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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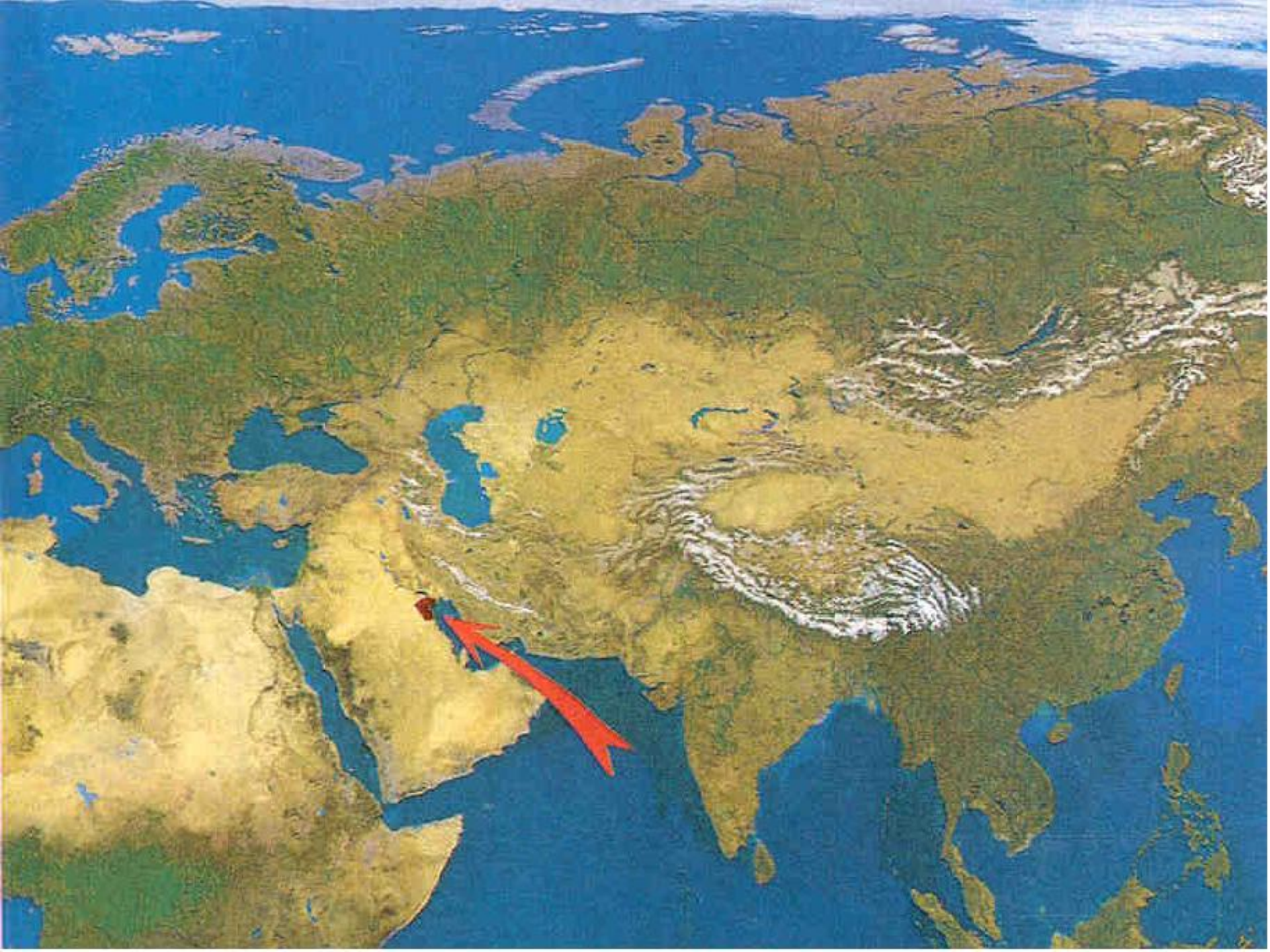
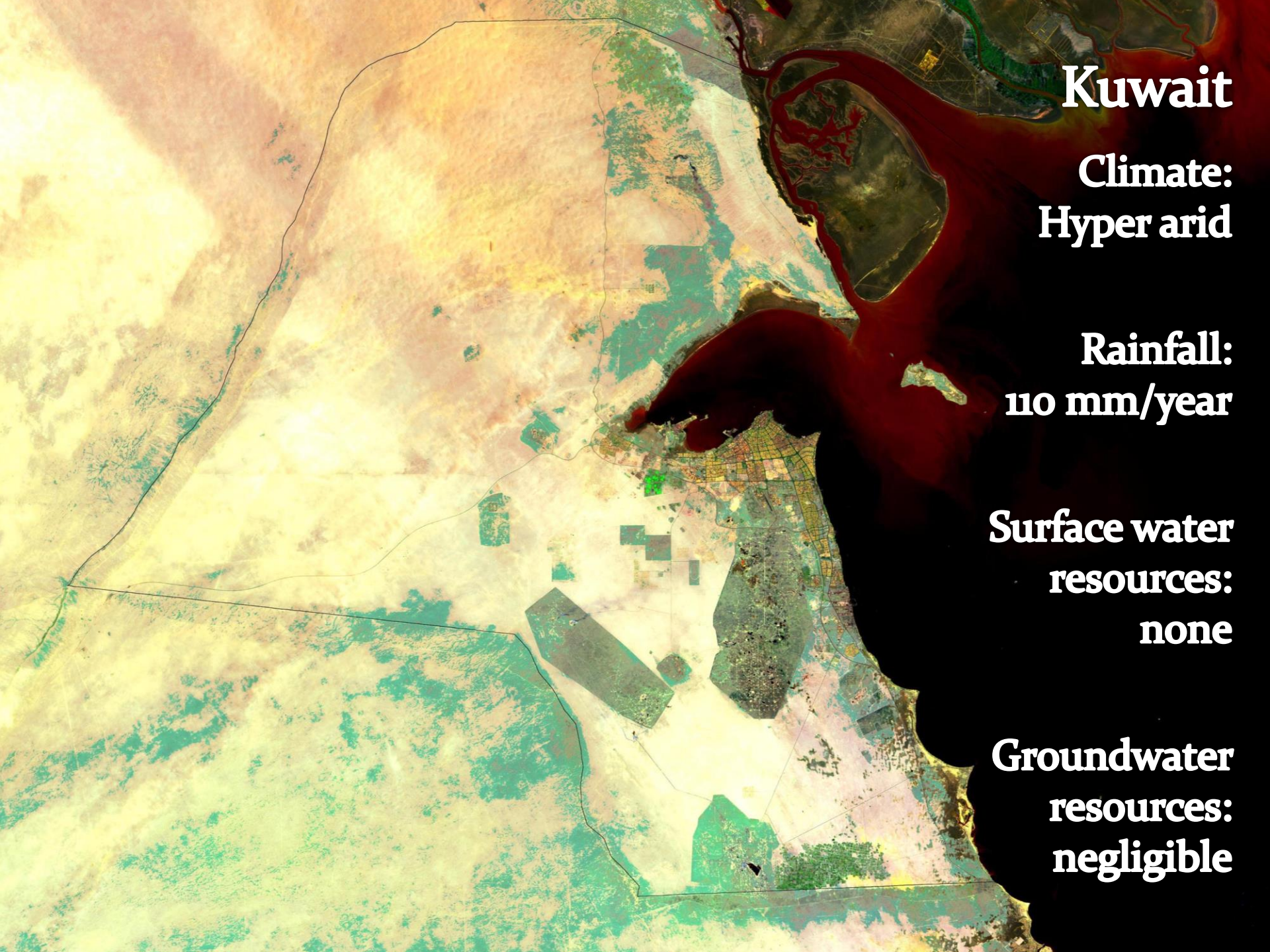
Overview

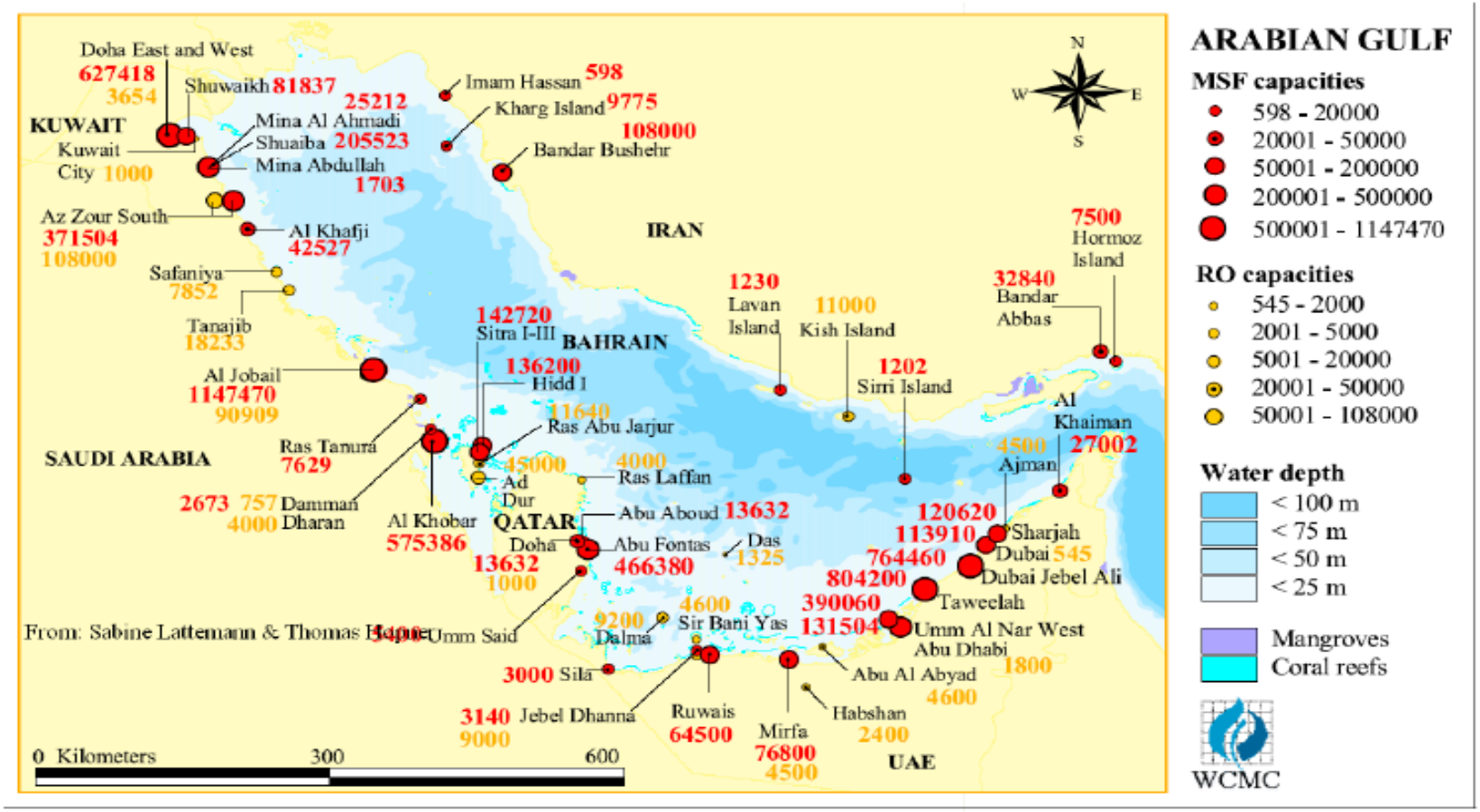
- Introduction
- Experimentation
- Results & Discussion
- Conclusions & Recommendations
- Acknowledgements

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 (MlGD) 2014 – 2018

Station	*Year*				
	2014	*2015*	*2016*	*2017*	*2018*
[a] Shuwaikh	49.5	49.5	49.5	49.5	49.5
Shuaiba	36	36	36	36	36
Doha East	42	42	42	42	42
Doha West	110.4	110.4	110.4	110.4	110.4
[b] Az-Zour South	145.2	145.2	145.2	145.2	145.2
Sabiya	100	100	100	100	100
Shuaiba North (G/T) Project	45	45	45	45	45
[c]Doha (Stage I)	-	-	-	-	50
[d] Doha (Stage II)	-	-	-	-	50
Total Installed Capacity	528.1	528.1	528.1	528.1	628.1

[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 MlGD

Considered approximately 20% water recovery

Kuwait Water Production 11-3-2019

Capacity: 623 MIGD
Production : 431MIGD 11-3-21019
Consumption : 400 MIGD 11-3-2019

Problem Statement

characteristic of brine

- High total dissolved solids (TDS:~ 54,000 - 80,000 mg/L),
- High temperature than that of seawater in case of thermal sesalination

Brine disposal is a major problem for costal & 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

Parameter	Units	Arabian Gulf Seawater	Arabian Gulf Beach-well Seawater	MSF Brine	RO Brine
pH	-	8.2	7.13	8.67	7.56
EC*	mS/cm	68.4	66.6	101.3	78.5
Ca^{2+}	mg/l	648	1,080	996	1,276
Mg^{2+}	mg/l	1,676.7	1,416.6	2,258	1,733
$(SO_4)^{2-}$	mg/l	4,200	3,900	5,700	4,500
$(HCO_3)^-$	mg/l as $CaCO_3$	180.8	175.6	299.9	221.6
Cl^-	mg/l	26,100	25,400	41,000	29,400
Na^+	mg/l	16,925	16,471	26,587	19,065
TDS	mg/l	48,116	47,843	75,370	55,866

Harvesting Salts and Other Useful Products

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

- ✓ NaCl
- ✓ KCl
- ✓ Na_2SO_4
- ✓ K_2SO_4
- ✓ $MgSO_4$
- ✓ $Mg(OH)_2$
- ✓ KNO_3
- ✓ Na_2NO_3 and … etc.

Mineral	Uses
NaCl	Textile dyeing, aquaculture, soil stabilization, and ice and snow removal
Cl_2	Polymers, plastics, and synthetic fibres
NaOH	Glass, rayon, synthetic fibres, plastics, polyester, soaps, and detergents
$NaSO_4$	Pulp and paper, dyes, and ceramic glazes
Na_2CO_3	Glass, pulp and paper, and rayon

Potential Products and Market Information

Product name	*Chemical composition*	*Potential applications and end uses*	*Cost Price/ton (2015)*
Sodium chloride (Halite)	NaCl	Chlor-alkali, soda ash, food industries. Water softening, de-icing road salt, glass, medicine, agriculture and firefighting.	180 US$ (Open pan salt) 8.5 US$ (Salt in brine)
Calcium sulfate	$CaSO_4$	Cements, gypsum, glass, textile, plastics, paints, tires and toothpaste.	9 US$ (Mine) 28 US$ (Plant)
Magnesium hydroxide	$Mg(OH)_2$	Electronic devices, cars industries, alloys, refractory, agriculture, medicine, chemical, material construction industries and wastewater treatment.	3,500 US$ (free Market)
Calcium Carbonate	$CaCO_3$	Agriculture, construction as a building material, medicine, iron industry, pH corrector, paints, ceramic and glass manufactures.	116 US$ (Quicklime) 139 US$ (Hydrate lime)
Sodium Carbonate	Na_2CO_3	Glass manufacture, food production, toothpastes, pulp, cotton industry and paper industries	290 US$ (Green River, USA) 138 US$ (Mine)
Lithium carbonate	Li_2CO_3	Batteries, industrial chemical, ceramic glaze, medicines, plastics, lubricants and grease.	6,600 US$
Potassium Oxide	K_2O	Fertilizers, alloys, catalysts and reducing agents in organic synthesis.	730 US $

Price of magnesium Oxide

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

US $1100.0-1300.0 / Ton

1 Ton (Min. Order)

2YRS Hebei Meishen Tec...

74.1%

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

US $200-1000 / Ton

20 Tons (Min. Order)

11YRS Liaoning Tianci Fi...

69.2%

Magnesium Stabilized Zirconia Powder/MgO stabilized

US $10-20 / Kilogram

1 Kilogram (Min. Order)

2YRS Nanjing Zirae Adva...

100.0%

Magnesium Oxide for livestock feed MgO 96% 95% China

US $240-290 / Metric Ton

25 Metric Tons (Min. Order)

5YRS Liaoning Metals &...

53.7%

Industrial grade fertilizer water soluble best price ...

US $180-350 / Metric Ton

20 Metric Tons (Min. Order)

5YRS Rs Maxunite Co., Ltd.

81.3%

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.

Parameters / Unit	*seawater Intake*	*SWRO brine*
Alkalinity as $CaCO_3$, mg/L	131.6	175
Ammonia, mg/L	<1	<1
Barium, 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
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	-
Phosphate, mg/L	0.2	-
Potassium, mg/L	316.4	997
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

Experimentation

Agilent Technologies,
7900 ICP-MS

Keysight 8500B FE-SEM

Thermo scientific,
Dionex ICS-5000^{+}DP

Spectrophotometer
LANGE DR2800

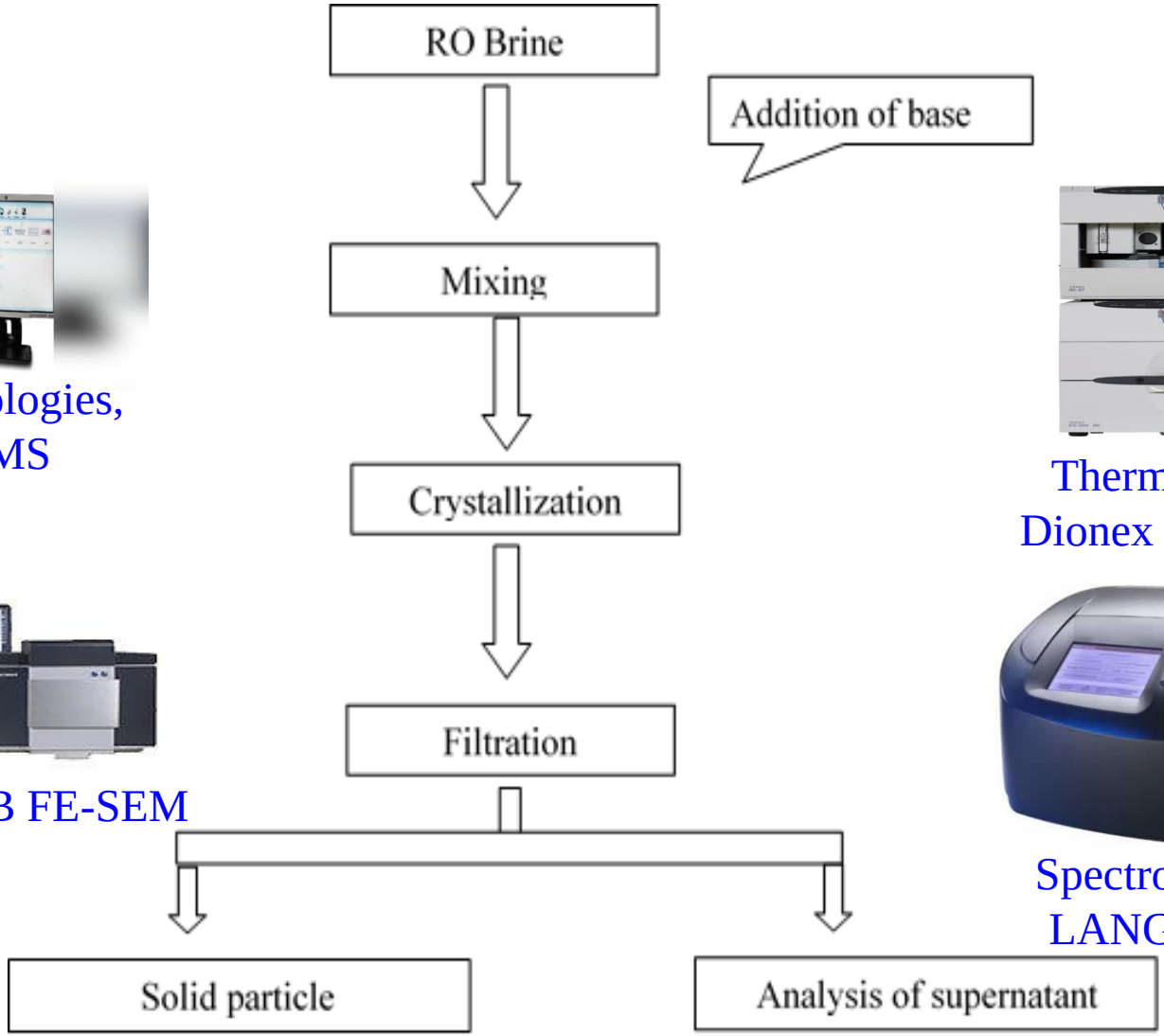
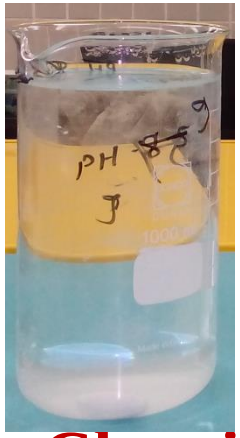


Figure 1. Flow diagram.

Experimentation



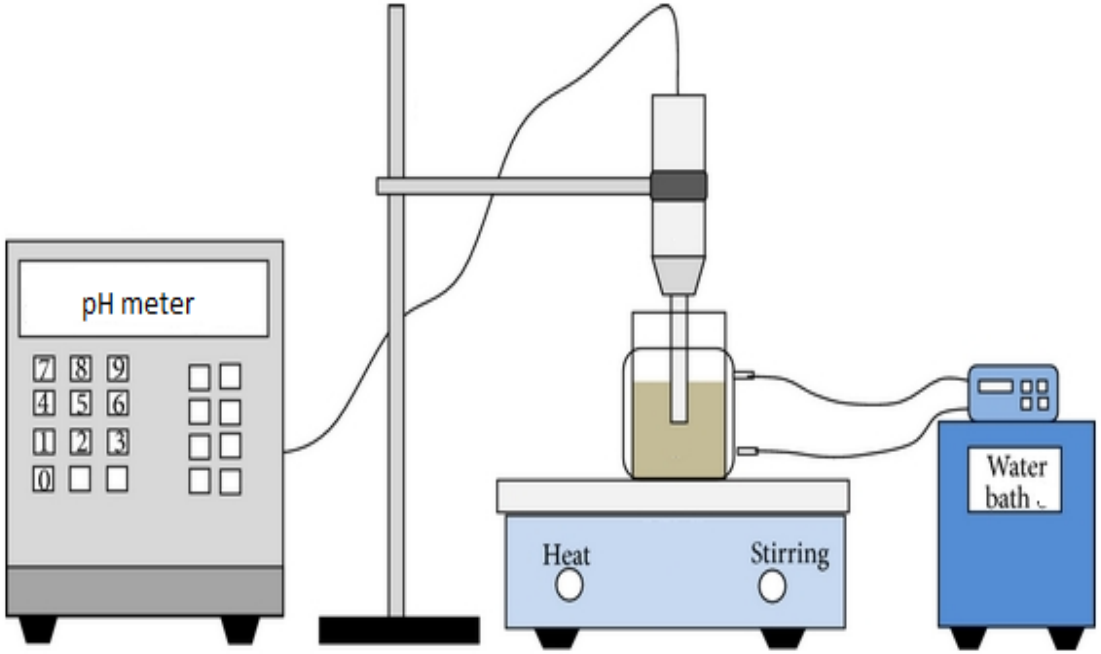


Figure 1. Experimental apparatus.

Chemical Reactions

$$\text{RO brine (MX)} + Ca(OH)_2 \longrightarrow MOH,\ M(OH)_2 + CaCl_2$$

$$\text{RO brine (MX)} + NH_4OH \longrightarrow MOH,\ M(OH)_2 + NH_3$$

$$\text{RO brine (MX)} + NaOH \longrightarrow MOH,\ M(OH)_2 + NaCl$$

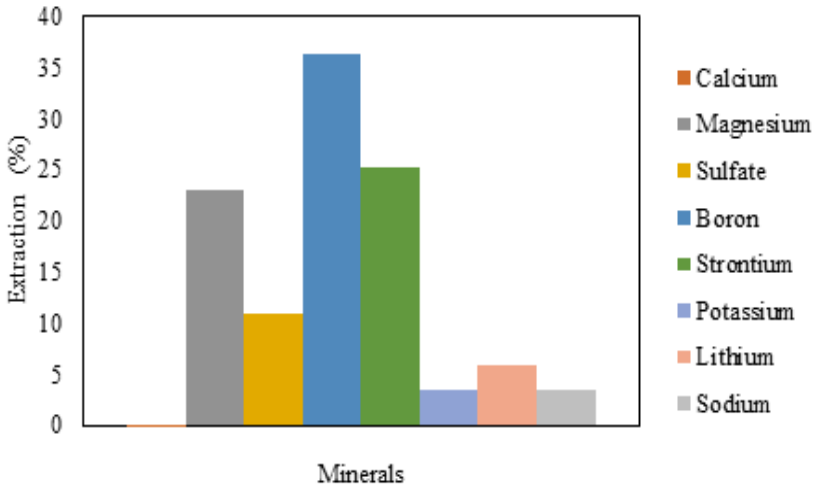
Where MX: Mineral halide and sulphate.

Results and Discussion

Effect of Base on Mineral Extraction (pH 9-Temp 90 °C)

Selected Base: $Ca(OH)_2$, NH_4OH, and NaOH

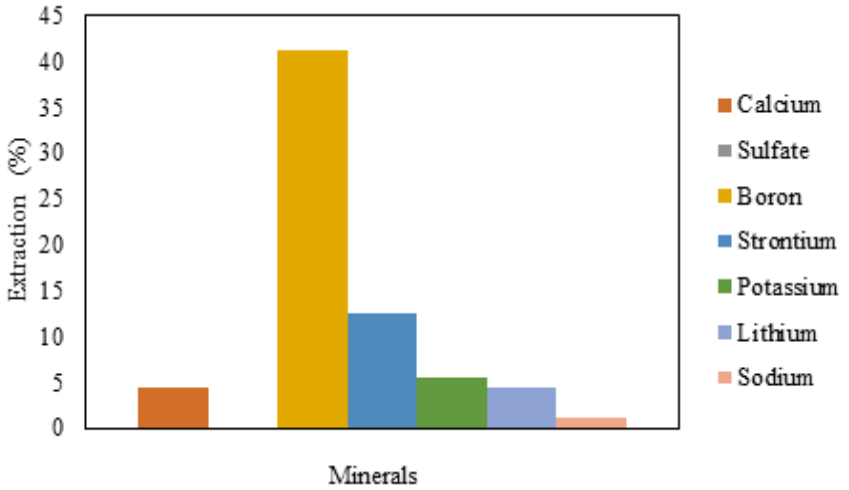
$Ca(OH)_2$ as base



Percentage of minerals extracted.

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

NH_4OH as base



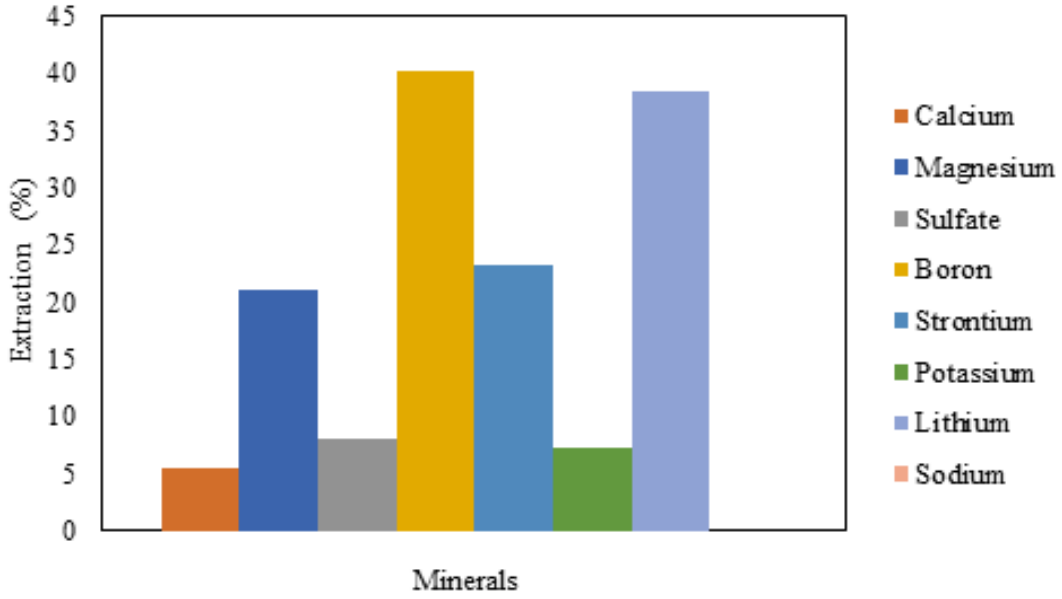
Percentage of minerals extracted.

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

Results and Discussion

Effect of Base on Mineral Extraction

NaOH as base



Percentage of minerals extracted.

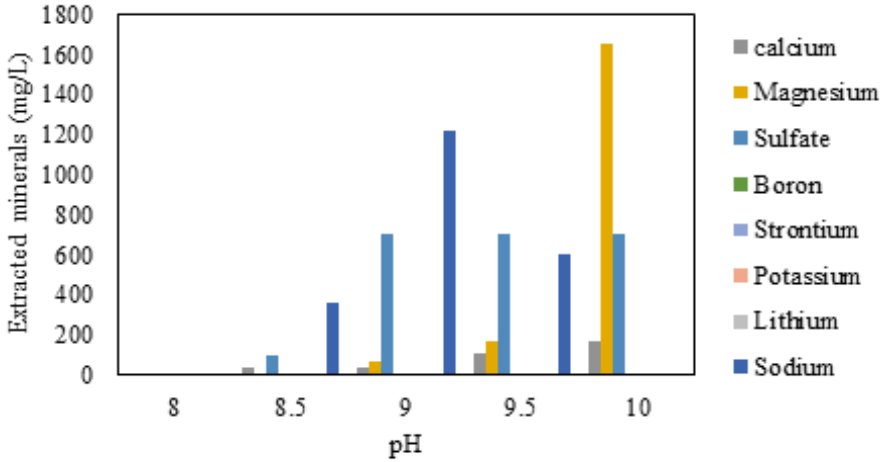
Extracted minerals:
Boron: 40%, lithium: 38%, strontium: 23% and magnesium: 20%.

- **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)**

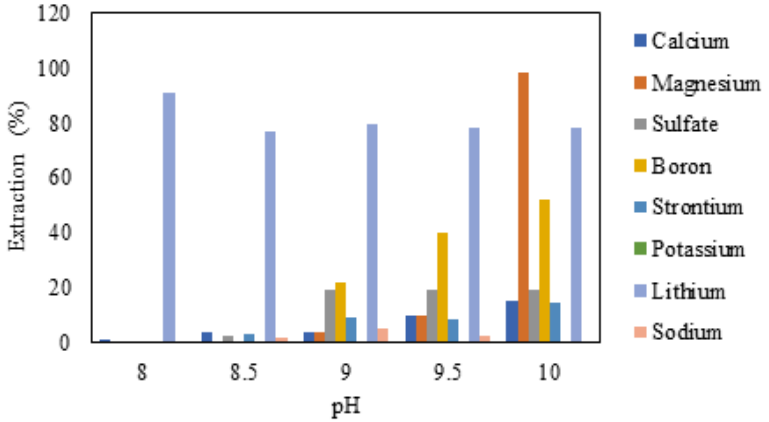
Results and Discussion

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.



Percentage of minerals extracted at 90 °C.

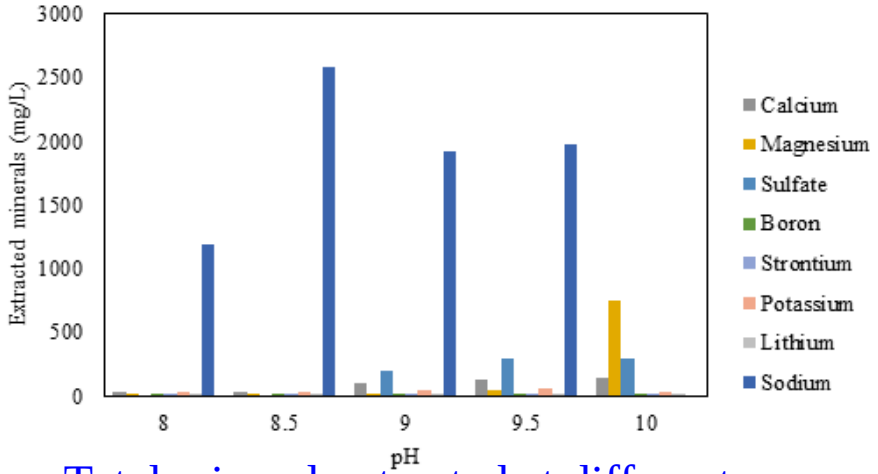
Magnesium: 1651 mg/L, sulfate: 700 mg/L and calcium: 168.8 mg/L.(ex.pH 10)

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

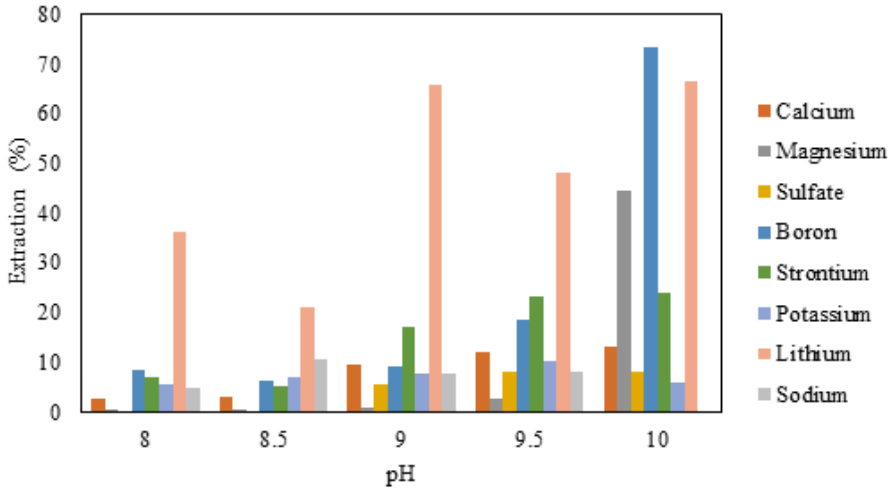
Results and Discussion

Effect of pH and Temperature on Mineral Extraction

Extraction of minerals at 8o °C and at different pH



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



Percentage of minerals extracted at 80 °C.

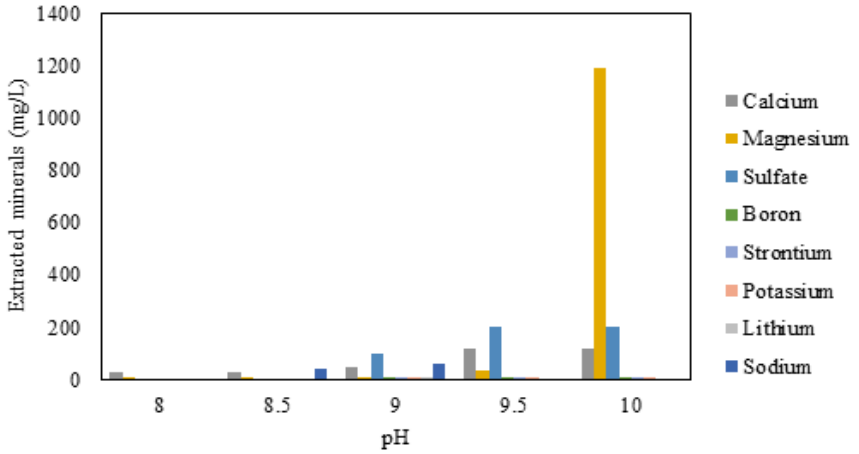
Magnesium: 750 mg/L, sulfate: 300 mg/L and calcium: 144 mg/L.(ex pH 10)

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

Results and Discussion

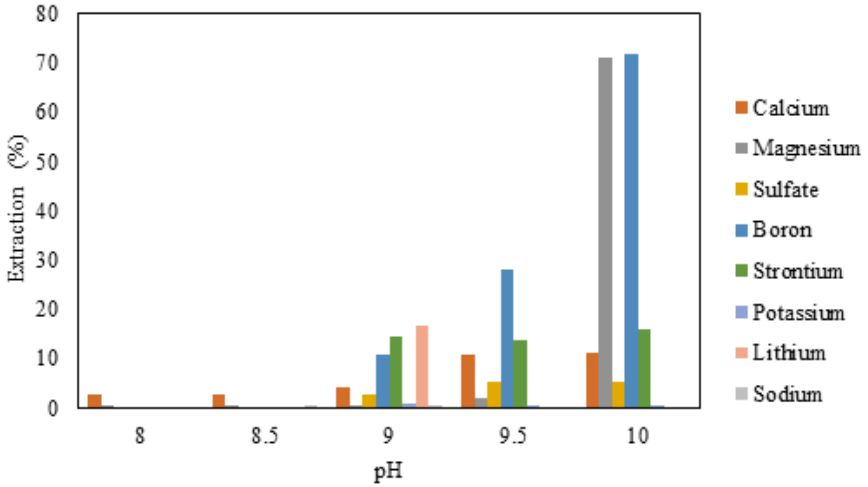
Effect of pH and Temperature on Mineral Extraction

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)



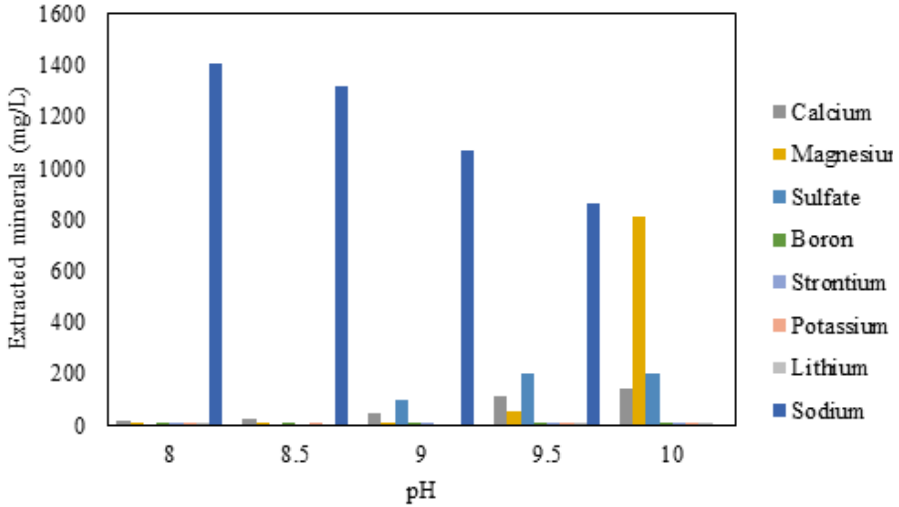
Percentage of minerals extracted at 70 °C.

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

Results and Discussion

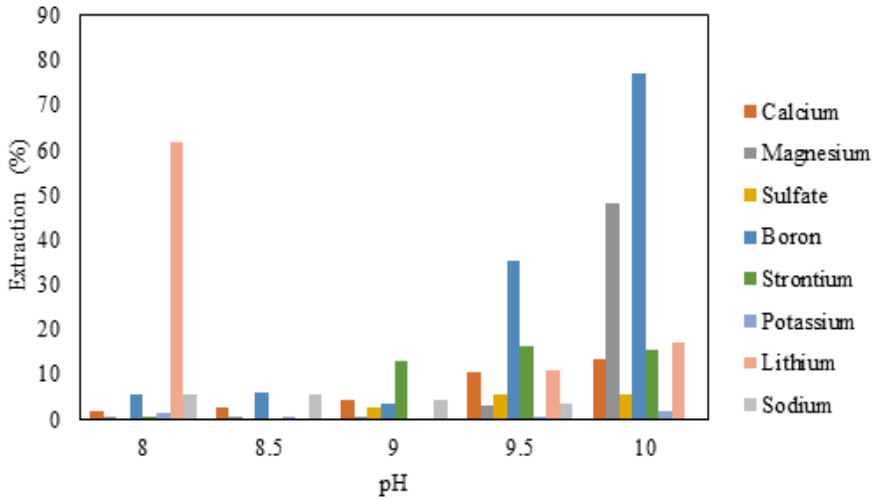
Effect of pH and Temperature on Mineral Extraction

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.

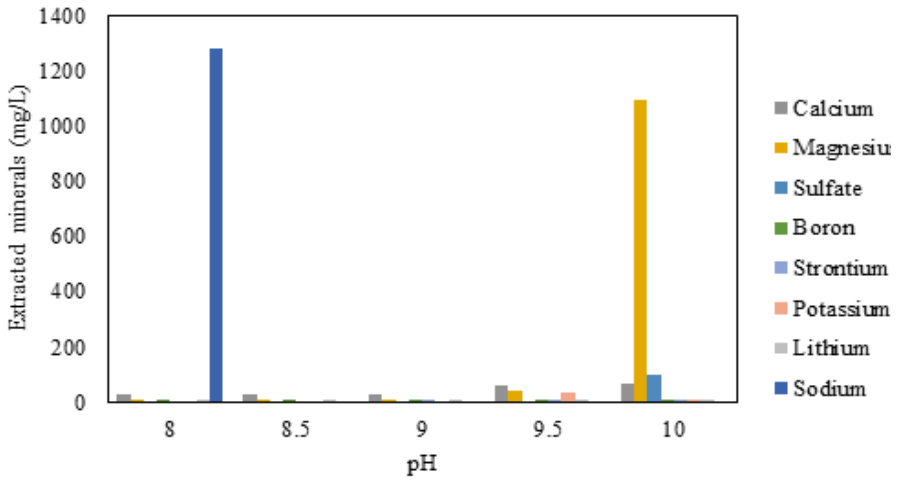
Boron: 77% and magnesium: 48% (ex pH 10),

Lithium: 61% (ex pH 8)

Results and Discussion

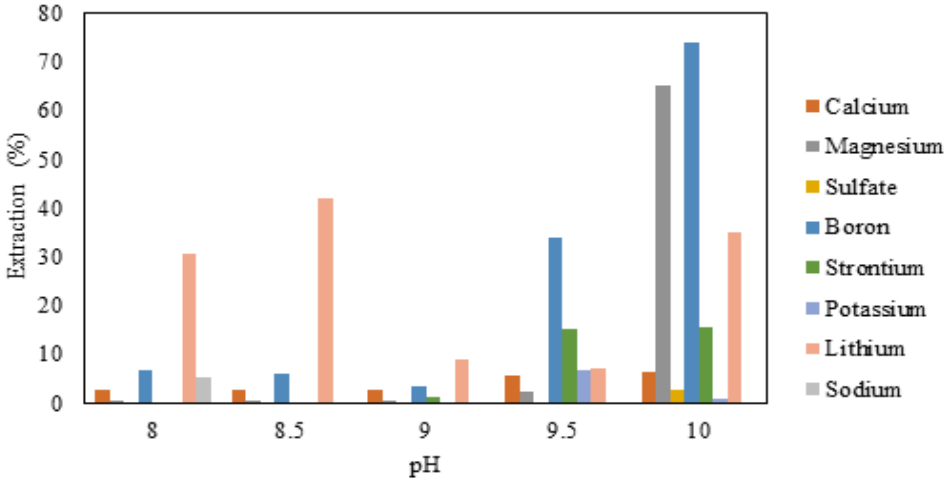
Effect of pH and Temperature on Mineral Extraction

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)

Results and Discussion

Preliminary Economic Evaluation of Magnesium Oxide Production Using DRP SWRO Brine

Production Capacity: 300 m^3/d.
Total Water Recovery: ≈30%.
TDS rejected from DRP plant: ≈54,000 ppm.

Rejected brine is approximately 700 m^3/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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