Reducing the specific energy consumption of 1st-pass seawater RO by application of high-flux membranes fed with high-pH, decarbonated seawater

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Civil & Environ. Eng. and GWRI, Technion
The Middle East
Funded: 1912; Location: Haifa (Northern Israel)

Shanghai world ranking 2014: 77 (44 in Engineering/18 CS)

Faculties: 18 (engineering and sciences)

Faculty Members: 615

Undergraduate Degree Programs: 53; Graduate Programs: 67

Students: 12,850 (+ ~ 3500 post grads)

Campus: 300 acres; Dorm Beds: 4000; Buildings on Campus: 87

Nobel Laureates: 3 (all in Chemistry)

Language of instruction: Hebrew; International school: English

Campus in NY: Technion-Cornell Innovation Institute (2.1 million square feet on Roosevelt Island)

Campus in China: Technion Guangdong Institute of Technology – TGIT (in Shantou)
Global desalination facts

• Constitutes ~1.7% of the world’s fresh water consumption (~80 Mm³/d; >16,000 plants).

• Average annual growth: 10% - 12%

• Reasons for growth: increased water stress (quantity- and quality-wise) and considerable reduction in RO costs.

• Major new desalinating countries: South Africa, Jordan, Mexico, Libya, Chile, India and China
Top 10 seawater desalinating countries

<table>
<thead>
<tr>
<th>Country</th>
<th>Commissioned seawater desalination capacity (m³/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saudi Arabia</td>
<td>9,170,391</td>
</tr>
<tr>
<td>UAE</td>
<td>8,381,299</td>
</tr>
<tr>
<td>Spain</td>
<td>3,781,314</td>
</tr>
<tr>
<td>Kuwait</td>
<td>2,586,761</td>
</tr>
<tr>
<td>Algeria</td>
<td>2,364,055</td>
</tr>
<tr>
<td>Australia</td>
<td>1,823,154</td>
</tr>
<tr>
<td>Qatar</td>
<td>1,780,708</td>
</tr>
<tr>
<td>Israel</td>
<td>1,532,723</td>
</tr>
<tr>
<td>China</td>
<td>1,494,198</td>
</tr>
<tr>
<td>Libya</td>
<td>1,048,424</td>
</tr>
</tbody>
</table>

Energy demand for seawater desalination ~3.7 kW·h/m³
## ISRAEL’s FRESH WATER DEMAND

<table>
<thead>
<tr>
<th></th>
<th>2008</th>
<th>2020</th>
<th>2030</th>
<th>2050</th>
</tr>
</thead>
<tbody>
<tr>
<td>Population (M)</td>
<td>7.0</td>
<td>8.5</td>
<td>10.1</td>
<td>14.2</td>
</tr>
<tr>
<td>Consumption per capita (m³/cap)</td>
<td>105</td>
<td>115</td>
<td>115</td>
<td>115</td>
</tr>
<tr>
<td>Municipal consumption (Mm³/y)</td>
<td>749</td>
<td>980</td>
<td>1,166</td>
<td>1,635</td>
</tr>
<tr>
<td>Agriculture</td>
<td>454</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>Industry</td>
<td>85</td>
<td>94</td>
<td>101</td>
<td>120</td>
</tr>
<tr>
<td>Allocation to nature</td>
<td>7</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Jordan</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Palestinian authority</td>
<td>80</td>
<td>131</td>
<td>194</td>
<td>425</td>
</tr>
<tr>
<td>Total (Mm³/y)</td>
<td>1,425</td>
<td>1,655</td>
<td>1,911</td>
<td>2,630</td>
</tr>
<tr>
<td>Gap (Mm³/y)</td>
<td>~450</td>
<td>~700</td>
<td>~500</td>
<td>~700</td>
</tr>
</tbody>
</table>

Natural average recharge: ~1200 Mm³/y
Current desalination in Israel

5 large seawater RO plants producing \( \sim 600 \text{ Mm}^3/\text{y} \)

Smaller brackish desalination plants: \( \sim 60 \text{ Mm}^3/\text{y} \)

Cost in latest bid: $0.53 per m\(^3\) of product water

Soreq: the largest RO desalination plant in the world: 150 Mm\(^3\)/y Will be doubled in 2020.

Desalination produces \( \sim 45\% \) of freshwater demand (85% of the demand on the shore)
Israeli water quality requirements for desalinated water (unique & stringent)

- Turbidity < 0.5 NTU
- $3 > \text{CCPP} < 10 \text{ mg/L as CaCO}_3$
- $80 < [\text{Ca}^{2+}] < 120 \text{ mg/L as CaCO}_3$
- Alkalinity > 80 mg/L as CaCO$_3$
- pH < 8.5
- B < 0.3/0.4 mg/L
- $[\text{Cl}^-] < 20; [\text{Na}^+] < 30 \text{ mg/L}$

Chemical stability
The most stringent regulations in the world, yet the cost per m$^3$ attained in recent bids was the lowest (~$0.53$/$m^3$)

Biological stability

Irrigation considerations

Typical water quality in recent bids around the world:
TDS < 500 mg/l; B < 0.5 mg/l
Focus on energy

Seawater desalination

A typical Reverse Osmosis plant layout

- Seawater intake
  - Subsurface intake
  - Open ocean intake
- Pretreatment
  - Conventional: coagulation & filtration
  - Membrane-based
- Reverse osmosis
  - Spiral wound modules with high-permeability membranes
- Post-treatment
  - Remineralization
  - Boron & chloride removal
  - Disinfection

Energy Consumption

- 2.5 kW·h/m³
- 3.7 kW·h/m³

Brine discharge
- Offshore ocean outfall
- Dilute with plant discharge
- Multiport diffuser

limeotech & Phillip, Science (2011)
Train module: seven membranes in series

To minimize chemical fouling, SWRO is always operated at R<50%

Since ions are rejected – TDS concentration and propensity of solids to precipitate increase along membrane train and in parallel – ΔP reduces. First solid to exceed $K_{sp} = \text{CaCO}_3(s)$
The pH value also evolves during RO filtration

**Reasons for changes in pH**

1. Ion concentrations increase, activity coefficients decrease, ion pairing intensifies.
2. Cross-membrane transport of (mostly) acidic species.

Chemical species depicted in the diagram include:
- B(OH)$_4^-$
- Ca$^{2+}$
- Na$^+$
- Cl$^-$
- HCO$_3^-$
- Mg$^{2+}$
- CO$_2$
- B(OH)$_3$
- H$^+$/OH$^-$. 
Coupling mass transport and chemical equilibrium models for improving the prediction of SWRO permeate boron concentrations

Oded Nir, Ori Lahav*

Faculty of Civil and Environmental Engineering, Technion, Haifa, 32,000, Israel
Modeling weak acids' reactive transport in reverse osmosis processes: A general framework and case studies for SWRO

Oded Nir *, Ori Lahav

Available online at www.sciencedirect.com

Accurate and self-consistent procedure for determining pH in seawater desalination brines and its manifestation in reverse osmosis modeling

Oded Nir a, *, Esra Marvin b, Ori Lahav a
Focus on boron

Agricultural use may be limited by residual boron

B in seawater: 5 mg/l as B

~4 mgB/l

B(OH)$_3$ + OH$^-$ $\rightarrow$ B(OH)$_4^-$

~1 mgB/l

Examples of boron-sensitive crops (affected at 0.3-0.75 mgB/l)

i.e. 1-2 mg/l as B in the permeate

0.2-0.5%

Na$^+$
Cl$^-$
B(OH)$_4^-$

%50-25

B(OH)$_3$

permeate

seawater
pH effect on boron RO rejection

Raising pH leads to increase in CaCO$_3$ scaling propensity
Conventional solution: 2\textsuperscript{nd} RO pass (additional cost of $\sim$0.05/m\textsuperscript{3})

Advantages:
- Low Na\textsuperscript{+}/Cl\textsuperscript{-} concentrations in product water

Drawbacks:
- High energy demand
- Loss of costly 1\textsuperscript{st} pass permeate
- Capital investment

\[ \text{B(OH)}_3 + \text{OH}^- \leftrightarrow \text{B(OH)}_4^- \]
Focus on SEC (specific energy demand)

• Energy consumption of seawater RO went down from ~26 kWh/m³ in 1980 to a current ~3.7 kWh/m³.

• Energy demand still amounts to ~40% of the overall cost and despite significant improvement SWRO is energy-intensive compared to conventional freshwater treatment technologies.
SEC reduction: state of the art research

• Current SEC in SWRO separation step \( \sim 2.5 \text{kW}\cdot\text{h/m}^3 \) product water (\( \sim 3.7 \text{kW}\cdot\text{h including pre- and post-treatment steps} \)). Thermodynamic theoretical demand \( \sim 1.0 \text{kW}\cdot\text{h/m}^3 \).
• Application of high flux RO membranes can reduce SEC by \( \sim 10\% \) (Subramani et al., 2014). Very low B rejection!
• Different arrangement of membranes in pressure vessels of 1\textsuperscript{st} and 2\textsuperscript{nd} passes (Altaee and Adel, 2014).
• Prante et al. (2014): suggested pressure retarded osmosis in conjunction with RO (40\% SEC reduction).
• Kishizawa et al. (2015) proposed a different RO system design (short 1\textsuperscript{st} pass, long 2\textsuperscript{nd} pass; \( \sim 20\% \) SEC reduction).
Rationale for new approach

• Aim: increase 1st pass recovery within currently used infrastructure and applied pressure. For example, 9% increase in R results in ~19% more product water and ~14% less brine.
• Limiting factor: CaCO$_3$ precipitation (and H$_2$O flux).
• CaCO$_3$ precipitation can be minimized by either reducing [Ca$^{2+}$] (10 mM in seawater) or [CO$_3^{2-}$] ($C_T = \sim$2mM).
• Use of conventional SWRO membranes is limited by H$_2$O flux at 70 bar external pressure. High flux membranes allow 20-30% higher flux, however B is poorly rejected.
• At pH>9 most of the boron weak acid system appears as B(OH)$_4^-$ or complexes thereof, thereby B rejection is high.
• To avoid CaCO$_3$ precipitation and allow for efficient B rejection $C_T$ has to be reduced (i.e. CO$_2$ stripped out).
• Hypothesis: Both chemical- and bio-fouling significantly reduced.
<table>
<thead>
<tr>
<th>The goal</th>
<th>SWRO using high flux membranes at water recovery &gt;50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limitation</td>
<td>Poor rejection of boron by high flux membranes</td>
</tr>
<tr>
<td>Solution</td>
<td>Increase the pH to ≈ 9.5</td>
</tr>
<tr>
<td>Obstacle</td>
<td>Precipitation of CaCO$_3$</td>
</tr>
<tr>
<td>Solution</td>
<td>Acidification and removal of carbonate species prior to SWRO</td>
</tr>
</tbody>
</table>
Filtered seawater
~37.5 g/l

Strong acid
Air Degasifier
Compressor
Stripped CO2 discharge
95% de-carbonation
Optional use at PT step

pH~4.0

High flux membrane
RO single pass
Brine discharge

pH~9.5

Product water
~375 mg/l TDS
~0.3 mgB/l

Optional use at PT step

2nd pass (optional)

TDS<30 mg/l
Experimental system
Results

TDS removal
(n=9)

(P = 66 bar)

B removal
(n=3)
Results of empirical & theoretical scenarios (varying limiting parameters)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Conventional process</th>
<th>Suggested process (experimental results)</th>
<th>Theoretical scenario 1 (Mg(OH)$_2$ precipitation)</th>
<th>Theoretical scenario 2 (BaSO$_4$/CaCO$_3$ precipitation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed pH</td>
<td>8.20</td>
<td>9.53</td>
<td>9.80</td>
<td>9.53</td>
</tr>
<tr>
<td>Recovery ratio [%]</td>
<td>47</td>
<td>56</td>
<td>60</td>
<td>67</td>
</tr>
<tr>
<td>Osmotic pressure [bar]</td>
<td>51.43</td>
<td>61.36</td>
<td>68.10</td>
<td>84.36</td>
</tr>
<tr>
<td>Energy demand [kWh/m$^3$ permeate]</td>
<td>2.523</td>
<td>2.270</td>
<td>2.419</td>
<td>2.956</td>
</tr>
<tr>
<td>Reduction in pre-treatment cost [%]</td>
<td>-</td>
<td>16.0</td>
<td>21.7</td>
<td>29.85</td>
</tr>
<tr>
<td>Reduction in brine-treatment costs [%]</td>
<td>-</td>
<td>-</td>
<td>40.9</td>
<td>56.3</td>
</tr>
<tr>
<td>Antiscalant application</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Scaling-limiting solid</td>
<td>CaCO$_3$</td>
<td>Mg(OH)$_2$</td>
<td>Mg(OH)$_2$</td>
<td>BaSO$_4$, CaCO$_3$</td>
</tr>
<tr>
<td>Permeate TDS concentration [mg/l]</td>
<td>197</td>
<td>375</td>
<td>440</td>
<td>497</td>
</tr>
<tr>
<td>Permeate B concentration [mgB/l]</td>
<td>0.85</td>
<td>0.30</td>
<td>0.22</td>
<td>0.31</td>
</tr>
</tbody>
</table>

14.0
Operational cost estimation for the considered scenarios (cent/m³ product water)

<table>
<thead>
<tr>
<th></th>
<th>Conventional process</th>
<th>Suggested process</th>
<th>Theoretical scenario 1</th>
<th>Theoretical scenario 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical power¹</td>
<td>17.36</td>
<td>15.62</td>
<td>16.64</td>
<td>20.39</td>
</tr>
<tr>
<td>Acid and base²</td>
<td>0</td>
<td>2.51+1.21</td>
<td>2.34+1.39</td>
<td>2.1+1.00</td>
</tr>
<tr>
<td>Antiscalants³</td>
<td>0.94</td>
<td>-</td>
<td>3.67</td>
<td>1.31</td>
</tr>
<tr>
<td>Degasification⁴</td>
<td>-</td>
<td>0.33</td>
<td>0.31</td>
<td>0.28</td>
</tr>
<tr>
<td>Pre-treatment⁵</td>
<td>12</td>
<td>10.08</td>
<td>9.4</td>
<td>8.42</td>
</tr>
<tr>
<td>Brine disposal⁶</td>
<td>5.5</td>
<td>3.83</td>
<td>3.25</td>
<td>2.4</td>
</tr>
<tr>
<td>B removal post-treatment⁷</td>
<td>4.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Total [$cent/m³]</strong></td>
<td><strong>40.50</strong></td>
<td><strong>33.58</strong></td>
<td><strong>37.00</strong></td>
<td><strong>34.59</strong></td>
</tr>
</tbody>
</table>

Estimated normalized cost of CO₂ stripping tower: 0.12 $cent/m³
Summary, conclusions and future work

- The suggested process results in 10% lower SEC and ~18% lower operational costs for attaining TDS < 500 mg/l; B < 0.5 mg/l.
- Overall potential saving in cost: $0.05-$0.07/m³.
- No need for antiscalants (environmental advantage)
- Probable reduction in biological fouling (hypothesis under investigation).
- 2\textsuperscript{nd} pass for TDS removal can be done at low pH/high R with high flux membranes since B removal not necessary.
Reducing the specific energy consumption of 1st-pass SWRO by application of high-flux membranes fed with high-pH, decarbonated seawater

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ARTICLE INFO

Article history:
Received 25 May 2015
Received in revised form
14 August 2015
Accepted 17 August 2015
Available online 20 August 2015

Keywords:
SWRO
SEC
High-flux membranes
Boron
Single pass

ABSTRACT

A new operational approach is presented which has the potential to substantially cut down on the energy and cost demand associated with seawater reverse osmosis (SWRO) desalination, without changing the currently-installed infrastructure. The approach comprises acidification/decarbonation of the feed seawater followed by high-pH single RO pass using high-flux membranes. Since the limitation imposed by CaCO₃(s) precipitation is overcome, the recovery ratio can be significantly increased. This work presents a new operational concept aimed at maximizing the benefits that can be obtained from new low-energy RO membranes available on the market. Results obtained from operating a pilot RO system revealed that following an acidification and decarbonation step, recovery ratio of 56% could be practically attained, along with effluent TDS and boron concentrations of 375 and 0.3 mg/l, respectively (feed water pH was adjusted to pH9.53 following the decarbonation step). The specific energy consumption (SEC) of this operation was calculated to be 5%–10% lower than the SEC typically associated with “conventional” SWRO operation. Two further scenarios were theoretically considered, under which the limiting operational parameter became Mg(OH)₂(s) and BaSO₄(s) precipitation. It was concluded that despite the fact that higher recovery ratios could be obtained, the