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# Salt Storage and Induced Crystallisation in Porous Asymmetric Inorganic Membranes

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## Abstract

Processing brines to recover strategic mineral salts using evaporation ponds requires large surface areas and are slow, even in arid climates. Here we show a novel membrane macropore storage mechanism that induces fast salt crystallisation in mesoporous top-layers in inorganic asymmetric membranes, stemming from 789 million nucleation points per metre square of surface area. During membrane pervaporation, dissolved salts are retained mainly in the macropores of the substrate which subsequently provide ideal conditions for crystal nucleation and growth on the membrane surface upon drying. This novel pore storage mechanism is attained owing to the solution flow modulation of the mesoporous titania and gamma-alumina layers that is counterbalanced by the flow of water during pervaporation. Therefore, pore size control is imperative to avoid flooding in the macroporous substrate. This work further shows the fundamental properties of the salt storage mechanism described by a single salt production coefficient, and a global salt production coefficient for metal chloride salts. This technology could potentially be considered for unlocking and process strategic global minerals from brines.

**Key words:** inorganic membranes; pore storage; pore size control; pervaporation; crystallisation.

## 1. Introduction

The demand for strategic minerals to meet our contemporary societies need for technological advancement is expanding. Meanwhile, conventional orebody grades are in decline, thus mineral brine mines will be an increasingly important source of salts and metals in the future. A clear example

41 is lithium, a relatively rare metal required for the production of highly efficient batteries for portable  
42 electronic devices [1], plug-in electrical cars [2] and increasingly for large scale power storage [3].  
43 The estimated global lithium brine reserves of 21.6 Mt is 5.6 times larger than non-brine lithium  
44 reserves [4]. Even larger reserves are the oceans of the world which are last frontier in mineral  
45 processing, holding vast quantities of dissolved metal ions of commercial interest, such as lithium  
46 ( $2.3 \times 10^5$  Mt), nickel (8,600 Mt), magnesium ( $1.3 \times 10^{12}$  Mt), gold (14.5 Mt), potassium ( $5.1 \times 10^8$  Mt),  
47 manganese (500 Mt) and uranium (4,300 Mt) among many others [5]. These elements find broad  
48 application in wealth generation (gold), and advanced materials such as magnesium for medical  
49 applications [6], manganese doped semiconductor quantum dots [7] and nickel as catalyst [8]. In  
50 addition, potassium plays a critical role in food production [9] and uranium is a key element to nuclear  
51 power production in a decarbonised economy [10]. However, extracting valuable elements from  
52 mineral brines is time and energy intensive and expensive, particularly in the case of diluted metal  
53 ions in oceans [11].

54  
55 Mineral brines are traditionally processed in evaporation ponds and industrial crystallisers.  
56 Essentially these processes evaporate water from a brine solution, leading to supersaturation and  
57 crystallisation. The crystallisation of evaporation ponds is very slow and highly dependable upon the  
58 weather conditions whilst industrial crystallisers deliver fast crystallisation rates though are energy  
59 intensive. Since the 1980s, polymeric hydrophobic membranes have become attractive to promote  
60 crystal nucleation and growth kinetics [12], using membrane distillation, also known as  
61 pervaporation. This process is known as membrane crystallisation, with proven applications for  
62 crystallising LiCl [13], NaCl [14, 15],  $\text{Na}_2\text{CO}_3$  [16] and  $\text{MgSO}_4$  [17]. Owing to the fast pervaporation  
63 of solvent via the hydrophobic polymeric membrane, ideal conditions are created at surface of the  
64 membrane at the feed side, leading to supersaturation, nucleation and crystallisation. Subsequently,  
65 two further downstream processes are required where (i) crystals are separated from the solution by  
66 filters and then (ii) dried in furnaces.

67

68 Although the state of the art in polymeric membrane crystallisation is well known, inorganic ceramic  
69 membranes remained absent [18] in this technological development until recently by the pioneering  
70 work of Motuzas and co-workers [19] who prepared porous hydrophobic carbon membranes to  
71 crystallise NaCl from mineral brine solutions. This process is known as membrane percrystallisation  
72 as solutes (i.e., crystals) and solvents were separated at a single step by a wet thin film under vacuum  
73 on the permeate side of the membrane. Subsequently, it was demonstrated that the process conditions  
74 (i.e., flow rates, temperature and vacuum pressure) in membrane percrystallisation altered the crystal  
75 NaCl particle size [20], and the crystal phase of NiSO<sub>4</sub> [21]. The use of hydrophilic inorganic  
76 membranes has eluded the field of membrane crystallisation to date.

77

78 Therefore, this work demonstrates for the first time that hydrophilic inorganic membranes can be  
79 used efficiently for crystallising mineral brines by a novel pore storage mechanism under  
80 pervaporation. It is shown that salt storage in the macropores of a ceramic membrane substrate under  
81 pervaporation can be attained only in the presence of a mesoporous inorganic top-layer with  
82 controlled pore sizes. Further, this work demonstrates that fundamental mass transfer properties in  
83 the pore storage are a function of feed concentrations for a single salt, and as a function of the  
84 molecular weight for chloride salts.

85

## 86 **2. Experimental**

### 87 **2.1 Sol-gel synthesis and xerogel characterisation**

88 An aqueous aluminium oxide (20%) sol with an average colloidal particle size of 0.05 µm (pseudo-  
89 boehmite from Alfa Aesar) was used as received for coating gamma alumina interlayers. The top  
90 layers were synthesised using a titania sol-gel method. Briefly, titanium (IV) isopropoxide (TIP,  
91 TiC<sub>12</sub>H<sub>28</sub>O<sub>4</sub>, 98%, Sigma-Aldrich) was added drop-wise into a solution of double-distilled water and  
92 hydrochloric acid under vigorous stirring. Then the mixture was maintained in a water bath at 30 °C

93 for 3 hours. The molar ratio of the final sol was TIP:HCl:H<sub>2</sub>O = 1:1:22. The sol was then dried in an  
94 oven at 60 °C for 3 h.

95

96 The preparation of xerogel (dried gel) was initially carried out by heat treatment at 150 °C to ensure  
97 the consolidation of the titania matrix. Subsequently, the titania xerogel was calcined at 350 °C to  
98 condense the matrix into a meso-structure. Heat treatment and calcination were carried out at a  
99 heating/cooling rate of 1 °C min<sup>-1</sup> and a dwell time of 1 h. Nitrogen sorption of titania xerogel samples  
100 was conducted on a Micromeritics TriStar 3020 analyser after degassing under vacuum on a  
101 Micromeritics VacPrep061 at 200 °C for a minimum of 12 h. The specific surface areas were  
102 calculated from the adsorption isotherms via the multi-points BET model at relative pressures  
103 of  $p/p_0=0.05-0.3$ . The pore size distribution was determined using Barrett–Joyner–Halenda (BJH)  
104 model, from the desorption branch of the isotherms of the mesoporous titania xerogel samples.

105

## 106 **2.2 Membrane preparation and characterisation**

107 Commercial porous alpha alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) tubes (OD = 1 cm, ID = 0.5 cm, L = 5.5 cm, Ceramic  
108 Oxide Fabricator Pty Ltd.) were used as membrane substrates. The substrates were pre-calcined at  
109 1000 °C for 8 h with a ramp rate of 5 °C min<sup>-1</sup> to improve the mechanical strength and to remove any  
110 organic impurities. Each coated layer was deposited separately by a dip-coating method at immersion  
111 and withdrawal rate of 5 cm min<sup>-1</sup> and a dwell time of 1 min. Both ends of the substrate were closed  
112 prior to dip-coating to allow layers to be coated on the outer shell of the substrate only. After each  
113 coated layer, the membranes were calcined in air at 500 °C (gamma alumina interlayers), 150 and  
114 350 °C (titania top layers) at a ramping/cooling rate of 1 °C min<sup>-1</sup> and a dwell time of 1 h. The latter  
115 followed a procedure proposed by Yacou et al. [22] in order to control the mesopore size of titania  
116 thin films. The final prepared membranes consisted of two gamma alumina interlayers and two titania  
117 top layers. Microstructural investigation of the membrane layers was carried out via a JEOL field

118 emission scanning electron microscope (FE-SEM, JEOL JSM-7001F) operating at 5 kV at a working  
119 distance of 10 mm.

120

### 121 **2.3 Membrane crystallisation**

122 Synthetic feed solutions were prepared by mixing chloride based salts ( $\text{mol}_s$ ) with the required amount  
123 of double-distilled water ( $L_w$ ) represented by  $\text{mol}_s L_w^{-1}$ . The salt concentration of the feed solution  
124 was determined via standard calibration curves (conductivity versus concentration) using a  
125 conductivity meter (labCHEM CP). The membrane outer shell was exposed to a pre-determined salty  
126 feed solution at atmospheric pressure and room temperature ( $\sim 20^\circ\text{C}$ ). The inner shell of the  
127 membrane (i.e., permeate side) was evacuated to 18 mbar using a vacuum pump, thus allowing water  
128 to evaporate and salt to remain in the pores of the membrane. The effective length of the membrane  
129 for pervaporation testing was 4.5 cm, as 0.5 cm at both ends of the substrate were covered with silicon  
130 tubes. The membranes were tested at time intervals from 10 to 30 min. The water vapour in the  
131 permeate stream was condensed and collected in a liquid nitrogen cold trap located downstream. The  
132 collected water was analysed using the conductivity meter to determine if any salt ions were entrained  
133 in the water vapour during water evaporation.

134

135 After testing, the membranes were transferred to a pre-heated oven at  $60^\circ\text{C}$  for 8 h to ensure a  
136 complete crystallization of salts on the  $\text{TiO}_2$  top layer took place on the outer shell of the membrane.  
137 The pervaporation schematic and salt growth on the membrane surface is depicted in the Appendix  
138 Fig. A1. The relative humidity of the oven chamber ( $\text{RH} = 67.3\%$ ) was controlled using  $\text{NaNO}_3$  brine  
139 solution. Salt crystals on the surface of the membranes were observed with JEOL field emission  
140 scanning electron microscope (FE-SEM, JEOL JSM-7001F) operating at 5 kV at a working distance  
141 of 10 mm.

142

143 The crystallised salts were removed from the outer surface of the membrane and the collected mass  
144 of salt crystals was measured in a high-precision laboratory scale. This allowed the production ( $J$ ) of  
145 crystallised salts to be determined as follows,

$$146 \quad J = \frac{m_{salt}}{tA} \quad (Eq. 1)$$

147 where  $m_{salt}$  is the mass of crystallised salt collected at a pre-determined membrane pervaporation time  
148 interval  $t$  (min), and  $A$  ( $m^2$ ) is membrane surface area. The membrane pervaporation followed by  
149 oven drying were replicated at least five times for all tested conditions. A Panasonic microwave  
150 (Genius 1100 MW) with variable power was also used for drying and crystallising chloride base salts.  
151 The membranes were microwave-dried at 900 W for 2 min. The mass and flux of crystallised chloride  
152 base salts after microwave-dried were calculated using a similar procedure as described above for the  
153 oven-dried membranes.

154

### 155 **3. Results and discussion**

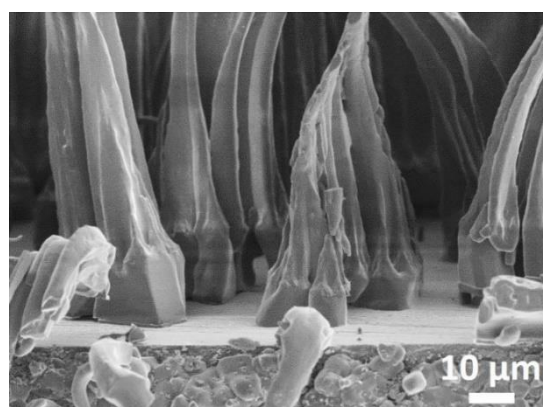
#### 156 **3.1 Induced Crystallisation and Membrane Characteristics**

157 Here we demonstrate for the first time that hydrophilic inorganic ceramic membranes are very  
158 efficient in processing mineral brines by a novel mechanism of induced salt crystallisation. We  
159 observed that under pervaporation of an aqueous NaCl solution, salts concentrated in the pores whilst  
160 water permeated through the membrane. Upon drying the membrane, capillary forces in the pores  
161 induced evaporation of water, leading to super-saturation, nucleation and crystal growth on the  
162 surface of the membrane. Fig. 1 displays NaCl crystals grown perpendicular to the membrane surface  
163 which appear as a salt crystal forest-type arrangement. The crystals are unusual, having a cubic shaped  
164 base at the interface of the membrane followed by an elongated pyramid shape, in sharp contrast to  
165 conventional NaCl cubic crystals. It is noteworthy that the crystals are approximately equidistant  
166 from each other.

167

168 Analysis of the SEM image (Fig. 1) suggests that the base of the crystal is of  $\sim 20.5 (\pm 2) \mu\text{m}$ , and the  
169 average distance between each crystal base is  $\sim 15.1 (\pm 1.5) \mu\text{m}$ . Therefore, one square metre of  
170 inorganic membrane area generates on the order of 789 million nucleation points of these unusual  
171 crystals in a single processing cycle of pervaporation, pore storage and crystallisation. As salt ions  
172 are expelled from the pores of the membrane, their concentration increases on the surface of the  
173 membrane. This process of mass transfer leads to spontaneous crystal nucleation in a supersaturated  
174 thin wet film on the surface of the membrane. Upon formation of the stable nuclei, crystal growth  
175 predominates which lowers the local supersaturation and inhibits further nucleation. Consequently,  
176 salt ions diffuse on the surface of the membrane from areas of high concentration to low concentration  
177 due to the chemical potential, thus favouring crystal growth.

178



179

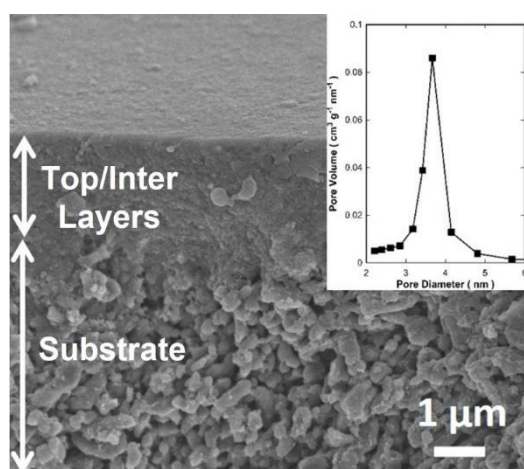
180 Fig. 1. SEM image of NaCl crystal pyramid-like shapes on a membrane dried at 60 °C.

181

182 Induced salt crystallisation occurred in asymmetric membranes (see representative SEM image in  
183 Fig. 2) composed of two top layers (titania) and two interlayers (gamma-alumina) with a combined  
184 average thickness of 1.95  $\mu\text{m}$  coated on an alpha-alumina support. The asymmetric configuration is  
185 based on the principle that the thin top layers are coated on a mechanically strong substrate, whilst  
186 the interlayer provides a smooth surface to form a defect free thin top layer [23]. A fundamental  
187 aspect of this induced pore crystallisation is the precise control of the sol-gel method to tailor the  
188 inorganic hydrophilic membrane pore diameter ( $d_p$ ). This was achieved by an acid sol-gel synthesis

189 of the titania top layers followed by a two-step calcination to 150 and 350 °C and using a low ramping  
190 rate of 1 °C min<sup>-1</sup>. A number of hydrophilic membranes were tested under pervaporation of aqueous  
191 NaCl solutions. The pore size of macroporous alpha alumina ( $d_p > 50$  nm) were too large, resulting  
192 in pore wetting and full permeation of the solution. In the case of microporous silica membranes ( $d_p$   
193  $< 0.5$  nm or 5 Å) [24], only water diffused through the membranes as the permeation of salt ions were  
194 hindered. Pore storage was observed for mesoporous titania top-layers ( $3 < d_p < 5$  nm) (Fig. 2 inset)  
195 and gamma alumina ( $3.7 < d_p < 8.9$  nm) [25] interlayers.

196



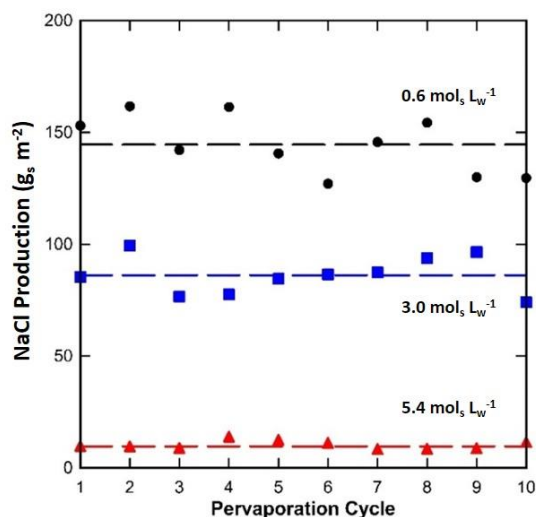
197

198 Fig. 2. SEM image of an asymmetric titania (top-layer) and gamma alumina (interlayer) where inset  
199 shows a pore size distribution based on Barrett, Joyner and Halenda (BJH) model.

200

### 201 3.2 Membrane Performance

202 Fig. 3 shows the stable cyclic performance of the titania/alumina membrane over 10 consecutive  
203 cycles of pervaporation and NaCl crystallisation. Increasing the NaCl feed concentration resulted in  
204 an increase in the production of NaCl crystals, suggesting an increase in the storage rate of NaCl in  
205 the pores of the membranes. Notably, the titania/alumina membrane was able to process a wide range  
206 of feed solution concentrations ranging from seawater ( $0.6 \text{ mol}_s \text{ L}_w^{-1} \text{ NaCl}$ ) to hypersaline brines ( $5.4$   
207  $\text{mol}_s \text{ L}_w^{-1} \text{ NaCl}$ ).

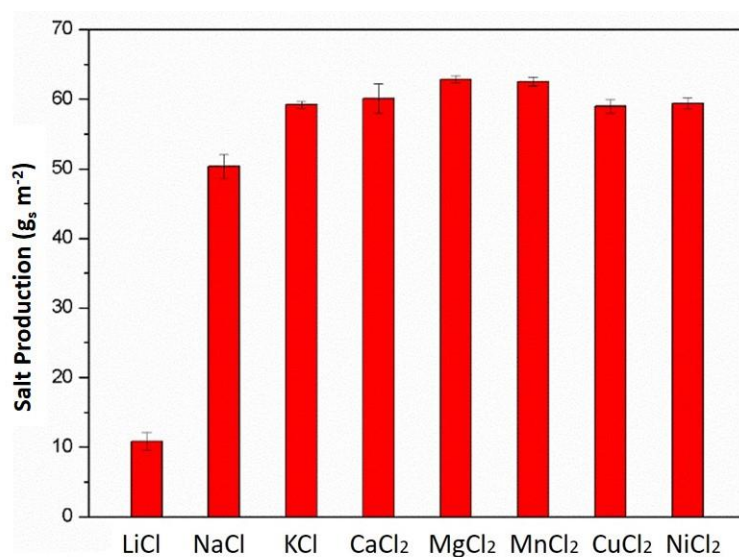


208

209 Fig. 3 NaCl production rate for 10 successive cycles of pervaporation of 30 min for various NaCl  
 210 feed concentrations (0.6, 3.0 and 5.4 mol<sub>s</sub> L<sub>w</sub><sup>-1</sup>). The membranes were oven-dried at 60 °C for 8 h  
 211 and RH = 67.3%.  
 212

213 This novel induced crystallisation proved to be very effective for a number of chloride salts as  
 214 displayed in Fig. 4. Under cycles of pervaporation of 10 min, the salt storage in the nanopores varied  
 215 between 50 to 63 g m<sup>-2</sup>, except for LiCl. It was observed that Li had reacted slightly with the  
 216 membrane as the top layer became darker instead of the typical white titania colour. The Li reaction  
 217 along with the relatively low molar mass of Li explains the lower LiCl storage per cycle.

218



219

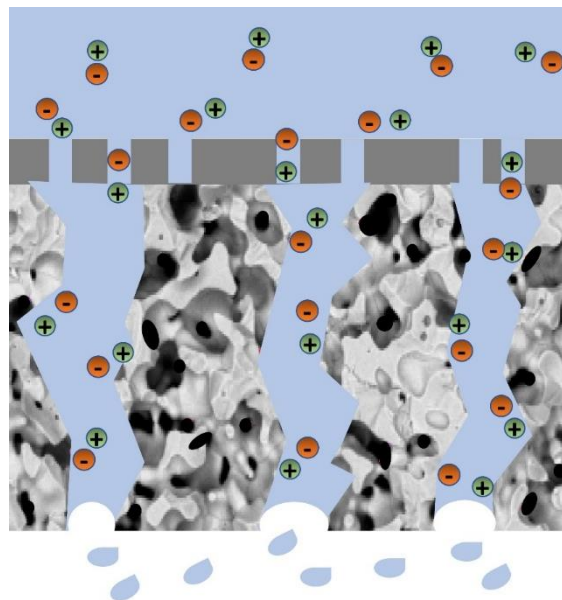
220 Fig. 4. Chloride salt production for feed concentrations (3 mol<sub>s</sub> L<sub>w</sub><sup>-1</sup>) at 20 °C with a pervaporation  
 221 time of 10 min. The membranes were microwave-dried at 900W for 2 min. Salt production includes  
 222 hydrated salts.

223






### 224 3.3 Novel pore storage mechanism

225 Salt crystallisation on the membrane surface proceeded via pervaporation as schematically depicted  
226 in Fig. 5. Upon contact of the dry membrane with an aqueous salt solution, capillary forces take effect  
227 immediately [26]. These forces induced salt solution penetration into the pores due to the hydrophilic  
228 nature of titania and gamma-alumina layers. Based on the results in Fig. 3 for a feed solution of 5.4  
229 mol<sub>s</sub> L<sub>w</sub><sup>-1</sup>, the NaCl production average is 144.5 g m<sup>-2</sup>. This is equivalent to a NaCl crust of NaCl with  
230 a thickness of 67 μm. The latter is 35 times thicker than the average thickness of the mesoporous  
231 titania and gamma-alumina layers of 1.95 μm. Therefore, the mass of salt that causes induced  
232 crystallisation can be directly attributed to salt storage in the membrane substrate that accounts to  
233 99.96% of the overall membrane thickness. Theoretical calculations in the Appendix Table A1 clearly  
234 confirms that this is the case as there is sufficient pore volume in the membrane substrate to  
235 accommodate the NaCl mass that induced crystallisation.

236



237

238 Fig. 5. Idealised schematic representing the salt storage in the membrane where  is the salt feed  
239 solution,  is the titania and gamma alumina mesoporous layers,  is the water meniscus,  is  
240 water vapour and  is the alpha alumina macroporous substrate.

241

242 It is noteworthy the role played by the mesoporous titania and gamma-alumina layers in avoiding  
243 membrane flooding under pervaporation. In this case, the mesoporous layers modulated the flow of  
244 salt ion solution into the larger macropores of the substrate. This flow modulation benefited the salt  
245 storage mechanism by entraining salt ions in the macropores of the substrate whilst avoiding solution  
246 flooding in the permeate side.

247

248 In this process, menisci are formed in the macropores of the substrate close to the surface of the inner  
249 shell of the tubes under pervaporation, thus controlling the water evaporation via the permeate stream.  
250 The water evaporation at the menisci is controlled by vapour-liquid equilibrium according to the  
251 Kelvin equation [27]. The water pervaporated through the membrane was condensed in a liquid  
252 nitrogen cold trap and analyses indicated salt rejections in excess of 99%, confirming that salt ion  
253 solution was mainly retained in the macropores of the substrate of the membrane.

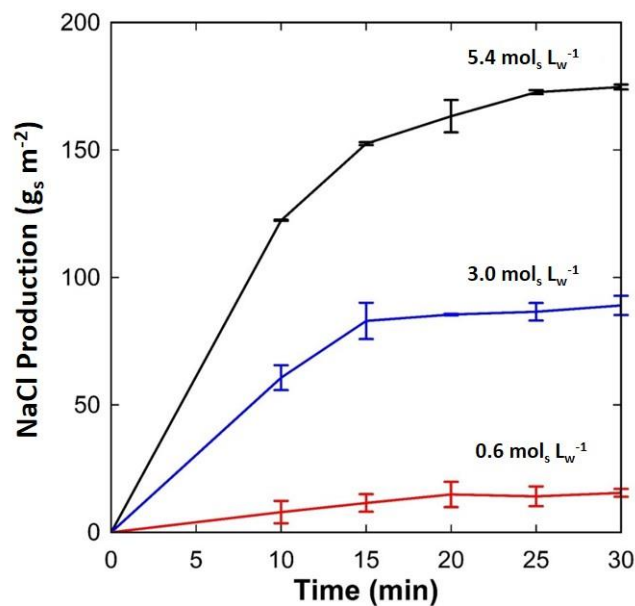
254

255 Upon drying the membrane, induced salt crystallisation on the surface of the mesoporous titania top  
256 layer took place. This process is directly controlled by capillary forces. As the macropores of the  
257 alpha-alumina substrate are interconnected to the mesopores of gamma-alumina interlayers and that  
258 to the mesopores of the titania layer, capillary pressure gradients force the salt ion solution stored in  
259 the substrate to permeate from the macropores to the mesopores. This is the case for two different  
260 saturated porous materials in hydraulic contact with each other and dried, the material with the largest  
261 pores starts to drain first [28]. Upon drying further, capillary forces bring the salt ion solution to the  
262 surface of the titania top layer where water evaporation increases rapidly. As a result, salt ions on the  
263 membrane surface reach supersaturation and lead to salt nucleation and salt growth induction as  
264 evidenced by Fig. 1.

265

266 **3.4 Transport phenomena, salt production and storage coefficients**

267 During the pervaporation stage, salt is being concentrated in the membrane pores ( $c_p$ ) as the process  
 268 is driven by vacuum evaporation of water. A concentration gradient ( $\Delta c$ ) is thus established between  
 269 the solution in the membrane pores and the solution in the feed. Fig. 6 shows the continuous built up  
 270 of NaCl in the membrane pores as a function of time until a maximum salt storage capacity is reached.  
 271 At this maximum capacity, the pores are fully saturated with salt solution and equilibrium is achieved  
 272 between the salt concentration in the feed solution and that in the macropores. In addition, the salt  
 273 production capacity also increased as a function of the NaCl feed concentration. Hence, the transport  
 274 phenomenon in this membrane pore storage mechanism is associated with the salt concentration in  
 275 the feed solution. The driving force for salt storage is at the highest at the beginning of pervaporation  
 276 ( $t=0$ ) and minimum at the maximum storage or saturation time ( $t=t_{sat}$ ). In other words, the membrane  
 277 pore storage mechanism is characterised by a batch process of salt loading.



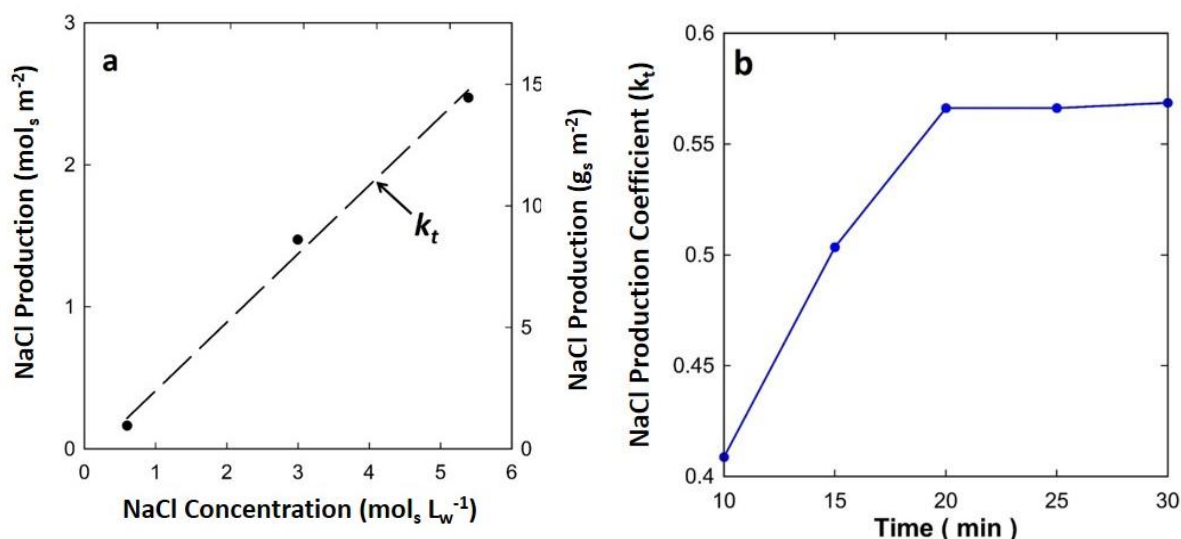
278  
 279 Fig. 6. NaCl production as a function of pervaporation time for a porous membrane tube thickness  
 280 of 2.5 mm for various NaCl feed concentration (0.6, 3.0 and 5.4 mol<sub>s</sub> L<sub>w</sub><sup>-1</sup>). The membranes were  
 281 oven dried at 60 °C for 8 h and RH = 67.3%.  
 282

283 Interestingly, the production of NaCl as a function of the feed concentration fitted well to a linear  
 284 relationship ( $R^2 > 0.99$ ) as demonstrated in Fig. 7a. We define the slope of this linear relationship as a  
 285 salt production coefficient ( $k_t$ ), which provides a fundamental parameter of this novel membrane pore  
 286 storage process. Owing to the batch process characteristics, the salt production coefficients were

287 plotted against time as shown in Fig. 7b, using data from Fig. A2 in the Appendix where all  $R^2 > 0.99$ .  
 288 After 20 min, NaCl accumulation in the pores reached saturation level ( $k_{sat}$ ), suggesting an approach  
 289 to equilibrium when the driving force is no longer significant. These results clearly indicate that the  
 290 mass storage mechanism in the membrane pores of the hydrophilic inorganic membrane follows Eq.  
 291 1 for a given condition, where  $P$  is the membrane surface specific salt production ( $\text{mol}_s \text{m}^{-2}$ ),  $t$  is  
 292 the pervaporation time,  $k$  is the salt production coefficient ( $\text{mol}_s \text{L}_w \text{mol}_s^{-1} \text{m}^{-2}$ ) and  $c_f$  is the feed salt  
 293 concentration ( $\text{mol}_s \text{L}_w^{-1}$ ).

$$P_t = k_t c_f \quad (\text{Eq. 2})$$

295



296

297 Fig. 7. (a) NaCl production versus feed concentration at 30 min pervaporation time, and (b) NaCl  
 298 production coefficient ( $k_t$ ) versus time.  
 299

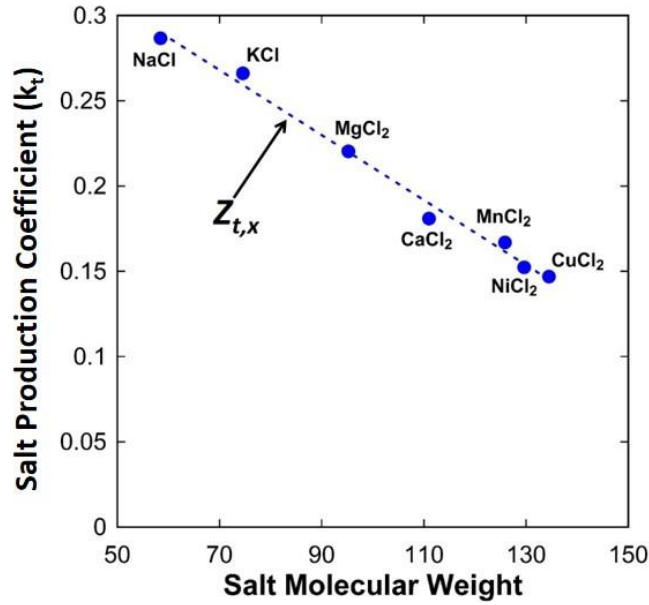
300 Another fundamental parameter for this novel pore storage mechanism is termed the global salt  
 301 production coefficient ( $Z$ ). The  $k_t$  values of the chloride salts in Fig. 8 derived from Fig. 4 were plotted  
 302 against their molecular weights, excluding LiCl which slightly reacted with the membrane to some  
 303 extent. Remarkably, the slope ( $Z$ ) shows a linear relation (also  $R^2 > 0.99$ ), clearly indicating that salt  
 304 production is also a function of the molecular weight of the non-reactive chloride salts tested in this  
 305 work. Therefore, Eq. 2 describes this property, where  $t$  is the pervaporation time,  $k$  is the salt

306 production coefficient and  $m$  is the molecular mass of salt  $x$ . The slope  $Z=-317m_x+187$  for the  
 307 chloride salts tested in this work.

308

309

$$k_{t,x} = Z_{t,x}m_x \text{ (Eq.3)}$$



310

311 Fig. 8. Global salt production coefficient ( $Z_{t,x}$ ) for a series of non-reactive chloride base salts (3 mol  
 312 L<sup>-1</sup> feed solutions at 20 °C) for a pervaporation time of 10 min and microwave drying at 900 W and  
 313 2 min. Salt production coefficient includes hydrated salts.  
 314

315 Essentially salt solutions were stored in the membrane during pervaporation, so the pore storage  
 316 coefficients are volumetric as a function of the membrane surface area and membrane thickness.

317 Hence, the mass storage coefficient ( $S_t$ ) is the mass of salt mainly stored in the macropores of the  
 318 substrate (mol<sub>s</sub> m<sup>-2</sup> m<sup>-1</sup>), per area (m<sup>2</sup>) per membrane thickness  $l$  (m), which can be derived from Eq.

319 2 as follows:

$$S_t = \frac{P_t}{l} \text{ (Eq.4)}$$

321

322 Likewise, the global salt storage coefficient  $GS_{t,x}$  for a membrane thickness  $l$  (m) can be derived from

323 Eq. 3. As the slopes of  $Z_{t,x}$  and  $GS_{t,x}$  remain the same irrespective of the thickness of the membrane,

324 than both global salt production and global salt storage coefficients for chloride hydrates are the same  
325 as follows:

$$326 \quad GS_{t,x} = Z_{t,x} \text{ (Eq. 5)}$$

327

328 In principle, the capability of the membrane to store salt is a function of the membrane specific  
329 structure. Hence, salt production values increase by increasing the thickness of the substrate, or by  
330 increasing the porosity of the substrate provided that membrane flooding is avoided. However, if  
331 increased in salt production are proportional to the feed concentration and/or to the chloride salt  
332 tested, then the slopes may remain the same. This means that the coefficients  $k_t$  and  $Z_t$  may not be  
333 affected by the membrane's specific structure if salt production proportionality is maintained.

334

#### 335 **4. Conclusions**

336 The induced crystallisation of mineral brines using hydrophilic inorganic membranes occurred via a  
337 novel mechanism of membrane pore salt storage during pervaporation. This phenomenon occurred  
338 due to the modulation of salt ion solution via the mesopores of titania and gamma-alumina layers,  
339 thus avoiding pore flooding in the substrate macropores. Fundamental properties of the membrane  
340 pore mass storage were established by determining salt production coefficient for single salts, and a  
341 global salt storage coefficient as a function of the molecular weight of chloride salts. These  
342 coefficients form the basis for the design of industrial plants for processing brines.

343

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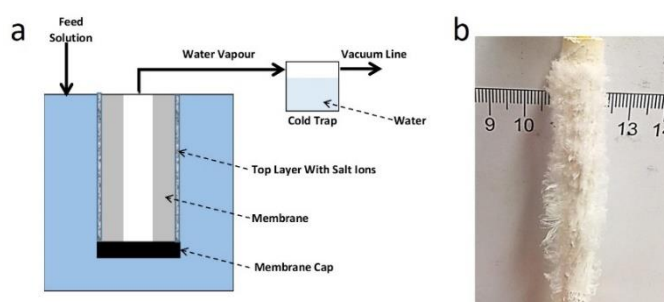
351

## 352 Competing interests

353 The authors declare no competing interests.

354

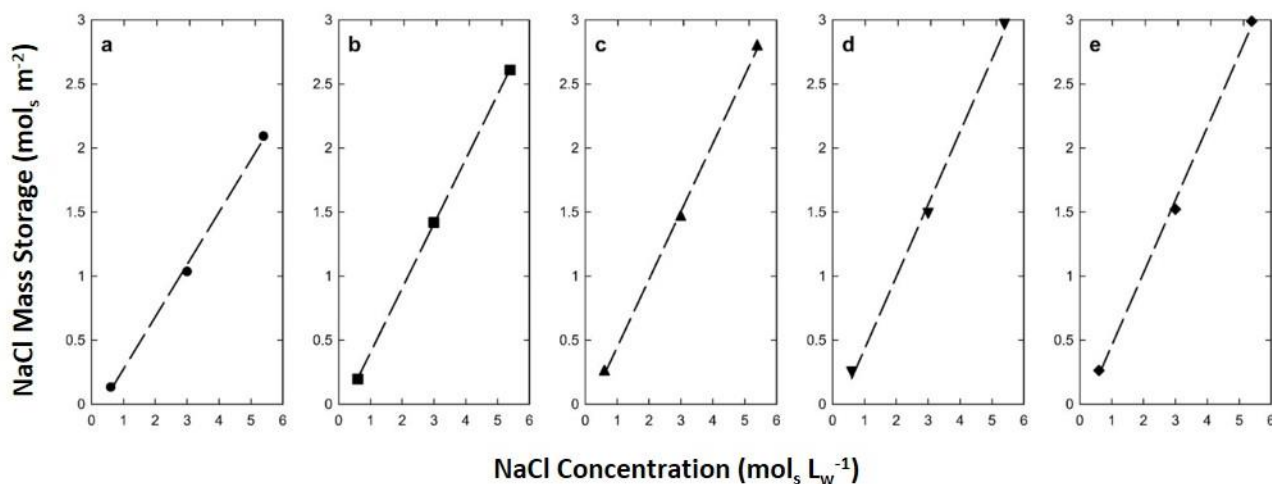
## 355 Appendix



356

357 Fig. A1. (a) Schematic of the pervaporation process and (b) image of an oven-dried membrane.

358



359

360 Fig. A2. Mass storage (average values) versus NaCl concentration for a series of pervaporation  
361 times: (a) 10 min, (b) 15 min, (c) 20 min, (d) 25 min and (e) 30 min where all  $R^2 > 0.99$ .

362

363 The alpha-alumina substrate porosity of 36% was determined from helium pycnometry. The  
364 substrate's pore volume ( $p_{vol}$ ) is 675 mL for a membrane tube with a surface area of  $1 \text{ m}^2$ , 1 cm outer  
365 shell diameter and a wall thickness of 2.5 mm. Table 1 lists the average density ( $\rho$ ) for the NaCl feed  
366 concentrations used in this work. The NaCl densities were determined based soaking conditions of a

367 a membrane with 1 m<sup>2</sup> surface area with a solution in equilibrium with the feed temperature. The  
 368 mass of salt (*M*) stored in the pores of the membrane is determined by  $M = \rho p_{vol}$ . Table A1 shows the  
 369 NaCl mass stored mainly in the macropores of the substrates which are 99.96% of the total porosity.  
 370 The NaCl production results from Fig. 3 are also listed. These results show that theoretical mass of  
 371 NaCl stored in the substrate is always higher than the mass produced per 1 m<sup>2</sup> of membrane surface  
 372 area.

373  
 374 Table A1. Theoretical NaCl mass stored in the membrane pores for a membrane with 1 m<sup>2</sup> of surface  
 375 area and pore volume of 675 mL.

Sol conc. (mol <sub>s</sub> L <sub>w</sub> <sup>-1</sup> )	Sol conc. Wt%	Av. density (g L <sup>-1</sup> )	Membrane Mass sol (g <sub>sol</sub> )	Membrane NaCl mass (g <sub>s</sub> )	Fig. 3 results NaCl mass (g <sub>s</sub> )
0.6	3.4	1022.3	690.4	23.5	16.2
3	14.9	1107.8	748.2	111.5	88.9
5.4	24	1180.4	797.2	191.3	174.0

376

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