



Facile supersaturation control strategies for regulating nucleation and crystal growth in membrane crystallisation[☆]

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ABSTRACT

The integration of crystallisation into membrane distillation has been proposed for brine mining as a method to effectively control primary nucleation which uses the excess supersaturation to create a new crystal phase. However, primary nucleation desaturates the solvent, subsequently introducing competition between crystal growth and nucleation mechanisms, which must be regulated to achieve a high yield and good product quality. This study therefore investigated supersaturation control strategies that can regulate nucleation and crystal growth mechanisms in membrane distillation crystallisation (MDC) following induction. Membrane area was used to adjust supersaturation, as this can modify kinetics without introducing changes to mass and heat transfer within the boundary layer. An increase in concentration rate shortened induction time and raised supersaturation at induction. This broadened the metastable zone width, and reduced scaling, due to the increased supersaturation driving force which favours a homogeneous primary nucleation pathway. Modulating supersaturation also repositioned the system within specific regions of the metastable zone that can favour crystal growth versus primary nucleation. Scaling was further mitigated using in-line filtration to ensure crystal retention within the crystalliser to reduce deposition. This permitted a consistent supersaturation rate to be sustained, enabling a longer hold-up time following induction. Population balance confirmed a reduction in nucleation rate with longer hold-up times, due to the desaturation of the solvent caused by crystal growth which resulted in larger crystal sizes. Through segregating the crystal phase into the bulk solution, growth can be more closely controlled to improve habit, shape and purity, independent of nucleation, due to the development of two discrete regions of supersaturation. The supersaturation control strategies described herein are unique to MDC and address the acknowledged challenge of supersaturation control within existing industrial evaporative crystalliser design.

1. Introduction

Crystallisation is one of the most important separation and purification processes for the manufacture of fine and bulk chemical products [1,2] and is emerging as a critical strategy for resource recovery in the environment sector [3]. The principle drawback to existing crystallisation technologies is that the undefined interfacial area introduces an uneven supersaturation rate (e.g. evaporation rate or cooling rate), which is challenging for the precise control of supersaturation level at induction, resulting in a poorly reproducible final crystal product [4,5,6]. Crystal properties can be critical to industrial applications, including crystal morphology (habit, shape, crystal size distribution (CSD)), purity (well-organised building blocks into the lattice) and crystal structure (polymorphism) [1,7]. Membrane distillation (MD) has

been proposed as a disruptive platform technology for crystallisation (MDC) as the fixed interfacial area and well-defined boundary layer ensure consistent control over heat and mass transfer processes, subsequently improving the regulation of supersaturation to advance governance over nucleation and crystal growth mechanisms [8,5,9,2].

Supersaturation is the driving force for the crystallisation process [10,11]. The metastable zone width (MSZW) represents the concentration difference between the solubility limit and the supersaturation level at the onset of nucleation (Fig. 1A) [12,13]. The extent of supersaturation when nucleation is induced determines the MSZW boundary limit and informs on which primary nucleation mechanism will predominate [11]. According to Sangwal [14], the metastable zone limit is kinetic in nature and is therefore dependent on the supersaturation rate (or concentrating rate) [9]. During crystallisation, operating below the metastable limit is preferable to avoid spontaneous primary nucleation

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Nomenclature

N	permeate flux, $\text{kg m}^{-2}\text{h}^{-1}$	$\text{NaCl g}^{-1}\text{ solution}$	
L	hollow fibre length, m	C_{fb}	feed bulk concentration, $\text{g NaCl g}^{-1}\text{ solution}$
A	effective membrane area, m^2	k_s	solute mass transfer coefficient, m s^{-1}
m	mass of permeate kg	Sh	Sherwood number, dimensionless
Q	heat transfer, W m^{-2}	Sc	Schmidt number, dimensionless
Q_v	latent heat of evaporation, W m^{-2}	J	nucleation rate based on CNT, $\text{No. m}^{-3}\text{ s}^{-1}$
Q_c	conductive heat flux through the membrane, W m^{-2}	ΔG^*	Gibb's free energy, kJ mol^{-1}
k_m	membrane thermal conductivity, $\text{W m}^{-1}\text{ K}^{-1}$	t_{ind}	induction time
k_p	polymer thermal conductivity, $\text{W m}^{-1}\text{ K}^{-1}$	k_B	Boltzmann constant, $1.38 \times 10^{-23}\text{ J K}^{-1}$
k_g	air thermal conductivity, $\text{W m}^{-1}\text{ K}^{-1}$	v_o	molecular volume, m^3
k_f	thermal conductivity of feed, $\text{W m}^{-1}\text{ K}^{-1}$	M	molar weight, kg mol^{-1}
k_p	thermal conductivity of permeate, $\text{W m}^{-1}\text{ K}^{-1}$	ρ_{cry}	crystal density, kg m^{-3}
T_{fm}	feed temperature adjacent to membrane surface, K	N_A	Avogadro's number ($6.022 \times 10^{23}\text{ molecules mol}^{-1}$)
T_{pm}	permeate temperature adjacent to membrane surface, K	T	nucleation temperature, K
T_f	bulk temperature in feed, K	A	pre-exponential parameter, $\text{m}^{-3}\text{ s}^{-1}$
T_p	bulk temperature in permeate, K	B	thermodynamic parameter for nucleation
d_i	outer diameter, mm	$\Delta C_{max, fm}$	maximum MSZW at membrane surface, $\text{mg g}^{-1}\text{ solution}$
d_o	outer diameter, mm	R'	concentrating rate, $\text{g } 100\text{ g}^{-1}\text{ solution h}^{-1}$
d_{hf}	hydraulic diameter of feed flow channel	F_p	permeate flow rate, kg h^{-1}
d_{hp}	hydraulic diameter of permeate flow channel	k	nucleation rate constant, $\text{No. m}^{-3-n}\text{ s}^{-1+n}$
$H_{V,T}$	vapour latent heat, kJ kg^{-1}	n	nucleation order, dimensionless
h_m	heat transfer coefficient of the membrane, $\text{W m}^{-2}\text{ K}^{-1}$	$n(L)$	crystal population density, m^{-4}
h_v	heat transfer coefficient of vapour, $\text{W m}^{-2}\text{ K}^{-1}$	n°	population density, m^{-1}
h_f	film heat transfer coefficients associated of feed side, $\text{W m}^{-2}\text{ K}^{-1}$	G	growth rate, m s^{-1}
h_p	film heat transfer coefficients associated of permeate side, $\text{W m}^{-2}\text{ K}^{-1}$	B_o	nucleation rate based on population balance theory, $\text{No. m}^{-3}\text{ s}^{-1}$
Nu	Nusselt's number	Greek letters	
Re	Reynold's number, dimensionless	δ_m	membrane thickness, m
Pr	Prandtl's number, dimensionless	ε	membrane porosity, %
v	velocity, m s^{-1}	ρ	density, kg m^{-3}
c_p	specific heat of feed/permeate, $\text{J kg}^{-1}\text{ K}^{-1}$	μ	viscosity, Pa s^{-1}
C_{fm}	interfacial concentration close to the membrane surface, g	γ	interfacial energy, mJ m^{-2}
		θ	contact angle, $^\circ$

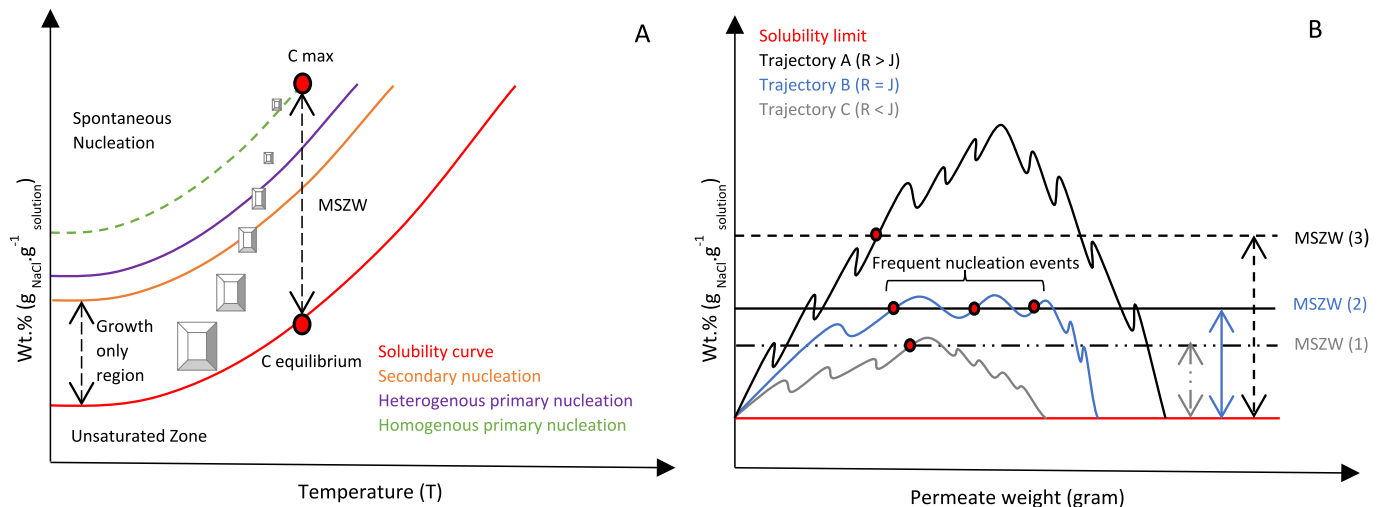


Fig. 1. (A) An illustration of metastable zone width boundaries; and (B) Schematic representation of the different supersaturation trajectories across the metastable zone width. For trajectory A, supersaturation rate following induction is greater than nucleation rate ($R > J$); trajectory B, supersaturation rate is equal to nucleation rate following induction ($R = J$); and trajectory C, supersaturation rate following induction is lower than nucleation rate ($R < J$).

which produces a high number of crystals that are small in size and may also be of poor quality[5,15]. However, primary nucleation can occur at various supersaturation levels, within a specific region of the metastable

zone, which is dependent upon the supersaturation rate. Toward the lower limit of the metastable zone (approaching the solubility line), considerably lower supersaturation is available as the driving force for

nucleation, which increases dependency on a heterogeneous substrate that can modify the interfacial energy sufficiently to lower the Gibbs free energy requirement for nucleation [16,5,17,11,18]. While this is thought to be a further advantage of the membrane surface in membrane crystallisation, the risk of membrane scaling via an adhesive growth mechanism is also introduced (which is generally presumed to be a *heterogeneous* primary nucleation mechanism) [18].

Following an initial primary nucleation event, further uncontrolled primary nucleation can occur due to the improper regulation of the supersaturation trajectory [19], where an overshoot by progressive concentration of the crystalline solution will introduce another new nucleation event [20] (Fig. 1B). This condition may pose a challenge within membrane distillation, where the elevated concentration within the boundary layer (or film) will lead to production of a large number of small crystals in a short timeframe within the vicinity of the membrane, which increases the potential for scaling through a deposition mechanism (*homogeneous* primary nucleation mechanism) [4,18]. The desaturation of solution caused by the initial nucleation event usually repositions the system for crystal growth within a less saturated region of the metastable zone, where growth may be sustained provided the supersaturation rate can match the consumption of supersaturation used for growth [21,22]. However, desaturation of the supersaturated fluid is either slower than, equal to or can exceed the supersaturation rate of the system. Therefore supersaturation control strategies (SSC) have been developed to regulate the supersaturation profile in conventional crystallisers by adjusting the supersaturation rate to promote crystal growth [21]. The concept of SSC is to control the kinetics of crystallisation by maintaining the supersaturation profile within the desired MSZW region, which significantly improves the crystal size distribution, quality and shape (Fig. 1B) [21]. However, the MSZW is a complex region where secondary nucleation cannot be avoided, resulting in the extensive generation of crystal fines [23,24]. The direct nucleation control (DNC) strategy has therefore been proposed which allows the system to cross the metastable boundary and induce primary nucleation, after which the supersaturation level is maintained at a lower saturation threshold (the ‘growth only’ zone) by sustaining particle number at a predetermined value using feedback control to regulate the supersaturation rate, therefore lowering the number of fines and ensuring a larger final crystal product size [25].

In MDC, supersaturation rate is typically modified through adjusting the membrane flux using feed temperature (T) or temperature difference (ΔT) to alter the vapour pressure difference across the membrane [26]. While evaporative crystallisation is generally preferred for salts with a relatively flat solubility-temperature dependency such as sodium chloride (NaCl) [10], adjustments to T or ΔT will nevertheless modify solubility and local solute concentration within the boundary layer, and will adjust complex mass and heat transfer processes across the membrane that can exacerbate polarisation within the boundary layer. Consequently, regulating the supersaturation rate to deliver a set supersaturation threshold is difficult to achieve making the kinetics of nucleation and crystal growth complicated to control, which restricts the opportunity to tailor final crystal quality [27,18,28]. This is an acknowledged limitation within conventional evaporative crystallisers, where temperature is the only regulatable variable and cannot be used as a method to initiate SSC or DNC strategies due to the limited precision of heating devices, and the long response times required to reach the desired temperature [21]. For MDC, the supersaturation rate must therefore be fixed to generate a sustained supersaturation gradient that can compensate for progressive primary nucleation events, while fostering reproducible crystal growth when transitioning across the MSZW. Jiang et al. [9] described the use of feed temperature and temperature difference (ΔT) in MDC to transition across the MSZW by regulating supersaturation rate (R) to demonstrate distinct nucleation kinetics, but the supersaturation trajectory following the onset of primary nucleation that determines the primary nucleation mechanism (heterogeneous or homogeneous), crystal growth mechanism and the

Table 1

Membrane and module specification.

Property	Units	Value	Fibre no.			
			3	7	19	37
Internal Diameter	(di, m)	0.0012				
Outer diameter	(do, m)	0.0018				
Wall Thickness	(m)	0.0003				
d_i/d_o	–	0.67				
Pore size	(μm)	0.45				
Porosity	(%)	73 ± 2				
Contact angle ^a	($^\circ$)	131				
Fibre Length	(m)	0.15				
Shell inner diameter	(m)	0.015				
Packing density	(%)		4.4	10.2	27.7	53.9
Membrane area	(cm^2)		25.5	59.4	161.2	313.9

^a Measured using water (Davey et al., 2020).

potential for subsequent nucleation events is yet to be described.

In this study, we therefore seek to characterise a set of fixed supersaturation rates that foster distinct kinetic trajectories across the metastable zone to determine how this informs on the primary nucleation mechanism and the subsequent evolution of nucleation and crystal growth following induction. Each supersaturation rate is modified by a change in membrane area rather than using T or ΔT , as a method to sustain comparable solution chemistry, and mass and heat transfer characteristics within the boundary layer, independent of modifications to the MSZW. This permits comparative conditions with which to discern whether sufficient adjustment of the supersaturation rate can be achieved to sustain a consistent supersaturation gradient that offsets the consumption of supersaturation to foster subsequent nucleation events and crystal growth within specific regions of the metastable zone. In-line filtration is introduced as a method to retain crystals from the bulk solution within the downstream crystalliser, to permit crystal growth within a region of supersaturation closer to the ‘growth only’ zone, and to reduce the probability for scaling through deposition which we propose will improve consistency in the supersaturation rate following the preliminary primary nucleation event. Specific objectives are to: (i) characterise different supersaturation trajectories following primary nucleation through modulating the supersaturation rate using membrane area; (ii) determine how the nucleation kinetics are modified based on the shape of the supersaturation trajectory through the metastable zone; (iii) identify how the primary nucleation mechanism is adjusted by the supersaturation trajectory as a method to mitigate membrane scaling; and (iv) relate crystal properties to where within the metastable zone that supersaturation is primarily consumed for growth.

2. Materials and methods

2.1. Experimental setup

The commercial polypropylene hollow fibre (HF) membrane (Accural PP 300/1200, 3 M, Wuppertal, Germany) comprised a $0.45 \mu\text{m}$ pore size, $300 \mu\text{m}$ wall thickness and porosity of $73 \pm 2\%$ (Table 1). The fibres were potted into predrilled holes on a set of end plates that ensured a consistent spacing arrangement and were used to construct four membrane modules composed of 3, 7, 19, and 37 HF. The HF bundles were then mounted in a resealable acrylic membrane housing with a 15 mm internal diameter and 150 mm effective membrane length. The MDC system was operated in a direct contact configuration (Fig. 2). The feed solution volume and initial concentration were 450 ml and 23.9 wt% sodium chloride (NaCl) concentration respectively. The feed solution was heated to $55 \pm 1^\circ\text{C}$ using a heat exchange assembly (Tornado TM IS6, HUBER Ministat230; Radleys, Saffron Walden, UK) and circulated to the shell side of the membrane module. Deionised water was cooled down using a chiller (LT ECOCOOL 150, Grant Instruments, Shepreth, UK) and circulated co-currently through the lumen side of the hollow fibres. The feed and permeate velocities were fixed at 0.06 m s^{-1} to

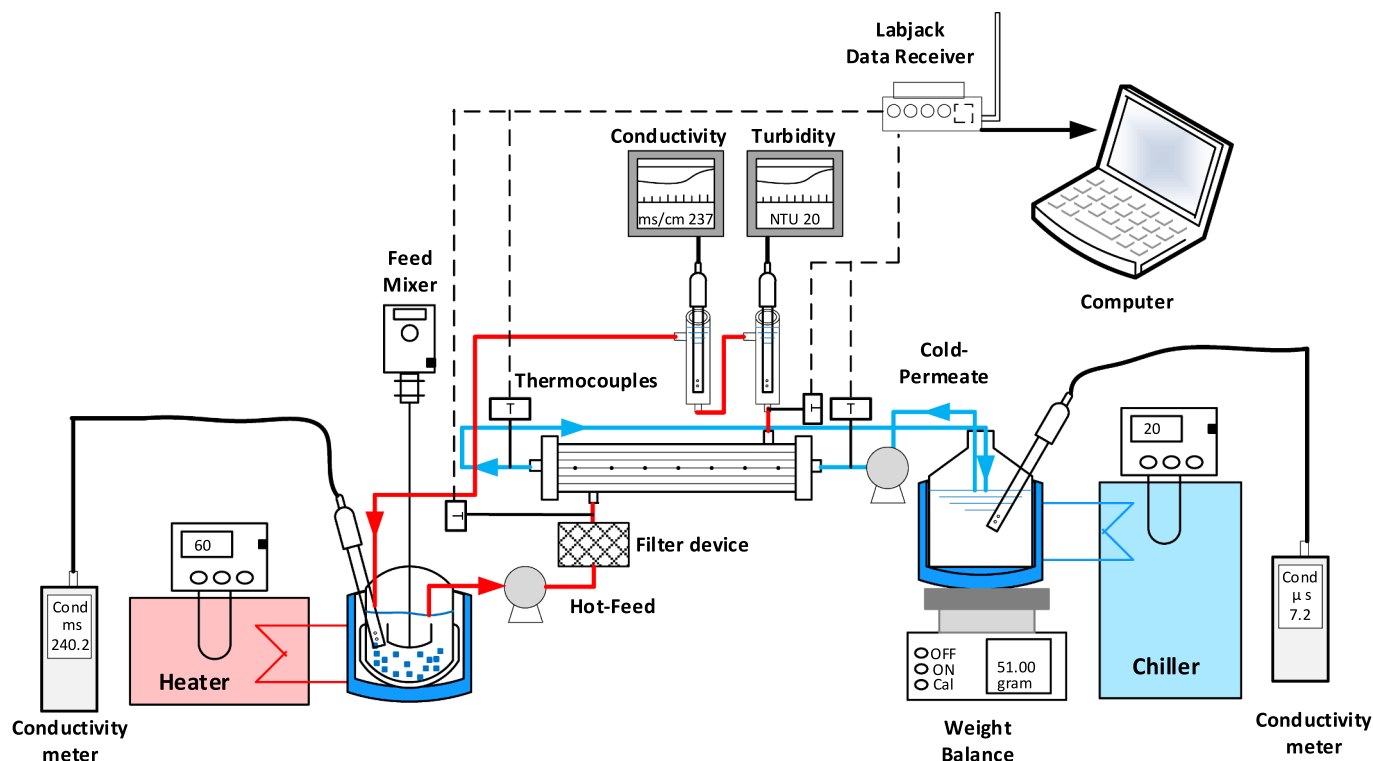


Fig. 2. Schematic diagram of the MDC setup.

provide a laminar flow regime within each membrane module (e.g. Re 134 for 37 HF) that provided a consistent transmembrane ΔT of $20 \pm 2^\circ\text{C}$ for each module. Due to the change in packing density, the flow rate was adjusted to ensure a comparable feed velocity was achieved in each membrane. The temperature was recorded in-line using thermocouples with an accuracy of $\pm 1^\circ\text{C}$ (EI1034 Temperature Prop, LabJack Corporation, Lakewood, USA). The permeate flux was calculated by weighing the cumulative permeate mass with a balance (± 0.5 g accuracy, LBX model bench scale, Adam Equipment Co Ltd, Milton Keynes, UK) and normalising to membrane area. In-line dual optic fibre turbidimetry was employed to determine induction time for nucleation (InPro8200/S/Epoxy/120, Mettler Toledo, Manchester, UK). The dual optic fibre construction provides extremely sensitive detection of the onset of nucleation through backscatter technique, enabling the accurate determination of induction time. The supersaturation profile developed within the feed solution was monitored using a conductivity sensor (InPro 7100i conductivity sensor, Mettler Toledo, Manchester, UK), offering responsive detection of conductivity changes following the utilisation of supersaturation for nucleation and crystal growth (range 0.02 to 500 mS cm^{-1} , accuracy ± 5 mS cm^{-1}). The transformation of conductivity data (mS cm^{-1}) to concentration (g NaCl g^{-1} solution) involved construction of a calibration curve that was developed through the direct measurement of conductivity within solutions of different supersaturation states (range between 24 and 29 g NaCl g^{-1} solution) at a comparative temperature to the proposed experiment. The filtration device that was implemented to retain crystals within the crystalliser, consisted of a coarse filter (polyester 10 μm square mesh fabric, Monodur™, Clear Edge Filtration, Geldern, Germany). A 'just-suspended' stirring speed was estimated for the crystalliser providing 'off-bottom' particle stratification to aid retention of the crystal phase within the crystalliser. Experiments were carried out in triplicate, with the average reported.

2.2. Crystals and membrane scaling analysis

The crystalline solution was filtered through a 0.45 μm nylon filter

(Whatman, Dorset, UK) to collect crystals from the bulk solution within the crystalliser. The crystals were weighed and sized after being dried over a desiccant (Genlabs drying cabinets 200L, Zoro, London, UK) for 48 h ($T \sim 23^\circ\text{C}$). CSD were characterised using optical microscopy (Lumenera Infinity 3-3 Camera with 5/0.12 160/- lens), with captured images analysed using Image ProPremier software (v9.2, Media Cybernetics, Rockville, US). Each CSD was performed in triplicate. At least 800 crystals were used to construct each CSD to minimise the standard error of the distribution. To determine the extent of crystal scaling via adhesive or deposition pathways, the membrane was dried over a desiccant for 48 h (temperature $\sim 23^\circ\text{C}$) and weighed using a high precision balance (0.02–62 g range, 0.0001 g precision, Fisherbrand™, Loughborough, UK). Morphology of the crystals generated on the membrane and in the bulk suspension were analysed using a scanning electron microscope (SEM) (TESCAN VEGA3, Cambridge, UK) at an accelerating voltage of 20 kV.

2.3. Mass and heat transfer in membrane distillation

Permeate flux N ($\text{kg m}^{-2} \text{h}^{-1}$) was calculated using [29]:

$$N = \frac{m}{A \times \Delta t} \quad (1)$$

where m is the permeate mass (kg), A is membrane area (m^2), and Δt is the time interval (h).

The heat transfer in membrane distillation comprises of conductive heat through the membrane Q_c (W m^{-2}), and the latent heat from vapor flux Q_v (W m^{-2}) [29]:

$$Q = Q_c + Q_v = \left(\frac{k_m}{\delta_m} \right) (T_{fm} - T_{pm}) + NH_{v,T} \quad (2)$$

where δ_m is the membrane thickness (m), k_m is membrane thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$), T_{fm} , T_{pm} are feed and permeate temperatures at membrane film and $H_{v,T}$ is the latent heat of vaporisation (kJ kg^{-1}) [30]:

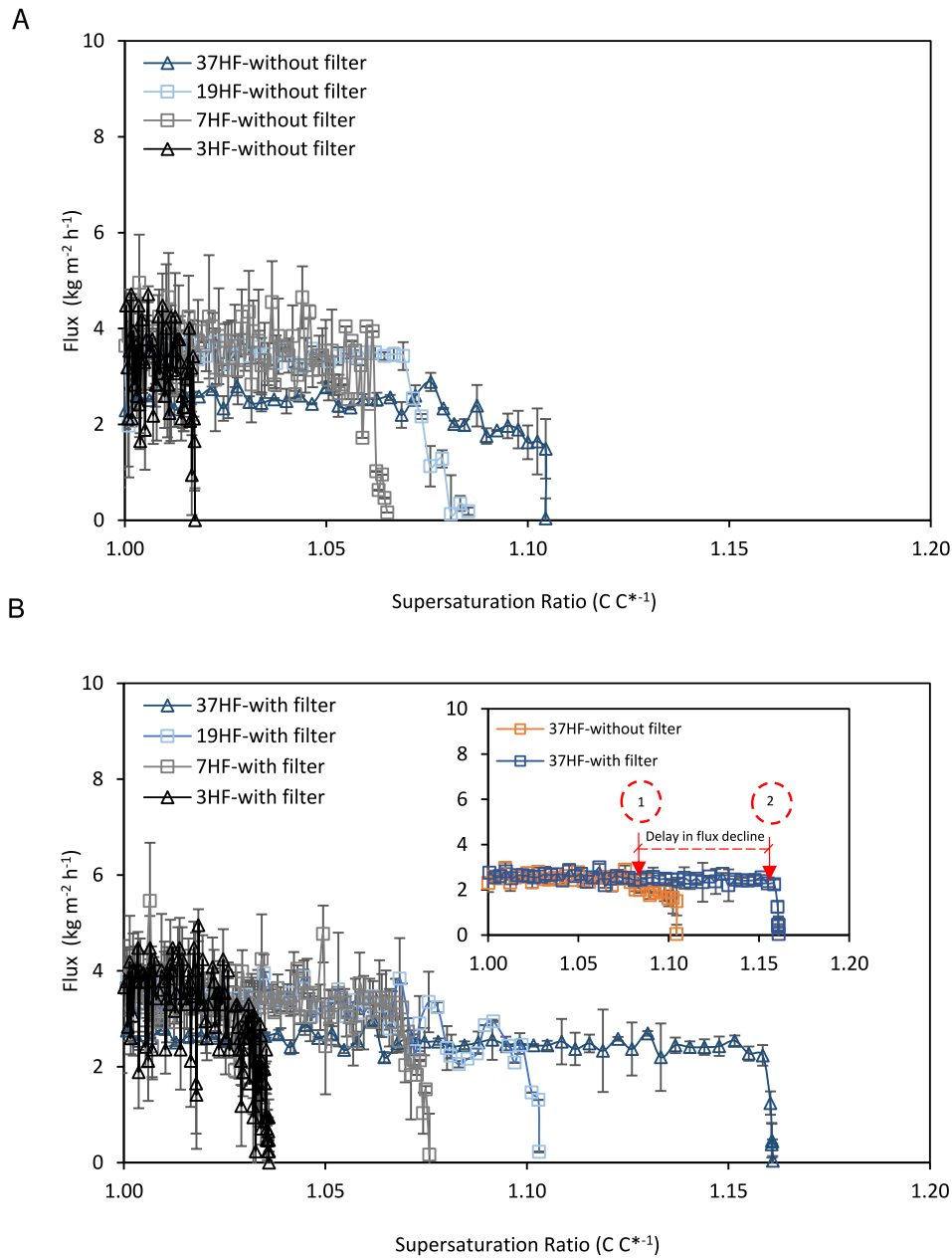


Fig. 3. Water vapour flux following progressive concentration of concentrated brine solution for different process configurations: (A) without filter device; and (B) with filter device. Comparison between A and B illustrates the extension to operation that is achievable with filtration, as underpinned by direct comparison between 37HF with and without filter (inset). Bulk supersaturation is calculated based on flux mass balance. Conditions: $T_{\text{bulk}} 55 \pm 1$ °C; $\Delta T 20 \pm 2$ °C; initial NaCl concentration, 23.9 wt%; feed and permeate velocity, 0.06 m s^{-1} .

$$k_m = k_p(1 - \varepsilon) + k_g \varepsilon \quad (3)$$

$$H_{v,T} = 1.7535 T_{m,\text{avg}} + 2024.3 \quad (4)$$

where k_p is polymer thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$), ε is membrane porosity, k_g is the air thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$), and $T_{m,\text{avg}}$ is the average of film temperature (K) [30,31]:

$$T_{m,\text{avg}} = \frac{T_{fm} + T_{pm}}{2} \quad (5)$$

The feed T_{fm} and permeate temperatures T_{pm} within the membrane film can be expressed as [26,29]:

$$T_{fm} = T_f - (T_f - T_p) \left[\frac{1/h_f \times d_i/d_o}{1/h_f \times d_i/d_o + 1/(h_m + h_v) + 1/h_p} \right] \quad (6)$$

$$T_{pm} = T_p - (T_f - T_p) \left[\frac{1/h_p}{1/h_f \times d_i/d_o + 1/(h_m + h_v) + 1/h_p} \right] \quad (7)$$

where d_i/d_o is inner/outer diameter ratio, bulk temperature in feed and permeate T_f and T_p (K), h_p is the permeate heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$), and h_f is feed heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$):

$$h_{fp} = Nu \times \frac{k_{fp}}{d_{hp}} \quad (8)$$

where k_f and k_p are thermal conductivity of feed and permeate ($\text{W m}^{-1} \text{K}^{-1}$), d_{hf} and d_{hp} are hydraulic diameter of feed and permeate flow channel (m), Nu is Nusselt's number, $h_m = k_m / \delta_m$ is the membrane heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$) and h_v is the vapour heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$):

$$h_v = \frac{NH_{v,(T_{fm}+T_{pm})/2}}{(T_{fm} - T_{pm})} \quad (9)$$

From this, the temperature polarisation coefficient (TPC) can be calculated by iteration:

$$TPC = \frac{T_{fm} - T_{pm}}{T_f - T_p} \quad (10)$$

The bulk solute concentration leading up to nucleation was estimated by mass balance, assuming negligible solute breakthrough into the permeate, which was confirmed by directly monitoring permeate conductivity during experimentation. The membrane film concentration was calculated from the concentration polarisation coefficient (CPC) based on the film model [32]

$$CPC = \frac{c_{fm}}{c_f} = \exp\left(\frac{N}{\rho \times k_s}\right) \quad (11)$$

where C_{fm} is the concentration adjacent to the membrane surface ($\text{g NaCl g}^{-1} \text{ solution}$), C_b is the bulk concentration ($\text{g NaCl g}^{-1} \text{ solution}$), ρ is the solution density (kg m^{-3}) and k_s is the solute mass transfer coefficient (m s^{-1}) which was calculated from Chilton-Colburn analogy based on the heat and mass transfer correlation [33,34].

$$\frac{Sh_f}{Sc_f^{0.33}} = \frac{Nu_f}{Pr_f^{0.33}} \quad (12)$$

where Sh is Sherwood number, Sc is Schmidt number, Pr_f is the Prandtl number of feed solution.

$$Sh_f = \frac{k_s D_h}{D_s} \quad (13)$$

$$Sc_f = \frac{\mu_f}{P_f D_s} \quad (14)$$

2.4. Characterisation of nucleation and crystal growth kinetics

The MSZW was calculated from the developed method proposed by Nývlt [9]. This approach assumes supersaturation to be linearly related to the MSZW in the range of concentration where nucleation first occurs (induction). Therefore, the upper supersaturation limit at the membrane film $\Delta C_{\max, fm}$ ($\text{mg NaCl g}^{-1} \text{ solution}$) is assumed to be proportional to the supersaturation rate R' ($\text{g.100 g solution}^{-1} \cdot \text{h}^{-1}$), where both correspond to the nucleation rate by the power-law equation as follows:

$$J = k(\Delta C_{\max, fm})^n = \left(\frac{dc_0}{dt}\right)_t = \frac{F_p C_0}{m_0 - \int_0^t F_p d\tau} \quad (15)$$

$$R' = \left(\frac{dC_0}{dt}\right)_t = \frac{F_p C_0}{m_0 - \int_0^t F_p d\tau} \quad (16)$$

where F_p is the permeate flow rate (kg h^{-1}), m_0 is the initial mass of the crystalline solution (kg), C_0 is the equilibrium concentration ($\text{g NaCl g}^{-1} \text{ solution}$), $\Delta C_{\max, fm}$ (which is, $c_{fm} - c^*$). The numerator ($F_p C_0$) represents the change in solute mass, while the denominator represents the change in solution volume, therefore collectively representing the rate of change in concentration. The kinetic parameters, k ($\text{No. m}^{-3-n} \text{s}^{-1+n}$) and n (—)

are the nucleation constant and nucleation order respectively and depend on the formation mechanism of the stable nucleus and its growth evolution into viable entities [35], which are determined from a linear fit between $\ln R'$ and $\ln \Delta C_{\max, fm}$ [9]:

$$\ln(\Delta C_{\max, fm}) = \frac{1}{n} \ln\left(\frac{C_0}{k}\right) + \frac{1}{n} \ln\left(\frac{F_p}{m_0 - \int_0^t F_p d\tau}\right) \quad (17)$$

Nucleation and crystal growth rates were calculated from the crystal suspension according to population balance theory [32]:

$$\frac{dn(l)}{dl} + \frac{n(l)}{Gt} = 0 \quad (18)$$

This assumes a well-mixed suspension during crystallisation and as crystal growth rate is independent of size at a given supersaturation (K. J. [36], Eq. (18)) can be expressed as:

$$n(L) = n(0) \exp - \frac{L}{Gt} \quad (19)$$

where $n(L)$ is the crystal population density (m^{-4}), n^0 is the population density at ($L = 0$) (m^{-1}), G is the growth rate (m s^{-1}), and t is the residence time (sec). From a linear fit of $\ln n(L)$ versus L , the intercept at ($L = 0$) is equal to population density (n^0) and the growth rate provided by the gradient ($-1/Gt$). The nucleation rate B^0 ($\text{No. m}^{-3} \text{s}^{-1}$) was therefore determined as follows:

$$B^0 = n^0 G \quad (20)$$

3. Result and discussion

3.1. Consistent primary nucleation is achieved with or without in-line filtration

Comparable initial permeation fluxes of around $3.6 \text{ kg m}^{-2} \text{ h}^{-1}$ were observed for each HF membrane examined (Fig. 3). This indicates consistent mass and heat transfer conditions were sustained when increasing membrane area; an assertion supported by the attainment of a comparable feed temperature and ΔT for each module of $55 \pm 1^\circ \text{C}$ and $20 \pm 2^\circ \text{C}$ respectively. The only exception was the 37 HF module, which recorded a marginally lower initial permeation flux of $2.6 \text{ kg m}^{-2} \text{ h}^{-1}$ (Fig. 3). While a comparable superficial velocity was developed within this module (V_L , 0.06 m s^{-1}), the small modification in flux may be attributed to an adjustment of the local superficial velocity due to the higher packing density [37]. Importantly, the increase in membrane area was demonstrated to enhance the supersaturation level that could be achieved. Each of the flux profiles comprised of three stages (Fig. 3b, inset): (i) a stable permeation flux that slightly decreased over time due to a reduction in water activity that is imposed by an increase in feed solution concentration [38,39,40]; (ii) a dramatic decline in permeation flux at a higher supersaturation level, which is thought to correspond to the onset of scaling, where a crystalline layer is initiated through either adhesive crystal growth (*heterogeneous* nucleation) or deposition of crystals formed within the bulk solution (*homogeneous* nucleation) which increases resistance to mass and heat transfer [32]; and (iii) the complete diminution of permeation flux [26,18]. Stage two flux decline was observed at higher levels of supersaturation as membrane area increased, while the time required to reach stage two was much less for modules comprising more HF. To illustrate, stage two flux decline was recorded at 338, 200, 78 and 56 min for 3, 7, 19 and 37 HF membrane modules respectively. Introducing filtration to advance crystal retention in the crystalliser downstream of membrane distillation, enabled the suppression of stage two flux decline to achieve a considerably higher supersaturation level. For example, the supersaturation level achieved at the onset of stage two flux decline with the 37 HF module, increased from $c/c^* 1.08$ to 1.15 when using filtration.

Turbidimetric measurements provided evidence for the onset of bulk

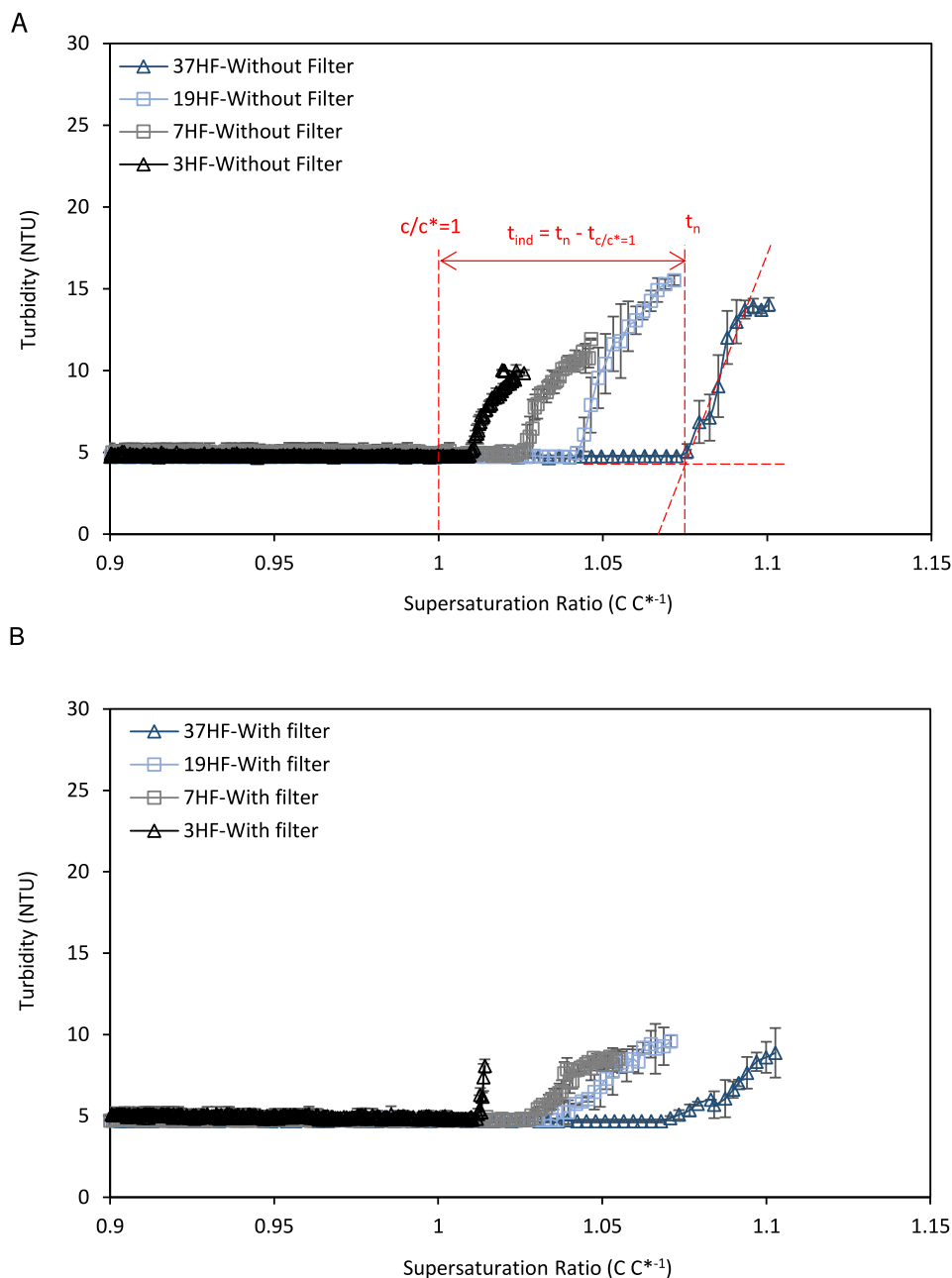


Fig. 4. Turbidity profiles characterising bulk nucleation events for operation: (A) without filter device; and (B) with filter device. Supersaturation at induction is increased by modifying membrane area. Conditions: $T_{bulk} 55 \pm 1$ °C; $\Delta T 20 \pm 2$ °C; initial NaCl concentration, 23.9 wt%; feed and permeate velocity, 0.06 m s^{-1} .

nucleation and confirmed observation from the flux trends that nucleation proceeds at higher supersaturation through an increase in membrane area (Fig. 4). The time elapsed from reaching a supersaturated state ($c/c^*, 1$) to the first appearance of the bulk crystal phase is defined as the induction time (J.W. [41,42]). While the inclusion of filtration downstream of MD was observed to increase the maximum supersaturation obtained for the duration of the experiment, both the supersaturation level and induction times achieved for primary nucleation were comparable regardless of whether filtration was used (Fig. 5). We suggest that the extended operation of MD with filtration may therefore be due to the reduction of deposition onto the membrane through restricting recycling of the crystal phase, which is supported by the lower turbidity values recorded when operating with filtration in place. This not only enables higher supersaturation to be achieved, but also creates a more consistent flux over a longer period, which implies a greater control over supersaturation rate and thus should provide for

closer control over the kinetics of nucleation and crystal growth. Critically, this study also demonstrates that the stage-two inflection point which many authors have previously employed as a surrogate measure for the onset of nucleation[32,2] is in fact mechanistically distinct from that of induction time as previously hypothesised by Horseman et al. [18].

3.2. Distinct supersaturation profiles develop when increasing membrane area

The supersaturation profiles developed within the boundary layer (film) and bulk solution were characterised to distinguish their implications for adjusting crystallisation kinetics at the onset of primary nucleation. Typically concentration and temperature polarisation are modified by the mass and heat transfer mechanisms established within the boundary layer [38,18]. In this study, by increasing supersaturation

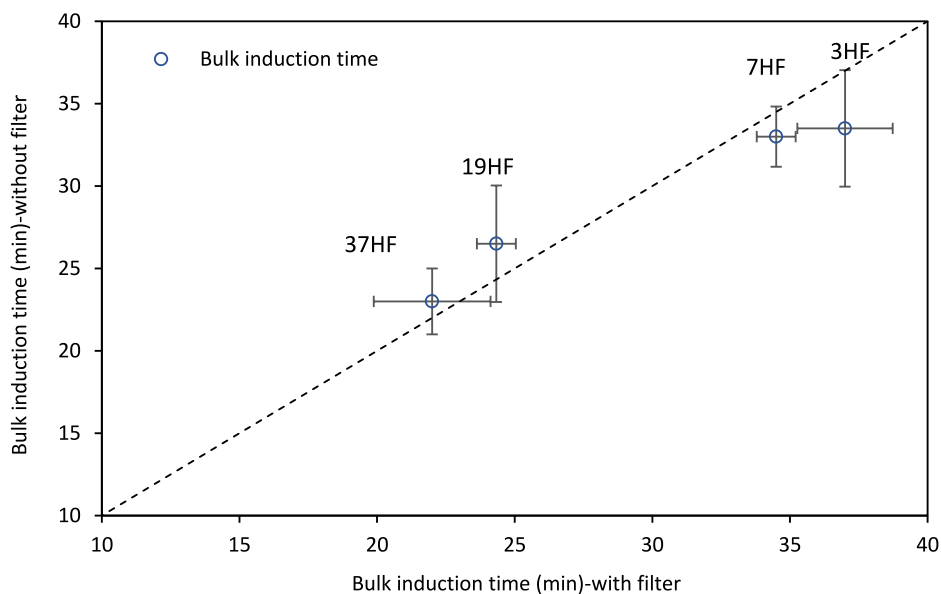


Fig. 5. Comparison of induction time between both MDC configurations (with and without in-line filtration) based on turbidity demonstrates that induction is achieved at the same time regardless of whether filtration is employed in the recycle line. Conditions: $T_{\text{bulk}} 55 \pm 1^\circ\text{C}$; $\Delta T 20 \pm 2^\circ\text{C}$; initial NaCl concentration, 23.9 wt%; feed and permeate velocity, 0.06 m s^{-1} .

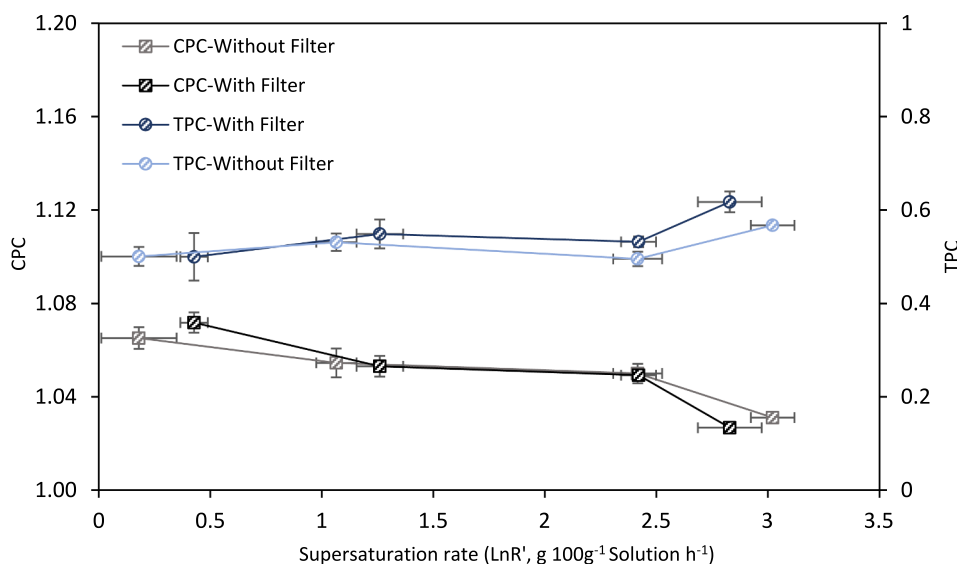


Fig. 6. Concentration and temperature polarisation coefficients (CPC and TPC) determined for each module determined when concentrating rate (LnR') is increased by membrane area. Comparison evidences boundary layer characteristics are similar at induction regardless of whether filtration is employed in the recycle line. Conditions: $T_{\text{bulk}} 55 \pm 1^\circ\text{C}$; $\Delta T 20 \pm 2^\circ\text{C}$; initial NaCl concentration, 23.9 wt%; feed and permeate velocity, 0.06 m s^{-1} .

rate with membrane area rather than T or ΔT , TPC and CPC were relatively consistent at the outset of filtration, due to the consistent flux established for each module, enabling total thermal losses to become proportional to membrane surface area, resulting in a constant ΔT of $20 \pm 2^\circ\text{C}$. However, at induction, a slight increase in TPC was noted (from 0.5 to 0.56) commensurate with a minor reduction in CPC (1.072 to 1.027 for 3 and 37 HF respectively when operating without filter) (Fig. 6). This is due to the increase in supersaturation that was achieved as supersaturation rate was elevated, which slightly reduced the vapour pressure (and thus flux) at induction, approximately in proportion to the membrane surface area.

While this thermal adjustment will introduce a subtle change in solute concentration in the boundary layer at induction, it is primarily the increase in membrane area that modifies the supersaturation rate and is

ultimately responsible for the supersaturation that is achieved at induction [18,9]. Since temperature is sustained within the bulk conditions and is not subject to polarisation, the trajectory across the MSZW is likely to be characteristically distinct between these regions, and will determine the kinetics of nucleation, crystal growth and the predominant primary nucleation mechanism (Fig. 7). For the bulk conditions, the MSZW at induction increased from 27.0 % to 28.8 % when the membrane module increased from 3HF to 37HF (0.18 to $3.02 \text{ g } 100 \text{ g}^{-1} \text{ solution h}^{-1}$). Comparable MSZW were developed for the initial primary nucleation event independent of whether in-line filtration was applied, consistent with the measured induction times. Polarisation phenomena in the film increased the MSZW that was attained within the film, ranging from 28.3 % for 3HF to 29.5 % for 37HF. The wider MSZW can be attributed to the higher supersaturation rate (higher driving force)

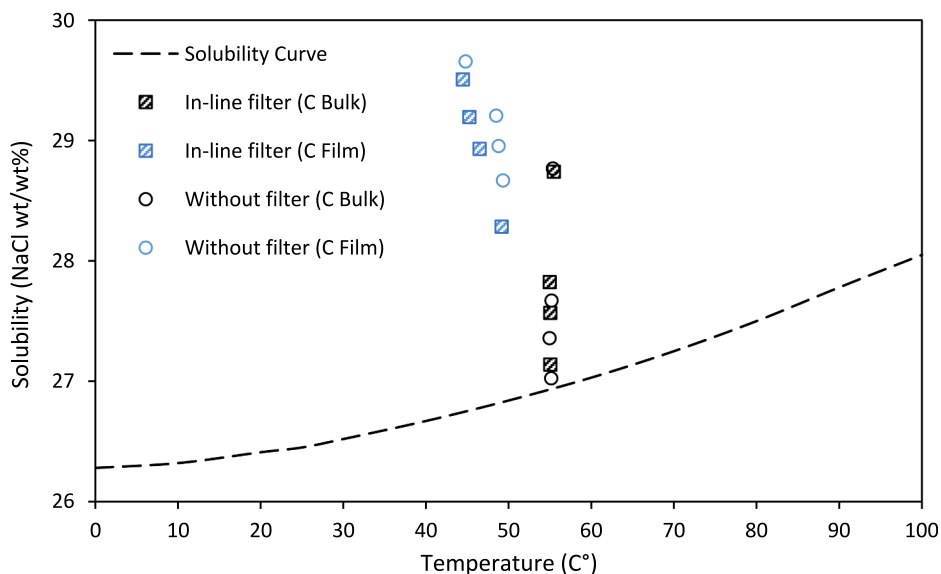


Fig. 7. The supersaturation achieved at induction is used to construct the metastable zone width (MSZW) using bulk and film concentrations (wt. NaCl/wt., %). Conditions: $T_{\text{bulk}} 55 \pm 1$ °C; $\Delta T 20 \pm 2$ °C; initial NaCl concentration, 23.9 wt%; feed and permeate velocity, 0.06 m s^{-1} .

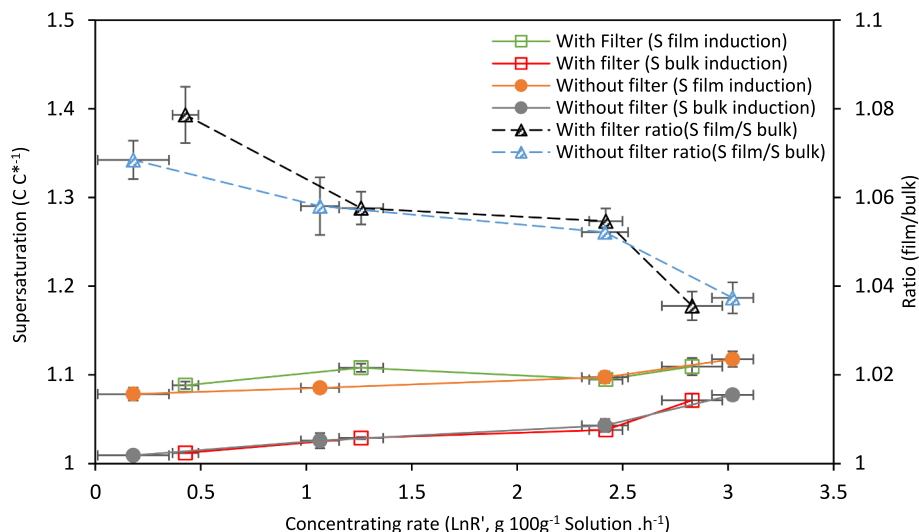


Fig. 8. Extent of supersaturation (c/c^*) achieved based on the concentrating rate (LnR') imposed by an increase in membrane area; supersaturation attained within bulk and boundary layer (film) are compared. Bulk supersaturation is calculated based on flux mass balance and film concentration is calculated according to CPC values. Conditions: $T_{\text{bulk}} 55 \pm 1$ °C; $\Delta T 20 \pm 2$ °C; initial NaCl concentration, 23.9 wt%; feed and permeate velocity, 0.06 m s^{-1} .

which introduces an excess free energy into a non-equilibrium condition bringing the critical free energy requirement for nucleation to a minimum [11,9,14](Fig. 8). The relative difference between supersaturation ratios achieved in the bulk and film reduced at higher supersaturation rates. This is due to the modification in vapour pressure at induction, which will be lowest at the highest concentrating rate due to the elevated supersaturation in the film, subsequently adjusting $C-C^*$ due to the slight modification in TPC and CPC [27,29]. While this constitutes a reduction in the relative difference between supersaturation achieved in the bulk and film at induction, the absolute difference in supersaturation between bulk and film remains significant for each condition (Fig. 7).

Membrane scaling was greatest when the minimum supersaturation rate was employed (Fig. 9), which corresponded to the lowest supersaturation level at induction, and the longest induction time (Figs. 4 and 5). This condition can be described through classical nucleation theory

as possessing a considerable free energy barrier to nucleation, increasing the relevance of a foreign substrate that can modify the interfacial energy of the system to permit primary heterogeneous nucleation to occur [2,43,44]. Previous authors have suggested that the modest reduction in film temperature identified in this study at the lowest supersaturation rate (3HF), will raise the probability for scaling through lowering of the solubility limit within the vicinity of the membrane [26,27]. However, the solubility-temperature dependency for NaCl is negligible [26]. As supersaturation increased, and induction time shortened, membrane scaling was considerably reduced. The higher supersaturation rate introduces the necessary excess free energy to lower the energy requirement for primary nucleation to proceed through a homogeneous mechanism [45,11]. Consequently, less scaling via adhesive growth (or heterogeneous primary nucleation) is observed at higher supersaturation rate. This transition to a primarily homogeneous mechanism is

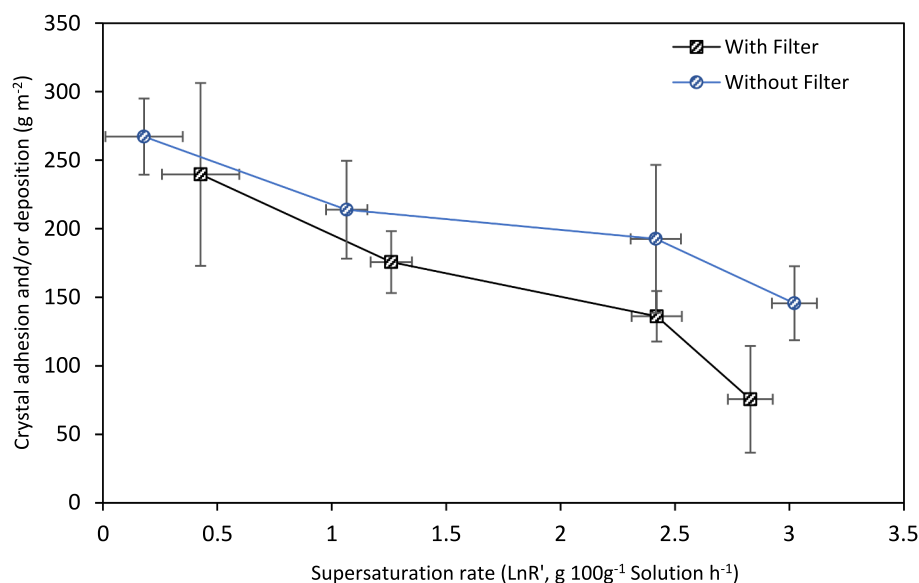


Fig. 9. The distinction in scaling mechanisms is observed, where the extent of surface adhesion and/or deposition at the membrane surface is dependent on the concentrating rate applied, and the presence of in-line filtration in the recycle line. Increasing concentrating rate (LnR') limits adhesive growth of scalant, while in-line filtration reduces deposition.

supported by comparison of scaling data from experiments with and without in-line filtration in place at high supersaturation rates. While the preliminary nucleation kinetics have been shown identical between the two scenarios (Figs. 4 and 5), the difference in scaling between the filter and no filter systems, evidences the contribution of deposition from crystals formed through a homogeneous mechanism begins to dominate scaling as supersaturation rate is increased. Identification of conditions that minimise scaling by adhesive growth are critical to sustaining the supersaturation trajectory following the preliminary nucleation event. Mitigating deposition through in-line filtration should also support a sustained and consistent supersaturation rate (Fig. 3b), providing greater control over crystallisation kinetics following induction.

Each supersaturation rate was evaluated (with in-line filtration applied) to ascertain how the supersaturation trajectory develops following the preliminary primary nucleation event, as this provides the driving force for crystallisation (Fig. 10). The supersaturation ($c-c^*$) achieved for an equivalent permeate mass at the outset of permeation are comparable (e.g. see data at intercept of y-axis), whereas an increase in supersaturation rate achieved a greater supersaturation ($c-c^*$ 0.021 for 37HF, versus 0.004 for 3HF) prior to nucleation within the metastable solution. Despite some slight oscillation within the developed supersaturation profile, three general trends are observed: (i) preliminary primary nucleation occurs at the highest $c-c^*$ that has been achieved up to that point for the specific supersaturation rate; (ii) a modest decline in supersaturation occurs shortly after primary nucleation, indicating the use of supersaturation within the nucleation process [25]; and (iii) following primary nucleation, a distinct supersaturation trajectory is observed dependent upon the supersaturation rate applied. The supersaturation profiles in the film and bulk solution are comparable in shape since the supersaturation rate is primarily determined by the relative increase in membrane area, but the distinction in trajectories is particularly evident within the film due to the higher $c-c^*$ that is developed through concentration and temperature polarisation. Specifically, at the lowest supersaturation rate, $c-c^*$ gradually declined following the first primary nucleation event, whereas for the highest supersaturation rate, $c-c^*$ progressively increased over time. Since supersaturation provides the driving force for both nucleation and crystal growth [11,21], it is postulated that these different trajectories across the MSZW following induction will determine the preference for

primary or secondary nucleation, and the competition between nucleation and crystal growth mechanisms [46,27,47].

3.3. Supersaturation trajectory determines crystal size, size distribution and morphology

The decline in solute concentration observed just after the onset of nucleation, implies an increase in total crystal surface area, indicating that crystalline particle growth is occurring within the system [22]. Construction of the metastable limits provides insight into the relative use of supersaturation following nucleation [27,48] (Fig. 11). Desaturation repositions the system supersaturation in a region of the metastable zone between the primary nucleation limit and the solubility curve, which minimises primary nucleation and favours crystal growth, but may also incur secondary nucleation when transitioning across this domain [46,49,50]. In-line filtration increased hold-up time after induction, which can further contribute to secondary nucleation as the higher crystal number increases the probability for collision, leading to the production of fines [27,51]. Comparison of CSDs produced with and without in-line filtration (37HF) evidenced how the extension in hold-up time (14 mins) negatively skewed the CSD (Fig. 12), indicating crystal growth is favoured over the production of fines (a response to secondary nucleation) [4,52,28]. For higher supersaturation gradients, secondary nucleation can be negligible, thus the elevated supersaturation is available to underpin crystal growth [49]. Similar growth rates of 5.31×10^{-8} and $5.05 \times 10^{-8} \text{ m s}^{-1}$ were observed within the systems with and without filtration respectively (Table 2), due to the comparable primary nucleation kinetics (and supersaturation trajectory) that were set at induction (Figs. 4 and 7). However, analysis of the population balance indicates a reduction in nucleation rate with a longer hold-up time, which may result from the competition for supersaturation between nucleation and growth within a crystallising solution comprised of a considerably higher crystal number density (yield 15.9 ± 3.9 and $7.9 \pm 0.1 \text{ g}$ respectively).

For low supersaturation rates, the MSZW is narrow, and the supersaturation frequently approached the solubility limit in a region characterised as the 'growth only' zone [43,53] (Fig. 11). The L_{50} of the final crystal product was $104 \pm 10 \mu\text{m}$ for the lowest supersaturation rate and progressively increased to $142 \pm 8 \mu\text{m}$ for the highest supersaturation rate (Table 3). Classical crystallisation generally favours fewer, larger

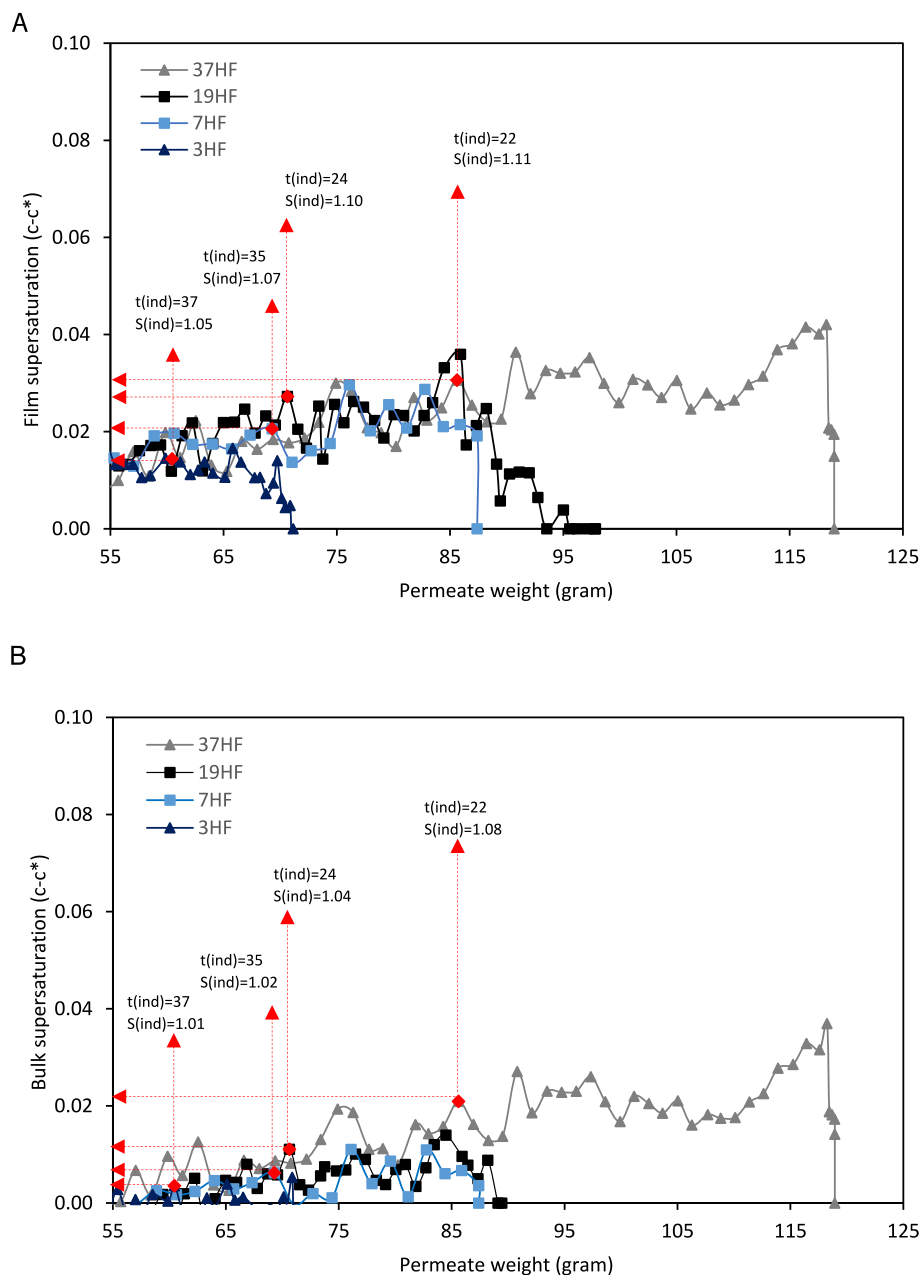


Fig. 10. Supersaturation profiles that develop before and after the initial primary nucleation event (induction), based on conductivity mass balance for: (A) boundary layer (or film) concentration; and (B) bulk solution concentration. Conditions: $T_{\text{bulk}} 55 \pm 1^\circ\text{C}$; $\Delta T 20 \pm 2^\circ\text{C}$; initial NaCl concentration, 23.9 wt%; feed and permeate velocity, 0.06 m s^{-1} .

crystals at low supersaturation [33], and can be explained by the preferential use of supersaturation for growth at an elevated supersaturation state initiated through the higher supersaturation rate [22]. However, the supersaturation state has implications for scaling and crystal product quality (Fig. 13). Detailed SEM imaging of the scaling layer revealed that even for a low supersaturation rate, the elevated supersaturation state in the film introduced imperfections within the crystal scaling morphology, as evidenced by hollows formed within the cubic structure (Fig. 13a). These so called ‘hopper’ crystals are symptomatic of growth induced when the diffusion of molecules into the crystal lattice is unstable [54,55]. At higher supersaturation rates, SEM imaging confirmed less scaling, whereas the extent of hollows apparent in the crystal morphology appear exacerbated, while crystal size is increased which is

consistent with the increase in local supersaturation providing the driving force for crystal growth. This is because higher supersaturation levels occur at edges and corners, rather than faces, subsequently generating these occlusions that can physically trap impurities, reducing product purity (Fig. 13b) [56,55]. Distinct morphology was evident for the crystal product formed within the crystalliser within the same conditions, permitting a characteristic cubic form with smooth surfaces and facets, suggesting that the lower supersaturation rate and supersaturation level that manifests in the bulk solution, enables sufficient time for more homogeneous molecular diffusion into the crystal lattice. This was coupled with a lower coefficient of variation (CV, 48 %), indicating narrowing of the distribution around the mean size. Consequently, segregating crystal growth into the bulk solution in MDC can provide

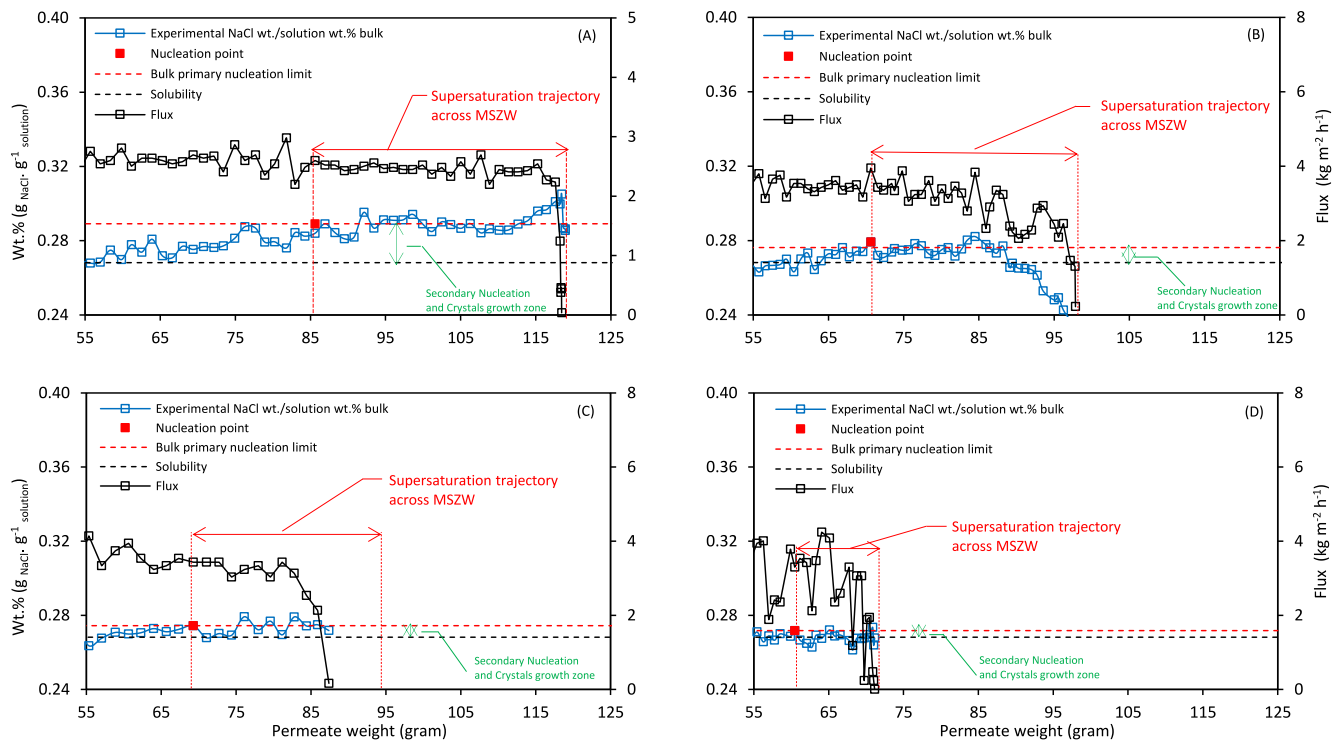


Fig. 11. Supersaturation trajectory during membrane distillation crystallisation, based on different supersaturation rates that are fixed by the membrane area used. In-line filtration is used in each configuration to limit deposition. The theoretical supersaturation profile is calculated based on conductivity mass balance assuming no consumption of NaCl for crystallisation, and compared to actual conductivity data, where the difference evidences where within the metastable zone width that nucleation and crystal growth are occurring: (A) 37HF; (B) 19HF; (C) 7HF; (D) 3HF. Conditions: T_{bulk} 55 ± 1 °C; ΔT 20 ± 2 °C; initial NaCl concentration, 23.9 wt%; feed and permeate velocity, 0.06 m s^{-1} .

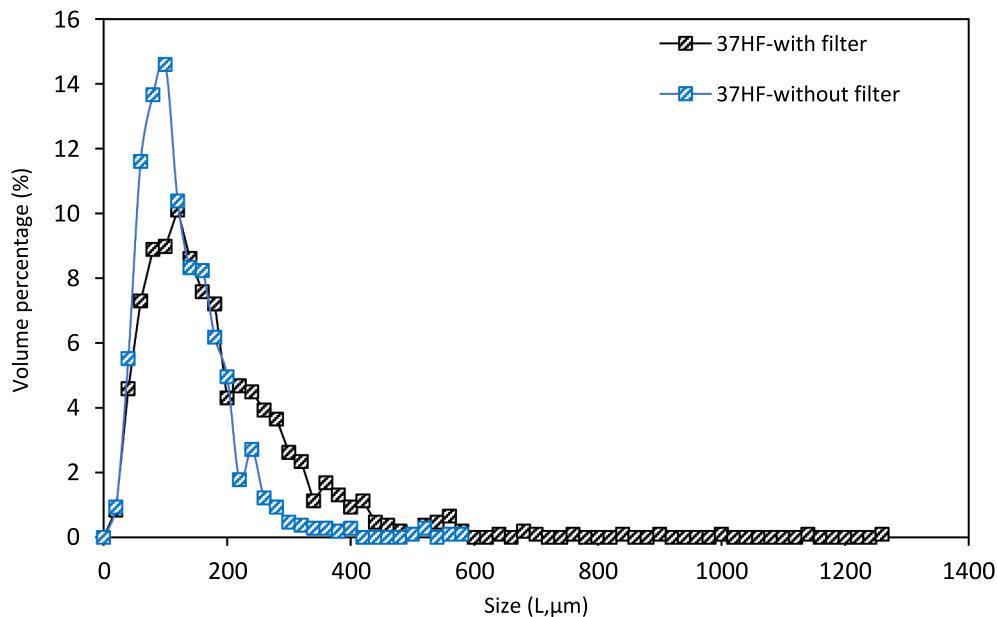


Fig. 12. Crystal size distributions (based on volume fraction, %) produced in the absence and presence of filtration to reduce deposition. The key difference is that in-line filtration extends residence time for crystal growth after induction which affects subsequent nucleation, crystal growth and yield. Conditions: T_{bulk} , 55 ± 1 °C; $\Delta T_{\text{membrane}}$, 20 ± 2 °C; initial NaCl concentration, 23.9 wt%; feed and permeate velocity, 0.06 m s^{-1} .

greater control over product quality, while independently promoting conditions that favour primary nucleation. However, cementation and aggregation are also indicated in the crystal product (Fig. 13c) which occur at high primary nucleation rates through collisions in the

significant population of small crystals, and may be unfavourable to product quality dependent on final application [57,58].

At the highest supersaturation rate, supersaturation exceeded the primary nucleation threshold (PNT) on several occasions, which

Table 2

Comparison of crystallisation kinetics at different batch time from 37 HF experiment. Extension in residence time is provided by in-line filtration to reduce deposition.

Parameters	Units	Without filter ^c	With filter ^c
Induction time	(min)	23 ± 2	22 ± 2
Concentrating rate at induction	(g.100 g ⁻¹ Solution h ⁻¹)	3.02 ± 0.09	2.83 ± 0.14
Supersaturation at induction (c-c*) ^b	(g NaCl g ⁻¹ solution)	0.022 ± 0.001	0.021 ± 0.007
Maximum supersaturation (c-c*) ^b	(g NaCl g ⁻¹ solution)	0.026 ± 0.003	0.037 ± 0.007
ln(ΔC _{fm,max})	(mg NaCl g ⁻¹ Solution)	3.45 ± 0.07	3.37 ± 0.12
Growth rate ^a	(m s ⁻¹) × 10 ⁻⁸	5.05 ± 3.5	5.31 ± 1.4
Nucleation rate ^a	(no. m ⁻³ s ⁻¹) × 10 ⁶	22.50 ± 0.15	1.95 ± 1.2
Hold-up time after induction	(min)	13 ± 1	27 ± 2
Crystals median size (L ₅₀)	(μm)	100 ± 15	142 ± 8
Crystals yield	(g)	7.9 ± 0.1	15.9 ± 3.9

^a Measured based on MSMPT theory.

^b Calculated based on conductivity measurements

^c The reported values represent the average and error of replicated experiments.

represents the supersaturation level at which primary nucleation first occurred (Fig. 14). While analysis of the population balance implied that extension of the residence time favoured growth over nucleation, when exceeding the PNT, it can be inferred that the free energy barrier was sufficiently reduced to initiate further primary nucleation events [33,9,59]. Supersaturation peaks up to a value of $\Delta c/c_{\text{pnt}}^*$ 0.006 were not observed to disturb flux, whereas flux was noted to decline shortly following a PNT peak of 0.016 which vastly exceeded the PNT threshold. While supersaturation peaks exceeding the PNT were fewer in number, and lower in value for lower supersaturation rates (enabled through membranes with fewer hollow-fibres), the stage three decline in flux was also preceded by a peak in supersaturation which exceeded the PNT (Table 4). It is therefore suggested that stage 3 flux decline is primarily a response to further primary nucleation events, where higher nucleation rates elicited at supersaturation >PNT can be detrimental to sustained operation. The relative insensitivity of flux for 37 HF (Fig. 14), implies that by broadening MSZW to favour homogeneous primary nucleation, membrane distillation crystallisation is more resilient to new primary nucleation events characterised by small transient PNT peaks. Desaturation of the supersaturated solution was greatest following the first primary nucleation event ($t = 0$, Fig. 14), whereas the consumption of supersaturation following subsequent PNT peaks was less, despite achieving higher levels of supersaturation. This can be attributed to the competition between nucleation and growth of the existing crystal phase. By shortening the residence time for crystal growth (reducing the particle population), more supersaturation will be consumed in the

creation of new nuclei which will lower the system supersaturation. In addition to mitigating stage 3 flux decline, this closer regulation of supersaturation can also reduce the effect of aggregation and cementation within the final product.

4. Conclusions

This study has demonstrated how facile supersaturation control strategies can be instigated within membrane crystallisation to enhance the governance over nucleation and crystal growth. While much research centres upon the control of primary nucleation, to our knowledge this is the first study to consider the management of supersaturation once nucleation has commenced, where competition between nucleation and crystal growth mechanisms subsequently exist. The significance to the literature, is that it is only within this region that crystal size, morphology and yield will ultimately be determined. In this study, adjustment of the metastable zone is illustrated independent of the boundary layer. This design strategy is unique to the MDC literature, which generally report tenacious scaling toward the outer limit of the metastable zone, limiting operation with higher nucleation rates or shorter induction times, that are important to controlling product morphology, process energy and system cost. A critical insight from this research, is that by modifying the metastable zone independent of the boundary layer, scaling can be controlled concomitant with bulk crystal morphology. This is distinct from classical evaporative crystalliser design and is due to the coupling of mass and heat transfer across a single interface in MDC to create a more controllable crystallisation environment. When complemented with in-line filtration, the secondary mechanism of scaling (deposition) can also be mitigated through isolation of the crystal phase from the solvent recycle. This increases crystal yield but can also sustain permeate flux at an equivalent value, sufficient to control supersaturation to a setpoint within the metastable zone, for improving quality assurance and narrowing of the crystal size distribution. Combining this new knowledge with feedback control strategies could further mitigate scaling by exploiting a supersaturation setpoint below the primary nucleation threshold. Importantly, through isolating the crystal phase within the crystalliser, high nucleation rates can be achieved within the boundary layer of MDC while cultivating a less saturated region to foster the preferred crystal habit with limited occlusions. Incorporation of a fluidised bed crystalliser would simplify recycle design to further enhance crystallisation control beyond that presently achievable within existing evaporative crystalliser technology.

CRedit authorship contribution statement

A. Ouda: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Y. Bajón-Fernández:** Writing – review & editing, Supervision. **E. McAdam:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation,

Table 3

Crystallisation kinetics across different supersaturation profiles developed when using in-line filter configuration.

Fibre No.	Induction time (min)	Concentrating rate at induction (g.100 g ⁻¹ Solution h ⁻¹)	Supersaturation at induction (c-c*) (g NaCl g ⁻¹ solution) ^a	Crystals yield (g)	Maximum Supersaturation (c-c*) (g NaCl g ⁻¹ solution) ^a	ln(ΔC _{fm,max}) (mg NaCl g ⁻¹ Solution)	Hold-up time after induction (min)	Median (L ₅₀) (μm) ^b	Coefficient of variation (CV, %)
37	22 ± 2	2.83 ± 0.14	0.021 ± 0.007	15.0 ± 3.9	0.037 ± 0.007	3.37 ± 0.09	27 ± 2	142 ± 8	0.63 ± 0.01
19	24 ± 1	2.42 ± 0.08	0.011 ± 0.002	11.5 ± 0.7	0.014 ± 0.004	3.23 ± 0.32	33 ± 9	133 ± 9	0.48 ± 0.02
7	35 ± 2	1.26 ± 0.11	0.006 ± 0.001	10.1 ± 2.9	0.011 ± 0.002	3.15 ± 0.05	87 ± 6	102 ± 6	0.55 ± 0.01
3	37 ± 1	0.43 ± 0.06	0.004 ± 0.001	9.3 ± 4.9	0.005 ± 0.0003	3.04 ± 0.02	89 ± 10	104 ± 10	0.69 ± 0.03

^a Calculated based on conductivity measurements.

^b Standard error was calculated based on differences in triplicate measurements.

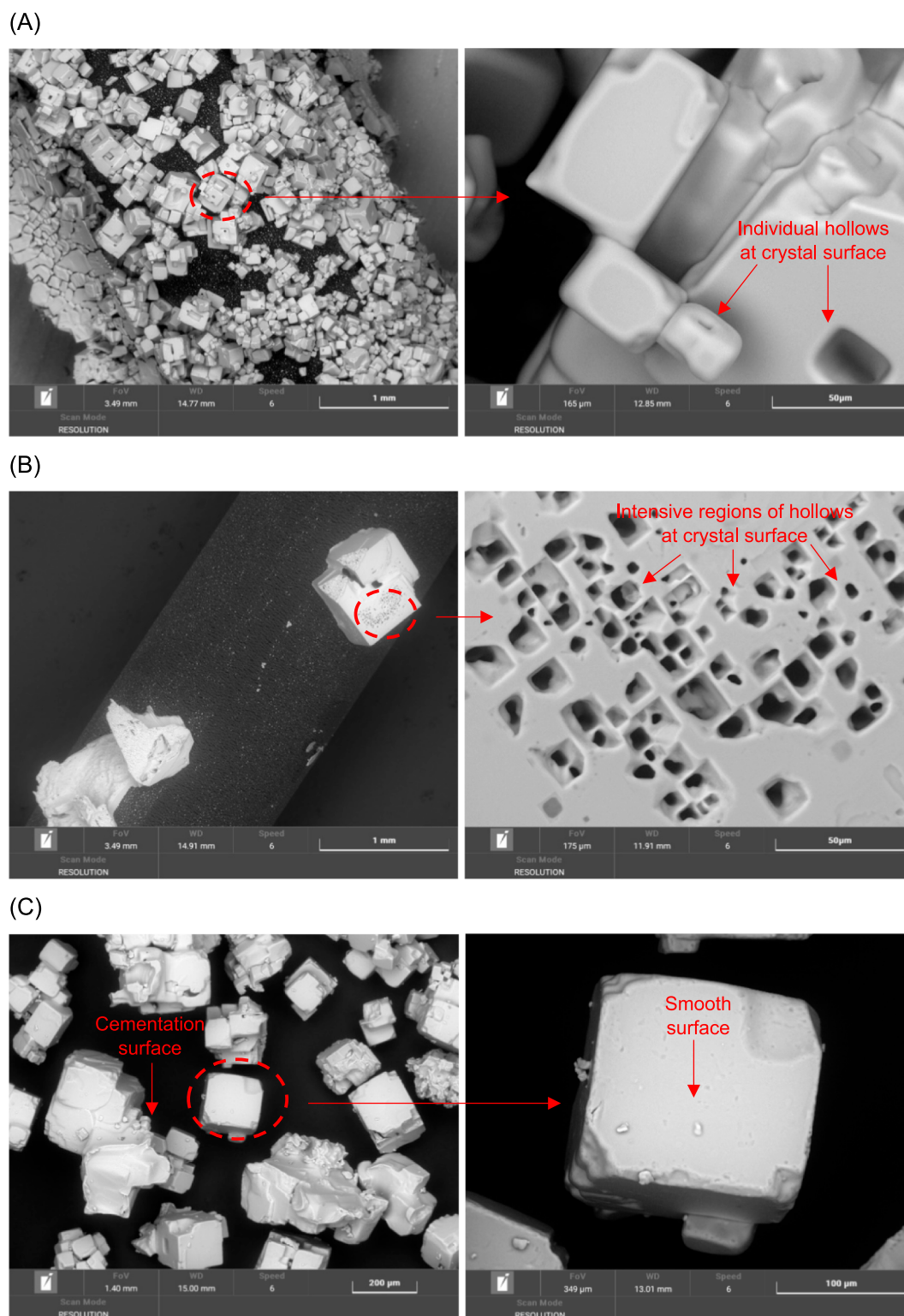


Fig. 13. Scanning electron microscopy (SEM) of produced crystals at the membrane surface and from the bulk solution: (A) 7HF, with filter device, sampled from membrane (c/c^* 1.07, residence time after induction, 89 min); (B) 19HF, with filter device, sampled from membrane (c/c^* 1.10, residence time after induction, 33 min); (C) 19HF, sampled from bulk solution in feed vessel, upstream of in-line filter configuration (c/c^* 1.04, residence time after induction, 33 min). Distinct crystal growth patterns observed at membrane surface dependent on supersaturating rate, and when crystals are produced in the bulk solution, evidencing the potential to improve crystal morphology.

Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

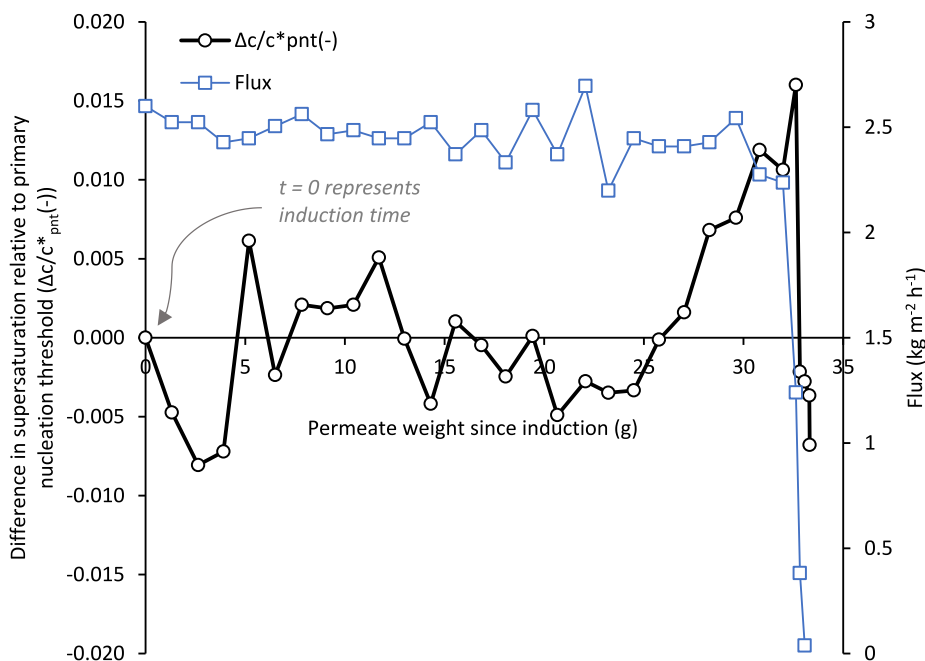


Fig. 14. Indicative illustration for how stage-three flux decline is seemingly dependent upon the system exceeding the supersaturation threshold for primary nucleation. 37 HF configuration used for illustration. Conditions: $T_{\text{bulk}} 55 \pm 1^\circ\text{C}$; $\Delta T 20 \pm 2^\circ\text{C}$; initial NaCl concentration, 23.9 wt%; feed and permeate velocity, 0.06 m s^{-1} .

Table 4

Primary nucleation exceedance (PNT) pattern of different supersaturation profiles.

FibreNo.	$\Delta c/c^*_{\text{pnt}}(-)$ ^a	$\Delta t(t_{\text{stage3}}-t_{\text{PNTexceedance}})^b(\text{min})$	$\Delta t(t_{\text{stage3}}-t_{\text{ind}})^c(\text{min})$
3	0	0	30
7	0.003	3	33
19	0.003	1	16
37	0.016	4	25

^a The extent of supersaturation that was achieved in excess of the PNT at stage 3 flux failure

^b Time lag between previous PNT exceedance and start of flux failure

^c Operating time between start of stage 3 flux decline and induction time.

the work reported in this paper.

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