
60	60	200	2.95
53	53	200	2.45
125	125	300	6.92
115	115	300	6.17
110	110	300	5.89
105	105	300	5.50
100	100	300	5.25
95	95	300	4.90
90	90	300	4.57
85	85	300	4.17
70	70	300	3.24
60	60	300	2.63
56	56	300	2.40

Text S1. Example PHREEQC input file used for gypsum saturation index (SI) calculation.

Representative PHREEQC input corresponding to Table S3 (Row 1): 42 mM $CaCl_2 \cdot 2H_2O$ and 42 mM Na_2SO_4 with no added background NaCl. Calculations were performed using PHREEQC Version 3 with the pitzer.dat database. It should be noted that the SI values obtained from PHREEQC are reported on a $\log_{10}$ basis.

```
# Representative PHREEQC input for Table S3 (Row 1)
# 42 mM CaCl2·2H2O + 42 mM Na2SO4, no added NaCl
# Database: pitzer.dat (PHREEQC Version 3, USGS)

SOLUTION 1 Table S3-Row1
temp      24
pH        6
pe        4
redox     pe
units     mmol/L
density   1
Cl        84
Ca        42
Na        84
S(6)      42
-water    1 # kg

SELECTED_OUTPUT
-reset false
-saturation indices Gypsum
END
```

Text S2. Example calculation of membrane-surface ion concentration and saturation index (SI_m)

A representative calculation of membrane-surface ion concentrations ($C_{m,i}$) using the film-theory mass-transfer model is presented for the BW30 membrane under the 24 mM gypsum scalants condition.

1. Bulk composition and rejection

Bulk concentrations (mol L^{-1}):
$C_{b,Na}$ = 0.048
$C_{b,Cl}$ = 0.048
$C_{b,Ca}$ = 0.024
$C_{b,SO4}$ = 0.024
Observed rejection:
R_{Na} = 0.970
R_{Cl} = 0.965
R_{Ca} = 0.988
R_{SO4} = 0.995

2. Hydrodynamic parameters

Crossflow velocity:
u = 0.213 m s^{-1}
Hydraulic diameter:
d_h = 5.38 × 10^{-3} m
Channel length:
L = 0.077 m
Kinematic viscosity:
υ = 9.131 × 10^{-7} m^2 s^{-1}
Initial water flux:
J_w = 30.50 L m^{-2} h^{-1}

3. Diffusion coefficients

D_{Ca} = 7.93 × 10^{-10} m^2 s^{-1}
D_{SO4} = 1.07 × 10^{-9} m^2 s^{-1}
D_{Na} = 1.33 × 10^{-9} m^2 s^{-1}
D_{Cl} = 2.03 × 10^{-9} m^2 s^{-1}

4. Reynolds number

$Re = \frac{u\, d_h}{\upsilon}$ (1)

$Re = \frac{(0.213)(5.38\times10^{-3})}{9.131 \times 10^{-7}} = 1.25 \times 10^3$

5. Schmidt number

$Sc_i = \frac{\upsilon}{D_i}$ (2)

Example (Ca^{2+}):

$Sc_{Ca} = \frac{9.131 \times 10^{-7}}{7.93 \times 10^{-10}} = 1151$

6. Sherwood number

$Sh_i = 1.85 \left(\frac{Re\, Sc_i\, d_h}{L}\right)^{0.333}$ (3)

Example (Ca^{2+}):

$$Sh_{Ca} = 1.85 \left(\frac{(1.25\times10^3)(1.15\times10^3)(5.38\times 10^{-3})}{0.077}\right)^{0.333} = 13.27$$

7. Mass transfer coefficient

$k_i = \frac{Sh_i\, D_i}{d_h}$ (4)

Example (Ca^{2+}):

$k_{Ca} = \frac{(13.27)(7.93\times 10^{-10})}{5.38 \times 10^{-3}} = 1.96 \times 10^{-6}$ m s^{-1}

8. Exponential term

$\exp(\frac{J_w}{k_i})$ (5)

For each ion:

$\exp(\frac{J_w}{k_{Ca}}) = 1.954$

$\exp(\frac{J_w}{k_{SO4}}) = 1.731$

$\exp(\frac{J_w}{k_{Na}}) = 1.607$

$\exp(\frac{J_w}{k_{Cl}}) = 1.430$

9. Membrane-surface concentration

$C_{m,i} = C_{b,i}\left[(1 - R_i) + R_i \exp\left(\frac{J_w}{k_i}\right)\right]$ (6)

Example: Ca^{2+}

$C_{m,Ca} = (0.024)[(1 - 0.988) + 0.988(1.954)] = 0.04662$ mol L^{-1}

10. Final calculated surface concentrations

$C_{m,Na}$= 0.07626 mol L^{-1}

$C_{m,Cl}$= 0.06793 mol L^{-1}

$C_{m,Ca}$= 0.04662 mol L^{-1}

$C_{m,SO4}$= 0.04145 mol L^{-1}

Finally, these membrane-surface concentrations were then used as input into PHREEQC (PITZER database) to calculate the membrane-surface saturation index SI_m, as described in Text S1.