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Mineral extraction from seawater reverse osmosis brine of Gulf seawater

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ABSTRACT

The brine disposal from desalination plants and its environmental impact are the major challenges faced by the desalination industry all over the world. The desalination brine contains higher concentration of inorganic compounds than that in seawater in addition to the chemical additives used by the pre-treatment units. The precipitation of minerals from brine reduces the fresh water production cost as well as minimizes the brine disposal problem. This article explores a systematic approach for the brine treatment problem by assessing the performance of mineral precipitation using chemical precipitation technique for precipitating valuable minerals, including magnesium, calcium, boron, sulfate, and strontium, from the rejected brine of two seawater reverse osmosis (SWRO) desalination plants in Kuwait. The preliminary mineral precipitation results showed that sodium hydroxide is the best suitable base for precipitation of all minerals compared with calcium hydroxide and ammonium hydroxide. Further, the mineral precipitation experiments were performed by using sodium hydroxide as base at different processing temperature and pH. The results showed that more than 78% of magnesium (Mg) was precipitated from RO brine at pH 10 and temperature of 90°C. The preliminary economic evaluation of magnesium oxide production using RO brine of desalination plants at Doha Desalination Research Plant and Shuwaikh sites of Kuwait are 228 and 97,909 tons per year, respectively. Overall, this study established optimum operating condition for effective precipitation of minerals from high saline Arabian Gulf SWRO brine with high efficiency and showed promising results for large-scale mining.

Keywords: Reverse osmosis brine; Mineral precipitation; Desalination plant; Chemical precipitation

1. Introduction

The increased urbanization and significant population growth has increased the demand for clean water. The report of Organization for Economic Co-operation and Development (OECD) 2008 revealed that 47% of world population will suffer from deficiency of fresh water by 2030 [1]. The desalination of seawater will become a reliable solution to the water shortages being experienced by the arid countries [2–4]. The main two categories of desalination are thermal- and membrane-based processes. Thermal processes cover distillation-based technologies such as multi-effect distillation (MED) and multi-stage flash (MSF) distillation [5]. Thermal-based desalination has been utilized for several years especially in the Middle East where the costs for energy requirements are significantly less in the region [6]. Membrane-based desalination processes are mainly reverse osmosis (RO), nanofiltration (NF) and electrodialysis (ED), with RO being the most widely used. In RO, high pressure is applied over a solution to allow the solvent only to pass through a selective membrane to the other side, thereby leaving behind the molecules and ions in the mother solution [7]. The most frequently used conventional seawater desalination technologies in Gulf Cooperation Council (GCC) countries are MSF [8,9] and RO [5]. The current desalination capacity of GCC is approximately 4,000 million imperial

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gallons a day (MIGD) and is set to increase more than 40% over the next 5 years [10], which will increase the impact on the Gulf ecosystem [11,12]. The State of Kuwait is fully dependent on conventional seawater desalination technologies due to the lack of fresh water resources. According to the Ministry of electricity and water, Kuwait has produced a total of 164,111 million gallons fresh water in 2017 (in which 146,922 million gallons of potable water and 17,189 million gallons brackish water) [13]. A recent study on global seawater desalination indicates that almost 80×10^6 m^3/d of desalinated water is produced every day, which leads to produce concentrated brine in the order of 100×10^6 m^3 every day [14].The reject from the desalination plants will be usually 10% to 15% more concentrated than usual seawater [15]. 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 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 [16,17]. The presence of inorganic compounds and higher salt concentration of the rejected concentrate causes major environmental and regulatory problems for seawater desalination industry [18]. 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 [19]. Thus, the reduction in brine volumes will reduce both potable water costs and, at the same time, the environmental impact of the desalination process.

There are a number of RO brine disposal and treatment methods such as deep well injection, discharge into the sea, sanitary sewers, evaporation ponds, forward osmosis (FO), vacuum membrane distillation (VMD), vacuum-enhanced direct contact membrane distillation (VEDCMD), RO–NF integrated system, bipolar membrane electrodialysis (BMED), ED, electro dialysis reversal (EDR), vibratory shear enhanced processing (VSEP), capacitive deionization, etc. [20]. The assessment of viability of applying the FO technology for brine concentration produced from brackish or seawater desalination plants were performed by Tang and Ng [4]. The study reported that FO process has the potential to concentrate the brine. VMD technology, which uses transmembrane pressure difference between feed partial vapor pressure on one side of a hydrophobic micro-porous membrane and a vacuum applied on the other side of the membrane, was applied for brine concentration. The study proved that a global recovery factor of 89% can be obtained by coupling RO and VMD [21]. Martinetti et al. [22] have studied VEDCMD for water recovery enhancement in desalination of brackish water and reported that VEDCMD achieved water recoveries up to 81% from the brines. Hilal et al. [23] conducted several preliminary tests based on the membrane electrochemical process, BMED, using NaCl solutions at high and low concentrations followed by tests with mixed salt solutions representing pretreated RO concentrate and finally with actual pretreated RO concentrate. The study reported that BMED process was technically viable for regenerating mixed acids and bases of reusable quality from RO concentrate [23]. The experiment on real RO concentrates using ED process suggests that the separation of salts from organics by electro dialysis is feasible [24]. Other research studies based on ED shows that the concentration of RO brine solution can be increased from 1.5% to 10% at an energy requirement of 7.0–8.0 kWh/m^3 [25]. The concentrations of the RO brine were reduced to 18–20 mN by ED and it can be mixed with RO permeate [25]. Research studies based on EDR for the treatment of inland brackish water RO concentrate was conducted by Turek et al. [26] The study reported that EDR can crystallize calcium sulfate and calcium bicarbonate in the concentrate [26]. VSEP treatment was used for RO reject from brackish well water. The study reported that 98% recovery of treated water was achieved, leaving only 2% of the volume to be disposed of as reject [27]. VSEP process, similar to EDR, would also decrease the amount of concentrate needing to be disposed [28].

The benefits of concentrate minimization and zero liquid discharge practices are often offset by their high operation and maintenance costs, and energy requirements [22,29,30]. 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 [31–35]. 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 [36]. 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 [37]. 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 [37]. 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 [37]. 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 and MSF) usually discharge a more diluted brine [15]. The recovery of gypsum, sodium chloride, magnesium hydroxide, calcium chloride, calcium carbonate, and sodium sulfate has been reported in literatures [38,39]. 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 [37].

The mineral extraction process is a thermodynamically and kinetically controlled process which involves the precipitation or separation based on the applied energy [40,41]. The chemical precipitation and crystallization methods are widely used methods for mineral precipitation from seawater and rejected brine from desalination plants. The major minerals in seawater are sodium, potassium, calcium, magnesium, strontium, lithium, boron, sulfate, and halogens [42,43].

The higher concentration of commercially valuable minerals in high saline brine discharged from Kuwait desalination plants has given a motivation to conduct this research study of mineral precipitation. The study covered the simple chemical precipitation method. A preliminary literature study was conducted to shortlist the available best process for SWRO mining [44–46] and accordingly precipitation 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, India and Merck, Germany, and used without any further purification. The quantitative and qualitative analysis was carried out using inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP 6000, Thermo Scientific, USA), conductivity meter (ORION STAR A222), spectrophotometer (LANGE DR 2800), and pH meter (ORION STAR A221) in standard analytical conditions. The laboratory scale mineral precipitation 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 m^3/d, respectively. The total dissolved solids (TDS) 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%. The average composition of seawater feed and SWRO brine discharged from DRP and Shuwaikh desalination plants are shown in Tables 1 and 2, respectively. The result shows that the TDS of rejected brine from Shuwaikh SWRO plant is significantly higher than that of the DRP SWRO desalination plant. This is mainly due to difference in feed intake system and difference in the water recovery ratio percentage. The feed intake system of DRP SWRO plant is beach well, while the Shuwaikh desalination plant is supplied directly from sea.

2.2. Mineral precipitation method

Precipitation 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 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

Table 1
Average composition of DRP SWRO feed seawater and brine

Parameters	Seawater	SWRO brine
Alkalinity as $CaCO_3$, mg/L	131.6	175
Ammonia, mg/L	<1	<1
Barium, mg/L	<1	<1
BOD, mg/L	<1	<1
Boron, mg/L	3.7	9.8
Bromine, mg/L	–	0.02
Calcium, mg/L	730	1,090
Chloride, mg/L	24,876	–
Chlorine, mg/L	–	0.02
Chromium, mg/L	<0.01	<0.01
COD, mg/L	90	–
Conductivity	58.3	69.4
Copper, mg/L	<0.01	<0.01
Fluoride, mg/L	5	–
Iodine, mg/L	–	0.02
Iron, mg/L	<0.01	<0.01
Lithium, mg/L	–	1.7
Magnesium, mg/L	1,325	1,673
Nitrate, mg/L	4.3	–
pH	7.3	7.13
Phosphate, mg/L	0.2	–
Potassium, mg/L	316.4	997
Silica, mg/L	2.1	–
Sodium, mg/L	14,488.5	17,905
Strontium, mg/L	14.6	121
Sulfate, mg/L	3,430.5	4,159
Total dissolved solids, mg/L	45,377	54,900
Total suspended solids, mg/L	0.75	–
Turbidity, NTU	1.06	0.35

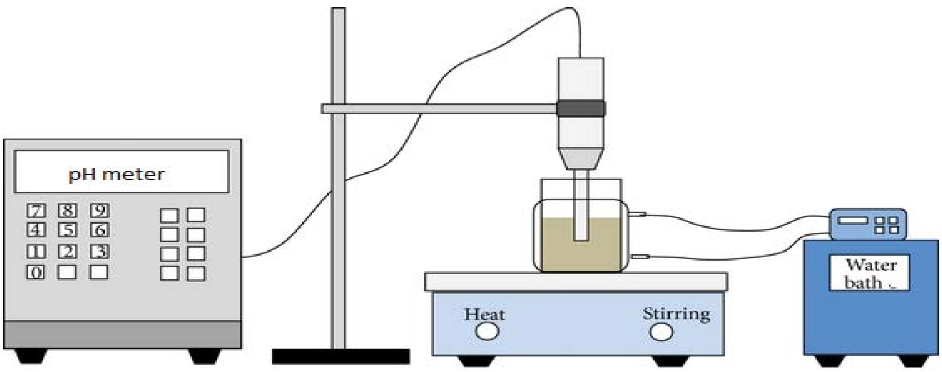

Fig. 1. Schematic diagram of the experimental apparatus assembly used for mineral precipitation.

Table 2
Average composition of Shuwaikh SWRO feed seawater and brine

Parameters	Seawater	SWRO brine
Alkalinity, mg/L	146.5	178.8
Ammonia, mg/L	<1	<1
Barium, mg/L	<1	<1
BOD, mg/L	<1	<1
Boron, mg/L	–	10.7
Bromine, mg/L	–	0.04
Calcium, mg/L	468	1,040
Chloride, mg/L	26,440.7	–
Chlorine, mg/L	–	0.04
Chromium, mg/L	<0.01	<0.01
COD, mg/L	90.65	–
Conductivity	63.3	98.7
Copper, mg/L	<0.01	<0.01
Fluoride, mg/L	3.66	–
Iodine, mg/L	–	0.04
Iron, mg/L	<0.01	<0.01
Lithium, mg/L	–	1.7
Magnesium, mg/L	1,712	2,703.2
Nitrate, mg/L	3.5	–
pH	8.1	7.04
Phosphate, mg/L	0.11	–
Potassium, mg/L	485	1,141.7
Silica, mg/L	0.5	–
Sodium, mg/L	14,991	27,802
Strontium, mg/L	6.6	50.4
Sulfate, mg/L	3,554	7,497.3
Total dissolved solids, mg/L	56,599	78,450
Total suspended solids, mg/L	1.7	–
Turbidity, NTU	1.1	0.66

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 precipitated minerals in the process. The flow diagram for the precipitation method is shown in Fig. 2.

2.3. Standardization of precipitation methods

The mineral precipitation capacity of different inorganic bases was studied. For these experiments, calcium hydroxide ($Ca(OH)_2$), sodium hydroxide (NaOH), and ammonium hydroxide (NH_4OH) 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 precipitated and % precipitation of each mineral was calculated using the below equations:

$$\text{Amount of mineral extracted}\left(\frac{\text{mg}}{\text{L}}\right)=\left(C_i-C_f\right) \tag{1}$$

$$\%\text{ of mineral extracted}=\frac{\left(C_i-C_f\right)}{C_i}\times 100 \tag{2}$$

where C_i = initial mineral concentration (mg/L), C_f = final mineral concentration (mg/L).

The chemical reactions involved in the precipitation process for different inorganic base are shown as follows:

$$\text{RO brine }\left(\text{MX}\right)+\text{Ca}\left(\text{OH}\right)_2\rightarrow\text{MOH, M}\left(\text{OH}\right)_2+\text{CaCl}_2 \quad \text{(I)}$$

$$\text{RO brine}\left(\text{MX}\right)+\text{NH}_4\text{OH}\rightarrow\text{MOH, M}\left(\text{OH}\right)_2+\text{NH}_3 \quad \text{(II)}$$

$$\text{RO brine}\left(\text{MX}\right)+\text{NaOH}\rightarrow\text{MOH, M}\left(\text{OH}\right)_2+\text{NaCl} \quad \text{(III)}$$

where MX: Mineral halide/sulfate.

2.4. Experimental procedure for mineral precipitation 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 precipitation. 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.

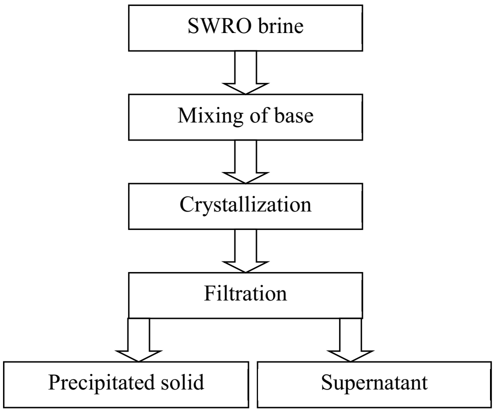

Fig. 2. Flow diagram of mineral precipitation from SWRO brine.

3. Results and discussion

3.1. Effect of base on mineral precipitation

The mineral precipitation capability of $Ca(OH)_2$, NH_4OH, and NaOH were studied at pH 9.0. The result showed the precipitation 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

The concentrations of mineral present in filtrate and precipitated amounts of minerals using $Ca(OH)_2$ are presented in Table 3. Fig. 3 shows the precipitation percentage of each mineral using $Ca(OH)_2$ as base. The minerals that were precipitated more are boron, strontium, magnesium, and sulfate with precipitation percentage of 36, 25, 23, and 11, respectively. Other minerals are precipitated at an extremely low percentage and a loss of 43% calcium hydroxide was observed in these experiments.

3.1.2. NH_4OH as base

Fig. 4 and Table 4 show the percentage and amount of precipitated mineral using NH_4OH as base. The minerals that were precipitated 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 precipitated while using NH_4OH as the base. In the case of magnesium, the precipitation percentage reduced to 6 from 23 (using $Ca(OH)_2$ base). Compared with $Ca(OH)_2$ base, precipitation percentage of minerals was less with NH_4OH base.

Table 3
Amount of precipitated minerals from DRP SWRO brine using $Ca(OH)_2$ as base

Parameters (mg/L)	Raw RO brine	Supernatant	Precipitated minerals
Calcium	1,092	1,564	–472
Magnesium	1,681.5	1,295.1	386.4
Sulfate	3,700	3,300	400
Bromine	<0.05	<0.05	<0.05
Chlorine	<0.05	<0.05	<0.05
Iodine	<0.05	<0.05	<0.05
Boron	6.187	3.935	2.252
Strontium	23.74	17.76	5.98
Potassium	548	528.9	19.1
Lithium	0.467	0.4393	0.0277
Sodium	24,770	23,930	840

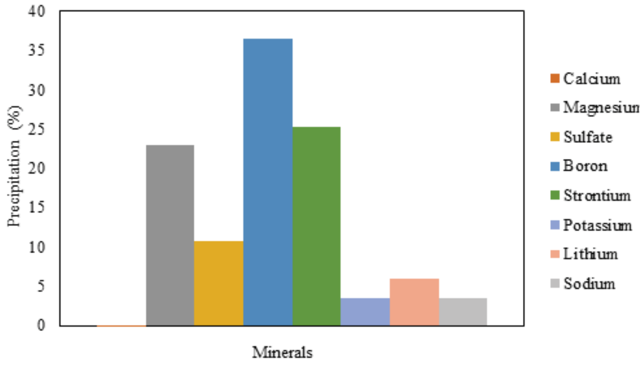

Fig. 3. Percentage of precipitated minerals using $Ca(OH)_2$ as base.

3.1.3. NaOH as base

The amount and percentage mineral precipitated using NaOH as base are presented in Table 5 and Fig. 5. The minerals that were precipitated are boron, lithium, strontium, and magnesium with percentages of 40, 38, 23, and 20, respectively. The precipitation process using NaOH as base was faster compared with $Ca(OH)_2$ and NH_4OH, and this is mainly due to faster reaction (conversion of chloride to hydroxide) and faster crystal growth of minerals in presence of NaOH [47,48]. The strong basicity and high soluble nature of the NaOH in the aqueous media is one of the reason for enhanced mineral precipitation compared with $Ca(OH)_2$ and NH_4OH as base [49]. Solubility of the mineral hydroxide played a major role in the quantity of precipitated minerals in all the experiments. The solubility concentration is depending

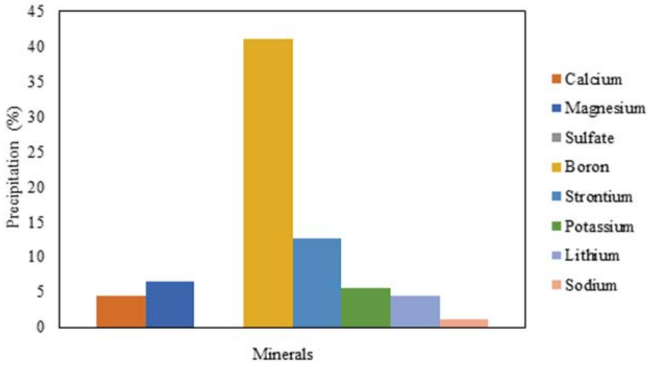

Fig. 4. Percentage of precipitated minerals using NH4OH as base.

Table 4
Amount of precipitated minerals from DRP SWRO brine using NH_4OH as base

Parameters (mg/L)	Raw RO brine	Supernatant	Precipitated minerals
Calcium	1,092	1,044	48
Magnesium	1,681.5	1,572.15	109.35
Sulfate	3,700	3,700	0
Bromine	<0.05	<0.05	<0.05
Chlorine	<0.05	<0.05	<0.05
Iodine	<0.05	<0.05	<0.05
Boron	6.187	3.644	2.543
Strontium	23.74	20.75	2.99
Potassium	548	517.5	30.5
Lithium	0.467	0.4462	0.0208
Sodium	24,770	24,490	280

Table 5
Amount of precipitated minerals from DRP SWRO brine using NaOH as base

Parameters (mg/L)	Raw RO brine	Supernatant	Precipitated minerals
Calcium	1,092	1,032	60
Magnesium	1,681.5	1,329.15	352.35
Sulfate	3,700	3,400	300
Bromine	<0.05	<0.05	<0.05
Chlorine	<0.05	<0.05	<0.05
Iodine	<0.05	<0.05	<0.05
Boron	6.187	3.697	2.49
Strontium	23.74	18.25	5.49
Potassium	548	508	40
Lithium	0.467	0.288	0.179
Sodium	24,770	27,750	–2,980

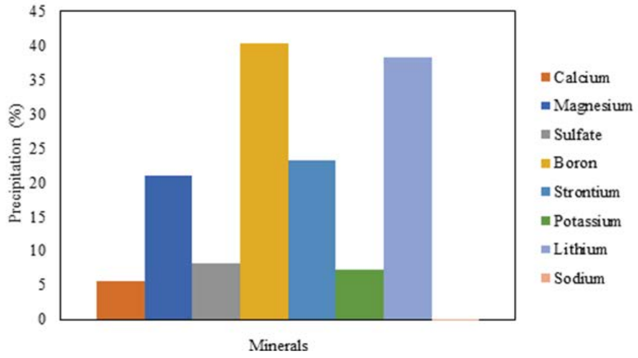

Fig. 5. Percentage of precipitated minerals using NaOH as base.

on pH of the aqueous media, temperature, and concentration of other impurities or competitive precipitating salts [50]. Based on the above experimental results, the amount and percentage of precipitated minerals are more using NaOH as base compared with $Ca(OH)_2$ and NH_4OH. 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 precipitation (DRP SWRO brine)

3.2.1. Precipitation of minerals at 90°C and at different pH

The effect of pH and temperature on mineral precipitation 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 precipitation percentage with an increase in pH as shown in Fig. 6. The increasing trend of mineral precipitation is mainly due to effect of increase of pH at higher temperature and ionic activity [51–53]. It is observed from Fig. 6 that the major minerals precipitated 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 precipitated at 90°C and pH 10.

3.2.2. Precipitation of minerals at 80°C and at different pH

The mineral precipitation 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 precipitation 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 precipitated when the pH was changed from 9.5 to 10 (41.5 to 750.8 mg/L) as shown in Fig. 8. The drastic change in magnesium precipitation at

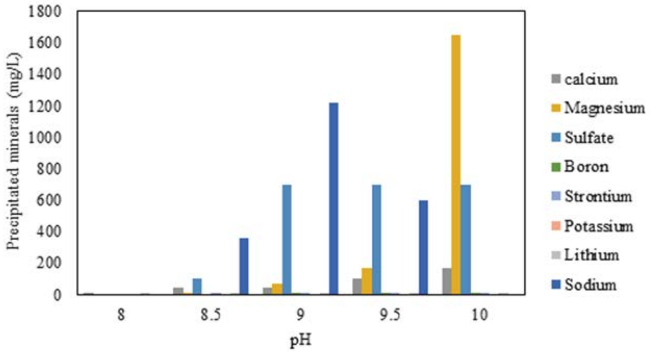

Fig. 6. Concentration of minerals precipitated at different pH at 90°C.

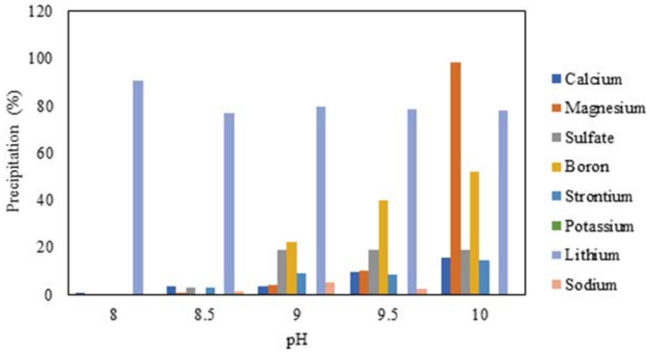

Fig. 7. Percentage of minerals precipitated at 90°C.

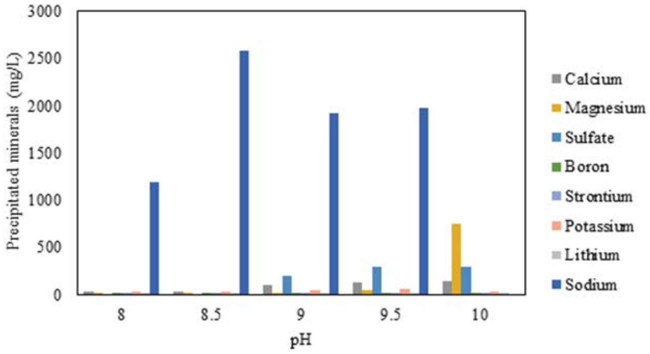

Fig. 8. Concentration of minerals precipitated at different pH at 80°C.

pH 9.5–10 may be due to decrease of solubility concentration of magnesium in the aqueous solution [50]. The precipitated minerals at 80°C and pH 10 are boron, lithium, magnesium, calcium, and sulfate with precipitation percentage of 73, 66, 44, 13, and 8, respectively, as shown in Fig. 9. It is observed that sulfate precipitation percentage was almost the same and not affected much by the change in pH from 9 to 10.

3.2.3. Precipitation of minerals at 70°C and at different pH

The precipitated 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 precipitated at pH 9.5 to 10 (116–120 mg/L). This shows that $Ca(OH)_2$ solubility concentration depends on the ion strength of the solution [50]. The drastic increase in precipitation of magnesium (from 34 to 1,193 g/L) was observed for pH 9.5 to 10 as with 80°C. Fig. 11 clearly shows that magnesium was the major precipitated mineral at 70°C and pH 10.

3.2.4. Precipitation of minerals at 60°C and at different pH

The mineral precipitation at 60°C shows a high percentage of lithium precipitation at pH 8.0. This may be due to the high reactivity and small size of the lithium ion [54]. Other major precipitated minerals at 60°C and pH 10 are boron and magnesium with precipitation percentage of 77 and 48, respectively. Fig. 12 clearly shows the decrease in the amount of sulfate precipitated with increasing pH from 8 to 10. But, the percentage of precipitation of sulfate is extremely low compared with lithium, boron, and magnesium for all pH at 60°C as shown in Fig. 13. The low percentage of sulfate precipitation at 60°C may be due to poor reactivity of sulfate ions at lower temperature.

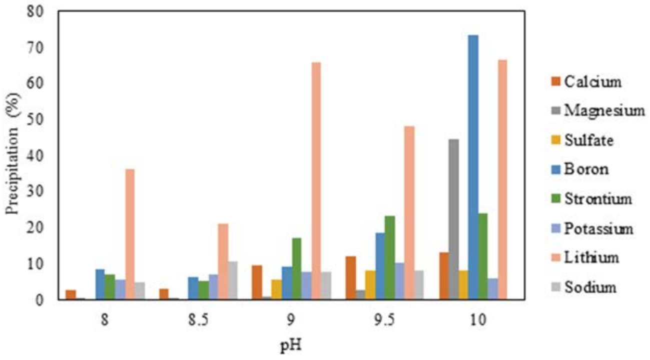

Fig. 9. Percentage of minerals precipitated at 80°C.

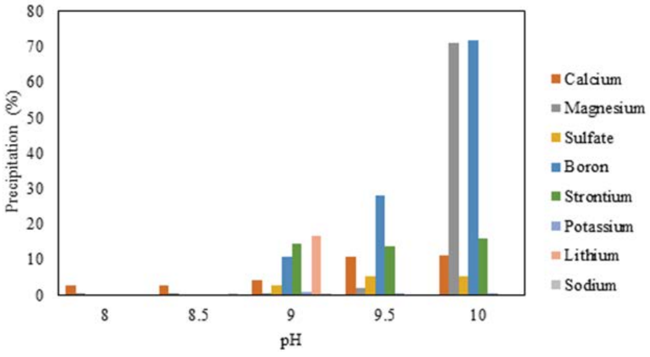

Fig. 10. Percentage of minerals precipitated at 70°C.

3.2.5. Precipitation of minerals at 50°C and at different pH

At 50°C there was an increase in mineral precipitation percentage with increase in pH, but the rate of increase was very less when compared with 90°C. The mineral precipitation increase with increase of temperature clearly shows

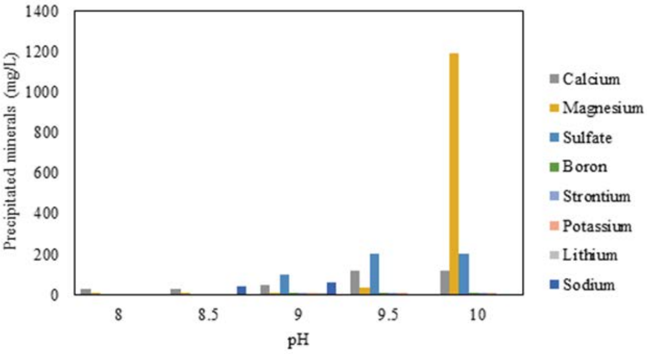

Fig. 11. Concentration of minerals precipitated at different pH at 70°C.

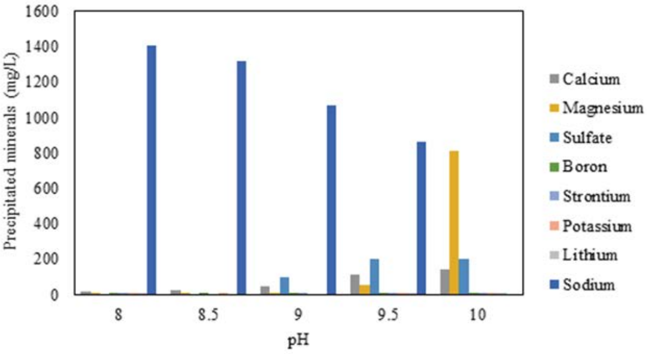

Fig. 12. Concentration of minerals precipitated at different pH at 60°C.

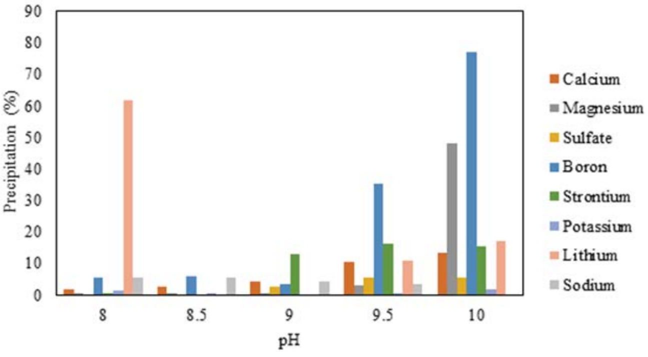

Fig. 13. Percentage of minerals precipitated at 60°C.

the effect of temperature on mineral precipitation. At higher temperature, the molecules rapidly dissociate into ions and results in faster reaction resulting in enhanced extraction [55]. At 50°C, there was a drastic change in the amount of magnesium precipitated 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 precipitated minerals are magnesium and boron with precipitation percentage of 73 and 65, respectively. Fig. 15 clearly shows that the amount of magnesium precipitated at pH 10 was very high compared with sulfate, boron, lithium, etc. It is important to note that magnesium precipitated 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 precipitation (Shuwaikh SWRO brine)

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

The effect of pH and temperature on mineral precipitation 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 at pH below 9.0 [47,48]. The filtrate analysis showed that there is an increase in the percentage of minerals precipitation with an increase in pH as shown in Fig. 16. The effect of increase in pH at higher temperature and ionic activity resulted in increased mineral precipitation [51–53]. The amount of NaOH 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 precipitated 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 precipitated by using sodium hydroxide as base at 10.0 pH. The precipitated mineral concentrations and percentage of precipitations are shown in Figs. 16 and 17.

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

The amount of minerals precipitated at 80°C is slightly less than the total mineral precipitated at 90°C. At 80°C with pH 9.5 to 10.0, a drastic increase in magnesium and boron precipitation was observed. The drastic change in magnesium and boron precipitation at pH 9.5 to 10 may be due to the decrease of solubility concentration of magnesium and boron in the aqueous solution [50,56,57]. The concentration of magnesium precipitated was only 12 mg/L at pH 9, but at pH 10 it was 2,060 mg/L. The major minerals precipitated 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. Precipitation of minerals at 70°C and at different pH

The precipitation of mineral at 70°C shows that there is a reduction in the total amount of minerals precipitated.

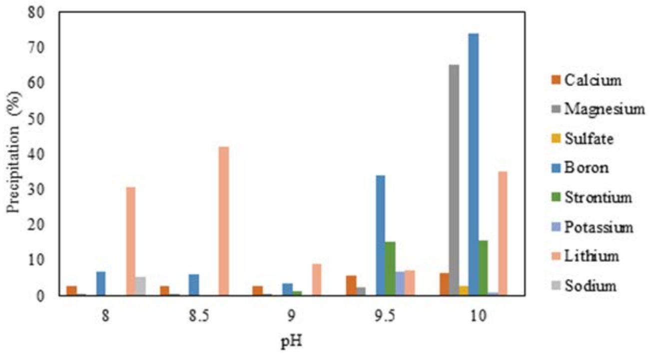

Fig. 14. Percentage of minerals precipitated at 50°C.

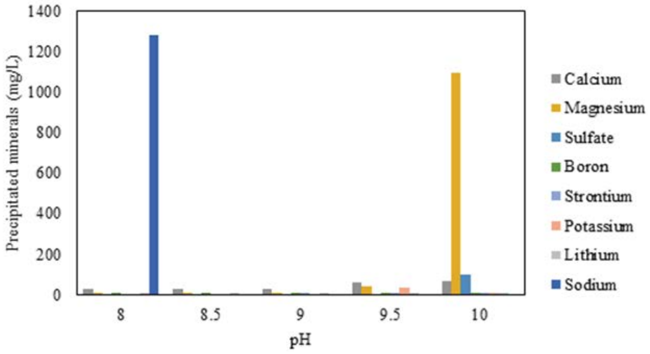

Fig. 15. Concentration of minerals precipitated at different pH at 50°C.

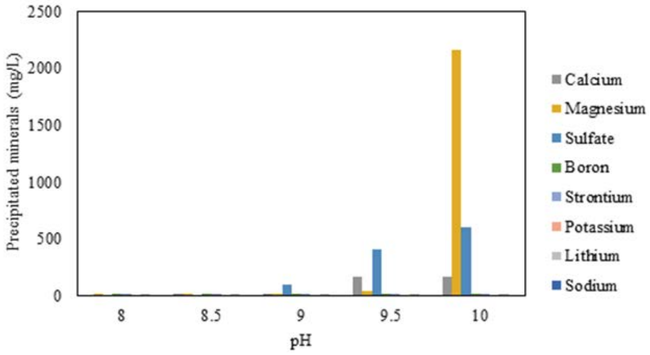

Fig. 16. Concentration of minerals precipitated at different pH at 90°C.

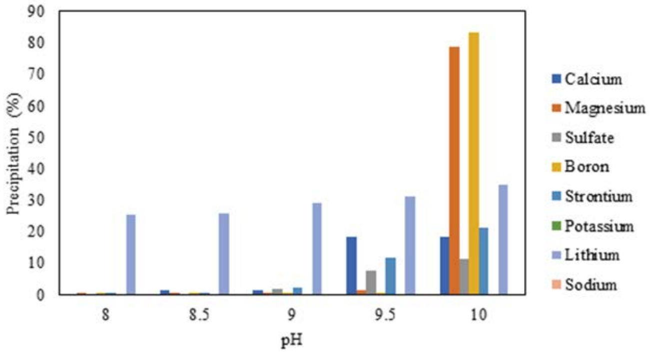

Fig. 17. Percentage of minerals precipitated at 90°C.

The major precipitated mineral was boron and is about 82%. The higher percentage precipitation of boron may be due to decrease of solubility concentration of borate in the aqueous solution with increase of pH [56,57]. The other precipitated minerals are magnesium (67%), lithium (67%), calcium (13%), and sulfate (7%). Figs. 20 and 21 clearly shows that the mineral precipitated at 70°C was less than the mineral precipitated at 90°C. The precipitated minerals are magnesium (1,856 mg/L), sulfate (400 mg/L), calcium (124 mg/L), and boron (6.0 mg/L).

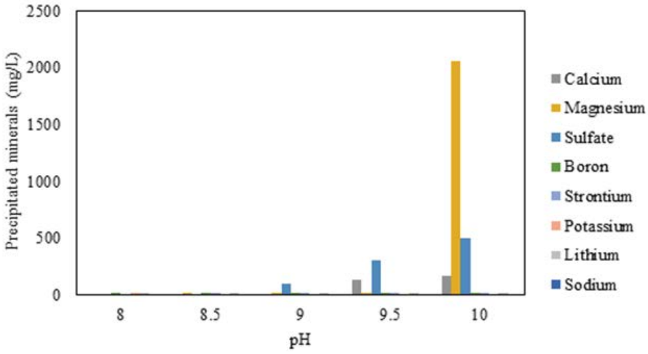

Fig. 18. Concentration of minerals precipitated at different pH at 80°C.

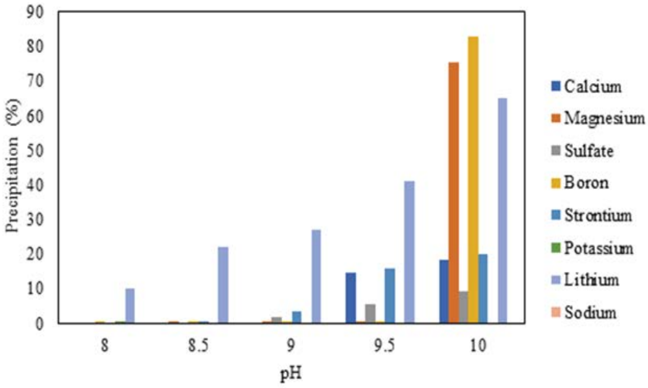

Fig. 19. Percentage of minerals precipitated at 80°C.

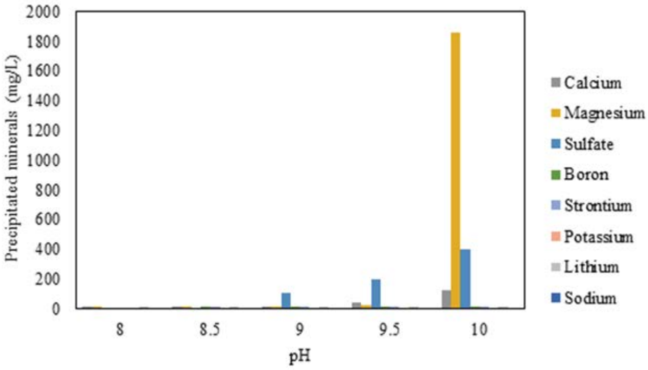

Fig. 20. Concentration of minerals precipitated at different pH at 70°C.

3.3.4. *Precipitation of minerals at 60°C and at different pH*

The mineral precipitation at 60°C shows that a high percentage of magnesium precipitation at pH 10.0. The percentage of magnesium precipitated was about 90%. Other major minerals precipitated 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 precipitated faster than the monovalent ions. The amount and percentage of precipitated minerals are shown in Figs. 22 and 23.

3.3.5. *Precipitation of minerals at 50°C and at different pH*

At 50°C the amount of mineral precipitated was considerably lesser than the amount of mineral precipitated at higher temperatures. It was observed that very less concentration of minerals precipitated below pH 10.0. The major precipitated 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 precipitated in good percentages even at lower temperatures by increasing the pH to 10. The increased percentage of magnesium at high pH and low temperature is due to high reactivity and low solubility concentration of magnesium [50].

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

The laboratory scale mineral precipitation experiments showed that magnesium was precipitated in more quantity

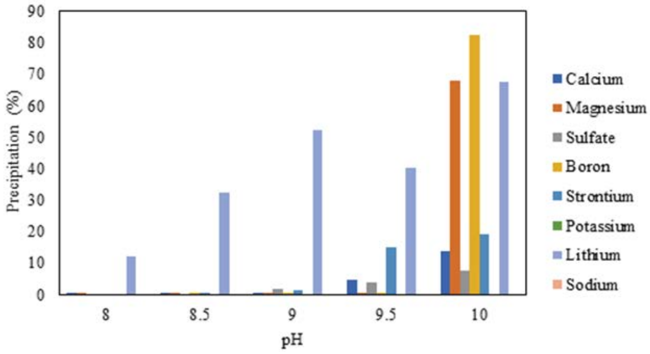

Fig. 21. Percentage of minerals precipitated at 70°C.

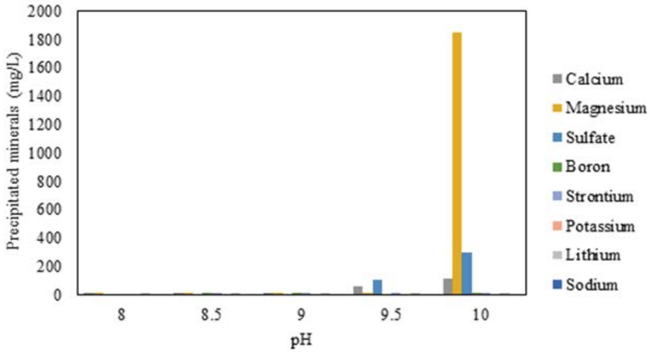

Fig. 22. Concentration of minerals precipitated at different pH at 60°C.

from SWRO brines. The SWRO brine of Kuwait contains higher concentration of magnesium compared with other minerals and the by-product of magnesium (MgO, $MgCl_2$, 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.

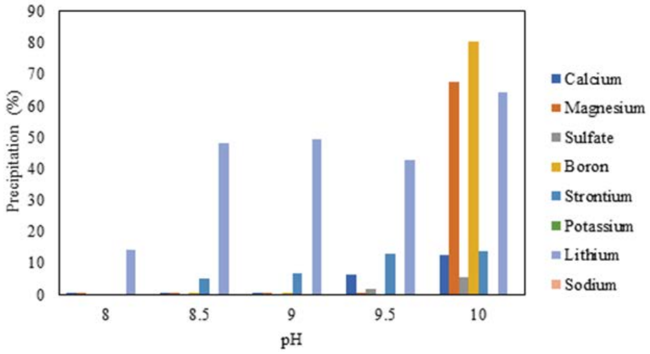

Fig. 23. Percentage of minerals precipitated at 60°C.

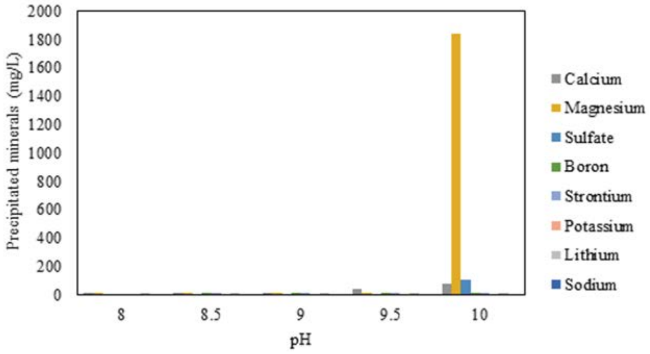

Fig. 24. Concentration of minerals precipitated at different pH at 50°C.

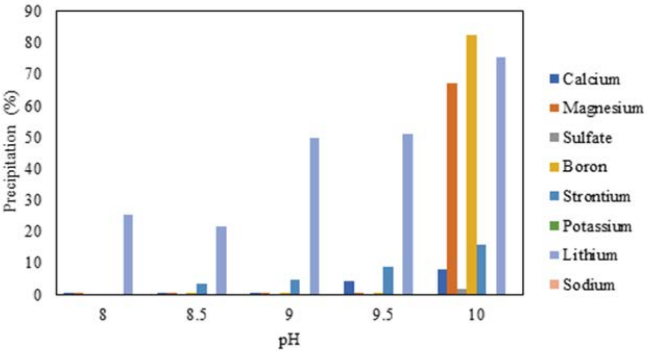

Fig. 25. Percentage of minerals precipitated at 50°C.

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 precipitated 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/ton, the annual benefit that can be achieved by extracting MgO from DRP SWRO brine is 572,010 USD/year. The chemicals used were NaOH and hydrochloric acid (HCl). The NaOH was used to increase the pH to 10 in the precipitation stage, whereas, HCl was used to reduce the pH to 7 in the post-treatment stage. The required quantity of NaOH and 0.1 N HCl is 6.0 and 8.0 g/L, respectively. The market price of commercial grade NaOH is USD 300 and HCl is

Table 6
Average composition of rejected brine after mineral precipitation at pH 10.0 and neutral pH 7.0

Parameters (mg/L)	Doha brine after precipitation	Shuwaikh brine after precipitation	Doha brine after neutralization	Shuwaikh brine after neutralization
Calcium	1,287	1,137	1,285	1,137
Magnesium	101	26	101	25
Chloride	29,920	42,318	30,128	44,082
Potassium	448	696	450	697
Sodium	21,267	30,272	21,394	31,407
Sulfate	3,688	4,966	3,688	4,967
Fluoride	11.1	11	10.8	10.9
Boron	1.34	2.20	1.33	2.19
Lithium	0.91	1.51	0.91	1.506
Strontium	9.52	4.97	9.56	5.09
TDS	53,489	74,307	54,790	75,866

USD 90. Accordingly, the total cost of chemicals required for precipitation and post-treatment is 138,025 USD/year.

Shuwaikh SWRO plant capacity is about 136,000 m^3/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 m^3/d. From the above data, it was calculated that 183,804 kg of magnesium is present in Shuwaikh SWRO brine per day.

Accordingly, the calculated amount of magnesium present in the rejected brine from Shuwaikh SWRO plant is approximately 73,967 ton/year. Based on the results obtained in this study and assuming that 78% of magnesium can be precipitated 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. 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/year. The required quantity of NaOH is 10.5 g/L and 0.1 N HCl is 16.0 g/L. The total cost of chemicals required for precipitation and post-treatment at Shuwaikh SWRO is 76,318,740 USD/year.

The TDS of feed (SWRO brine), filtrate after extraction and post-treated (neutralized) are almost same and contains less concentration of divalent ions as shown in Table 6. The neutralized reject after mineral extraction can be used for further water extraction using thermal desalination process by increasing the top brine temperature, high pressure RO, FO, and membrane distillation [58,59].

4. Conclusion

The mineral precipitation from actual SWRO brines was conducted using chemical precipitation process. In the process, mineral precipitation 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 precipitation. The mineral precipitation results showed that there is a change in total concentration of precipitated 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 precipitated minerals are magnesium, lithium, boron, sulfate, calcium, and strontium. The experimental results showed that the precipitation of minerals started only at pH above 9.0 and decrease of temperature reduced the total precipitated 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/year from DRP and Shuwaikh SWRO brine, respectively. Therefore, the integration of mineral precipitation plants to seawater desalination plants reduces brine disposal problem, and the economic return from mineral precipitation will benefit in reduction of overall water production cost.

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