Extraction of Valuable Minerals from Reverse Osmosis Brine in Kuwait

استخلاص العناصر القيمة من المحاليل الملحية المركزة الناتجة عن عمليات تحلية مياه البحر بالتناضح العكسي في دولة الكويت

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Overview

• Introduction
• Experimentation
• Results & Discussion
• Conclusions & Recommendations
• Acknowledgements
Introduction
Kuwait

Climate: Hyper arid

Rainfall: 110 mm/year

Surface water resources: none

Groundwater resources: negligible
Most of Fresh Water Demands Provided by the Desalination of Seawater by Thermal or Membrane Technologies
Estimates of Distillation Plants, Kuwait
Installed Capacity (MIGD) 2014 – 2018

<table>
<thead>
<tr>
<th>Station</th>
<th>2014</th>
<th>2015</th>
<th>2016</th>
<th>2017</th>
<th>2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Shuwaikh</td>
<td>49.5</td>
<td>49.5</td>
<td>49.5</td>
<td>49.5</td>
<td>49.5</td>
</tr>
<tr>
<td>Shuaiba</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>36</td>
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<tr>
<td>Doha East</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
<td>42</td>
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<tr>
<td>Doha West</td>
<td>110.4</td>
<td>110.4</td>
<td>110.4</td>
<td>110.4</td>
<td>110.4</td>
</tr>
<tr>
<td>b Az-Zour South</td>
<td>145.2</td>
<td>145.2</td>
<td>145.2</td>
<td>145.2</td>
<td>145.2</td>
</tr>
<tr>
<td>Sabiya</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Shuaiba North (G/T) Project</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>d Doha (Stage I)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>d Doha (Stage II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Total Installed Capacity</td>
<td>528.1</td>
<td>528.1</td>
<td>528.1</td>
<td>528.1</td>
<td>628.1</td>
</tr>
</tbody>
</table>

* a New seawater desalination plant (RO) having capacity of 30 MIGPD added to reach the total installed capacity of 49.5 MIGPD during 2011.
* b It is expected to add seawater desalination plant (RO) plant at Az-Zour South station having capacity of 30 MIGPD during 2014 to reach the total installed capacity of 145.2 MIGPD.
* c It is expected to add seawater desalination plant (RO) plant at Doha station (Stage I) having capacity of 50 MIGPD during 2017.
* d It is expected to add seawater desalination plant (RO) plant at Doha station (Stage II) having capacity of 50 MIGPD during 2018.

Source: MEW, 2014

Approximate rejected brine: 2500 MIGD
Considered approximately 20% water recovery
Capacity: 623 MIGD
Production: 431 MIGD 11-3-2019
Consumption: 400 MIGD 11-3-2019
Brine disposal is a major problem for coastal & inland desalination plants.
Current Disposal Methods

- Deep well injection;
- Irrigation of plants tolerant to high salinities;
- Disposal to municipal sewers;
- Evaporation ponds;
- Chemical treatment;
- Disposal into surface water bodies.
## Major Components In Seawater and Desalination Brines

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Arabian Gulf Seawater</th>
<th>Arabian Gulf Beach-well Seawater</th>
<th>MSF Brine</th>
<th>RO Brine</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>8.2</td>
<td>7.13</td>
<td>8.67</td>
<td>7.56</td>
</tr>
<tr>
<td>EC*</td>
<td>mS/cm</td>
<td>68.4</td>
<td>66.6</td>
<td>101.3</td>
<td>78.5</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>mg/l</td>
<td>648</td>
<td>1,080</td>
<td>996</td>
<td>1,276</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>mg/l</td>
<td>1,676.7</td>
<td>1,416.6</td>
<td>2,258</td>
<td>1,733</td>
</tr>
<tr>
<td>(SO(_4))(^{2-})</td>
<td>mg/l</td>
<td>4,200</td>
<td>3,900</td>
<td>5,700</td>
<td>4,500</td>
</tr>
<tr>
<td>(HCO(_3))(^{-})</td>
<td>mg/l as CaCO(_3)</td>
<td>180.8</td>
<td>175.6</td>
<td>299.9</td>
<td>221.6</td>
</tr>
<tr>
<td>Cl(^{-})</td>
<td>mg/l</td>
<td>26,100</td>
<td>25,400</td>
<td>41,000</td>
<td>29,400</td>
</tr>
<tr>
<td>Na(^{+})</td>
<td>mg/l</td>
<td>16,925</td>
<td>16,471</td>
<td>26,587</td>
<td>19,065</td>
</tr>
<tr>
<td>TDS</td>
<td>mg/l</td>
<td>48,116</td>
<td>47,843</td>
<td>75,370</td>
<td>55,866</td>
</tr>
</tbody>
</table>
Harvesting Salts and Other Useful Products

Many marketable mineral salts can be produced from reject brines such as [Howe, 2009]:

- NaCl
- KCl
- Na₂SO₄
- K₂SO₄
- MgSO₄
- Mg(OH)₂
- KNO₃
- Na₂NO₃ and ... etc.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Textile dyeing, aquaculture, soil stabilization, and ice and snow removal</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Polymers, plastics, and synthetic fibres</td>
</tr>
<tr>
<td>NaOH</td>
<td>Glass, rayon, synthetic fibres, plastics, polyester, soaps, and detergents</td>
</tr>
<tr>
<td>NaSO₄</td>
<td>Pulp and paper, dyes, and ceramic glazes</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>Glass, pulp and paper, and rayon</td>
</tr>
<tr>
<td>Product name</td>
<td>Chemical name</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Sodium chloride (Halite)</td>
<td>NaCl</td>
</tr>
<tr>
<td>Calcium sulfate</td>
<td>CaSO₄</td>
</tr>
<tr>
<td>Magnesium hydroxide</td>
<td>Mg(OH)₂</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Na₂CO₃</td>
</tr>
<tr>
<td>Lithium carbonate</td>
<td>Li₂CO₃</td>
</tr>
<tr>
<td>Potassium oxide</td>
<td>K₂O</td>
</tr>
</tbody>
</table>

(Open pan salt) (Salt in brine) (free Market) (Quicklime) (Hydrate lime) (Green River, USA) (Mine)
Price of magnesium Oxide

**Industrial grade Magnesium Oxide**
Price 20kg/bag White

JS $1100.0-1300.0 / Ton
1 Ton (Min. Order)

2YRS Hebei Meishen Tec...

**Magnesium oxide** (MgO 80%
85%-90%-92%-94%)

US $200-1000 / Ton
20 Tons (Min. Order)

11YRS Liaoning Tianci Fi...

**Magnesium Stabilized Zirconia**
Powder/MgO stabilized

US $10-20 / Kilogram
1 Kilogram (Min. Order)

2YRS Nanjing Zirae Adv...

**Magnesium Oxide** for livestock feed MgO 96% 95% China

US $240-290 / Metric Ton
25 Metric Tons (Min. Order)

5YRS Liaoning Metals &...
Case Study at KISR
Experimentation

Sampling and Physicochemical Parameters Determination

Sample: Sample was collected from DRP which is located at Doha East Power Generation and Water Desalination Plant in Kuwait.

Production Capacity: 300 m$^3$/d.

Total Water Recovery: ≈30%.

Total Dissolved Solid (TDS) rejected from DRP plant: ≈54,000 ppm.

<table>
<thead>
<tr>
<th>Parameters / Unit</th>
<th>seawater Intake</th>
<th>SWRO brine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity as CaCO$_3$, mg/L</td>
<td>131.6</td>
<td>175</td>
</tr>
<tr>
<td>Ammonia, mg/L</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Barium, mg/L</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Boron, mg/L</td>
<td>3.7</td>
<td>9.8</td>
</tr>
<tr>
<td>Bromine, mg/L</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>Calcium, mg/L</td>
<td>730</td>
<td>1,090</td>
</tr>
<tr>
<td>Chloride, mg/L</td>
<td>24,876</td>
<td>-</td>
</tr>
<tr>
<td>Chlorine, mg/L</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>Chromium, mg/L</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Copper, mg/L</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Fluoride, mg/L</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Iodine, mg/L</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>Iron, mg/L</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Lithium, mg/L</td>
<td>-</td>
<td>1.7</td>
</tr>
<tr>
<td>Magnesium, mg/L</td>
<td>1,325</td>
<td>1,673</td>
</tr>
<tr>
<td>Nitrate, mg/L</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>Phosphate, mg/L</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>Potassium, mg/L</td>
<td>316.4</td>
<td>997</td>
</tr>
<tr>
<td>Sodium, mg/L</td>
<td>14,488.5</td>
<td>17,905</td>
</tr>
<tr>
<td>Strontium, mg/L</td>
<td>14.6</td>
<td>121</td>
</tr>
<tr>
<td>Sulfate, mg/L</td>
<td>3,430.5</td>
<td>4,159</td>
</tr>
<tr>
<td>Total dissolved solids, mg/L</td>
<td>45,377</td>
<td>54,900</td>
</tr>
</tbody>
</table>
Experimentation

Agilent Technologies, 7900 ICP-MS

Thermo scientific, Dionex ICS-5000+DP

Keysight 8500B FE-SEM

Spectrophotometer LANGE DR2800

Figure 1. Flow diagram.
Experimentation

**Chemical Reactions**

\[
\begin{align*}
\text{RO brine (MX) + Ca(OH)_2} & \rightarrow \text{MOH, M(OH)_2 + CaCl}_2 \\
\text{RO brine (MX) + NH}_4\text{OH} & \rightarrow \text{MOH, M(OH)_2 + NH}_3 \\
\text{RO brine (MX) + NaOH} & \rightarrow \text{MOH, M(OH)_2 + NaCl}
\end{align*}
\]

Where MX: Mineral halide and sulphate.
Results and Discussion

Effect of Base on Mineral Extraction (pH 9-Temp 90 °C)
Selected Base: Ca(OH)$_2$, NH$_4$OH, and NaOH

**Ca(OH)$_2$ as base**

Extracted minerals:
- Boron: 36%, strontium: 25%, magnesium: 23% and sulfate: 11%.

**NH$_4$OH as base**

Extracted minerals:
- Boron: 41%, strontium: 12%, magnesium: 6% and potassium: 6%.

Percentage of minerals extracted.
Effect of Base on Mineral Extraction

NaOH as base

Results and Discussion

- NaOH is the best suitable base for extracting minerals from Kuwait SWRO brine (precipitation faster due to faster reaction and faster crystal growth of minerals in presence of NaOH)

Extracted minerals:
Boron: 40%, lithium: 38%, strontium: 23% and magnesium: 20%.
Results and Discussion

Effect of pH and Temperature on Mineral Extraction

Extraction of minerals at 90 °C and at different pH

Total mineral extracted at different pH (mg/L) at 90 °C.

Magnesium: 1651 mg/L, sulfate: 700 mg/L and calcium: 168.8 mg/L. (ex pH 10)

Percentage of minerals extracted at 90 °C.

Magnesium: 98%, Lithium: 78%, boron: 51%. (ex pH 10)
Results and Discussion

Effect of pH and Temperature on Mineral Extraction

Extraction of minerals at 80 °C and at different pH

Total mineral extracted at different pH (mg/L) at 80 °C.

- Magnesium: 750 mg/L, sulfate: 300 mg/L
- and calcium: 144 mg/L. (ex pH 10)

Percentage of minerals extracted at 80 °C.

- Boron: 71%, magnesium: 44%, strontium: 15% and calcium: 10%. (ex pH 10)
Results and Discussion

Effect of pH and Temperature on Mineral Extraction

Extraction of minerals at 70 °C and at different pH

Total mineral extracted at different pH (mg/L) at 70 °C.

Magnesium: 1193 mg/L, sulfate: 200 mg/L and calcium: 120 mg/L.(ex pH 10)

Percentage of minerals extracted at 70 °C.

Boron: 71%, magnesium: 70%, strontium: 15% and calcium: 10%. (ex pH 10)
Results and Discussion

Effect of pH and Temperature on Mineral Extraction

Extraction of minerals at 60 °C and at different pH

Total mineral extracted at different pH (mg/L) at 60 °C.

Magnesium: 809 mg/L, Sulfate: 200 mg/L and calcium: 144 mg/L. (ex pH 10)

Percentage of minerals extracted at 60 °C.

Boron: 77% and magnesium: 48% (ex pH 10), Lithium: 61% (ex pH 8)
Results and Discussion

Effect of pH and Temperature on Mineral Extraction

Extraction of minerals at 50 °C and at different pH

Total mineral extracted at different pH (mg/L) at 50 °C.

Magnesium: 1095 mg/L, sulfate: 100 mg/L and calcium: 68 mg/L.(ex pH 10)

Percentage of minerals extracted at 50 °C.

Boron: 73%, magnesium: 65%, and calcium: 6%. (ex pH 10)
Preliminary Economic Evaluation of Magnesium Oxide Production Using DRP SWRO Brine

Production Capacity: 300 m³/d.
Total Water Recovery: ≈30%.
TDS rejected from DRP plant: ≈54,000 ppm.

Rejected brine is approximately 700 m³/d
Amount of magnesium present: 1,771 kg per day and 646 ton/year.
Based on our study: Extracted magnesium using NaOH as base at 90 °C and pH 10 is ≈ 633 ton/year.

Theoretically, 1 gm of magnesium (Mg) can produce 1.658 gms of magnesium oxide (MgO)
The total amount of magnesium oxide (MgO) that can be produced per year from DRP SWRO brine is 1000 ton/year.

Considering the market price of MgO at (800-2,500) USD per ton, the annual benefit that can be achieved by extracting MgO from DRP SWRO brine is 800,000 USD per year.
Conclusion & Recommendations

• The mineral extraction from actual SWRO brine was conducted using chemical precipitation process,
• Mineral extraction capability of three different inorganic base was studied,
• The study proved that NaOH is the best suitable base for extracting minerals from Kuwait SWRO brine
• The effect of pH and temperature was conducted for maximum mineral extraction,
• The mineral extraction results showed that there is change in total concentration of extracted mineral with increase in temperature from 50 °C to 90 °C as well as with increase of pH from 8.0 to 10.0,
Conclusion & Recommendations

• The extracted minerals are magnesium, lithium, boron, sulfate, and calcium,

• The economic gains obtained by extracting minerals depend mainly on the concentration of minerals in brine, the market price of these minerals, the recovery of the extraction and the purity of the mineral extracted.
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