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I certify that the work in this thesis has not previously been submitted for degree nor has it been submitted as part of requirement for a degree except as fully acknowledge within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information source and literature used are indicated in the thesis.

This research is supported by the Australian Government Research Training Program (RTP).

Signature of Candidate

YOUNGKWON CHOI

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JOURNAL ARTICLE PUBLISHED OR SUBMITTED


* Articles related to the Thesis. ** Publications made during the PhD candidature including articles not entirely related to the Thesis.

CONFERENCE PAPERS AND PRESENTATIONS


Presentation made during the PhD candidature including proceedings, oral and poster presentations.
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGMD</td>
<td>Air gap membrane distillation</td>
</tr>
<tr>
<td>CG</td>
<td>Concentration gradient</td>
</tr>
<tr>
<td>CG ratio</td>
<td>Concentration gradient ratio ($C_{\text{Bottom}}/C_{\text{Top}}$)</td>
</tr>
<tr>
<td>CI</td>
<td>Concentration increase ($C_t/C_0$)</td>
</tr>
<tr>
<td>CP</td>
<td>Concentration polarization</td>
</tr>
<tr>
<td>Cr</td>
<td>Crystallizer</td>
</tr>
<tr>
<td>CSD</td>
<td>Crystal size distribution</td>
</tr>
<tr>
<td>DCMD</td>
<td>Direct contact membrane distillation</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DiPA</td>
<td>Diisopropylamine</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
</tr>
<tr>
<td>F-SMDC</td>
<td>Fractional-submerged membrane distillation crystallizer</td>
</tr>
<tr>
<td>GOR</td>
<td>Gain output ratio</td>
</tr>
<tr>
<td>HF</td>
<td>Hollow fiber</td>
</tr>
<tr>
<td>HOC</td>
<td>Hydrophobic organic compound</td>
</tr>
<tr>
<td>IP</td>
<td>Ionic production</td>
</tr>
<tr>
<td>KCuFC</td>
<td>Potassium copper hexacyanoferrate</td>
</tr>
<tr>
<td>LEP</td>
<td>Liquid entry pressure</td>
</tr>
<tr>
<td>LMW</td>
<td>Low molecular weight</td>
</tr>
<tr>
<td>MC</td>
<td>Membrane contactor</td>
</tr>
<tr>
<td>MD</td>
<td>Membrane distillation</td>
</tr>
<tr>
<td>MDC</td>
<td>Membrane distillation crystallization</td>
</tr>
<tr>
<td>MSF</td>
<td>Multi-stage flash</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>OD</td>
<td>Osmotic membrane distillation</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
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PW  Produced water
R   Recovery ratio
RC  Reaction crystallization
RO  Reverse osmosis
SGMD Sweep gas membrane distillation
SGPW Shale gas produced water
SWRO Seawater reverse osmosis
S-DCMD Submerged-direct contact membrane distillation
S-MD Submerged-membrane distillation
S-VMD Submerged-vacuum membrane distillation
S-VDCMD Submerged-vacuum enhanced direct contact membrane distillation
TG  Temperature gradient
TOC Total organic carbon
TP  Temperature polarization
VCF Volume concentration factor
VDCMD Vacuum enhanced direct contact membrane distillation
VMD Vacuum membrane distillation
VMDC Vacuum membrane distillation crystallization
ZLD Zero liquid discharge
### LIST OF SYMBOLS

<table>
<thead>
<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>C</td>
<td>Concentration</td>
</tr>
<tr>
<td>$C_{Bottom}$</td>
<td>Concentration at the bottom portion in F-SMDC</td>
</tr>
<tr>
<td>$C_f$</td>
<td>Concentration at feed solution side</td>
</tr>
<tr>
<td>$C_{fm}$</td>
<td>Concentration on membrane surface in feed side</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Concentration in permeate stream</td>
</tr>
<tr>
<td>$C_t$</td>
<td>Concentration at specific time</td>
</tr>
<tr>
<td>$C_{Top}$</td>
<td>Concentration at the top portion in F-SMDC</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Initial concentration</td>
</tr>
<tr>
<td>J</td>
<td>Flux</td>
</tr>
<tr>
<td>$J_t$</td>
<td>Flux at specific time</td>
</tr>
<tr>
<td>$J_0$</td>
<td>Initial flux</td>
</tr>
<tr>
<td>$K_{sp}$</td>
<td>Solubility product constant</td>
</tr>
<tr>
<td>m</td>
<td>Mass</td>
</tr>
<tr>
<td>$m_t$</td>
<td>Mass at specific time</td>
</tr>
<tr>
<td>$m_0$</td>
<td>Initial mass</td>
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<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Temperature of coolant in condenser</td>
</tr>
<tr>
<td>$T_f$</td>
<td>Temperature of feed solution</td>
</tr>
<tr>
<td>$T_{fm}$</td>
<td>Temperature on membrane surface in feed side</td>
</tr>
<tr>
<td>$T_p$</td>
<td>Temperature of permeate</td>
</tr>
<tr>
<td>$T_{pm}$</td>
<td>Temperature on membrane surface in permeate side</td>
</tr>
<tr>
<td>$P_f$</td>
<td>Hydraulic pressure of feed solution</td>
</tr>
<tr>
<td>$P_p$</td>
<td>Hydraulic pressure of permeate</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>Q</td>
<td>Volumetric flow rate</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>( v )</td>
<td>Flow rate</td>
</tr>
<tr>
<td>( v_P )</td>
<td>Flow rate of permeate stream</td>
</tr>
<tr>
<td>( V_{\text{Reactor}} )</td>
<td>Volume of reactor</td>
</tr>
<tr>
<td>( V_{\text{Total,permeate}} )</td>
<td>Total amount of permeate produced</td>
</tr>
<tr>
<td>( \Delta P )</td>
<td>Vapor pressure gradient</td>
</tr>
<tr>
<td>( \Delta t )</td>
<td>Time difference</td>
</tr>
<tr>
<td>( \Delta T )</td>
<td>Temperature difference</td>
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ABSTRACT

Seawater reverse osmosis (SWRO) brine management is an important component in sustainable desalination. Improving additional water production from brine with resource recovery can substantially enhance the overall efficiency of desalination process. SWRO plants generate a large amount of concentrated brine as the recovery rate from RO is still limited to 30-50%. Recently, membrane distillation (MD) has emerged as one of the alternative technologies for systematic reduction of the amount of brine as it leads to the additional production of high-quality water. MD process is driven by vapor pressure between high temperature feed solution and low temperature permeate stream. The vapor evaporated from the feed solution to permeate stream is transported through a porous hydrophobic membrane. MD can lead to the treatment of high concentration and zero liquid discharge (ZLD) as there is no hydraulic pressure restriction in MD. Other aspect of MD is the concentration of the feed solution, resulting to a supersaturation condition of salt present in SWRO brine. It enhances the potential of resource recovery in crystal form. MD can thus be combined with a crystallization technique known as membrane distillation-crystallization (MDC). In MDC process, there are two streams produced: the high-quality water and crystals as resource. MD concentrates the feed solution continuously via the production of clean water from feed solution. This makes a favorable condition for forming crystals. Also, the extraction of salt by crystallization from feed solution mitigates the adverse influence of high concentration on mass transfer in MD.

This research focused on the investigation of hybrid systems with submerged-membrane distillation (S-MD) for resource recovery and producing additional water recovery from SWRO brine. In this study, S-MD was coupled with other technologies such as crystallization and adsorption technologies to achieve resource recovery and volume minimization of SWRO brine.
A new concept of MDC named in this study as fractional-submerged membrane distillation crystallizer (F-SMDC) was investigated to improve the water recovery and resource recovery simultaneously.

Performance of S-MD with different configuration in treatment of SWRO brine

S-MD offers an additional advantage of a compact system compared to cross-flow MD. The performances of three different S-MD configurations were evaluated in this study, namely; submerged direct contact membrane distillation (S-DCMD), submerged vacuum direct contact membrane distillation (S-VDCMD) and submerged vacuum membrane distillation (S-VMD) for SWRO brine treatment. A 13-77% higher water flux was obtained by S-MDs with incorporation of vacuum (S-VMD and S-VDCMD) compared to S-DCMD due to higher driving force. Evaluation on the influence of feed concentration and permeate temperature revealed that S-MD with high vacuum was significantly affected by feed concentration. Meanwhile S-DCMD was severely affected by feed temperature losses, due to the membrane pore crystallization formation. Moreover, the crystallization on the membrane surface was influenced by the presence of vacuum pressure. A repeated cycle of S-DCMD with membrane air-backwashing was effective for flux recovery and to reduce membrane crystallization. This enabling to concentrate SWRO brine by 2.8 times of volume concentration factor (VCF).

Integrated SMD-adsorption system to recover the rubidium (Rb) and clean water

An integrated SMD with adsorption using granular potassium copper hexacyanoferrate (KCuFC) as adsorbent was evaluated for improving water recovery from brine while extracting valuable Rb. KCuFC showed good capacity for Rb extraction. The thermal S-MD process (55 °C) with a continuous supply of Rb-rich SWRO brine enabled Rb to be concentrated (99%
rejection) while producing additional fresh water. The thermal condition with concentrated Rb helped to improve the performance of granular KCuFC in Rb extraction. An optimum dose (0.24 g/L) KCuFC was identified based on 98% Rb adsorption (9.78 mg as Rb) from RbCl solution without a continuous supply of feed. The integrated submerged MD-adsorption system was able to achieve more than 85% water recovery and Rb extraction in continuous feed supply with two repeated cycles. The presence of Ca in SWRO brine resulted in CaSO₄ crystallization deposition onto the membrane and on the surface of the granular KCuFC submerged in the feed reactor. This led to a reduced recovery rate and Rb adsorption. Significantly better MD water recovery was obtained upon removal of Ca in SWRO brine while achieving a total of 6.65 mg of Rb extraction. A comparative study conducted on the performance of different KCuFC forms (granular, particle and powder) showed that the particle form of KCuFC exhibited 10–47% higher capacity in terms of Rb adsorption.

**Resource recovery from high salinity solution using F-SMDC**

MDC is an attractive process for high saline SWRO brine treatment. MDC produces additional fresh water while simultaneously recovering valuable resources. In this study, a novel approach of fractional-submerged MDC (F-SMDC) process was developed and tested. In this system, MD and crystallizer are integrated in a feed tank with a submerged membrane. F-SMDC principle is based on the presence of concentration/temperature gradient (CG/TG) in the feed reactor. The conditions provided at the top portion of the feed reactor (higher temperature and lower feed concentration) was well suited for MD operation, while the bottom portion of the reactor (lower temperature and higher concentration) was favorable for crystal growth. F-SMDC performance with direct contact MD to treat brine and produce sodium sulfate (Na₂SO₄) crystals showed positive results. The presence of CG/TG in F-SMDC enabled to achieve higher
water recovery for brine treatment with a VCF of over 3.5 compared to VCF of 2.9 with a conventional S-MDC set-up. Further, the high feed concentration and low temperature at the reactor bottom in F-SMDC enabled the formation of Na₂SO₄ crystals with narrow crystal size distribution.

Moreover, the reactor of F-SMDC contained the submerged hollow-fiber membrane. This enables water and salt recovery to occur simultaneously in a single reactor. The influence of inorganic and organic compounds present in brine solutions on the development and stability of CG/TG in F-SMDC was evaluated in detail. The results showed that properties of inorganic compounds (such as molecular weight and electronegativity) played a significant role in influencing CG/TG in F-SMDC. A high CG ratio (between 1.51 to 1.83 after crystallization) was observed when using feed solutions with inorganic compounds such as KCl, MgSO₄, and Na₂SO₄. However, only low CG ratio (between 0.94 to 1.46) was achieved in feed solutions containing lower molecular weight compounds, NH₄Cl and NaCl. High CG ratio with KCl resulted in the occurrence of salt crystallization at a faster rate (from VCF 2.4 onwards) compared to the predicted theoretical salt saturation point of VCF 3.0. On the other hand, Na₂SO₄ showed lower flux decline (12.56 % flux decline) compared to MgSO₄ (55.93 % flux decline). This is due to lower cation electronegativity of Na⁺. The presence of CG in F-SMDC by concentrated inorganic compounds also enhanced organic compounds to gravitate downwards to the bottom of the reactor, potentially mitigating organic deposition on the membrane.

F-SMDC was used to recover Na₂SO₄ from simulated SWRO brine. CG and TG in the reactor enhanced the water recovery by MD and Na₂SO₄ crystallization by crystallizer. The crystals were not obtained at the bottom portion of F-SMDC due to deposition of calcium sulfate (CaSO₄) on the membrane surface and negative influence of low temperature-sensitivity.
solubility slat such as NaCl. In order to obtain the higher degree of supersaturation of Na₂SO₄, sulfate-rich condition was created by adding salts such as Na₂SO₄, MgSO₄ and (NH₄)₂SO₄. In the case of addition of Na₂SO₄ and MgSO₄, the concentration increase at the top portion was observed, resulting in low CG ratio (around 1.7). On the other hand, the addition of (NH₄)₂SO₄ achieved faster Na₂SO₄ crystallization (VCF 1.42) at the bottom portion with higher CG ratio of over 2.0. Total water recovery ratio of 72 % and 223.73 g Na₂SO₄ crystals was achieved in the laboratory-scale F-SMDC unit used while treating simulated SWRO brine.

Tendency of CaSO₄ crystallization in high salinity solution

Discharge of brine back into the sea through submarine pipelines affects the marine ecosystem. MDC can produce additional amount of clean water with valuable resources recovery from the concentrated brine. The SWRO brine contains salts, which contributes to scaling development during the MDC operation. Hence, this research also investigated the crystallization tendency of calcium sulfate (CaSO₄) under high salinity and examined the effects of other inorganic and organic compounds in forming CaSO₄ crystallization. The crystallization tendency of CaSO₄ in SWRO brine was examined at different conditions such as: temperatures; changes in pH values; and in the presence of co-existing ions such as chemical agents, and organic matters. The results showed that the size and quantity of crystals formed increased with the increase in temperature. Furthermore, an increase in the pH values (from 5 to 9) increased the crystal size. At higher pH, the complexion of NaCl along with CaSO₄ was observed.