Extraction of valuable minerals from reverse osmosis brine in Kuwait

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**Abstract**

The availability of freshwater on earth is very less and a noticeable worry about the shortage of freshwater has emerged during the last decade especially in the Middle East and North Africa (MENA) countries. Most of the freshwater demands are provided by the desalination of seawater both thermal or membrane desalination technologies and desalination plants produce huge volumes of concentrated brine which are discharged back to the sea. This brine contains greater concentration of commercially valuable minerals than that in seawater. The literatures reported that the current disposal options have a number of severe limitations that are associated with technical challenges and environmental issues. As such, research studies have remarkably carried out into the development of mineral extraction processes with aim of producing valuable minerals from desalination brine. Therefore, this paper will review the appraisal of extraction of valuable minerals from Kuwait seawater desalination brine. To achieve this goal, bench-scale experiments were conducted by adopting suitable technologies present in the recent literature. Chemical precipitation method was experimentally implemented at Water Research Center (WRC) of Kuwait Institute for Scientific Research (KISR) with aim of extracting valuable minerals, including magnesium, calcium, boron, sulfate, and strontium, from the rejected brine of the main seawater reverse osmosis desalination units of Desalination Research Plant (DRP) and Shuwaikh Water Distillation Plant (SWDP). The mineral extraction experiments were performed by using sodium hydroxide as base at different processing temperature and pH. The results showed that the amount of extraction of minerals from Doha RO brine was 7.280 g/L. The major extracted mineral magnesium is about 98% and other minerals are lithium 78%, boron 51%, sulfate 18%, calcium 15%, and strontium 14%. For Shuwaikh brine, percentage of extracted minerals are boron 83%, magnesium 78%, lithium 34%, strontium 21%, calcium 18%, and sulfate 11% at 90°C at 10.0 pH. Based on the experimental data and mathematical calculations, the production of magnesium oxide from DRP and Shuwaikh RO plants is around 231 and 97,910 ton per year. The annual benefit from magnesium oxide production using Doha and Shuwaikh brine are 577,500 US$/Y and 244,775,000 US$/Y, respectively.

**Keywords:** Desalination brine; Chemical precipitation; Solubility; Brine management

1. Introduction

The State of Kuwait is fully dependent on conventional seawater desalination technologies due to the lack of fresh natural water resources. According to the Ministry of Electricity and Water (MEW), Kuwait has produced a total of 164,111 million gallons fresh water in 2017 (in which 146,922 million gallons are potable water and 17,189 million gallons are brackish water) (Statistical Review 2017).

A recent study on global seawater desalination indicates that almost $80 \times 10^6$ m$^3$/d of desalinated water is produced every day, which leads to production of concentrated brine in the order of $100 \times 10^6$ m$^3$ every day (Tedesco et al. 2015). The reject from the desalination plants will be usually 10% to 15% more concentrated than usual seawater (Cipollina et al. 2012). The brine from seawater desalination plants that are installed in the coastal areas are commonly discharged back to the sea. The continuous release of rejected brines

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from desalination plants which is characterized by having a higher salinity and/or temperature than that of feed seawater will increase the seawater salinity level and harm the marine creatures (Latorre 2005; Peters & Pinto 2008). The presence of inorganic compounds and higher salt concentration of the rejected concentrate causes major environmental and regulatory problems for seawater desalination industry (Younos 2005). In addition, the cost of brine disposal varies from 5% to 33% of the total cost of desalination, depending on the amount of brine, the level of treatment before disposal, the nature of the surrounding environment and the disposal method (Glueckstern & Priel 1996). Thus, the reduction in brine volumes will reduce both potable water costs and, at the same time, the environmental impact of the desalination process.

The benefits of concentrate minimization and zero liquid discharge practices are often offset by their high operation and maintenance costs, and energy requirements (Koppol et al. 2004). As a result, the mineral extraction from seawater and brine rejected from the desalination plants attracted researchers all over the world due to the benefits in reducing the environmental effect and desalination cost as well as diversifying the land mining process (Bazedi et al. 2014). The concept of recovering valuable constituents from desalination concentrate was likely first proposed by Dr. John F. Mero in 1964, who claimed that rejected brines from desalination facilities would play a major role in future production of minerals from seawater (Mero 1965). The advantage of seawater mining of minerals is that seawater is homogeneous and there is no mineral grade difference as there is in the land (Loganathan et al. 2017). The developing nations can produce fertilisers containing plant nutrients (K, Mg, Ca, S, and B) from seawater at affordable prices compared with commercial fertilisers available on the market (Loganathan et al. 2017). The economic gains obtained by extracting minerals depend mainly on the concentration of minerals in brine and the market price of these minerals. It has been reported that Na, Ca, Mg, K, Li, Sr, Br, B, and U are potentially attractive for extraction (Loganathan et al. 2017). The minerals that can be recovered from the rejected brines of desalination plants vary depending on the desalination process and the feed water quality. Seawater reverse osmosis (SWRO) plants produce brine with concentration in the range of 65,000–85,000 ppm, whereas thermal desalination plants (MED, MSF) usually discharge a more diluted brine (Cipollina et al. 2012). The recovery of gypsum, sodium chloride, magnesium hydroxide, calcium chloride, calcium carbonate and sodium sulfate has been reported in literatures (Ahmed et al. 2003; Arakel et al. 2004). The main methods of recovery of minerals are solar evaporation, ED, MDC, and adsorption/desorption. Of these, the first three can recover only minerals such as Na, Mg, and Ca which are found at high concentrations (Loganathan et al. 2017).

The higher concentration of commercially valuable minerals in high saline brine discharged from Kuwait desalination plants has prompted us to conduct this research study of the mineral extraction. The study covered the simple chemical precipitation method. A preliminary literature study was conducted to shortlist the available best process for SWRO mining (Attia et al. 2015; Quist-Jensen et al. 2016) and accordingly extraction process is selected in the present article.

2. Materials and methods

All the chemicals and reagents required for the laboratory experiments, calibration and analysis were purchased from Sigma-Aldrich, Merck and used without any further purification. The quantitative and qualitative analysis was carried out using inductively coupled plasma optical emission spectrometry (ICP-OES: Thermo Scientific: iCAP 6000), conductivity meter (ORION STAR A222), spectrophotometer (LANGE DR 2800), and pH meter (ORION STAR A221) in standard analytical conditions. The laboratory scale mineral extraction experiments were conducted in a customized apparatus as shown in Fig. 1.

2.1. Sampling and physicochemical parameters determination

The rejected brine samples were collected from two SWRO desalination plants in Kuwait. The RO desalination units are at Desalination Research Plant (DRP) Doha and Shuwaikh with production capacity of 300 and 136,000 m3/d, respectively. The total dissolved solids (TDSs) of rejected brine from DRP and Shuwaikh is ≈58,000 and ≈78,000 ppm, respectively. The total recovery of DRP RO plant is ≈40% whereas; of Shuwaikh SWRO plant is ≈50%–60%.

2.2. Mineral extraction method

Extraction of minerals from SWRO brines was conducted using laboratory scale assembly as shown in Fig. 1. Laboratory scale apparatus consists of a magnetic stirrer, pH

Fig. 1. Schematic diagram of the experimental apparatus assembly used for mineral extraction.
meter, and a glass beaker. One litre of RO brine was taken in a beaker with magnetic bead, and sodium hydroxide powder was added to achieve the required pH. After reaching constant pH, the curdy solution was kept in the oven for 1 h at a constant temperature in a closed vessel and the precipitate (crystal growth) was allowed to settle at room temperature. The precipitated mineral was separated using Buchner funnel under vacuum and dried at 90°C. The filtrate was analyzed to check the extracted minerals in the process. The flow diagram for the extraction method is shown in Fig. 2.

2.3. Standardization of precipitation methods

The mineral extraction capacity of different inorganic bases was studied. For these experiments, calcium hydroxide (Ca(OH)₂), sodium hydroxide (NaOH) and ammonium hydroxide (NH₄OH) were selected, and experiments were conducted as follows. A known quantity of (1 L) RO brine was taken in the beaker and powdered base was added to adjust the pH of the solution (pH: 9.0). The solution was stirred for 15 min and pH change was continuously monitored. The curdy solution was kept in the oven for 60 min at 90°C and, then allowed for crystallization at room temperature for 6 h. The precipitate was filtered and dried under vacuum for 10 h. The filtrate was analyzed using standard analytical protocols to verify the remaining minerals in mother liquid.

The amount of mineral extracted and % extraction of each mineral was calculated using the below equations:

\[
\text{Amount of mineral extracted} = (C_i - C_f) \\
\%	ext{ of mineral extracted} = \left(\frac{C_i - C_f}{C_i}\right) \times 100
\]

where

\[C_i = \text{Initial mineral concentration (mg/L)}\]
\[C_f = \text{Final mineral concentration (mg/L)}\]

The chemical reactions involved in the extraction process for different inorganic base are shown below:

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

where MX: mineral halide/sulfate.

2.4. Experimental procedure for mineral extraction at different temperature and pH

One litre of SWRO brine was treated with NaOH powder at different pH (8, 8.5, 9, 9.5, and 10). The solution was stirred for 15 min to stabilize the pH of the solution and continuously monitored the change in pH using pH meter. After observing the constant pH, the solution was kept for 1 h at different temperature (50°C, 60°C, 70°C, 80°C, and 90°C) to check the effect of temperature and pH on the mineral extraction. After 1 h, the curdy solution was kept at room temperature for crystallization and crystal growth. The precipitated minerals were filtered using Buchner funnel and solid particles were dried in an oven and filtrate was taken for analysis to check the remaining minerals in filtrate. The experiments were conducted in triplicate and mean values are considered.

3. Results and discussion

3.1. Effect of base on mineral extraction

The mineral extraction capability of Ca(OH)₂, NH₄OH, and NaOH were studied at pH 9.0. The result showed the extraction of calcium, magnesium, sulfate, boron, strontium, potassium, lithium, and sodium, and there was no change in halogen concentration.

3.1.1. Ca(OH)₂ as base

Fig. 3 shows the extraction percentage of each mineral using Ca(OH)₂ as base. The minerals that were extracted more are boron, strontium, magnesium, and sulfate with extraction percentage of 36, 25, 23, and 11, respectively. Other minerals are extracted at an extremely low percentage and a loss of 43% calcium hydroxide was observed in these experiments.

3.1.2. NH₄OH as base

Fig. 4 shows the percentage of extracted mineral using NH₄OH as base. The minerals that were extracted are boron, strontium, magnesium, and potassium with extracting percentages of 41, 12, 6, and 6, respectively. It is important to note that sulfate was not extracted while using NH₄OH as the base. In the case of magnesium, the extraction percentage reduced to 6% from 23% (using Ca(OH)₂ base). Compared
with Ca(OH)$_2$ base, extraction percentage of minerals were less with NH$_4$OH base.

### 3.1.3. NaOH as base

The percentage mineral extracted using NaOH as base are presented in Fig. 5. The minerals that were extracted are boron, lithium, strontium, and magnesium with percentages of 40, 38, 23, and 20, respectively. The extraction process using NaOH as base was faster compared with Ca(OH)$_2$ and NH$_4$OH, and this is mainly due to faster reaction (conversion of chloride to hydroxide) and faster crystal growth of minerals in presence of NaOH. Based on the above experimental results, the amount and percentage of extracted minerals are more using NaOH as base compared with Ca(OH)$_2$ and NH$_4$OH. Therefore, all further experiments were conducted using sodium hydroxide as base with different pH and temperatures.

### 3.2. Effect of pH and temperature on mineral extraction (DRP SWRO brine)

#### 3.2.1. Extraction of minerals at 90°C and at different pH

The effect of pH and temperature on mineral extraction was studied using NaOH as base. The experiment was carried out at 90°C and different pH ranging from 8.0 to 10. The precipitation of minerals started at pH 9.0 and no visible precipitation was observed at pH below 9.0. The filtrate analysis showed an increasing trend of mineral extraction percentage with an increase in pH as shown in Fig. 6. It is observed from Fig. 6 that the major minerals extracted at 90°C and pH 10 are magnesium, sulfate, and calcium at concentration of 1,651; 700; and 168.8 mg/L, respectively. As shown in Fig. 7, approximately 98% of magnesium was extracted at 90°C and pH 10.

#### 3.2.2. Extraction of minerals at 80°C and at different pH

The mineral extraction experiment was carried out at 80°C and different pH ranging from 8.0 to 10. At 80°C there was an increase in mineral extraction percentage with the increase in pH, but the rate of increase was less when compared with 90°C. At 80°C, there was a drastic change in the quantity of magnesium extracted when the pH was changed from 9.5 to 10 (41.5 to 750.8 mg/L) as shown in Fig. 8. The extracted minerals at 80°C and pH 10 are boron, lithium, magnesium, calcium, and sulfate with extraction percentage of 73, 66, 44, 13, and 8, respectively as shown in Fig. 9. It is observed that sulfate extraction percentage was almost the same and not affected much by the change in pH from 9 to 10.

#### 3.2.3. Extraction of minerals at 70°C and at different pH

The extracted minerals at 70°C and pH 10 are boron, magnesium, strontium, and calcium with the percentage of 71, 70, 15, and 10, respectively (Fig. 10). A constant amount of calcium was extracted at pH 9.5 to 10 (116–120 mg/L) and a drastic increase in extraction ratio was observed for magnesium (from 34 to 1,193 g/L). Fig. 11 clearly shows that magnesium was the major extracted mineral at 70°C and pH 10.

#### 3.2.4. Extraction of minerals at 60°C and at different pH

The mineral extraction at 60°C shows a high percentage of lithium extraction at pH 8.0. This may be due to the high reactivity and small size of the lithium ion. Other major extracted minerals at 60°C and pH 10 are boron, magnesium, strontium, and calcium with the percentage of 71, 70, 15, and 10, respectively (Fig. 10). A constant amount of calcium was extracted at pH 9.5 to 10 (116–120 mg/L) and a drastic increase in extraction ratio was observed for magnesium (from 34 to 1,193 g/L). Fig. 11 clearly shows that magnesium was the major extracted mineral at 70°C and pH 10.
3.2.5. Extraction of minerals at 50°C and at different pH

At 50°C there was an increase in mineral extraction percentage with increase in pH, but the rate of increase was very less when compared with 90°C. At 50°C, there was a drastic change in the amount of magnesium extracted when the pH was changed from 9.5 to 10 (38 to 1,095 mg/L). It was observed from Fig. 14 that at pH 10 the major extracted minerals are magnesium and boron with extraction percentage of 73 and 65, respectively. Fig. 15 clearly shows that the amount of magnesium extracted at pH 10 was very high compared with sulfate, boron, lithium, etc. It is important to note that magnesium extracted at pH 10 was the best condition to isolate pure magnesium from the DRP SWRO brine compared with higher temperature.

3.3. Effect of pH and temperature on mineral extraction (Shuwaikh SWRO brine)

3.3.1. Extraction of minerals at 90°C and at different pH

The effect of pH and temperature on mineral extraction for Shuwaikh SWRO brine was studied using NaOH as base. The experiment was carried out at 90°C and different pH ranging from 8.0 to 10. There was no visible precipitation was observed at pH below 9.0. The filtrate analysis showed that there is an increase in the percentage of minerals extraction with an increase in pH as shown in Fig. 16. The amount of sodium hydroxide consumed for extracting minerals from Shuwaikh SWRO brine was almost double.
than the amount used for extracting minerals from DRP SWRO brine. This consumption is mainly due to more concentration of convertible (mineral chlorides) minerals in Shuwaikh SWRO brine. The major extracted minerals are calcium (164 mg/L), magnesium (2,157 mg/L) and sulfate (600 mg/L). More than 80% of boron and 78% of magnesium was extracted by using sodium hydroxide as base at 10.0 pH. The extracted mineral concentrations and percentage of extractions are shown in Figs. 15 and 17.

3.3.2. Extraction of minerals at 80°C and at different pH

The amount of minerals extracted at 80°C is slightly less than the total mineral extracted at 90°C. At 80°C with pH 9.5 to 10.0, a drastic increase in magnesium and boron extraction was observed. The concentration of magnesium extracted was only 12 mg/L at pH 9, but at pH 10 it was 2,060 mg/L. The major minerals extracted from these experiments are calcium (165 mg/L), magnesium (2,060 mg/L), sulfate (500 mg/L), and boron (6 mg/L). The graphical representations are shown in Figs. 18 and 19.

3.3.3. Extraction of minerals at 70°C and at different pH

The extraction of mineral at 70°C shows that there is a reduction in the total amount of minerals extracted. The major extracted mineral was boron and is about 82%. The other extracted minerals are magnesium (67%), lithium (67%), calcium (13%), and sulfate (7%). Figs. 20 and 21
clearly shows that the mineral extracted at 70°C was less than the mineral extracted at 90°C. The extracted minerals are magnesium (1,856 mg/L), sulfate (400 mg/L), calcium (124 mg/L), and boron (6.0 mg/L).

3.3.4. Extraction of minerals at 60°C and at different pH

The mineral extraction at 60°C shows that a high percentage of magnesium extraction at pH 10.0 the percentage of magnesium extracted was about 90%. Other major minerals extracted at 60°C are calcium, sulfate, boron, and strontium at concentrations of 112, 300, 5.89, and 1.7 mg/L, respectively. In these experiments, most of the divalent cations extracted faster than the monovalent ions. The amount and percentage of extracted minerals are shown in Figs. 22 and 23.

3.3.5. Extraction of minerals at 50°C and at different pH

At 50°C the amount of mineral extracted was considerably lesser than the amount of mineral extracted at higher temperatures. It was observed that very less concentration of minerals extracted below pH 10.0. The major extracted minerals at 50°C and pH 10.0 are magnesium and boron at 82% and 67%, respectively. From Figs. 24 and 25, it is evident that magnesium can be extracted in good percentages even at lower temperatures by increasing the pH to 10.

3.4. Preliminary economic evaluation of magnesium oxide production using SWRO brines

The laboratory scale mineral extraction experiments showed that magnesium was extracted in more quantity from SWRO brines. The SWRO brine of Kuwait contains higher concentration of magnesium compared with other minerals and the by-product of magnesium (MgO, MgCl₂, etc.) are widely used in constructions and chemical industries and have high commercial values. Therefore, the preliminary economic evaluation of magnesium oxide production using Kuwait SWRO brines was performed.

DRP SWRO plant capacity is about 300 m³/d and TDS in brine is approximately 54,900 ppm. The amount of magnesium present in DRP SWRO brine is 1,673 mg/L. The recovery ratio is about 25%–30% and quantity of the rejected brine is approximately 210 m³/d. From the above data, it was calculated that 351.33 kg of magnesium is present in DRP SWRO brine per day.

Accordingly, the amount of magnesium present in the rejected brine from DRP SWRO plant calculated is approximately 141 ton/year. Based on the results obtained in this study and assuming that 98% of magnesium can be extracted using NaOH as base at 90°C and pH 10, then the amount of magnesium that can be produced per year is 138 ton/year.

The molar mass of Mg is 24.3050 g/mol, whereas, molar mass of MgO is 40.3044 g/mol. So, theoretically, 1 g of magnesium can produce 1.658 g of magnesium oxide. Accordingly, the total amount of magnesium oxide (MgO) that can be produced per year from DRP SWRO brine is 228 ton/year.

Considering the market price of MgO at 2,500 USD per ton, the annual benefit that can be achieved by extracting MgO from DRP SWRO brine is 572,010 USD per year.
Shuwaikh SWRO plant capacity is about 136,000 m³/d (30 MIGD) and TDS in brine is approximately 78,000 ppm. The amount of magnesium present in Shuwaikh SWRO brine is 2,703 mg/L. The recovery ratio is about 50%–60% and quantity of the rejected brine is approximately 68,000 m³/d. From the above data, it was calculated that 183,804 kg of magnesium is present in Shuwaikh SWRO brine per day.

Accordingly, the amount of magnesium present in the rejected brine from Shuwaikh SWRO plant calculated is approximately 73,967 ton/year. Based on the results obtained in this study and assuming that 78% of magnesium can be extracted using NaOH as base at 90°C and pH 10, then the amount of magnesium that can be produced per year is ≈59,053 ton/year.

Accordingly, the total amount of magnesium oxide (MgO) that can be produced per year from Shuwaikh SWRO brine is 97,909 ton/year. Considering the market price of MgO at 2,500 USD per ton, the annual benefit that can be achieved by extracting MgO from Shuwaikh SWRO brine is 244,772,500 USD per year.

4. Conclusion

The mineral extraction from actual SWRO brines was conducted using chemical precipitation process. In the process, mineral extraction capability of three different inorganic bases was studied. The study proved that NaOH is the best suitable base for extracting minerals from Kuwait SWRO brine. In addition, the effect of basicity and temperature was conducted for DRP and Shuwaikh SWRO brine at standardized conditions for maximum mineral extraction. The mineral extraction results showed that there is a change in total concentration of extracted mineral with an increase in temperature from 50°C to 90°C as well as with the increase of pH from 8.0 to 10.0. The extracted minerals are magnesium, lithium, boron, sulfate, calcium, and strontium. The experimental results showed that the precipitation or extraction of minerals started only at pH above 9.0 and decrease of temperature reduced the total extracted mineral concentration. The preliminary calculation showed that approximately 228 and 97,909 ton/year of magnesium oxide can be produced from DRP and Shuwaikh SWRO brine, respectively. Accordingly, the annual benefit from the produced magnesium oxide is 572,010 and 244,772,500 USD per year from DRP and Shuwaikh SWRO brine, respectively.

Therefore, the integration of mineral extraction plants to seawater desalination plants reduces brine disposal problem, and the economic return from mineral extraction will benefit in reduction of overall water production cost.

References


