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Comparison of Membrane Distillation and Freeze Crystallizer as Alternatives for Reverse Osmosis Concentrate Treatment

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Abstract

Membrane distillation (MD) and freeze crystallizer (FC) were evaluated as alternative reverse osmosis concentrate (ROC) treatment options. A direct contact MD (DCMD) was capable of obtaining 60% water recovery with chemically pretreated ROC. Nevertheless, in repeated cycles, DCMD displayed a trend of reduced water recovery and declining permeate quality. At elevated concentrations, ROC caused scaling and membrane hydrophobicity reduction, indicating reduced membrane life span. On the other hand, FC in three-stage freeze/thaw approach was able to concentrate ROC by 2.3 time, achieving a 57% water recovery with no scaling issues. The fresh ice water quality (total dissolved solids) obtained from FC was within the range of 0.08-0.37 g/L. A brief techno-economic evaluation highlighted advantages and limitations of both options. The efficiency of DCMD as a compact, low thermal process for ROC treatment was compromised by membrane scaling, indicating the necessity for a scaling mitigation pretreatment. This invariably incurs an additional cost. FC was advantageous as a scaling and chemical free process. The high freezing requirement of FC could be met by coupling with refrigerant coolant from liquefied natural gas. Nevertheless, the practical industrial application of FC is inherently restricted due to complex scaling up issues.

25 **Keywords:** Direct contact membrane distillation; freeze crystallizer; reverse osmosis concentrate.

26

27

28 **1. Introduction**

29 Presently reverse osmosis (RO) technology has gained worldwide acceptance for desalination
30 and wastewater treatment. Globally, RO dominates 60% of total desalination plants [1] due to its
31 techno-economic benefits and high quality water production capacity. RO is a pressure-driven process
32 in which a semi-permeable membrane rejects dissolved constituents present in the feed water [2]. The
33 mechanisms of rejection are due to size exclusion, charge exclusion and physical–chemical
34 interactions between solute, solvent and membrane [2,3].

35 In Australia, RO technology has taken a prominent role for saline water treatment to meet the
36 rapidly growing demands of irrigation, domestic water **supply**, mining, coal seam gas (CSG), and
37 power station industry. Presently, Australia has around 10 - 15 major plants and more than 300 small
38 plants using RO technology (**Table S1**) [4-7].

39 Although highly reliable, the major limitation of RO is its relatively low recovery at around
40 35-45%, resulting in large volume of concentrate especially for highly saline feed solutions such as
41 seawater [2]. For coastal plants, RO concentrate (ROC) is discharged back into the ocean. Disposal of
42 ROC containing high salt contents and other chemical compounds could lead to significant
43 environmental issues [3,8]. Mitigation approaches such as dilution are used to reduce ROC salinity
44 prior to ocean discharge as well as dedicated infrastructures such as long and large pipeline for ocean
45 outfall. This incurs an additional operation cost to the RO plant [5,9,10]. For instance, Perth seawater
46 RO plant, one of Australia’s largest coastal RO plant [7], adheres to stringent ocean discharge
47 regulations. This includes 45 times of ROC dilution, post treatment removal of ferric oxyhydroxide
48 flocs from ROC (via a centrifuge and subsequent disposal of the concentrate to landfill) to prevent
49 staining of the white beaches of Cockburn Sound, long pipeline infrastructure as well as constant
50 monitoring of the ocean’s dissolved oxygen level at the discharge vicinity [10,11].

51 For inland RO plants, ROC management is a major challenge as the option of ocean discharge
52 is not available [5,9,11]. The major established inland ROC treatment methods used in Australia are

53 evaporation ponds, deep well injection to aquifer, and brine crystallizer [5,11]. Although low in cost,
54 these technologies are limited for handling high volume flow of ROC, requires large land area and are
55 susceptible to leakage and groundwater pollution [5,9,11]. In the 1980's, only low capacity inland RO
56 plants were applied in Australian mining, and the relatively small ROC volume generated was
57 manageable using evaporation ponds. More recently, the boom in CSG and mining industries resulted
58 in the installation of large treatment plants using RO. For instance, in Queensland, the development of
59 CSG resources in the Surat and Bowen Basins has seen major growth with the state's annual CSG
60 production, surging from 4 petrajoules in 1998/1999 to 285 petrajoules in 2013/2014 [12,13]. CSG
61 extraction generates highly saline wastewater [12,13]. In Australia, RO is predominantly adopted to
62 treat saline CSG wastewater, invariably resulting in substantially large ROC volume. This coincided
63 with greater focus on ROC discharge regulations in Australia.

64 Ideally, achieving close to zero liquid discharge would be the ideal management solution for
65 ROC. One such technology that exhibit promising concentrate treatment is membrane distillation
66 (MD). MD is a thermal membrane distillation process that operates by transporting water vapor to the
67 distillate (permeate) side through the pores of a hydrophobic membrane [14,15]. As a vapor pressure
68 driven process, MD is not significantly affected by salinity, which accentuates its suitability for
69 treating highly saline ROC. Moreover, the vapor mass transfer mechanism in MD potentially offers
70 complete rejection of ions, enabling the production of additional fresh water from ROC. The low
71 thermal requirement (at 50-80 °C of feed temperature) in MD can be met by solar or heat waste
72 integration [15,16], which is an added advantage over other thermal technologies. However, treating
73 hypersaline ROC which contains high amount of dissolved ions in a thermal based membrane process
74 such as MD, may lead to high inorganic ion precipitation. This phenomenon was highlighted by a
75 number of MD studies [17-20]. For instance, Martinetti et al. [18] demonstrated that the water recovery
76 of vacuum-enhanced direct contact MD operated with ROC was limited by precipitation of inorganic
77 ions such as calcium (Ca) based ion precipitation on the membrane surface. Similarly, Naidu et al. [19]

78 observed the susceptibility of MD towards CaSO_4 precipitation. Specifically, these studies identified
79 Ca as the main scalant in ROC, due to its inverse solubility under thermal condition. Ca then serves as
80 nucleation sites for other species such as Na and Mg. Scaling precipitation could potentially limit MD's
81 long-term performance for ROC treatment. Hence, removing Ca from ROC could potentially reduce
82 scaling issues in MD operation. Scaling mitigation techniques such as inorganic pretreatments could
83 enhance the performance of MD [17,20-22]. A few MD studies have evaluated scaling mitigation
84 techniques such as antiscalant [17], chemical softening [20], membrane cleaning and air back washing
85 [21,22]. However, repeated cycles of operation are essential in determining the feasibility of MD for
86 ROC treatment and the effectiveness of pretreatment as well as the implication of additional
87 pretreatment cost.

88 Given the susceptibility of scaling in membrane processes, it is worth evaluating the potential
89 of a non-membrane based technology for ROC treatment. In this regard, freeze crystallization (FC) is
90 a non-membrane based technology that show promise for concentrate treatment. The principle of FC
91 is based on liquid-solid phase in which, fresh water ice forms during freezing, while highly soluble
92 dissolved salts concentrate remains in the liquid phase [23,24]. This leads to the separation of ice and
93 concentrate [24-29]. Nevertheless, a major challenge of FC is the co-adsorption of salts with ice
94 crystals. A large number of small sized ice crystals (ice slurry) are generated in FC, resulting in high
95 specific surface area. These surfaces are usually covered by a slew of salts due to the strong adhesive
96 force between ice and salt concentrate [27-29]. This entails washing to remove the salts. For instance,
97 Chang et al. [28] highlighted that under optimal FC operating condition for seawater, the optional
98 amount of washing water to clean raw ice was about 50% of the raw ice produced. Minimizing washing
99 would enhance FC performance as well as avoid the dilution of concentrate. A potential way of
100 minimizing washing is to reduce the surface area of ice formed. The prospect of treating ROC using
101 FC with minimal washing is explored in this study.

102 This study aims to evaluate the performance of MD and FC as alternative ROC treatment
103 technologies. The potential of pre-treated ROC for improving the performance of MD was considered.
104 Repeated cycles of MD operation was carried out to determine the membrane life span and
105 effectiveness of pre-treatment. The approach of FC with minimal washing requirement was explored.
106 Water recovery ratio, fresh water quality, tendency of scaling development as well as membrane life
107 span were the main factors used in comparing the performance of MD and FC for ROC treatment.

2. Materials and methods

2.1. Direct contact membrane distillation (DCMD)

In this study, MD performance capacity for ROC treatment was evaluated with a bench scale DCMD (**Fig. 1** and **Fig. S1**). In this set-up, an acrylic membrane cell with depth, width, and length of 0.2 cm, 5.0 cm and 8.0 cm (40 cm² effective membrane area) was used. A commercial hydrophobic polytetrafluoroethylene (PTFE) flat sheet membrane (General Electric, US) with a support layer of polypropylene was used. The porosity, average pore size and membrane thickness provided by the supplier were 70–80%, 0.2 μm, and 179 μm, respectively [21]. DCMD experiments were carried out at a moderate feed temperature (T_f) of 55 °C. Deionized (DI) water was used as the cooling/initial permeate solution, which was set at a permeate temperature (T_p) of 25 °C. The bulk temperatures were maintained within the variation of ± 3 °C for all experiments. The feed solution (1.5 L of actual and pretreated ROC) and permeate solution (1.5 L deionized water (DI)) were channelled into the membrane cell at a feed and permeate flow velocity of 1.1 m/s in a counter current mode with a gear pump.

The DCMD operation was carried out up to the point where the initial feed volume (1.5 L) was reduced to around 0.5-0.6 L (achieving 60-65% water recovery) or until a significant permeate flux decline occurred. Three repeated cycles of DCMD operation (cycle 1-3) were carried out using the same membrane. After each cycle, DI water (0.1 L) was flushed at low velocity (0.6 m/s) into the feed module to clean the membrane. At the end of cycle 3, the used membrane was removed from the module for further analysis as described in **Section 2.4.2**.

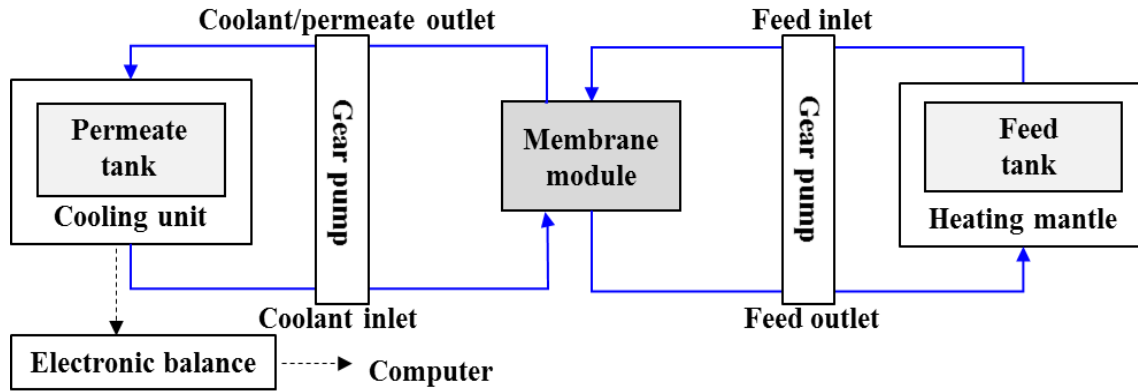


Fig. 1. Experimental setup of DCMD.

2.2. Freeze Crystallizer (FC)

This study used a batch reactor FC set-up (**Fig. 2**), comprising of four reactor tanks (bulk, crystallizer, ice and thawing tank). The bulk ROC (1.5 L) was precooled to 0 °C. The ROC was channeled to a slurry tank (placed in a chiller unit), which was maintained at -8 to -11 °C based on previous studies [24-27] that established the freezing points of salt solution with up to 10% NaCl mass at these temperature ranges (**Fig. S2**). The ROC in the slurry tank was stirred at 300 rpm to promote faster ice growth in suspension, enabling ice slurry formation to float on the top of the tank, while concentrated ROC gravitates to the bottom of the tank (on the principle of higher density of salt to ice) [27,29]. The ice slurry formation was removed periodically and placed in an ice tank and left in the chiller for 10 h to form solid ice slabs. Thereafter, the ice slab was thawed at room temperature on a wired tray with a collection drain at the bottom. The collection drain was equipped with a water quality probe to consistently measure the total dissolved solids (TDS) level of the runoff melting from the ice slab.

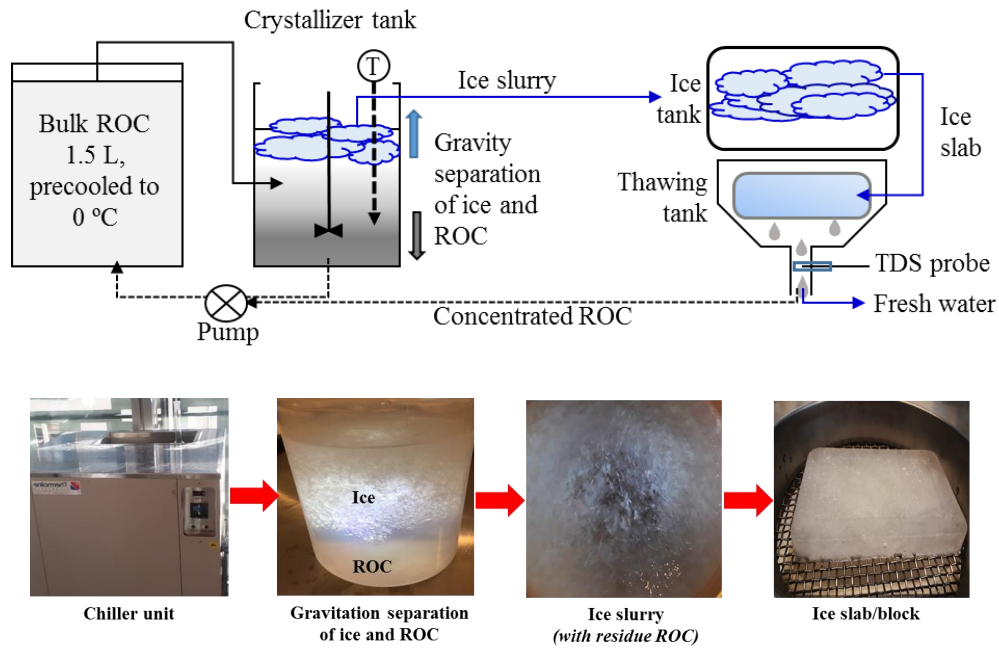


Fig. 2. Batch reactor freeze crystallizer (FC) set-up.

2.3. Feed solutions

2.3.1. Actual ROC

Experiments were carried out using actual ROC obtained from a seawater desalination plant [21,30]. The major ion contents of the ROC is listed **Table 1**. The pH and conductivity of the ROC was 7.9 ± 0.2 and 105.3 ± 0.3 mS/cm respectively.

Table 1 Major ion contents of actual ROC.

Major ion contents	Actual ROC (mg/L)
Ca	894.1
Mg	2571.3
Na	22100.0
K	783.5
Sr	15.6
SO ₄	8051.0
Cl	41400.0

2.3.2. Chemical pretreatment

Based on the prevalent Ca based scaling in MD, the chemical pretreatment focused on Ca removal from ROC. In a batch beaker test, Ca removal rate in ROC was tested using phosphate (as KH_2PO_4), carbonate (as KHCO_3) and hydroxide (as NaOH) based alkalizing chemical agents. All chemical reagents were of analytical grade (Sigma Aldrich) and used without further purification. The results showed that the highest Ca removal rate from ROC was achieved with carbonate based alkalizing agent (as KHCO_3) (**Fig. S3a**). This was in line with a number of studies that established the favourable precipitation of Ca as CaCO_3 in the presence of carbonate based alkalizing agents such as Na_2CO_3 and KHCO_3 [20,31]. At the same time, KHCO_3 batch test, carried out at different doses (1.0 to 4.0 g/L), showed that at a dose of 3.0 g/L onwards, more than 95% Ca removal was achieved (**Fig. S3b**).

Chemical pretreatment experiments were carried out in a multiple stirrer jar test apparatus (PB-900TM, Phipps and Bird, USA) equipped with variable speed control in the range of 0 – 100 rpm at room temperature ($24.5 \pm 0.5^\circ\text{C}$). Based on the batch beaker test, KHCO_3 (3 g/L) was added into jars containing 0.5 L ROC respectively. Solution in the jar was rapidly mixed (100 rpm) for 15 min, followed by slow stirring (50 rpm) for 24 h. Thereafter, the pretreated ROC solution was filtered through a glass microfiber filter with a mean pore size of 1.1 μm (Filtech, Australia).

2.4. Analytical measurements

2.4.1. Water quality and ionic characterization

The pH and conductivity of feed and permeate solutions were measured using HQ40d portable meter (Hach, USA). The concentration of major inorganic cations and anions of the concentrate and original ROC were measured with inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500, Agilent, USA) and Metrohm ion chromatograph (IC) (model 790 Personal IC) respectively.

178 **2.4.2. Membrane characterization**

179 **2.4.2.1. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS)**

180 The morphology of the virgin and used membrane surface was examined using a scanning
181 electron microscope (SEM, Zeiss Supra 55VP). It was coupled with a Bruker XFlash silicon drift
182 detector energy-dispersive spectroscopy (EDS) to obtain the chemical composition information of
183 crystal deposition on the MD membrane. Prior to SEM analysis, the membrane samples were dried in
184 a desiccator and subsequently analysed without any further treatment. SEM imaging was conducted at
185 a voltage of 15 kV while a spot diameter of about 3 nm was used for the EDS analysis.

186

187 **2.4.2.2. Water contact angle**

188 Water contact angle measurement on MD membrane was used to determine the
189 hydrophobicity of the membrane upon MD operation (used MD membranes) and the new MD
190 membranes (virgin membrane). The water contact angle measurement was carried out by sessile drop
191 method using a goniometer (Theta Lite) with 1.8–2.0 mL of MQ water droplet on the dried membrane
192 surface. Measurements were repeated 3 times and the average reading was reported.

193

194 3. Results and discussion

195 3.1. Direct contact membrane distillation (DCMD)

196 DCMD was operated with actual and chemically pretreated ROC. Each set of operation was
197 carried out in three repeated cycles with membrane cleaning after each cycle.

198

199 3.1.1. Actual ROC feed solution

200 3.1.1.1 Permeate flux and quality

201 An initial permeate flux of around 90-92 L/m²h (LMH) (volume concentration factor, VCF
202 1.0) was achieved with actual ROC solution in cycle 1 (**Fig. 3**). Given the small membrane area of
203 0.004 m², this translates to a production rate of 0.36-0.37 L/h. This production rate was in line with
204 values reported by previous DCMD studies using similar temperature difference [18,20,32]. For
205 instance, Duong et al. [32] reported an initial permeate flux of 30-32 LMH (production rate of 0.30
206 L/h with a membrane area of 0.01m²) at a feed temperature of 50 °C. Similarly, Sanmartino et al. [20]
207 obtained a flux of 65-80 LMH (production rate of 0.26-0.32 L/h) with a membrane area of 0.004 m²).
208 Martinetti et al. [18] reported a flux of 40 LMH (production rate of 0.40 L/h) with a membrane area of
209 0.014 m² using a vacuum enhanced DCMD at a feed temperature of 40 °C for treating ROC. A 38-
210 40% permeate flux decline was observed as the feed solution was concentrated from VCF 1.0 to VCF
211 2.6 (60% water recovery). Subsequently, from VCF 2.6 to VCF 2.7, a sharp permeate flux decline to
212 20 LMH occurred. At the end of cycle 1, membrane washing was carried out by circulating 100 ml of
213 DI water into the feed side of the membrane module. In comparison to cycle 1, the following cycles
214 showed lower initial permeate flux (cycle 2 = 85-87 LMH; cycle 3 = 73-76 LMH) as well as the
215 occurrence of sharp permeate flux decline at lower feed concentration rate, corresponding to VCF 2.2
216 (57% water recovery) and VCF 2.0 (51% water recovery) respectively. Further, the permeate
217 conductivity showed an increasing trend, from 10-15 µS/cm in cycle 1, to 62-66 µS/cm in cycle 3. The

flux decline pattern and increased permeate conductivity suggest wetting occurrence by cycle 3 of the DCMD operation.

3.1.1.2 Membrane analysis

The presence of crystals were evident on the SEM images (at high magnification) of the used membrane with actual ROC feed solution compared to the virgin membrane (**Fig. 4**). The EDX analysis detected Ca as the main elements on the used membrane with small peaks of S, Cl, and Na (**Fig 4b**), indicating that CaSO_4 was the main scalant deposited on the membrane. This is in line with a number of MD studies that have highlighted similar results, establishing CaSO_4 as the dominant scalant with ROC as feed solution [17-19]. It is also worth highlighting that the CaSO_4 crystal shape (**Fig 4b**) on the used membrane in this study, was significantly different compared to the generally long needle-like CaSO_4 observed on used MD membranes in other studies [19]. In this study, the crystals on the used membrane appeared to be broken and flatly adhered onto the membrane. This could be due to the repeated cycle of operation on the same membrane. Also, membrane cleaning may have contributed to breaking down of large crystals into smaller crystals but was most likely not effective enough to remove the crystals from the membrane in repeated cycles. Further, the water contact angle of the used membrane ($109.2 \pm 2.4^\circ$) (**Fig. 4b**) showed 22% reduction from the virgin membrane ($140.3 \pm 1.7^\circ$) (**Fig. 4a**), indicating the reduction of membrane hydrophobicity after three cycles.

The results demonstrated the compromised DCMD performance in repeated cycles using ROC, which was primarily attributed to significant CaSO_4 scaling deposition on the membrane as well as reduced vapor pressure with increased feed solution concentration [19,21]. Reducing the inorganic ion contents in ROC could potentially enhance DCMD performance. In light of this, chemical precipitation to reduce the inorganic ion contents in ROC was carried out and thereafter, the performance of DCMD with chemically pretreated ROC was evaluated.

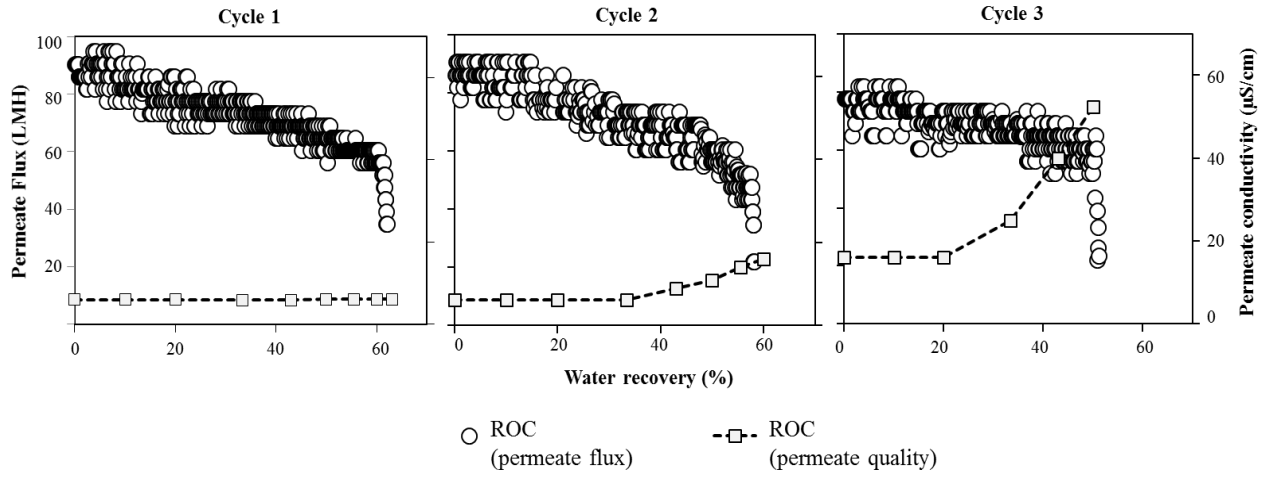
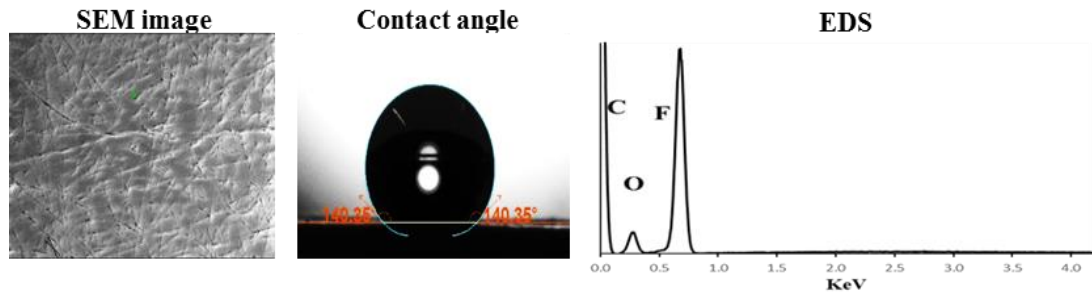
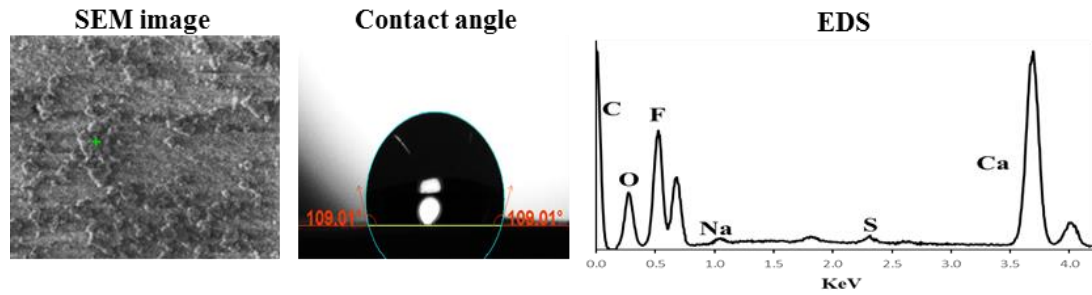


Fig. 3. Performance of DCMD with actual ROC in terms of permeate flux and permeate quality in three repeated cycles ($T_f = 55\text{ }^{\circ}\text{C}$, $T_p = 25\text{ }^{\circ}\text{C}$).



(a)



(b)

Fig. 4. Membrane analysis (SEM image, EDS spectrum and contact angle) of (a) virgin and (b) used ROC membrane.

3.1.2. Chemically pretreated ROC feed solution

Chemical softening/precipitation enabled to reduce the inorganic ion contents in ROC, achieving more than 95% reduction of Ca and Sr and around 41% reduction of Mg (**Table 2**). The high reduction of Ca and Sr was attributed to its precipitation as CaCO_3 and SrCO_3 [20,31]. The high solubility limit of Na resulted in minimal changes while, the significant increase of K in the pretreated ROC was due to KHCO_3 , the chemical agent used for the pre-treatment.

Table 2 Comparison of major ion contents in actual ROC and chemically pretreated ROC.

Major ion contents	ROC (g/L)	Pretreated ROC (g/L)
Ca	894.1	40.2
Mg	2571.3	1522.7
Na	22100.0	22100.0
K	783.5	2411.0
Sr	15.6	0.3

3.1.2.1 Permeate flux and quality

DCMD performance with pretreated ROC in cycle 1 and 2, was considerably improved compared to actual/untreated ROC. This was evident in terms of achieving more stable permeate flux up to a water recovery rate of 60% while maintaining good permeate quality (permeate conductivity remained low within the range of 10-15 $\mu\text{S}/\text{cm}$) (**Fig. 5a**). Nevertheless, by cycle 3, a trend of significant permeate flux decline and permeate conductivity increment was observed, similar to the performance with actual/untreated ROC.

3.1.2.2 Membrane analysis

The presence of significant amount of rhombohedron and hexagon shaped crystals likened to carbonate crystals [33] were evident on the SEM images of the used MD membrane with chemically

269 pretreated ROC (**Fig. 5b**). In line with this, the EDX analysis of the used membrane showed significant
270 Na peak as well as visible peaks of Mg, K and Cl. Element peaks related to Ca and S were not detected,
271 unlike the used membrane with actual ROC (**Fig. 4b**). This suggest that Na_2CO_3 precipitation most
272 likely occurred during the DCMD operation with pretreated ROC, which deposited on the membrane.

273 Overall, the results showed that chemical pretreatment was effective in removing most Ca from
274 ROC, which systematically eliminated CaSO_4 formation, a dominant scalant in MD operation. As a
275 result of this, DCMD performance with chemically pretreated ROC achieved improved performance
276 in the first two cycles. Moreover, the 8.3% membrane hydrophobicity reduction ($128.7 \pm 3.5^\circ$) of used
277 membrane with pretreated ROC (**Fig 5b**) was considerably lower to the 22% membrane
278 hydrophobicity reduction of the used membrane with actual ROC (**Fig. 4b**). This indicated that the
279 inorganic chemical pretreatment does play a role in improving MD membrane scaling to a certain
280 degree. Nevertheless, by cycle 3, DCMD performance with pretreated ROC was still compromised
281 due to carbonate based salt precipitation. The presence of carbonate was due to the addition of KHCO_3
282 during chemical pre-treatment. The results indicated, a simple chemical pre-treatment was not
283 sufficient for eliminating scaling issues in MD operation on long-term basis, and therefore more
284 complex alkalizing chemical combinations may have to be considered. Further, exploring other
285 inorganic pretreatment options such as NF or anti scalants may be beneficial in identifying a more
286 suitable scaling mitigation approach for MD. However, the additional cost incurred to the MD
287 operation due to complex pretreatment must be given due consideration.

288 Given that ROC is a complex solution containing high inorganic ions, membrane scaling is
289 inevitable, especially in a thermal membrane process such as MD. In view of this, the potential of a
290 non-membrane technology for ROC treatment, freeze crystallizer (FC) was evaluated in the subsequent
291 section.

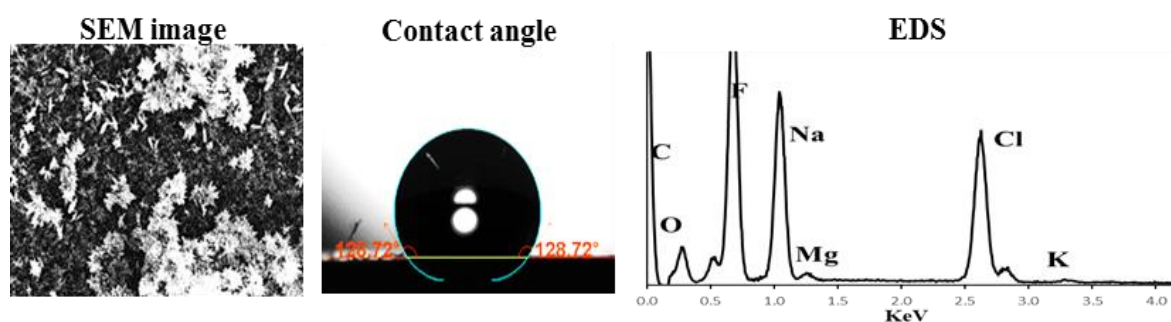
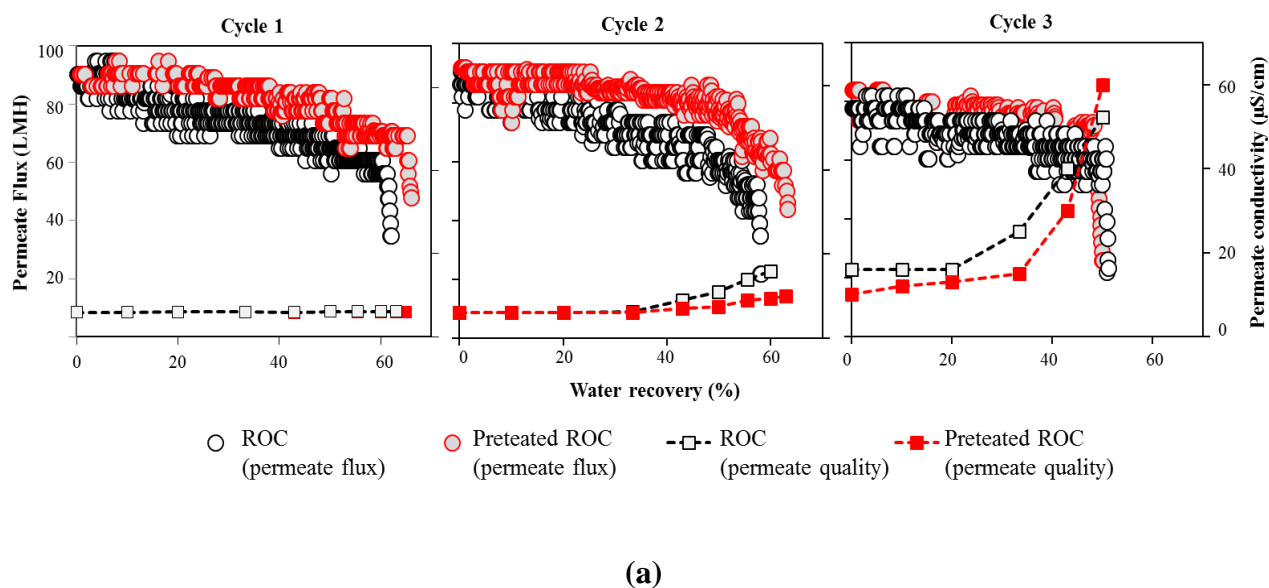


Fig. 5. Performance of DCMD with chemically pretreated ROC (a) permeate flux and quality comparison with actual ROC for three cycles ($T_f = 55\text{ }^{\circ}\text{C}$, $T_p = 25\text{ }^{\circ}\text{C}$) (b) used membrane analysis after cycle 3.

3.2. Freeze Crystallizer (FC)

The performance of FC (as a non-membrane technology) for ROC treatment was evaluated in a three-stage freeze/thaw system (**Fig. 6**). The ROC was pre-cooled in a freezer to $0.1 \pm 0.2\text{ }^{\circ}\text{C}$ before being transferred into a crystallizer tank. In the first FC stage, ROC in the crystallizer tank was placed in a chilling unit at a temperature of $-7.5 \pm 0.2\text{ }^{\circ}\text{C}$ and stirred at a speed of 300 rpm. After a specified time duration (1.0 h), the ice slurry (containing fresh water with salt residues) was transferred to an ice container and left to freeze at $-4.0 \pm 0.2\text{ }^{\circ}\text{C}$ for 10 h to form solid ice slabs. The thawing of ice slabs was

303 carried out at room temperature on a mesh wired tray with a collection drain at the bottom. The quality
304 of the melted runoff from the ice slab was measured consistently with a TDS probe. The onset run-off
305 from the ice slab contained concentrated salt, which was channelled back to the bulk ROC tank for a
306 second freeze/thaw stage. Meanwhile, melted ice with TDS below 0.5 g/L was collected in a separate
307 container as fresh water. The initial concentrated salt runoff was likely due to the formation of unfrozen
308 salt pockets in the ice slab that melted at the onset of thawing at increased temperature (room
309 temperature). This phenomena was established by a number of studies that evaluated the warming of
310 sea ice [34,35]. During the freezing of ice slurry into ice slabs, the ROC residue in the ice slurry
311 developed fine channels of unfrozen concentrate at the base of the ice mass. As the ice slurry layer
312 became colder and firmer, these channel pathways were partially blocked by the firmly formed ice
313 layer, resulting in isolated concentrate pockets in the fully formed ice slab. Warming the ice slab at
314 room temperature during the thawing cycle enabled to melt the fragile crystal boundaries containing
315 concentrated salt pockets prior to the melting of the core ice slab. This allowed concentrated ROC to
316 flow from the ice to the collection drain. The freeze/thaw approach of a solid ice slab was effective at
317 concentrating and separating ROC from fresh ice. More importantly, this approach enabled to
318 eliminate water washing columns used in freeze crystallizer processes [24-29]. The washing required
319 additional usage of water and diluted the ROC while the freeze/thaw enabled to concentrate the ROC.

320 The approach of freeze/thaw in stages was adopted because a single 1.5 L crystallizer could
321 not achieve the same concentration as that obtained by cascading concentration procedure. Moreover,
322 the solid content of more than 35% ice during the crystallization process made the separation of ice
323 slurry from the ROC extremely difficult as the entire crystallizer was filled with ice from top to bottom.
324 Through the multiple stage approach, ice slurry could be drained from the crystallizer at different time
325 duration (1.0 h to 3.0 h), ensuring no more that 30-35% ice slurry formed at one time in the tank.
326 Further, multiple stages enables to control the freezing temperature based on the solution concentration
327 (- 8.0 °C to -11.0 °C). Based on the initial salt concentration of 55-59 g/kg (5.5-5.9% NaCl), the

freezing point was set at -7.5 ± 0.5 °C (**Fig. S2**). However, as ice slurry was separated from the ROC, the remaining ROC solution became more concentrated. The freezing point was therefore further depressed as depicted in the phase diagram (**Fig. S2**) [28]. The second FC stage constituted of higher concentration of ROC and therefore the freezing temperature and time duration was increased to -9.0 ± 0.3 °C and 2.5 h. Likewise, a third FC stage was carried out in the same procedure with an increased freezing temperature and time duration of -10.5 ± 0.3 °C and 3.0 h respectively.

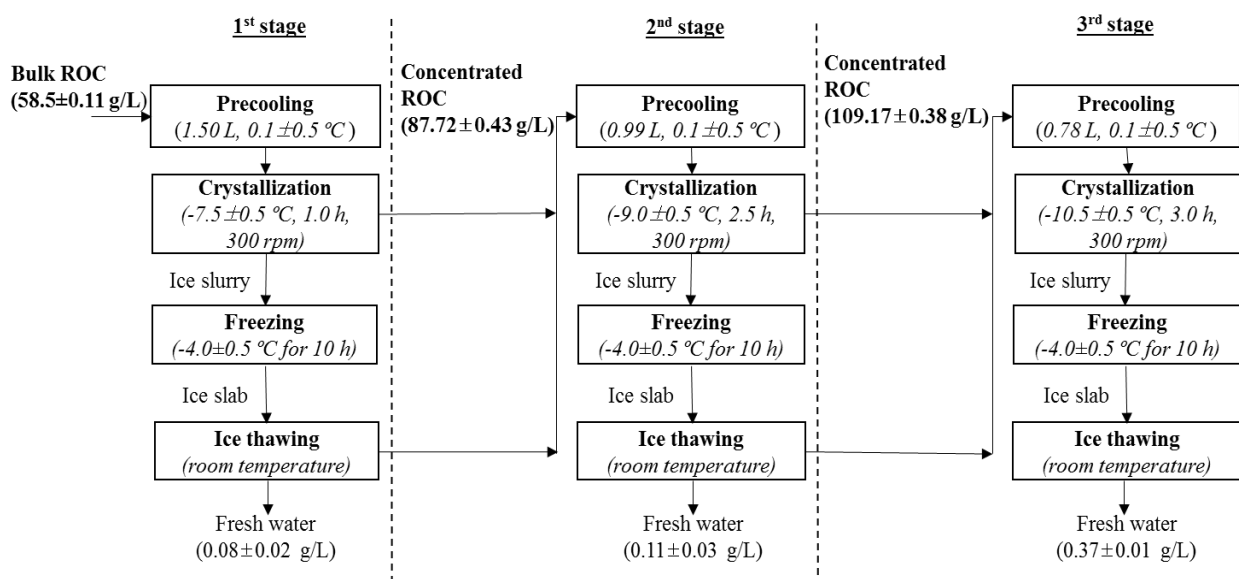


Fig. 6. FC treatment with ROC using multi stage freeze/thaw approach.

3.2.1. Ice/fresh water recovery rate

Upon final FC stage, the actual ROC solution with an initial TDS of 58.5 g/L was concentrated by 2.3 times, achieving a final TDS of 136.2 g/L. In line with this, 57% water recovery was obtained with fresh water quality in the range of 0.08 to 0.37 g/L (**Table 3**).

The FC enabled to concentrate the actual ROC by 2.3 times. Nevertheless, negligible salt crystallization occurred. This could be related to the high solubility of dissolved ion constituents in ROC that did not result in any salt crystallization with only 2.3 times of concentration. Comparatively, a FC study using a solution containing only CuSO_4 enabled to obtain 21 kg/h/m³ of CuSO_4 salt at the

end of the operation [36]. Similarly, Randall et al. [27] reported on the capacity of FC to achieve highly pure CaSO_4 and Na_2SO_4 salts along with potable water from highly concentrated ROC. Previous studies have highlighted that factors such as ice seeding, stirring speeds, reactor design and hybrid integration can potentially enhance FC performance [24,26,27]. It is worth exploring these factors in detail to enable to achieve higher ROC water recovery rate with FC as well as recover valuable elements, which in turn, could offset the operation cost of FC.

Table 3 Three stage FC operation (Initial ROC volume =1500 ml; TDS = 58.51 g/L).

	End of stage 1	End of stage 2	End of stage 3
ROC volume (ml)	987.5±1.5	772.0±1.4	640.3±1.0
Fresh water volume (ml)	500.2±1.0	204.5±1.2	127.0±1.5
Fresh water TDS (g/L)	0.08±0.02	0.11±0.03	0.37±0.01
ROC TDS (g/L)	87.72±0.43	109.17±0.38	135.24±0.38

3.3. Techno economic comparison of DCMD and FC for ROC treatment

DCMD and FC show promising performance for ROC treatment, given that both the systems were able to produce additional fresh water from ROC (57-60% water recovery). In this regard, FC offers a number of advantages for ROC treatment such as a chemical-free operation that is not limited by scaling. In comparison, to achieve the same water recovery rate, DCMD was susceptible to scaling and membrane wetting which suggest the limitation of the membrane life-span in long term operation. Further, FC only requires easy maintenance as a non-membrane process and simple construction materials as a system that is not influenced by corrosion. Nevertheless, in spite of the advantages that FC offer, it must be acknowledged that the major challenges of FC is the difficulty to separate ice slurry from the ROC solution and co-adsorption of salts on the ice crystal surface, which significantly

compromised its efficiency and thus limits its practical application. On the other hand, as a membrane process, DCMD offers a practical, reliable and compact operation.

Given that both DCMD and FC exhibit advantages and limitations, a brief techno economic comparison was carried out based on factors such as energy requirement, production capacity and recovery rate.

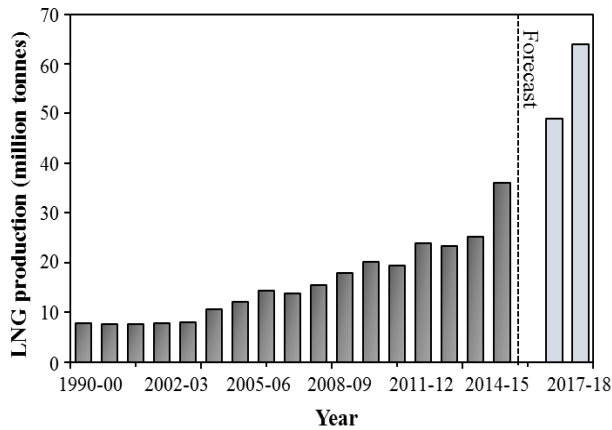
3.3.1. Energy requirement

In terms of energy requirement, it is well established that the moderate thermal/heating requirement of DCMD operation in the range of 50 to 80 °C makes it possible for an integration with alternative heat/energy sources such as solar and waste heat. For instance, Banat and Jwaied [16] reported on the capacity of a large pilot scale MD coupled with solar to obtain up to 0.5 kL/day water production. Recently, Schwantes et al. [37] demonstrated the potential of operating three pilot-scale parallel multi MD modules for seawater desalination with diesel waste heat and solar collector at design capacities of 3.5–5.0 kL/day. This factor substantially reduces the energy requirement for MD operation, making it an attractive option for ROC treatment.

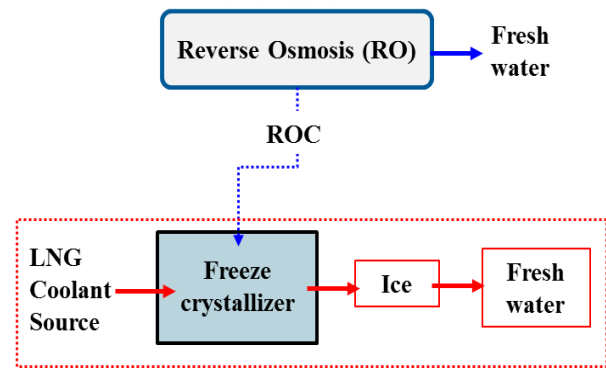
Meanwhile, detail energy requirement of FC process has not been widely evaluated and various assumptions are used in estimating the energy requirement of the process, resulting in varying energy values. For instance, Van der Ham et al. [36] used eutectic based FC with cooled disk column crystallizer for treating wastewater containing NaNO₃ and CuSO₄, and reported energy requirements in the range of 1037 - 1282 kJ/kg. Meanwhile, Attia et al. [38] indicated that around 420 kJ/kg was required to remove salt and produce 1 kg of fresh water using a new efficient FC system.

The high freezing requirement is indicated to be one of the major limitation of FC process. The potential of coupling FC with alternative coolant waste source such as liquefied natural gas (LNG) would enable to reduce its energy requirement [28,39]. This is especially relevant in Australian context due to the substantial growth of LNG production in recent times [40] (Fig. 7a). Natural gas is converted

into LNG by compression and cooling at -160°C to -200°C . Freeze crystallizer could be coupled to the LNG refrigerant coolant source (**Fig. 7b**), given that majority of LNG plants are located on sea coast [41].



(a)



(b)

Fig. 7. Relationship of LNG production and FC on the basis of (a) projected LNG production increment trend in Australia [40] (b) potential coupling of LNG refrigerant coolant with FC.

3.3.2. Recovery rate

FC was able to achieve a 56-57% water recovery with ROC. Nevertheless, a multistage approach was required to obtain this rate of recovery. On the other hand, DCMD was able to concentrate the ROC, achieving an average 60% water recovery with an efficient single stage compact system. In DCMD, the presence of membrane play an important role in enabling an efficient heat and mass transfer of the water vapour, resulting in a competent operation to produce high quality fresh water from ROC. However, it was also the presence of membrane that compromised the DCMD performance attributed to scaling. Further, the results of this study indicated that the MD water recovery was reduced in repeated cycles of operation and the occurrence of wetting (declined permeate quality and membrane hydrophobicity reduction) strongly suggest the compromised lifespan of the membrane for a long-term MD operation with ROC treatment. Chemical pretreatment evaluated in

this study did not effectively mitigate the scaling issue in long term MD operation. Perhaps, the scaling effect could be mitigated by exploring other methods such as NF or antiscalant. Nevertheless, the additional cost associated with such pretreatments must be given due consideration.

FC on the other hand, was not susceptible to scaling and hence required no pretreatment. Further, the concentration of specific elements in the final concentrated ROC varied in FC from that in DCMD (using actual and pre-treated ROC) (**Table 4**). For instance, the final MD and pretrated MD showed mass reduction/losses of elements such as Ca, Mg, Li and Sr and this was attributed to the initial removal during inorganic pre-treatment (for the pretreated ROC) as well as salt co-precipitation of these elements during thermal MD operation. Contrarily, as a freezing process, FC managed to concentrate these elements to a higher level without any mass losses. This factor is an added advantage for subsequent selective extraction of these elements by methods such as ion exchange adsorbents upon FC. Extraction of valuable elements such as Rb, Li, Sr and Mg could offset the ROC operating cost as indicated in our recent papers [21,42].

Table 4 ROC ion contents (as mass in mg) upon DCMD and FC operation.

Mass (mg)	Treatment process	Ca	Mg	Sr	Li	Rb
Initial ROC		1341.1	3856.7	23.4	0.6	0.3
Final ROC	Upon FC	1340.0	3853.0	23.4	0.6	0.3
	Upon DCMD (with ROC)	988.7	2971.3	15.3	0.4	0.3
	Upon DCMD (with pretreated ROC)	50.3	1978.4	<0.05	0.2	0.3

Presently, only few researchers have evaluated and reported the operation cost of MD and FC [15,24,29]. This is because both these technologies are still under research evaluation and not fully applied in industrial scale. Therefore, a number of assumptions are used to compute the cost of these processes. This has somewhat resulted in a wide dispersion in the cost value estimation. The operation cost of freeze desalination, specifically FC has not been evaluated in detail thus far. A few studies have

429 indicated the operating cost of freeze desalination in the range of \$0.90-0.93/m³. This was based on
430 the price indication of using electricity power consumption [24,29]. Meanwhile, MD operation cost
431 have been indicated to be as low as \$0.64 -0.93/m³ when using low grade heat or alternative energy
432 source. Energy requirement is one of the main cost of MD operation, which can be overcome by
433 alternative energy source. However, apart from energy, the membrane cost is another factor that must
434 be considered in MD. Generally, MD membrane cost is estimated on the basis of average 15-20%
435 membrane replacement rate per year [15]. Given the results of this study, membrane replacement may
436 have to be more frequent. Invariably, this would incur additional cost to the MD operation process.

437 This evaluation proved the effectiveness of both DCMD and FC for ROC treatment.
438 Nevertheless, there are some inherent issues that limits the effective of these processes. Although the
439 principle and performance of MD and FC have been widely evaluated on laboratory basis, both these
440 processes still do not have significant commercial uptake. A major reason is the operation complexity
441 that limits the performance capabilities of these processes in large scale set-ups. More research focus
442 must be carried out to overcome these factors.

4. Conclusion

The performance of DCMD and FC was evaluated as potential alternative treatment technology for ROC. The results showed that:

- DCMD was able to achieve 60% water recovery of untreated ROC. However, in repeated cycles of operation, prevalent CaSO_4 scaling and wetting occurred;
- Chemical pretreatment enabled to reduce Ca content in ROC by more than 95%. Enhanced DCMD performance was observed initially (cycles 1 and 2) with chemically pretreated ROC compared to its performance with untreated ROC. However, in subsequent cycles, DCMD performance depreciated due to carbonate based salt precipitation on the membrane;
- FC in multi stage freeze/thaw approach achieved 56-57% water recovery with good quality fresh water ice (TDS less than 0.08 – 0.37 g/L);
- A techno economic comparison of FC and DCMD showed that both the options exhibit benefits and limitations for ROC treatment. DCMD was advantageous as a compact efficient membrane system with the limitation of scaling and related issues of frequent membrane maintenance and replacement. FC was advantageous as a chemical free process that was insensitive to scaling. In Australian context, the potential of coupling FC with LNG refrigerant coolant would be an added advantage. Nevertheless, the challenge of separating ice slurry from ROC limits the efficiency of FC for practical implementation. Further, the FC process took almost 2 days to achieve 57% water recovery. Process design improvement is necessary to reduce the FC operation duration.

Acknowledgments

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Supporting information

**Comparison of Membrane Distillation and Freeze Crystallizer as Alternatives for
Reverse Osmosis Concentrate Treatment**

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The supporting information provides additional detail as following:

583 **Table S1** List of major RO plants in Australia [1-4].

Plant location	Type/Purpose	Capacity(ML/day)	Commissioned date
Perth, Western Australia (WA)	Seawater RO	143	2006
Southern Plant, WA	plants	150	2012
Gold Coast, Queensland		250	2009
Adelaide, South Australia		270	2012
Kurnell, NSW		246	2010
Wonthaggi, Victoria		450	2012
Townsville, Queensland	Inland RO related	10	2006
Cape Preston, WA	to mining, CSG	140	2013
Woleebee Creek, Northern Treatment Plant, Queensland	and power plant industry	100	2014
Kenya Treatment Plant, Chinchilla, Queensland		100	2011
Talinga, Eastern Treatment Plant, Queensland		20	2013
Condabri, Eastern Treatment Plant, Queensland		40	2013
Spring Gully, Eastern Water Treatment Plant, Queensland		12	2007
Reedy Creek		40	2015
Fairview ROP2		20	2011

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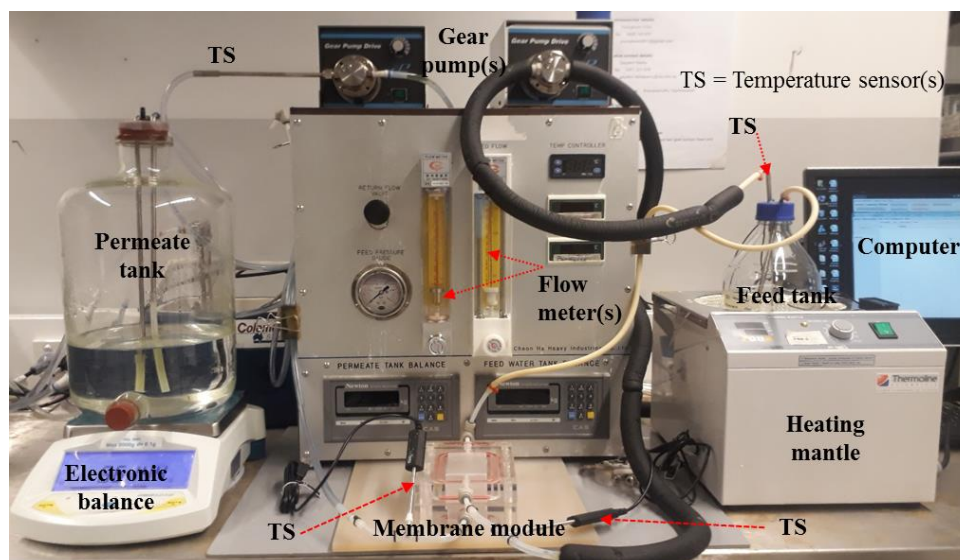
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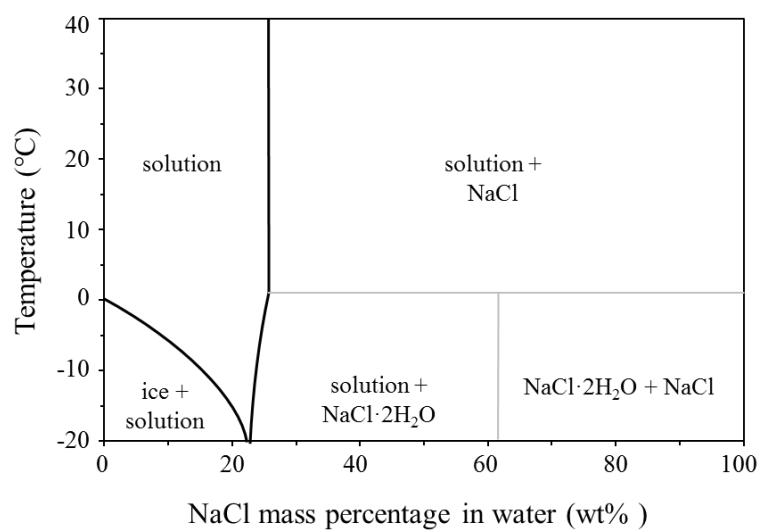
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592 **Fig. S1.** Photo illustration of DCMD experimental setup.

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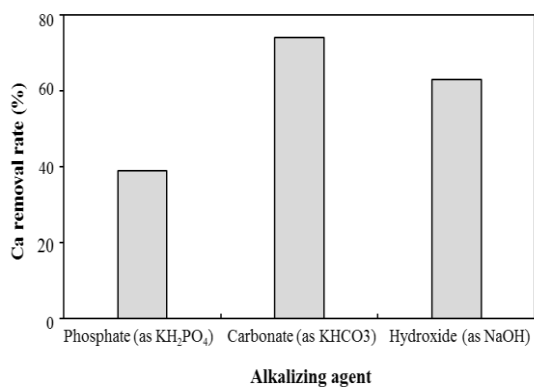
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595 **Fig. S2.** Phase diagram of binary salt-water mixture showing the freezing points based on mass
 596 percentage of NaCl [5].

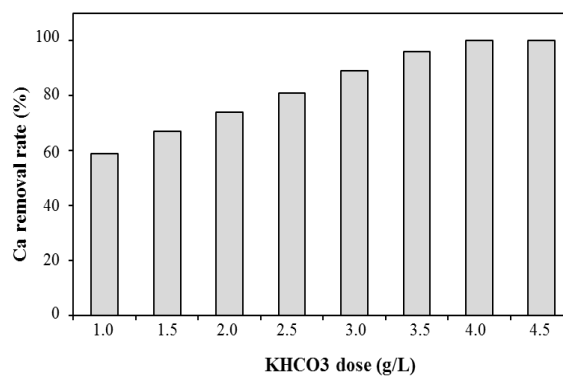
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(a)



(b)

600 **Fig. S3.** Batch beaker test of Ca reduction rate in ROC using (a) different alkalizing agent (2 g/L) and
 601 (b) different doses of KHCO_3 (100 ml ROC solution at $24.5 \pm 0.5^\circ\text{C}$ for a duration of 24 h).

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Supplementary References

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