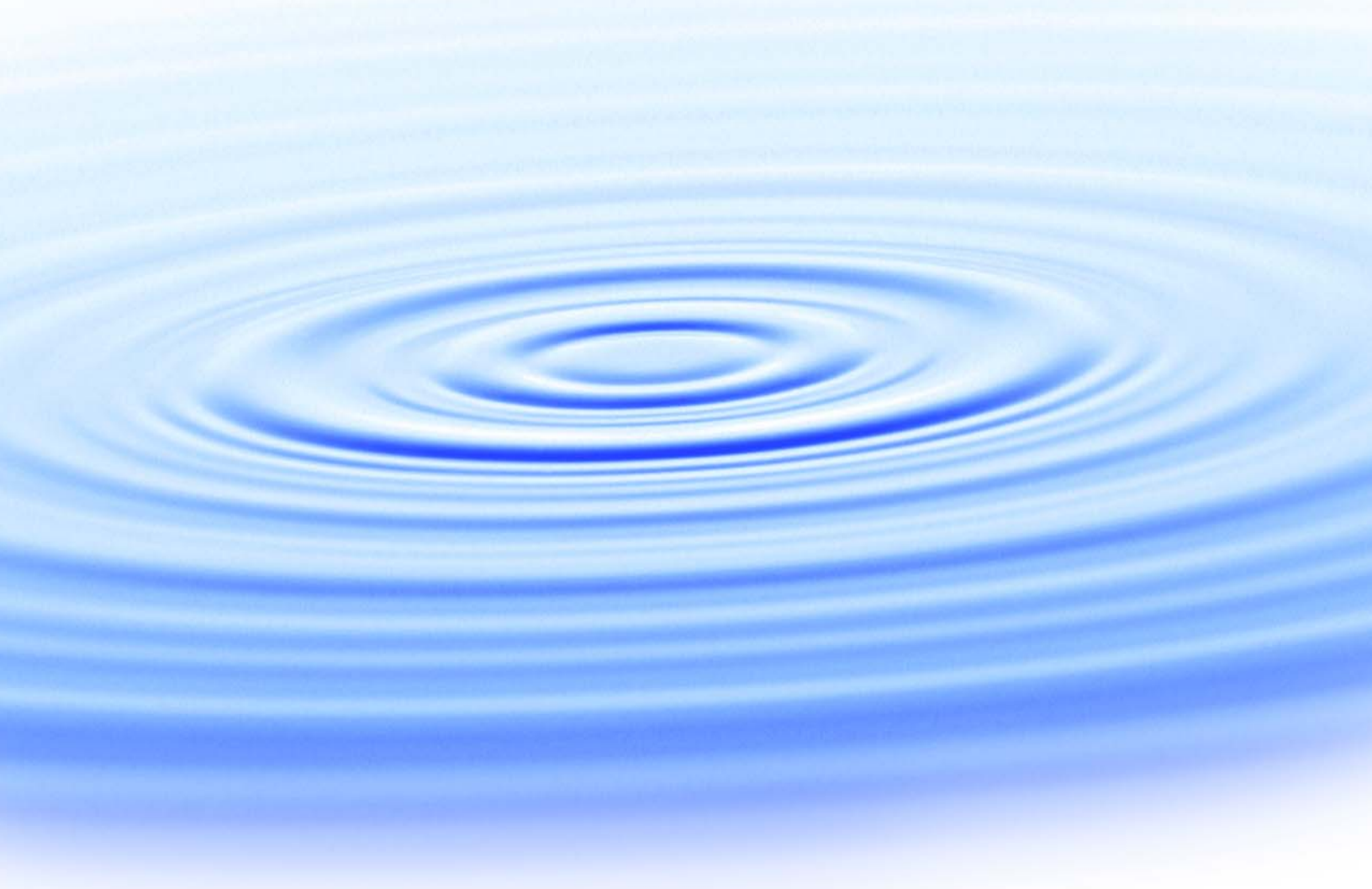




# **Selection of Salt, Metal, Radionuclide, and Other Valuable Material Recovery Approaches**



**WaterReuse Research Foundation**



## Selection of Salt, Metal, Radionuclide, and Other Valuable Material Recovery Approaches



## About the WateReuse Research Foundation

The mission of the WateReuse Research Foundation is to build support for water reuse through research and education. The Foundation's research advances the science of water reuse and supports communities across the United States and abroad in their efforts to create new sources of high quality water for various uses through reclamation, recycling, reuse, and desalination while protecting public health and the environment.

The Foundation sponsors research on all aspects of water reuse, including emerging chemical contaminants, microbiological agents, treatment technologies, reduction of energy requirements, concentrate management and desalination, public perception and acceptance, economics, and marketing. The Foundation's research informs the public of the safety of reclaimed water and provides water professionals with the tools and knowledge to meet their commitment of providing a reliable, safe product for its intended use.

The Foundation's funding partners include the supporters of the California Direct Potable Reuse Initiative, Water Services Association of Australia, Pentair Foundation, and Bureau of Reclamation. Funding is also provided by the Foundation's subscribers, water and wastewater agencies, and other interested organizations.

# Selection of Salt, Metal, Radionuclide, and Other Valuable Material Recovery Approaches

Christopher L. Bellona, Ph.D.  
Ashley Waldron  
*Clarkson University*

Joon Min, Ph.D.  
Liyan Jin  
*BKT United*

**Cosponsor**  
Bureau of Reclamation



WateReuse Research Foundation  
Alexandria, VA



**Disclaimer**

This report was sponsored by the WateReuse Research Foundation and cosponsored by the Bureau of Reclamation. The Foundation and its Board Members assume no responsibility for the content reported in this publication or for the opinions or statements of facts expressed in the report. The mention of trade names of commercial products does not represent or imply the approval or endorsement of the WateReuse Research Foundation. This report is published solely for informational purposes.

**For more information, contact:**

WateReuse Research Foundation  
1199 North Fairfax Street, Suite 410  
Alexandria, VA 22314  
703-548-0880  
703-548-5085 (fax)  
[www.WateReuse.org/Foundation](http://www.WateReuse.org/Foundation)

© Copyright 2015 by the WateReuse Research Foundation. All rights reserved. Permission to copy must be obtained from the WateReuse Foundation.

WateReuse Research Foundation Project Number: 10-09  
ISBN: 978-1-941242-28-5





# Contents

---

List of Figures .....	viii
List of Tables .....	x
List of Abbreviations and Acronyms .....	xii
Foreword .....	xv
Acknowledgments.....	xvi
Executive Summary .....	xvii
<b>Chapter 1. Introduction.....</b>	<b>1</b>
1.1 Background .....	1
1.2 Objectives.....	2
<b>Chapter 2. Motivation for Extraction of Valuable Materials from Desalination Facilities .....</b>	<b>5</b>
2.1 Historical Examples of Valuable Material Extraction .....	5
2.1.1 Extraction from Seawater.....	5
2.1.2 Extraction from Brackish Groundwater or Brines .....	8
2.3 Desalination Brine/Concentrate Composition.....	8
2.3.1 Seawater Desalination.....	8
2.3.2 Brackish Water Desalination.....	14
2.3.3 Wastewater Desalination.....	15
<b>Chapter 3. Technologies for Extraction of Materials from Aqueous Solutions .....</b>	<b>17</b>
3.1 Summary of Potential Unit Processes for Material Extraction .....	17
3.1.1 Membrane Processes.....	17
3.1.2 Evaporation.....	22
3.1.3 Sorption Processes .....	23
3.1.4 Precipitation and Crystallization .....	24
3.1.5 Flotation .....	30
3.1.6 Electrowinning .....	30
<b>Chapter 4. Materials Targeted for Extraction from Desalination Brines .....</b>	<b>31</b>
4.1 Summary of Literature and Patent Information .....	31
4.1.1 Boron.....	31
4.1.2 Bromine.....	34
4.1.3 Calcium .....	37
4.1.4 Cesium .....	41
4.1.5 Chlorine and Sodium Hydroxide .....	43
4.1.6 Lithium.....	46
4.1.7 Magnesium.....	60

4.1.8	Molybdenum.....	74
4.1.9	Nitrogen.....	75
4.1.10	Phosphorus .....	76
4.1.11	Potassium.....	78
4.1.12	Rubidium .....	81
4.1.13	Sodium.....	85
4.1.14	Strontium .....	88
4.1.15	Uranium.....	90
4.1.16	Other Constituents Receiving Attention in the Literature .....	97
4.2	Summary of Proposed Extraction Schemes.....	98
4.3	General Considerations Toward Material Extraction .....	101
4.3.1	Economic Considerations.....	101
4.3.2	Product Considerations.....	101
4.3.3	Facility Considerations .....	101
4.4	Assessment of Material Extraction.....	102
4.4.1	Seawater Desalination .....	102
4.4.2	Brackish Water Desalination .....	115
<b>Chapter 5. Extraction Case Studies .....</b>		<b>117</b>
5.1	Intentional Material Recovery from Production Lines .....	117
5.1.1	Case Study 1—Colloidal Silica Recovery from Chemical Production Plant.....	117
5.1.2	Case Study 2—Orange Juice Pulp Concentration for Use in Industrial Applications.....	119
5.1.3	Case Study 3—Maple Tree Sap Concentration for Maple Syrup Production.....	120
5.1.4	Case Study 4—Silica Recovery from Geothermal Fluids .....	121
5.2	Material Recovery from Industrial Waste and Wastewater.....	124
5.2.1	Case Study 5—Lysine Recovery from Production Wastewater.....	124
5.2.2	Case Study 6—Ammonium Nitrate Recovery from Fertilizer Production Wastewater.....	126
5.2.3	Case Study 7—Ethanol Wastewater Treatment .....	127
5.2.4	Case Study 8—Copper Recovery from a Waste Stream in a Casting Plant Using Electrowinning Technology .....	128
5.2.5	Case Study 9—Nutrient Recovery from Digestate in a Biogas Plant.....	131
5.2.6	Case Study 10—Polymer Production Wastewater Treatment and Alternative Carbon Source .....	136
5.2.7	Case Study 11—Grain Recovery from High Strength Brewery Wastewater .....	139
5.3	Material Recovery from Brines .....	143
5.3.1	Case Study 12—Mineral Recovery from RO Concentrate Using Isothermal Evaporation .....	143

5.3.2 Case Study 13—Calcium Recovery from RO Concentrate Using a Fluidized-Bed Crystallizer .....	146
<b>Chapter 6. Conclusions.....</b>	<b>151</b>
<b>References.....</b>	<b>157</b>
<b>Appendix: Patent Summary Tables .....</b>	<b>181</b>

# Figures

3.1	Concentration factor as a function of rejection (R) and % recovery .....	18
3.2	Schematic of the ED process .....	20
3.3	Schematic of the EDM process .....	21
3.4	Common crystallizer configurations: (a) fluidized-bed crystallizer, (b) forced-circulation crystallizer .....	29
4.1	Reported lithium end products in 2007 .....	46
4.2	Market shares of lithium-based commodities.....	47
4.3	Types of lithium resources, reserves, products, and major end-use applications.....	47
4.4	Simplified process flow charts for lithium carbonate production from three resource types.....	48
4.5	Unadjusted and inflation-adjusted lithium carbonate pricing.....	49
4.6	Comparison of lithium uptake from a seawater matrix for different adsorbent materials .....	54
4.7	Proposed process for extraction of bromine, salt, and magnesium from RO brine....	66
4.8	Schematic of Merck and Co.'s process for magnesium extraction from seawater.....	68
4.9	Schematic of Kaiser Aluminum and Chemical Company's magnesia from seawater process .....	69
4.10	Overhead view of Ube Material Industries' magnesia from seawater plant .....	70
4.11	Preliminary screening of profitable elements in RO concentrate for plants with different brine flow rates .....	103
4.12	Cash flow diagram for the MgO plant.....	106
4.13	Cash flow diagram for the Cl <sub>2</sub> -NaOH plant .....	109
4.14	Proposed schemes for extraction of constituents from RO brine/concentrate.....	114
4.15	Additional proposed schemes for extraction of constituents from RO brine/concentrate .....	115
4.16	Proposed process for recovery of calcium carbonate from BWRO desalination brine .....	116
5.1	Process flow diagram for colloidal silica concentration.....	119
5.2	Process flow diagram for the recovery and concentration of orange juice pulp.....	120
5.3	Process flow diagram for the concentration of maple sap prior to evaporation.....	120
5.4	Process of silica recovery from geothermal fluid.....	121
5.5	Process flow diagram for lysine extraction and fermentation bacterial recovery from production wastewater .....	125
5.6	Process flow diagram for ammonium nitrate recovery and concentration .....	126
5.7	Process flow diagram for the recovery of solids from ethanol wastewater.....	127
5.8	A schematic of copper recovery from waste cleaning solution.....	129
5.9	Schematic of digestate treatment using a vortex-enhanced membrane system and conventional RO .....	131
5.10	Market prices of different fertilizers with different nitrogen levels .....	134

5.11	Comparison of conventional treatment process and membrane treatment process .....	136
5.12	Process flow diagram in brewery wastewater treatment.....	140
5.13	Process schematic for desalination effluent management.....	143
5.14	Products recoverable from evaporation/crystallization of Scottsdale concentrate at 25° C .....	144
5.15	Schematic of brackish water treatment and mineral recovery .....	147

# Tables

---

2.1	Concentrations of the Major Ions in Surface Seawater .....	9
2.2	Concentrations of the Minor Ions (umol and nmol) in Surface Seawater .....	10
2.3	Concentrations of the Minor Ions (pmol and fmol) in Surface Seawater.....	11
2.4	Example of Measured Water Quality in Seawater Reverse Osmosis Brine .....	13
2.5	Major Ion Composition of Several Brackish Groundwaters .....	14
2.6	Wastewater Reverse Osmosis Concentrate Measured Water Quality at Two Wastewater Reclamation Facilities. ....	16
4.1	Boron Summary .....	33
4.2	Summary of Patents Related to Boron Extraction.....	34
4.3	Bromine Summary .....	36
4.4	Summary of Patents Related to Bromine Extraction.....	37
4.5	Calcium Overview.....	40
4.6	Summary of Patents Related to Calcium Extraction .....	41
4.7	Cesium Overview .....	42
4.8	Summary of Patents Related to Cesium Extraction .....	43
4.9	Chlorine and Sodium Hydroxide Overview .....	45
4.10	Metal Composition of the Dried Precipitate Salt .....	52
4.11	Summary of Technologies for Lithium Extraction.....	56
4.12	Lithium Overview .....	59
4.13	Summary of Patents Related to Lithium Extraction.....	60
4.14	2006 Year-End Prices for Various Magnesium Compounds .....	62
4.15	Average Composition of Caustic-Calcined Magnesia.....	63
4.16	Magnesium Overview .....	72
4.17	Summary of Patents Related to Lithium Extraction.....	73
4.18	Molybdenum Overview.....	74
4.19	Nitrogen Overview .....	76
4.20	Phosphorus Overview.....	78
4.21	Potassium Overview .....	80
4.22	Summary of Patents Related to Potassium Extraction .....	81
4.23	Rubidium Overview .....	84
4.24	Summary of Patents Related to Rubidium Extraction.....	84
4.25	Sodium Overview .....	87
4.26	Summary of Patents Related to Sodium Extraction .....	88
4.27	Strontium Overview .....	89
4.28	Summary of Patents Related to Sodium Extraction .....	90
4.29	Summary of Sorbent Materials for Uptake of Uranium from Aqueous Solutions. ....	95
4.30	Uranium Overview .....	96

4.31	Summary of Patents Related to Uranium Extraction .....	97
4.32	Summary of Studies Evaluating the Extraction of Dissolved Constituents from Desalination Brine/Concentrate .....	99
4.33	Summarized Commodity Prices and Potential Revenue from Commodity Sales ....	104
4.34	Calculated Cost for Different Units of MgO Extraction Plant.....	105
4.35	Calculated O&M for MgO Extraction Plant .....	105
4.36	Calculated Cost for Different Units of Cl <sub>2</sub> and NaOH Extraction Plant .....	107
4.37	Calculated O&M Cost for Cl <sub>2</sub> and NaOH Extraction Plant.....	108
4.38	Calculated Cost for Different Units of NaCl Extraction Plant Using MED .....	110
4.39	Calculated Cost for Different Units of NaCl Extraction Plant Using MVC .....	110
4.40	Calculated O&M Cost of NaCl Extraction Plant Using MED.....	110
4.41	Calculated O&M Cost for Different Units of NaCl Extraction Plant Using MVC ..	111
4.42	Calculated Cost for Different Units of Mg(OH), Br, Salt Extraction Plant Using MED .....	112
4.43	Calculated Cost for Different Units of Mg(OH), Br, Salt Extraction Plant Using MVC.....	112
4.44	O&M Costs for Mg(OH), Br, Salt Extraction Plant Using MED and MVC .....	113
4.45	Net Present Value and Payback Period for Different Extraction Plants .....	113
5.1	Overview of Case Studies .....	118
5.2	Performance and Mass Balance of RO System .....	122
5.3	Economic Analysis of Silica Recovery at Mammoth Lakes.....	124
5.4	Specifications of Copper Electrowinning System .....	129
5.5	Economic Analysis of Copper Electrowinning System .....	130
5.6	Operating Conditions of UF and RO Membranes .....	132
5.7	Mass Balance of Nutrients from UF and RO Membranes .....	132
5.8	Factors That Affect Liquid Fertilizer Market Value .....	133
5.9	Market Analysis of Fertilizers Used .....	134
5.10	Potential Value of RO Concentrate as Organic Liquid Fertilizer .....	135
5.11	Operating Conditions for the Membrane System Used in Methylcellulose Wastewater Treatment .....	137
5.12	Operational Cost–Benefit Analysis of Membrane Methylcellulose Recovery Process Versus Conventional Process .....	138
5.13	Operating Conditions of Vortex Membrane System.....	141
5.14	Economic Analysis for Grain Recovery from Brewery Wastewater .....	142
5.15	Main Composition of the Byproducts in Different Steps of Mineral Recovery from RO Concentrates .....	145
5.16	Economic Analysis of Mineral Recovery from Scottsdale’s Reclaimed Water RO System .....	146
5.17	Economic Analysis of Mineral (Pellet) Recovery from Chino II Desalter .....	149
6.1	Summary of Extraction of Potentially Profitable Compounds from Seawater and RO Concentrate .....	153

# Abbreviations and Acronyms

---

AEM	Anion exchange membrane
BARC	Bhabha Atomic Research Centre
BOD	biological oxygen demand
BWRO	brackish water reverse osmosis
CBDA	Chino Basin Desalter Authority
CEM	cation exchange membrane
COD	chemical oxygen demand
DAF	dissolved air flotation
DOC	dissolved organic carbon
ECU	electrochemical unit
ED	electrodialysis
EDM	electrodialysis metathesis
EDR	electrodialysis reversal
EFC	eutectic freezing crystallization
FBC	fluidized-bed crystallizer
FC	forced circulation
IAP	ion activity product
IXSS	ion exchange supersaturation
LCA	life-cycle assessment
LIB	lithium ion battery
MCr	membrane crystallization
MED	multiple-effect distillation
MF	microfiltration
MSF	multi-stage flash
MVC	mechanical vapor compression
MWCO	molecular weight cutoff
NF	nanofiltration
NPV	net present value
NTU	nephelometric turbidity units
O&M	operation and maintenance
PLE	polymeric ligand exchange
RO	reverse osmosis
SARI	Santa Ana Regional Interceptor
SLM	supported liquid membrane
SOP	sulfate of potash
SWRO	seawater reverse osmosis
TDS	total dissolved solids
TS	total solids
TSS	total suspended solids



TVC	thermal vapor compression
UF	ultrafiltration
USGS	United States Geological Survey
ZLD	zero liquid discharge



# Foreword

---

The WateReuse Research Foundation, a nonprofit corporation, sponsors research that advances the science of water reclamation, recycling, reuse, and desalination. The Foundation funds projects that meet the water reuse and desalination research needs of water and wastewater agencies and the public. The goal of the Foundation's research is to ensure that water reuse and desalination projects provide sustainable sources of high quality water, protect public health, and improve the environment.

An Operating Plan guides the Foundation's research program. Under the plan, a research agenda of high priority topics is maintained. The agenda is developed in cooperation with the water reuse and desalination communities, including water professionals, academics, and Foundation subscribers. The Foundation's research focuses on a broad range of water reuse and desalination research topics including:

- Defining and addressing emerging contaminants, including chemicals and pathogens
- Determining effective and efficient treatment technologies to create "fit for purpose" water
- Understanding public perceptions and increasing acceptance of water reuse
- Enhancing management practices related to direct and indirect potable reuse
- Managing concentrate resulting from desalination and potable reuse operations
- Demonstrating the feasibility and safety of direct potable reuse

The Operating Plan outlines the role of the Foundation's Research Advisory Committee (RAC), Project Advisory Committees (PACs), and Foundation staff. The RAC sets priorities, recommends projects for funding, and provides advice and recommendations on the Foundation's research agenda and other related efforts. PACs are convened for each project to provide technical review and oversight. The Foundation's RAC and PACs consist of experts in their fields and provide the Foundation with an independent review, which ensures the credibility of the Foundation's research results. The Foundation's Project Managers facilitate the efforts of the RAC and PACs and provide overall management of projects.

Multiple issues currently impede the widespread application of desalination. Besides high energy requirements and treatment costs, concentrate management and disposal are two of the most divisive aspects of desalination and often the decisive factors determining the feasibility of a desalination project. One possible strategy to recover costs and reduce brine volume/concentrations from desalination applications is through the selective recovery of valuable constituents in desalination brine/concentrate streams. The major goal of this project was to examine current and past efforts aimed at recovering materials from aqueous solutions with the goal of recovering valuable compounds from desalination brine/concentrate streams.

**Douglas Owen**  
*Chair*  
WateReuse Research Foundation

**Melissa Meeker**  
*Executive Director*  
WateReuse Research Foundation

# Acknowledgments

---

This project was funded by the WateReuse Research Foundation in cooperation with the Bureau of Reclamation.

This study would not have been possible without the insights and dedication of many individuals. These include members of the research team and PAC and the WateReuse Research Foundation's project managers, Anna Durden, Deana Bollaci, and Kristan Cwalina. The research team thanks participating utilities, including Orange County Water District, WaterSecure/Veolia, Eastern Municipal Water District, and the Water Replenishment District of Southern California.

The research team also thanks the WateReuse Research Foundation for funding this research project and the Water Replenishment District of Southern California for its in-kind contributions.

## **Principal Investigator and Project Manager**

Christopher Bellona, Ph.D., *Clarkson University*

## **Research Project Team**

Liyan Jin, Ph.D., *BKT*

Joon Min, Ph.D., *BKT*

Ashley Waldron, *Clarkson University*

## **Project Advisory Committee**

Patrick Brady, *Sandia National Laboratory*

Robert Cheng, *Coachella Valley Water District*

Saied Delagah, *Bureau of Reclamation*

John Pellegrino, *University of Colorado*

# Executive Summary

---

Because of increasing demands on conventional water sources, communities in the United States and abroad are turning toward unconventional water resources such as brackish groundwater, wastewater effluent, irrigation return water, and seawater to meet current and future water demands. Although desalination applications have become an important alternative for securing additional potable water supplies for certain locations, there are multiple issues associated with desalination that currently impede its widespread application. Besides high energy requirements and treatment costs, concentrate management and disposal are among two of the most divisive aspects of desalination and often the decisive factors determining the feasibility of a desalination project.

As a result of the issues associated with concentrate management and disposal, there is increased interest in developing methods and technologies for the minimization of reverse osmosis (RO) concentrate volumes with the ultimate goal of zero liquid discharge (ZLD) from desalination facilities. Unfortunately, the obvious benefits of concentrate minimization and ZLD practices are often offset by their high operation and maintenance (O&M) costs and energy requirements. One possible strategy to recover costs from ZLD implementation is through the selective recovery of valuable constituents in RO concentrate streams. These constituents potentially could be marketed to increase the profitability of desalination facilities, which could in turn increase private investment in the desalination sector.

The main objective of this project was to examine and summarize the state of the science regarding the recovery of materials from aqueous solutions with the goal of determining the feasibility of valuable material recovery from desalination brine/concentrate streams. A comprehensive literature and patent review was performed to identify viable methods for and case studies on the extraction of metals, salts, and other valuable commodities from fluids. Commodity economic information and extraction technology costing evaluations were then used to screen for economically viable extraction scenarios. Finally, information gained from literature and patent reviews was summarized into a searchable bibliography software database.

From a technical standpoint, the extraction of most major ions in desalination brine/concentrate is currently viable; however, the feasibility of producing commodities at profit from desalination brine/concentrate is dependent on numerous factors that require careful consideration. Economic factors that influence the feasibility of material extraction include commodity demand and pricing, energy consumption and cost, labor requirements, and the overall costs of production. Other major considerations include facility siting (e.g., availability of raw materials, transportation, and cheap energy; close proximity to consumers), product purity and uniformity, safety, material handling, storage, and transport.

Historically, mining of water for economic gain has received significant attention and for several commodities has been a lucrative business. Besides sodium chloride, in the recent past bromine and magnesium were almost exclusively produced from seawater in the United States. In addition, appreciable quantities of iodine and lithium have been and are still produced from concentrated brines. Over the past century, a significant amount of effort has been put towards the extraction of gold, lithium, and uranium from seawater, with very limited success. Currently, sodium chloride and magnesium compounds (magnesium hydroxide and magnesia) are the only compounds extracted from seawater at any appreciable

extent. With the exception of a planned process to produce calcium carbonate at a desalination facility in Southern California, only one documented case of full-scale valuable material extraction from desalination brine for economic gain was identified: sodium chloride is produced from seawater reverse osmosis brine in evaporation ponds in Israel.

A preliminary screening exercise was performed to identify constituents in seawater that could potentially be extracted for a profit based on their concentration and value. Of the constituents evaluated, the results demonstrated that extraction of bromine, magnesium (as magnesium hydroxide or magnesia), rubidium, sodium, and strontium is potentially profitable at desalination facilities of an appreciable size ( $>10,000 \text{ m}^3/\text{day}$ ). In addition, several researchers have concluded that chlorine and sodium hydroxide could also be produced from desalination brine for a profit. Because the global demand for rubidium is extremely low and strontium lacks a viable extraction technology and its market is dominated by China and Spain, these commodities were not evaluated further.

Cost analyses were performed on several reported schemes for the production of the aforementioned commodities to evaluate the economics of extraction. The cost analyses indicated that magnesia (and potentially magnesium hydroxide) and potentially chlorine and sodium hydroxide are economical products derived from seawater desalination brine. The profitability of extracting chlorine and sodium hydroxide is strongly dependent upon the efficiency of the electrolytic cell, and more research is required to evaluate the efficiency of chlorine and sodium hydroxide production using purified desalination brine as feed stock.

Although cost analyses indicated that most extraction scenarios are not currently economically feasible, several scenarios were identified where extraction was or could be beneficial at a desalination facility. In one case, a brackish water desalination facility in Southern California is using intermediate softening to improve the overall membrane system's recovery to reduce brine flow rates sent to a discharge line. Through intermediate softening, a salable calcium carbonate product is produced, which is sold to a building material manufacturer. Through this approach, the utility reduces treatment costs by producing a salable product while simultaneously reducing costs associated with brine discharge.

Other potential applications of extraction include producing chemicals (e.g., acid, chlorine, magnesium hydroxide) or byproduct streams for desalinated water stabilization. For the latter, hybrid desalination processes have been proposed where nanofiltration (NF) is used as pretreatment to RO or thermal-based desalination processes. In this approach, NF permeate low in divalent ion concentrations is sent to the main desalination process (i.e., RO or thermal), thereby reducing energy requirements of RO and thermal-based desalination processes. A portion of the NF concentrate with elevated multivalent ion concentration can then be used to stabilize and remineralize desalinated water. These potential extraction applications would require analysis on a case-by-case basis to assess whether they would reduce the cost of desalination.

To gain perspective on the adoption of extraction methodologies in any industry, case studies were developed to identify commonly applied technologies, constituents of interest, and economic impacts. Developed case studies of industrial and water treatment applications indicate that numerous industries are applying or considering the integration of material extraction into their current operation. Depending on the industry, significant benefits can be

realized that extend beyond maximizing profits (e.g., waste minimization). As commodity prices increase because of demand and increased pressure on terrestrial resources, extraction of materials from desalination brine may become more economically feasible.





## *Chapter 1*

# **Introduction**

---

## **1.1 Background**

Because of increasing demands on conventional water sources, communities in the United States and abroad are turning toward unconventional water resources such as brackish groundwater, wastewater effluent, irrigation return water, and seawater to meet current and future water demands [1–4]. Although desalination applications (e.g., indirect potable reuse, brackish water desalination, seawater desalination) using reverse osmosis (RO) have become an important alternative for securing additional potable water supplies for certain locations (e.g., Australia, Israel, Saudi Arabia, Spain, United Arab Emirates, United States), there are multiple issues associated with desalination that currently impede its widespread application. Besides high energy requirements and treatment costs, concentrate management and disposal are two of the most divisive aspects of desalination and often the decisive factors determining the feasibility of a desalination project [3, 5, 6].

Desalination facilities primarily rely on discharge to wastewater treatment plants (indirect potable reuse applications, inland brackish water desalination), groundwater injection (inland brackish water desalination), and ocean discharge (seawater desalination, inland brackish water desalination, indirect potable reuse applications) for concentrate disposal [5, 7–10]. These disposal options are becoming increasingly scrutinized because of concerns regarding human and environmental health, impact on receiving water quality, and inability of wastewater treatment plants to accommodate increased salinity [5, 7, 10–12]. Furthermore, the costs associated with concentrate disposal can be a significant portion of the total project costs depending on the volume of concentrate and type of discharge required [3, 9, 13].

As a result of the issues associated with concentrate management and disposal, there is increased interest in developing methods and technologies for the minimization of RO concentrate volumes, with the ultimate goal of zero liquid discharge (ZLD) from desalination facilities. Unfortunately, the obvious benefits of concentrate minimization and ZLD practices are often offset by their high operation and maintenance (O&M) costs and energy requirements [1, 2, 13, 14]. One possible strategy to recover costs from ZLD implementation is through the selective recovery of valuable constituents in RO concentrate streams. These constituents potentially could be marketed to increase the profitability of desalination facilities, which could in turn increase private investment in the desalination sector. The feasibility of recovering valuable materials from desalination waste streams is dependent not only upon technical, energy, and cost considerations of the extraction technology [15] but also market fluctuations for the minerals extracted [16].

The concept of recovering valuable constituents from a desalination facility's waste stream was likely first proposed by Dr. John F. Mero, a pioneer in the field of mining the sea, who postulated in 1964 that brine from seawater conversion plants (i.e., thermal desalination for drinking water production) would play an important role in future production of minerals from seawater [17]:

By using these brines for the extraction of minerals, several important advantages are gained; the cost of pumping is carried by the conversion plant, the brine temperature is relatively high, and the concentrations are increased as high as four.

Petersen [18] revisited this concept in 1994 and published a good review article on the recovery of metals from seawater and desalination facility brine in which he argued:

Where it [seawater] has to be used to produce fresh water, why not try to obtain as many byproducts as are economically viable?...Or why not place a minerals industry in a region where byproduct water would be desirable?

In the past [19, 20], researchers have noted that seawater is not commonly used for obtaining minerals and pointed to the value and concentration of the various elements and compounds in it to make the case for why the concept is unfeasible. Given the cost of disposal of RO brine, however, and the fact that many desalination facilities produce millions of gallons of brine per day, there is a need to evaluate the concept of extracting valuable materials from desalination brine with the ultimate goal of reducing the volume of brine requiring disposal.

## **1.2 Objectives**

The major goal of this project was to examine current and past efforts aimed at recovering materials from aqueous solutions, with the goal of recovering valuable compounds from desalination brine/concentrate streams. The objectives of this study, therefore, were to

- Review and summarize available literature pertaining to the extraction of metals, salts, and other valuable constituents.
- Organize this literature into searchable EndNote databases.
- Evaluate and determine the feasibility of valuable material extraction from desalination brine/concentrate.
- Summarize relevant industrial case studies in which extraction was evaluated or performed.

To achieve this objective, the project was divided into four major tasks:

### **Task 1. Literature Review**

The goal of Task 1 was to review all pertinent information on the potential for extraction of valuable materials from desalination concentrate streams and develop a database containing information on the following categories, which are listed as subtasks below:

(1) water quality information; (2) summary of technologies for brine minimization and extraction of materials; and (3) industrial examples where extraction has occurred.

## **Task 2. Patent Literature Review**

The purpose of Task 2 was to review patent literature as it relates to concentrate minimization and recovery of materials from various water sources. For the patent literature search, several sources of information were utilized, including:

- Online searchable databases for U.S. patents, including Google patent search, FreePatentsOnline.com, GetthePatent.com
- The U.S. Patent and Trademark Office resource, which includes an online searchable database
- U.S. Patent and Trademark Depository Library
- European Patent Office online database, GB Esp@cenet
- World Intellectual Property Organization PatentScope Database

## **Task 3. Identification of Targeted Materials**

The purpose of Task 3 was to develop a short list of materials of which the extraction from desalination concentrate would be technologically and economically feasible. Information gained from the completion of Tasks 1 and 2 was used to develop this list along with a preliminary cost analysis of several extraction schemes.

## **Task 4. Develop Case Studies**

The purpose of Task 4 was to identify and describe several real-world examples from any industry in which selective extraction was used or attempted.



## *Chapter 2*

# **Motivation for Extraction of Valuable Materials from Desalination Facilities**

---

## **2.1 Historical Examples of Valuable Material Extraction**

### **2.1.1 Extraction from Seawater**

The concept of mining water for economic gain is relatively old, first thought to be practiced by the Chinese in 2200 BCE to extract salt from seawater [17, 21, 22]. The Maya, a civilization that flourished approximately 1200 years ago, also are thought to have extracted salt from the sea in order to meet daily salt demands. With no apparent terrestrial source (their mostly vegetarian diet would not have met the required daily salt requirement) and an approximate population of 45,000 (circa 841), the city of Tikal would have required roughly 15,000 tons of salt per year [22]. It is believed that the Maya harvested salt from seawater, and the remains of ancient salt works have been discovered along the coast of the Yucatan Peninsula [22].

In the late 19th century, scientists believed the concentration of gold in seawater to be between 2 and 64 ppb, which attracted large amounts of interest from prospectors, including Dr. Fritz Haber (a Nobel Prize winner), who promised to pay off Germany's World War I debt by mining gold from the sea [23]. Only after concentrations were later estimated to be in the range of 0.001 ppb did scientists conclude that mining gold from the sea was uneconomical [17, 23]. The pursuit to extract other minerals from the sea continued unabated, and by the early half of the 20th century numerous extract facilities were operating in the United States for common salt (NaCl), bromine, and magnesium [17, 24].

By 1965, only four constituents in seawater had been commercially extracted in a significant quantity: sodium and chloride in the form of common salt, magnesium and some of its compounds, and bromine. Several potassium and calcium salts have also been produced as byproducts in salt or magnesium extraction processes. Today, solar salt composes a large fraction of the total salt consumed in many countries. At these solar salt production facilities, such as the San Francisco salt works, seawater is taken into evaporation ponds and allowed to evaporate until salt precipitation begins to occur. In the first pond, calcium sulfate, the first salt to crystallize, settles to the bottom. The remaining brine is then moved into another crystallizing pond and further concentrated by evaporation until sodium chloride begins to precipitate. Eventually, magnesium salts will begin to precipitate, after which the remaining liquid, termed bittern, is drawn off of the crystallizing pond and further processed for recovery of magnesium compounds and bromine. Once an appreciable layer (4–6 in.) of sodium chloride has formed through this process, it is harvested mechanically, rinsed with salt water, and stored in piles. This refined product is over 99.9% NaCl, which is sufficient for human consumption.

### **2.1.1.1 Bromine**

Bromine was first produced from seawater in 1926 by treating the bitterns from the California solar salt operations. The development of antiknock gasoline created a very large demand for bromine [17]. By the late 1920s, the increased use of ethylene dibromide in the treatment of gasoline for motor fuel had sparked concerns that terrestrial sources of bromine could not meet demand [25, 26]. In response, both Dow Chemical Company and Ethyl Gasoline Corporation (later combined to Dow-Ethyl Corporation) began exploring means to extract bromine from seawater. The process first used (U.S. Pat. No. 2,323,549) precipitated bromine directly from unconcentrated seawater as tribromoaniline using aniline and chlorine. The process was first instigated aboard a ship capable of producing approximately 75,000 lbs of bromine per month using 250 tons of concentrated sulfuric acid, 25 tons of aniline, and 66 tons of chlorine. According to Mero [17], the original process was conducted at sea to avoid dilution with the discharged waste effluent; however, by 1933 Dow-Ethyl had begun operating a land-based facility at Kure Beach, NC. Siting of the carefully selected facility ultimately allowed for production of 20,000 tons of bromine per year.

The process was eventually modified to produce hydrobromic acid, which could be more easily refined to elemental bromine. Two facilities based on the tribromoaniline precipitation or hydrobromic acid process were later constructed in Freeport, TX; by 1965, these accounted for 80% of the bromine consumed in the United States. Both processes were capable of operating at extraction efficiencies of 90%; however, by 1965, the hydrobromic acid process emerged as dominant. The Kure Beach facility was shuttered after World War II, but the Freeport facilities operated until 1998.

### **2.1.1.2 Magnesium**

Prior to World War I, Germany was the only country actively producing magnesium metal [24]. World War I and the British blockade of Germany led to the development of numerous magnesium production facilities in the United States, with Dow and several other U.S.-based companies producing it from deep-well brines, primarily in Michigan. Most of these facilities were closed after World War I, when demand for magnesium decreased substantially [24]. During World War II, when global steel production significantly increased again, magnesium metal was in high demand, leading to the development of processes using seawater as a source. Both Britain and the United States put significant effort into the production of magnesium metal and magnesium compounds from seawater.

#### **2.1.1.2.1 Magnesium Production in Britain**

During World War II, Britain became very active in processing magnesia from seawater and built and operated several plants. These plants included the Harrington and Hartpool facilities. The Hartpool facility operated until around 2005 and by 2000 had produced 7 million tons of magnesia from seawater. The decline of the British magnesia industry is attributed to decreasing demand for magnesia, increasing fuel cost, and the overall global recessions [27]. At the Hartpool facility, approximately 700 tons of magnesia was produced per day, requiring 4000 gpm of seawater [28]. Britain was able to economically produce magnesia from seawater for such a long period of time because of its close proximity to cheap sources of limestone (e.g., the Coxhoe Works and Quarry) and a mature system for transport of raw and finished materials.

#### 2.1.1.2.2 *Magnesium Production in the United States*

**Dow Chemical Company.** Although the British were the first to successfully extract magnesium from seawater, the first large-scale magnesium processing plant using seawater was built in Freeport, TX in 1941. Built and operated by Dow, the facility utilized a multistep chemical precipitation process using slaked lime ( $\text{Ca}(\text{OH})_2$ ) and hydrochloric acid ( $\text{HCl}$ ) to produce magnesium chloride [17]. The facility was sited in Freeport for its availability of cheap natural gas (for production of heat and electricity) and lime [29].

Producing magnesium metal from seawater requires an extraction step, a refinement step to produce magnesium oxide or magnesium chloride, and electrolytic reduction to magnesium metal. The Dow process used lime addition to produce a slurry of magnesium hydroxide followed by a settling process to yield a concentrated solution. Addition of hydrochloric acid yielded a magnesium chloride solution that was evaporated to reduce the solubility of salts carried over from the seawater. By adding magnesium sulfate, gypsum was precipitated and the remaining solution further evaporated to about 50% concentration of magnesium sulfate. This solution was then heated ( $170^\circ\text{C}$ ) and sprayed onto solid magnesium chloride. The solid was then dried and fed into an electrolytic cell to yield magnesium metal and chlorine gas. The gas was used to make hydrochloric acid for the process and the metal cast into ingots. The overall process produced around 99.8% magnesium metal [17].

A second government-owned Dow facility was eventually built in Velasco, TX in 1942, and by the end of the year the two facilities produced more than 92,000 tons of magnesium metal annually and 84% of the total U.S. output of magnesium metal [29]. By the 1960s, both magnesium metal and magnesium compounds were produced from seawater at these two facilities, and by the 1970s Texas produced more than half of the world's magnesium [29]. These magnesium compounds were used by the chemical, sugar, paper, rayon, fertilizer, rubber, ceramic, and petroleum industries, for preparation of special cements, and in refractories. Dow increased its capacity in 1969 and 1970 to 120,000 tons a year, while its major competitor, American Magnesium, which began operations in 1969, produced smaller quantities. Specific values were not disclosed, but in 1980 magnesium had the highest value of metallic minerals produced in Texas.

Although Dow dominated the global magnesium market through the 1970s and 1980s, during this time several other U.S. companies (Alcoa, NL Industries, AMAX Inc.) began entering the market. Considerable technological advancements had been made worldwide to improve magnesium production efficiency, but Dow managed to hold onto its share of the market by cutting prices and increasing output, which deterred competitors from committing to significant magnesium production. By the 1990s, tariff reductions and increased global production significantly decreased the price of magnesium, and the United States became a net importer [24]. In 1998, Dow's Freeport facility was damaged by lightning, Hurricane Francis, and rainstorms and abandoned at the end of the year. According to Lieberman [24]: "Dow's exit signaled the declining role of US producers in the increasingly global magnesium industry."

**Kaiser Aluminum and Chemical Corporation.** Magnesium compounds such as magnesium oxide ( $\text{MgO}$ ), magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) and magnesium chloride ( $\text{MgCl}_2$ ) were also commercially extracted from seawater and used as a refractory material in a variety of products as early as 1941. A facility was operated at Moss Landing, CA by Kaiser Aluminum and Chemical Corporation to produce magnesium hydroxide and various grades of

magnesium oxide from seawater [17]. Seawater was mixed with calcined dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) to precipitate magnesium hydroxide. After settling and thickening, the slurry was washed to remove impurities and filtered to reduce water content. The filter cake could be used directly or further processed (calcined) to produce magnesium oxide. This facility closed in 1999, and currently part of the Kaiser facility is being used by Calera Corporation to develop its process for producing calcium carbonate from seawater [30].

### **2.1.2 Extraction from Brackish Groundwater or Brines**

Groundwater or brines rich in valuable ions have long been used for the production of commodity-grade materials. Dow Chemical Company began producing bromine from underground brines in Midland, MI around 1890 and later developed a process for the production of chlorine and sodium hydroxide. In the United States, bromine, lithium, and iodine are exclusively produced from underground brines, and materials extracted from the Great Salt Lake include sodium chloride, magnesium chloride, potassium sulfate, and chlorine. Zinc metal was once produced from the Salton Sea by Cal Energy, although production ceased in early 2000 because of operational difficulties.

## **2.3 Desalination Brine/Concentrate Composition**

### **2.3.1 Seawater Desalination**

The major ions of seawater are (somewhat arbitrarily) defined as those with concentrations greater than 1 ppm that contribute significantly to its salinity [22, 31]. Thus, there are 11 major ions in seawater, listed in Table 2.1 with concentration data obtained from Pilson [22]. Major ion data reported by Pilson was generated in the 1960s through the analysis of more than 100 seawater samples [32–34]. The ionic composition of seawater is dominated by NaCl, which composes more than 86% of the salt content by mass. Salinity and specific ion concentrations of seawater can vary significantly from one location to another depending on climate conditions and surface water runoff.

A summary of minor ions present in seawater at a range of micromolar and nanomolar concentrations is presented in Table 2.2, and those at picomolar and femtomolar concentrations are presented in Table 2.3. Several researchers have argued that the extraction of constituents at concentrations lower than boron is unfeasible because of the volume of water requiring processing and the insignificant added value of the extracted minor ions compared to extraction costs [17, 20, 35]. Seawater desalination facilities typically operate at between 30 and 50% recovery, which results in a brine stream nearly twice as concentrated as the influent seawater. As a reference, the concentration of major ions in several seawater RO desalination brine streams is presented in Table 2.4.



**Table 2.1. Concentrations of the Major Ions in Surface Seawater**

<b>Ion</b>	<b>Abbreviation</b>	<b>mmol/kg</b>	<b>Concentration (‰)</b>
Sodium	Na	468.96	10.781
Potassium	K	10.21	0.399
Magnesium	Mg	52.83	1.284
Calcium*	Ca	10.28	0.4119
Strontium*	Sr	0.0906	0.0079
Chloride	Cl	545.88	19.353
Sulfate	SO <sub>4</sub>	28.23	2.712
Bicarbonate*	HCO <sub>3</sub>	2.06	0.126
Bromide	Br	0.844	0.0673
Boric acid	B(OH) <sub>3</sub>	0.416	0.0257
Fluoride	F	0.068	0.0013

*Source:* Pilson [22]

*Note:* \*Considered nonconservative—concentrations change with depth.

**Table 2.2. Concentrations of the Minor Ions (μmol and nmol) in Surface Seawater**

Element	Units per kg	Approx. Mean Concentration	Minimum Value	Maximum Value	Mean Conc. ppb (μg/kg)
Iodine	umol	0.4	0.2	0.5	50.8
Lithium	umol	25	NA	NA	173.5
Nitrogen (NO <sub>3</sub> )	umol	30	<0.1	45	1860.2
Phosphorus	umol	2.3	<0.1	3.5	71.2
Rubidium	umol	1.4	NA	NA	119.7
Silicon	umol	100	<1	200	2808.6
Aluminum	nmol	10	0.1	40	0.27
Antimony*	nmol	1.2	NA	NA	0.146
Arsenic	nmol	23	15	25	1.723
Barium	nmol	100	32	150	13.733
Cadmium	nmol	0.7	0.001	1.1	0.079
Cesium	nmol	2.2	NA	NA	0.292
Chromium	nmol	4	2	5	0.208
Copper	nmol	4	0.5	6	0.254
Iron	nmol	1	0.1	2.5	0.056
Manganese	nmol	0.5	0.2	3	0.027
Molybdenum	nmol	100	92.	105	9.594
Nickel	nmol	8	2	12	0.47
Selenium	nmol	1.7	0.5	2.3	0.134
Uranium	nmol	13.6	13.872	13.328	3.237
Vanadium	nmol	30	20	35	1.528
Zinc	nmol	6	0.05	9	0.392

Source: Pilson [22]

Notes: \*=not well established; NA=not available.

**Table 2.3. Concentrations of the Minor Ions (pmol and fmol) in Surface Seawater**

<b>Element</b>	<b>Units per kg</b>	<b>Approx. Mean Concentration</b>	<b>Minimum Value</b>	<b>Maximum Value</b>	<b>Mean Concentration ppb (µg/kg)</b>
Beryllium	pmol	20	4	30	0.0001802
Bismuth*	pmol	0.1	<0.015	0.24	0.0000209
Cerium	pmol	20	16	26	0.0028024
Cobalt	pmol	20	10	100	0.0011787
Dysprosium	pmol	8	2	12	0.0013
Erbium	pmol	8	2	10	0.0013381
Europium	pmol	1	0.3	1.7	0.000152
Gadolinium	pmol	6	2	9	0.0009435
Gallium	pmol	20	2	50	0.0013945
Germanium	pmol	70	<7	115	0.0050827
Hafnium*	pmol	20	NA	NA	0.0035698
Holmium	pmol	2.5	0.5	3	0.0004123
Indium*	pmol	0.1	0.05	0.15	0.0000115
Lanthanum	pmol	30	8	57	0.0041672
Lead	pmol	10	5	175	0.002072
Lutetium	pmol	1	0.2	1.8	0.000175
Mercury	pmol	2	0.5	12	0.0004012
Neodymium	pmol	25	5	40	0.003606
Niobium*	pmol	<50	NA	NA	0.0046453
Palladium	pmol	0.6	0.2	0.6	0.0000639
Platinum	pmol	1	0.54	1.64	0.0001951
Praeseodymium	pmol	5	1	8	0.0007046
Rhenium	pmol	40.	NA	NA	0.0074484
Rhodium	pmol	0.8	0.3	1	0.0000823
Samarium	pmol	4	1	6	0.0006014
Scandium	pmol	15	8	20	0.0006743
Silver	pmol	25	0.5	45	0.0026967
Tantalum*	pmol	14	NA	NA	0.0025333
Tellurium	pmol	0.6	0.4	1.7	0.0000766
Terbium*	pmol	1	0.2	1.5	0.0001589
Thallium	pmol	60	NA	NA	0.0122628
Thulium	pmol	1	0.3	1.5	0.0001689
Tin*	pmol	4	1	12	0.0004748

<b>Element</b>	<b>Units per kg</b>	<b>Approx. Mean Concentration</b>	<b>Minimum Value</b>	<b>Maximum Value</b>	<b>Mean Concentration ppb (µg/kg)</b>
Titanium	pmol	200	4	300	0.0095734
Tungsten	pmol	56	45	67	0.010295
Ytterbium	pmol	7	1.5	11	0.0012113
Yttrium	pmol	250	80	300	0.0222265
Zirconium	pmol	200	12	300	0.0182448
Gold	fmol	50	20	200	0.0000098
Iridium*	fmol	0.7	0.5	0.9	0.0000001
Osmium*	fmol	9	NA	NA	0.0000017
Ruthenium*	fmol	20	NA	NA	0.000002

*Source:* Pilson [22]

*Notes:* \*=not well established; NA=not available.

**Table 2.4. Example of Measured Water Quality in Seawater Reverse Osmosis Brine**

Facility		Qidfa I <sup>a</sup>	Qidfa II <sup>a</sup>	Not Disclosed <sup>b</sup>	Lab Test <sup>c</sup>
Location		UAE	UAE	NA	Tyrrhenian Sea
Recovery		40%	35%	NA	30%
Water quality parameter	Unit				
Calcium	mg/L	617	730	891.2	625
Magnesium	mg/L	2150	2240	2877	2020
Sodium	mg/L	15,100	15,800	24,649	15,500
Potassium	mg/L	767	805	888	NA
Strontium	mg/L	7.19	11.5	ND	NA
Silicon	mg/L as SiO <sub>2</sub>	1.07	19.9	NA	NA
pH	-	6.76	6.97	7	NA
Bicarbonate	mg/L	117	125	315.3	199
Chloride	mg/L	30,540	32,004	43,661	28,800
Sulfate	mg/L	3931	4500	6745	3060
Nitrate	mg/N/L	0.7	0.7	NA	NA
Fluoride	mg/L	2.1	0.9	NA	NA
TDS	mg/L	53,177	56,158	80,028	50,200
Alkalinity	mg/L	96	102	NA	NA
Hardness	mg/L	10,409	11,067	NA	NA
Copper	µg/L	NA	NA	15	NA
Nickel	µg/L	NA	NA	3	NA
Iron	µg/L	NA	NA	13	NA
Chromium	µg/L	NA	NA	3.5	NA
Molybdenum	µg/L	NA	NA	0.4	NA

Sources: a [36]; b=[37]; c=[38]

Notes: NA=not available; TDS=total dissolved solids.

### 2.3.2 Brackish Water Desalination

Brackish water is a loosely defined term mostly referring to waters with intermediate salinity (e.g., seawater diluted by freshwater, such as conditions found in estuarine systems, or groundwater with elevated total dissolved solid [TDS] concentrations). The chemical composition of estuarine waters is somewhat similar to seawater, although usually more dilute from input of freshwater sources [39]. Estuary systems, however, have significantly more temporal and spatial variability of salinity than seawater and estuaries receiving large volumes of inland water. Anthropogenic input may also contain significantly more dissolved metals, nutrients, and potential for algal blooms [40]. It is worth noting that the water chemistry of estuaries is rather complex because of inland-derived colloidal material and particulates reacting with dissolved metals in saline environments [41]. It is expected that, in general, estuarine waters will have lower concentrations of valuable materials than seawater.

The composition of inland brackish water depends on the surrounding geologic formation, hydrological recharge mechanisms, anthropogenic impact, and influence of seawater on the aquifer. In many inland brackish water sources of the southwestern United States, waters are enriched in calcium and depleted in sodium relative to seawater [42]. In addition, silica is often found at higher concentrations than seawater, and the predominant anion is often sulfate rather than chloride [42]. Besides silica (and in certain cases bromine, iodine, and lithium), however, individual constituents are typically at lower concentrations than seawater. This fact, however, does not preclude brackish water from potential mineral recovery, especially considering that RO concentrates from brackish water applications are expected to have greater concentration factors than seawater RO facilities; this is due to operation of RO systems at higher recovery. A good summary of major ion concentrations in various U.S. brackish water sources is provided by Brady, et al. [42], and several are shown in Table 2.5.

**Table 2.5. Major Ion Composition of Several Brackish Groundwaters**

<b>Ion</b>	<b>Groundwater Tularosa Basin, NM</b>	<b>Groundwater Las Vegas, NV</b>	<b>Groundwater Hueco Bolson, TX</b>	<b>Oil and Gas Prod. Water Eddy Co., NM</b>
Sodium	114	755	116	3430
Potassium	2	72	7	NA
Calcium	420	576	136	600
Magnesium	163	296	33	171
Chloride	170	954	202	4460
Nitrate	10	31	NA	NA
Phosphate	0	NA	NA	NA
Sulfate	1370	2290	294	2660
Bicarbonate	270	210	190	488
Silicon dioxide	22	77	31	NA
TDS	2630	5270	1200	11900

*Source:* Adapted from [42]

*Notes:* All values in units of mg/L; TDS=total dissolved solids.

### **2.3.3 Wastewater Desalination**

Typical wastewater desalination or reclamation facilities treat secondary or tertiary treated wastewater effluent using low-pressure membrane (i.e., microfiltration [MF] or ultrafiltration [UF]) filtration pretreatment followed by RO. RO systems are typically operated at recoveries of 75 to 85% resulting in streams that are roughly six times as concentrated as the influent wastewater effluent. Concentrate composition is dependent upon the numerous factors controlling the composition of wastewater, including regional drinking water composition, industrial wastewater inputs, infiltration, stormwater collection, and the level of wastewater treatment. As a reference, the measured composition of two wastewater reclamation RO concentrate streams is presented in Table 2.6.

**Table 2.6. Wastewater Reverse Osmosis Concentrate Measured Water Quality at Two Wastewater Reclamation Facilities**

Analyte	Detection Limits	Facility 1	Facility 2	
		RO Concentrate ppm (n=2)	Average Deviation	RO Concentrate ppm (n=1)
Aluminum	0.018	0.16	0.05	0.10
Antimony	0.016	BDL	NA	BDL
Arsenic	0.039	BDL	NA	BDL
Barium	0.0003	0.36	0.09	0.19
Beryllium	0.0002	BDL	NA	BDL
Boron	0.053	0.66	0.04	BDL
Cadmium	0.001	BDL	NA	0.02
Calcium	0.01	439.44	109.87	482.00
Chromium	0.003	BDL	NA	BDL
Cobalt	0.004	BDL	NA	0.01
Copper	0.003	0.03	0.00	0.02
Iron	0.002	0.33	0.08	0.77
Lead	0.013	BDL	NA	BDL
Lithium	0.003	0.06	0.03	0.12
Magnesium	0.0004	104.31	26.08	156.62
Manganese	0.0003	0.33	0.10	0.34
Molybdenum	0.002	0.09	0.03	0.12
Nickel	0.002	BDL	NA	0.04
Phosphorus	0.1	1.85	0.45	2.78
Potassium	0.19	118.26	29.50	111.91
Selenium	0.04	BDL	NA	BDL
Silica	0.11	71.44	13.53	61.49
Silver	0.004	BDL	NA	BDL
Sodium	0.005	1148.88	224.89	1398.53
Strontium	0.023	4.73	1.23	4.23
Tin	0.01	BDL	NA	BDL
Titanium	0.001	BDL	NA	BDL
Vanadium	0.001	BDL	NA	0.01
Zinc	0.001	0.21	0.07	NA

Notes: The RO system was operated at approximately 85% recovery (n=number of samples); BDL=below detection limit; NA=not available; RO=reverse osmosis.



## Chapter 3

# Technologies for Extraction of Materials from Aqueous Solutions

---

### 3.1 Summary of Potential Unit Processes for Material Extraction

#### 3.1.1 Membrane Processes

##### 3.1.1.1 Reverse Osmosis and Nanofiltration

RO is a pressure-driven membrane process that has, along with thermal processes (e.g., multistage flash [MSF]), become a dominant technology for seawater, brackish water, and wastewater desalination [7]. Commercial RO membranes are predominately thin film composite with a thin polyamide active layer cast on a porous support layer. RO membranes can be classified by salt rejection and pressure requirement, and the main categories include seawater RO, brackish water RO, and low-pressure RO. Modern RO membranes are capable of achieving greater than 98% sodium chloride rejection where rejection ( $R_s$ ) is given by

$$R_s = \text{Rejection} = \left( 1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}} \right) \quad (3.1)$$

NF represents a relatively recent development in membrane technology with characteristics that fall between UF and RO. NF has been engineered to provide selective separation of solutes and now consists of a wide range of membrane materials and configurations that can be used for a variety of applications. Whereas RO membranes dominate the seawater desalination industry, NF is employed in a variety of water treatment and industrial applications for the selective removal of ions and organic substances and in certain seawater desalination applications.

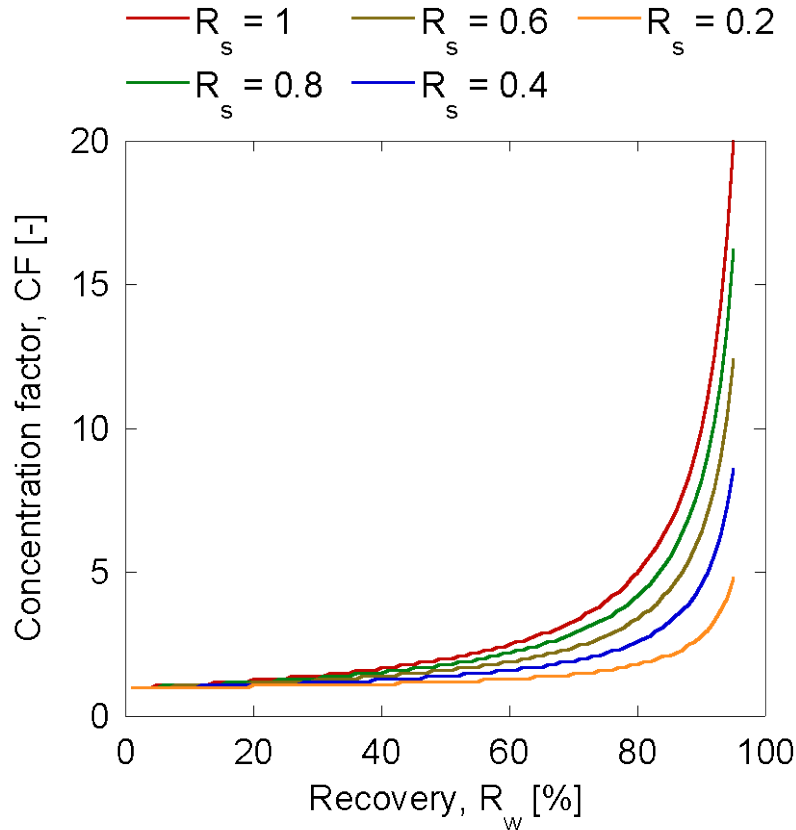
As physical separation processes, RO and NF membrane systems are limited by the percentage of feed water that becomes permeate, which is termed recovery ( $R_w$ ) and given by

$$R_w = \text{Recovery} = \frac{Q_{\text{permeate}}}{Q_{\text{feed}}} \quad (3.2)$$

Membrane system recovery is governed by a number of factors, including feed water ionic composition and salinity, level of pretreatment, and optimum conditions for minimizing energy consumption. Seawater RO (SWRO) membrane systems are operated at a low recovery (35–55%) compared with RO and NF applications for low to moderately saline source waters (up to 85%) primarily because of the high osmotic pressure of seawater. Besides determining the amount of brine/concentrate requiring disposal or treatment, recovery dictates the brine/concentrate concentration factor given by

$$CF = \left( \frac{1}{1 - R_w} \right) [1 - R_w (1 - R_s)] \quad (3.3)$$

and the concentration of constituents in the brine/concentrate stream. The impact of rejection and recovery on the concentration factor is illustrated in Figure 3.1. Given a salt rejection of 99%, SWRO systems operating between 35 and 50% will have brine streams one and a half to two times as concentrated as the feed water.



**Figure 3.1. Concentration factor as a function of rejection (R) and % recovery.**

Compared to RO, NF has been proposed only for certain niche applications in the desalination industry. These applications include a dual NF system that was extensively piloted by the Long Beach Water Department in Southern California and NF as a pretreatment to RO or MSF for seawater desalination. Hassan et al. [43] proposed a desalination process using NF as a pretreatment step to SWRO or MSF, which has subsequently been pilot- and demonstration-tested at the Umm Lujj facility in Saudi Arabia. The advantage of NF pretreatment is reported to be the reduction in sparingly soluble salts, microorganisms, organic foulants, turbidity, and TDS, which allows the SWRO to operate at lower energy consumption and higher recovery (70%) and the MSF at a higher brine temperature and recovery (80%). Subsequent pilot testing indicated that hybridization of RO and MSF desalination processes by introducing NF could reduce typical SWRO desalination costs by approximately 30% [44]. On the basis of these results, the Umm Lujj desalination

facility was retrofitted with NF pretreatment for long-term demonstration testing of the NF/SWRO process [45]. Although the NF membranes used had organic fouling issues, process modifications (i.e., addition of more NF elements to reduce the flux of lead elements) have reportedly solved any issues [45]. Macedonio et al. [46] conducted a cost and energy analysis on several integrated desalination processes (RO, MSF, membrane crystallization [MCr], including NF pretreatment and reported that although NF can significantly increase the recovery of desalination systems, the cost savings are only marginal when energy recovery devices are used. However, the application of MCr to treat NF brine has been proposed as a method to yield salable products such as calcium carbonate, sodium chloride, and magnesium sulfate [47, 48].

### **3.1.1.2 Microfiltration and Ultrafiltration**

MF and UF are porous, low-pressure membrane technologies used in a variety of applications including water and wastewater treatment, food and beverage manufacturing, biomedical processing, and high purity product manufacturing. Although normally used as pretreatment for RO membranes in desalination applications, several hybrid MF or UF processes have been developed into processes or could be used for the extraction of constituents from aqueous streams. Such processes include adsorption membrane filtration for boron removal [49], micellar or polymer enhanced UF for heavy metal removal [50, 51], and fluidized bed crystallization (FBC) coupled with MF [2].

### **3.1.1.3 Dialysis**

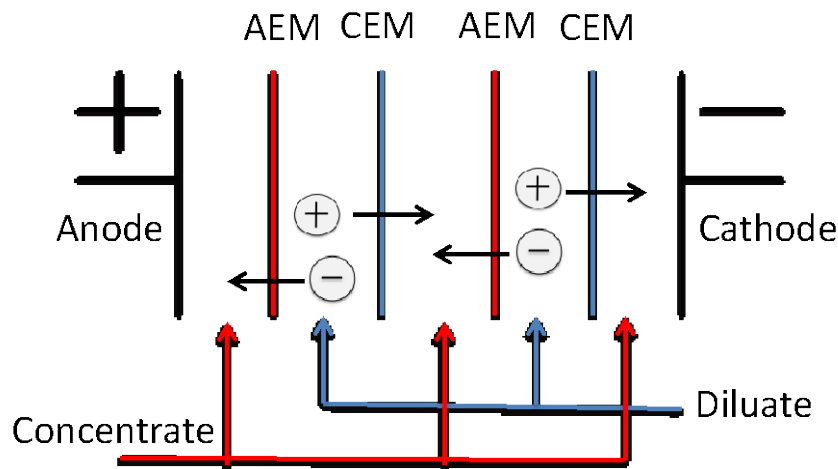
Donnan dialysis utilizes ion-exchange membranes and concentration gradients between the feed stream and a sweep stream to allow for selective passage of ions. Donnan dialysis is based on Donnan equilibrium theory, which states that, for two solutions separated by an ion-selective membrane, ions will diffuse across the membrane to achieve minimum potential energy and electroneutrality at equilibrium. By selecting the appropriate membrane and ion composition and concentration in the sweep solution, preferential transport of the ion of interest from the feed solution can be achieved (although it is worth noting that the sweep co-ion must also diffuse from the sweep to the feed solution). Compared to electrodialysis (ED), the advantages of Donnan dialysis include resistance to fouling and low energy requirements and cost [52]. The dialysis process has been used for product purification and removal or recovery of cations and anions from various process streams and sludges, including calcium, magnesium, heavy metals (e.g., aluminum, copper, gold, silver), oxyanions (e.g., bicarbonate, nitrate, sulfate), and organic acids [52–54]. The main disadvantages to Donnan dialysis include low ion flux, long treatment times, and reverse diffusion of sweep ions.

### **3.1.1.4 Electrodialysis and Electrodialysis Reversal**

ED is an electrochemical (i.e., current driven) membrane process that uses numerous cells of anion exchange membranes (AEM) and cation exchange membranes (CEM) for the removal of ions from a source water. In ED, ions migrate toward the electrodes, with anion transport maintained through AEMs toward the anode and cation transport maintained through CEM membranes toward the cathode (Figure 3.2). Ions transported from the diluate stream accumulate in a concentrate stream that is partially recycled through the system. Electrodialysis reversal (EDR) is a variation of the ED process in that the polarity of the electrodes is reversed at predetermined intervals (e.g., 15–20 minutes). Reversal of ion migration and switching of the diluate channel to the brine channel (and vice versa) remove

accumulated ions from the membrane, allowing operation at high recovery and eliminating the need for chemicals to prevent scaling. The major advantages of EDR (particularly compared with RO) include ability to treat waters with elevated turbidity (up to 2 NTU) and silica, potential for product water recoveries up to 94%, reduced antiscalant chemical use, and robustness of membranes [55]. EDR systems are limited by feed water salinity (the process is economical up to 8000 ppm TDS) and are typically used for desalting water with 800 to 2000 ppm TDS [55, 56].

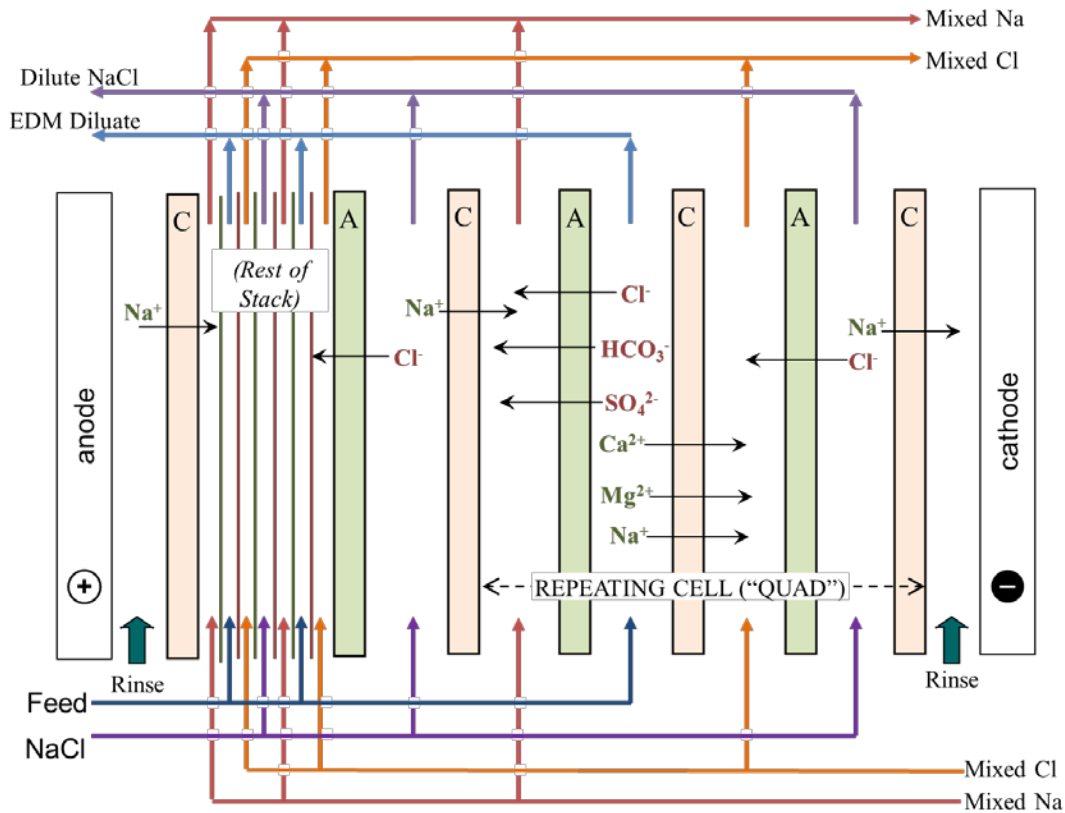
A number of treatment schemes using ED and EDR have been proposed for desalination, RO brine/concentrate minimization, ZLD applications, and salt production from brine and concentrates [13, 57–62]. Typically in these processes, ED or EDR is proposed to treat desalination system brine or concentrate to increase system recovery and for further concentration prior to evaporation or crystallization for salable salt recovery [57, 58, 62]. Most of the studies evaluating such approaches are limited to laboratory-scale investigations; however, such an approach is used to produce food-grade salt from seawater in Japan, Korea, and Taiwan. Tanaka et al. [58] analyzed costs and energy requirements associated with sodium chloride production from RO brine using ED and evaporation and reported that it required 80% of the energy associated with sodium chloride production from seawater.



**Figure 3.2. Schematic of the ED process.**

An additional ED technology receiving considerable recent attention for concentrate minimization is termed electrodialysis metathesis (EDM). EDM differs from ED in that it has two diluting streams (EDM feed and NaCl) and two concentrating streams that are normally called mixed Cl and mixed Na. The EDM feed can be brackish water or RO Concentrate. Anions from the EDM feed mix with Na from NaCl to produce various sodium salts ( $\text{Na}_2\text{SO}_4$ , NaCl,  $\text{NaHCO}_3$ , etc). Cations from the EDM feed mix with Cl from NaCl to produce various chloride salts ( $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , NaCl) (see Figure 3.3). This configuration is designed to separate ions from the raw water into two streams of highly soluble salts (sodium salts and chloride salts) and therefore achieve high recoveries when treating RO concentrate [63]. Through pilot-scale testing, Bond et al. [63] developed cost and energy requirements associated with ZLD using EDM followed by crystallization. The results indicated that the EDM/crystallizer process could be significantly cheaper (between \$0.64 and \$11.21/kgal depending on the raw water TDS) than thermal evaporation processes when the feed water (RO concentrate) TDS was less than 6000 mg/L. EDM system recoveries have been reported

at 99% when raw water TDS is less than 2000 mg/L. Veolia has purchased the rights to the technology and is apparently developing a commercial EDM system called Zero Discharge Desalination [64]. Several sources of information have alluded that sequential precipitation processes could be performed on EDM concentrate to obtain salable products (e.g., calcium carbonate, calcium sulfate, sodium sulfate); however, limited information is available as to feasibility [64, 65].



**Figure 3.3. Schematic of the EDM process.**

Source: [65]

### 3.1.1.5 Liquid Membranes

Numerous liquid membrane systems have been developed for the separation and enrichment of ionic constituents from various source waters and solutions [66, 67]. Comprehensive reviews on liquid membrane systems for metal extraction or removal can be found in Gyves and de San Miguel [67] and Nghiem et al. [68]. Liquid membranes can be of two types: supported liquid membranes (SLM) and nonsupported liquid membranes. SLMs are usually a solvent-resistant, polymeric flat sheet or hollow-fiber membrane impregnated with a solvent containing a carrier molecule (ionophore) capable of binding a metal or compound [67]. Transport of a species from the source water to a receiving phase against a concentration gradient can occur in the presence of a second species that moves down a concentration gradient (i.e., coupled transport). Various carriers, carrier solutions, membrane types, and

designs have been proposed for liquid membrane systems, and although efficient separations have been demonstrated, issues with SLMs include poor stability, low solute fluxes, and difficulty in developing large systems.

### **3.1.2 Evaporation**

#### **3.1.2.1 Evaporation Ponds**

Although not very common in the United States, evaporation ponds are a brine/concentrate disposal option in arid regions with high evaporation rates and inexpensive land. According to Mickley [11], the cost of evaporation ponds becomes excessive when brine/concentrate flow rates exceed 0.3 mgd. Good reviews and analysis of the use of evaporation ponds for desalination brine/concentrate disposal can be found in several references [10, 11, 69, 70]. Although solar salt is commonly produced from evaporation ponds, literature does not suggest that this method has been significantly explored for salt production from desalination brine/concentrate. One exception is a publication by Ravizky and Nadav [71], which describes a partnership between Mekorot Water Company (Israel) and Israel Salt Company for SWRO disposal in evaporation ponds and subsequent production of food-grade salt. In the process, the entire brine stream from the SWRO desalination facility is blended with seawater and sent to a series of evaporation ponds. According to the authors, this arrangement has led to a 30% increase in salt production compared to seawater alone. Difficulties encountered include elevated calcium in the brine (leading to biogrowth in the pond), accelerated precipitation of calcium sulfate, and initial salt purity issues. Process changes to the SWRO system (e.g., use of antiscalants in lieu of pH adjustment to prevent membrane scaling) and evaporation pond system reportedly solved all issues, and the brine disposal salt production system had been in operation for 9 years by the time the paper was published in 2007.

#### **3.1.2.2 Distillation and Evaporation Systems**

There are a number of distillation/evaporation processes that can be used for the goal of brine/concentrate minimization, ZLD, or extraction of constituents from waste streams. For the extraction of materials, evaporators can be used to precipitate salts and, when used upstream of other processes (e.g., crystallizers), can increase solute concentrations and reduce the volume of brine/concentrate being treated. The selection of one evaporator design over another is based on a number of factors including cost, energy requirements, access to waste heat, flow rate, and feed water dissolved solids concentration. Several distillation and evaporation processes are discussed in this and the following sections.

Multiple-effect distillation (MED) is a process consisting of multiple vessels or effects and was once commonly used for seawater desalination. MED uses steam and steam condensation as heat to evaporate water, and vapor produced in each vessel is used in subsequent vessels as a heat source. As such, MED only requires an external heat source in the first chamber and cooling of the final distillate. Because the boiling point of water decreases with decreasing pressure and the vapor pressure decreases with each subsequent vessel, MED systems can operate at relatively low temperatures (~70° C).

MSF evaporators use a series of stages in which the feed water is first warmed in pipes (by steam condensing from flash chambers) prior to heating to its maximum temperature in a brine heater fed by low-pressure steam. The water is then fed to a series of flash chambers with lower temperature and pressure, where a small fraction of the water boils (i.e., flashes), condenses on the feed water pipe (thereby warming the feed water prior to the brine heater),

and is collected. MSF is considered one of the simplest evaporation processes and produces approximately 40% of the world's desalinated water (it is by far the most common desalination technique in the Middle East) [7].

Although MED is more thermodynamically efficient than MSF and can achieve higher recoveries (~20% for MSF versus ~50% for MED), MSF is favored in the desalination sector for its relative simplicity and reduced issues with scaling. MED and MSF units are typically sized for flow rates of 1 mgd and greater, and when used with waste heat sources to generate steam, both can have relatively low energy consumption (1.2–4 kWh/m<sup>3</sup>). In the absence of waste heat, however, both processes are energy intensive. Capital costs for both processes are high, with significant O&M costs.

Both MED and MSF have been proposed in treatment schemes for extraction of constituents from desalination brine/concentrate. For example, MED and MSF have been used or proposed as evaporation steps after ED for production of food-grade salt [58], sodium hydroxide, and chlorine [16, 72].

As opposed to MED and MSF, mechanical vapor compression (MVC) and thermal vapor compression (TVC) evaporators can be used to treat small flows of highly concentrated brines and achieve high recoveries [13]. Often termed brine concentrators, both processes generate mechanically the energy required to evaporate water. For typical systems, water vapor is compressed and fed to heat exchangers to evaporate a feed stream with the heat of the distilled water and brine reclaimed for heating purposes. Similar to MED and MSF, energy requirements increase with increasing feed stream concentration, and energy requirements for VCM and TVC are reportedly between 8.5 and 23 kWh/m<sup>3</sup>. Brine concentrators have been considered for ZLD systems [13] and the production of salt from RO brine/concentrate [72].

### **3.1.3 Sorption Processes**

#### **3.1.3.1 Ion Exchange**

Ion-exchange processes use the interchange or exchange of ions through electrostatic interactions between two phases (i.e., water and ion-exchange material) to separate ions. The exchange of ions in solution is dependent upon numerous factors but largely depends on the concentration of ions in solution and the affinity of the ions for the ion-exchange material relative to the solution phase. Various natural materials (e.g., inorganic solids) act as ion-exchange resins; however, ion-exchange resins have been engineered from various polymers to provide high affinity and selectivity for specific ions. Hundreds of ion-exchange resins have been developed over the past 100 years using various polymers and ligands, and a good historical review of ion-exchange resin development can be found in Alexandratos [73].

A large amount of research has been conducted to develop and optimize ion-exchange materials and resins for the separation of valuable constituents from aqueous solutions. A comprehensive review of ion-exchange processes developed for metal extraction from seawater (up until 1984) can be found in Schwochau [21]. Schwochau's review demonstrates that significant effort has been put towards the development of ion-exchange resins for metal extraction from seawater, particularly lithium, magnesium, and uranium. An additional and more recent review was also given by Khamizov et al. [74]. In particular, ion-exchange resins have been proposed or evaluated for the extraction of ions from seawater and desalination

brine/concentrate, including ammonia, boron, cesium, lithium, magnesium, molybdenum, phosphorus, potassium, rubidium, and uranium. More discussion on the use of ion-exchange resins for these metals is provided in subsequent sections.

#### **3.1.3.3 Molecular or Ion Sieves**

Molecular sieves (often termed ion sieves) are engineered inorganic adsorbents with high selectivity towards specific ions. Generally regarded as an ion-exchange process, molecular sieves obtain high selectivity by incorporating the ion of interest into hydrous oxides of tetravalent and pentavalent metals. Once the ion is removed from the metal oxide (usually through acid rinsing), a lattice or nanoporous structure is created that sterically excludes metals besides the ion of interest [75, 76]. Various types of molecular sieves have been developed, with one of the main focuses being on the extraction of lithium from seawater.

#### **3.1.4 Precipitation and Crystallization**

Precipitation and crystallization are processes by which dissolved constituents in supersaturated solutions interact to form a solid. They are generally discussed as occurring in three stages: nucleation, crystal growth (or crystallization), and ageing. Nucleation is considered the stage where lattice ions form clusters of sufficient size to lead to the spontaneous deposition of additional lattice ions during the crystal growth stage [77]. Nucleation can occur through either random collisions between lattice ions (homogeneous nucleation) or surface interactions with other particles or impurities (heterogeneous nucleation). Heterogeneous nucleation is often observed in water treatment applications because of the abundance of foreign particles and dissolved constituents.

Crystal growth or crystallization refers to the stage whereby lattice ions are transported to (through diffusion and advection) and incorporated into the lattice structure. Crystal growth depends on both the rate of transport and the surface area available for adsorption; however, the rate of crystallization is typically controlled by either diffusion or interface [77, 78]. Even in supersaturated solutions, nucleation and the initial stages of crystallization may require significant time to occur, referred to as the induction time. The kinetics of precipitation can be considered as both the length of the induction period and the rate of change in the concentration as precipitation occurs [79].

Once precipitated, the structure of ionic solids may change over time depending on the conditions and whether crystals are kept in the initial solution. Ageing refers to the shift from amorphous (noncrystalline), microcrystalline (<1–2  $\mu\text{m}$ ), or polymorphous (small crystallites) solid forms to a more stable crystal form [77]. The shift in smaller crystals to larger ones is termed Oswald ripening.

Precipitation and crystallization are processes by which materials could potentially be extracted from RO brine, namely abundant metal salts such as calcium, magnesium, potassium, and sodium. Both processes have received significant interest recently, particularly for maximizing the recovery of RO systems (e.g., intermediate softening) and ZLD systems [2, 13, 80–82]. Whereas precipitation and crystallization refer to unit operations or processes that generate a solid from a supersaturated solution, precipitation is often used to describe the process of solid formation in highly supersaturated solutions achieved through chemical additions (i.e., manipulating the ion activity product [IAP]) [83]. Precipitation is typically fast and irreversible and may produce amorphous solids in addition to microcrystals. Crystallization refers to the formation of ionic solids through manipulation of solubility



conditions, including solvent removal through evaporation and changes in temperature and pressure (e.g., manipulating  $K_{s0}$ ). In both precipitation and crystallization, formation of solids follows the same processes as described previously; however, precipitation performed at high supersaturation typically results in the formation of small crystals. Solids recirculation during a precipitation process increases the surface area available for crystal growth, leading to larger crystals [77].

### 3.1.4.1 Solubility Equilibria and Supersaturation

Whether a salt will precipitate can be evaluated by comparing IAP to equilibria constants or equilibrium solubility products (e.g.,  $K_{s0}$ ). For the dissolution reaction of a generic solute  $A_xB_y(s)$  the dissolution reaction can be expressed as,



where A and B are lattice ions and x and y are stoichiometric coefficients. The solubility product constant ( $K_{s0}$ ) can be expressed as

$$K_{s0} = [A^{y+}]^x [B^{x-}]^y \quad (3.5)$$

The IAP (often referred to as Q) can be expressed as

$$IAP = \gamma_A [A^{y+}]^x \gamma_B [B^{x-}]^y = \{A\}^x \{B\}^y \quad (3.6)$$

where  $\gamma$  is an ion's activity coefficient and  $\{ \}$  denotes an ion's activity. Comparison of the IAP with  $K_{s0}$  indicates the state of the system regarding saturation. If  $IAP > K_{s0}$ , the solution is supersaturated with respect to  $A_xB_y(s)$ , and precipitation could potentially occur. Saturation can also be expressed as

$$S = \left( \frac{IAP}{K_{s0}} \right)^{\frac{1}{x+y}} \quad (3.7)$$

where S is the saturation state of the system, and  $S > 1$  indicates the potential for precipitation. Evaluating the potential for precipitation requires corrections for activity and temperature, among other considerations. Activity coefficients ( $\gamma$ ) can be estimated using several different activity models, including the Debye-Huckel equation, extended Debye-Huckel equation, Davies equation, Bronsted–Guggenheim ion interaction model, and Pitzer equation, among others [84].

For high ionic strength systems, the Pitzer equation or ion interaction model is commonly used to calculate ion activity coefficients with the purpose of obtaining the instantaneous IAP for calculation of the degree of saturation. However, past research has demonstrated that equilibrium activity products ( $K_{sp}$  or  $K_{s0}$ ) and IAP can depend on the ionic makeup of the solution and not just the ionic strength or concentrations of ions. For example, Chong and Sheikholeslami [85] demonstrated that the presence of calcium sulfate at levels between

0.002 and 0.01 M increased the calcium carbonate solubility product by more than an order of magnitude.

Calculations performed to assess an ionic salt's precipitation potential can be complex and yield inaccurate results. According to Randtke [77], inaccuracies arise through incorrect assumptions regarding dissolved constituent speciation and solid-phase composition, complex formation, presence of threshold inhibitors (antiscalants), erroneous solubility product constants and activity coefficients, and failure to reach equilibrium. Supersaturated solutions can exist indefinitely in a metastable state where no solids precipitate, and precipitation can proceed very slowly once instigated [2]. Precipitation induction times and rates are typically dependent upon the saturation state of the system (S), with higher supersaturation yielding quicker induction times and rates of precipitation. In general, heterogeneous nucleation occurs at lower supersaturation compared with homogenous nucleation [2].

### 3.1.4.2 Kinetics of Precipitation and Crystallization

**Nucleation.** The rate of precipitation depends on the kinetics of nucleation and crystal growth. A significant amount of research has been conducted over the past 50 years to both understand precipitation kinetics and model the rate of nucleation crystal growth. The following discussion presents a summary of several important concepts, and more information can be found in several textbooks [86, 87].

As previously discussed, the condition of supersaturation is not always sufficient to promote precipitation or crystallization. Prior to crystal growth, molecules must collide and form a number of sufficiently sized nuclei from which crystals grow. For homogenous nucleation, the free energy change associated with the formation of a solid phase is the sum of the free energy change associated with the creation of a surface ( $\Delta G_s$ , a positive quantity) and the free energy change associated with ion aggregation ( $\Delta G_v$ , a negative quantity)

$$\Delta G_n = \Delta G_s + \Delta G_v \quad (3.8)$$

which, can be written as

$$\Delta G_n = 8\pi r\sigma + 4\pi r^3\Delta G_v \quad (3.9)$$

where  $r$  is the nucleus radius and  $\sigma$  is the surface energy. The radius of the critical nucleus ( $r_c$ ) is obtained when

$$\frac{d\Delta G}{dr} = 8\pi r\sigma + 4\pi r^3\Delta G_v = 0 \quad (3.10)$$

and thus, the critical radius ( $r_c$ ) is

$$r_c = \frac{-2\sigma}{\Delta G_v} \quad (3.11)$$

Nuclei with radii larger than  $r_c$  are stable because free energy is reduced as they grow. Conversely, nuclei with radii smaller than  $r_c$  must dissolve for free energy to be reduced. The

critical free energy change ( $\Delta G_{\text{crit}}$ ) associated with formation of stable nuclei can be expressed as

$$\Delta G_{\text{crit}} = \frac{16 \pi \sigma^3}{3(\Delta G_v)^2} = \frac{4 \pi r_c^2}{3} \quad (3.12)$$

The saturation state (S) can be introduced into Eqn. (3.13) through the relationship

$$\ln S = \frac{2 \sigma v}{k T r} \quad (3.13)$$

where k is the Boltzman constant, v is the molecular volume, and T is temperature. The critical free energy change ( $\Delta G_{\text{crit}}$ ) becomes

$$\Delta G_{\text{crit}} = \frac{16 \pi \sigma^3 v^2}{3(k T \ln S)^2} \quad (3.15)$$

The rate of nucleation (J) can be expressed as

$$J = A \exp(-\Delta G / k T) \quad (3.16)$$

where A is a constant, and J is typically reported in units of number of nuclei per second per  $\text{cm}^3$ . Inserting Eqn. (3.15) into the nucleation rate equation yields

$$J = A \exp \left[ -\frac{16 \pi \sigma^3 v^2}{3 k^3 T^3 (\ln S)^2} \right] \quad (3.17)$$

which indicates that the nucleation rate is dependent upon temperature, degree of supersaturation, and surface energy. According to Mullin [86], a critical degree of supersaturation leading to homogenous nucleation is approximately  $S=4$ . In the presence of “foreign body” surfaces capable of participating in the nucleation process (i.e., heterogeneous nucleation), the critical free energy change ( $\Delta G_{\text{crit}}$ ) is lower than for homogenous nucleation owing to reduction in the free energy associated with surface formation.

### 3.1.4.3 Crystallization Technologies

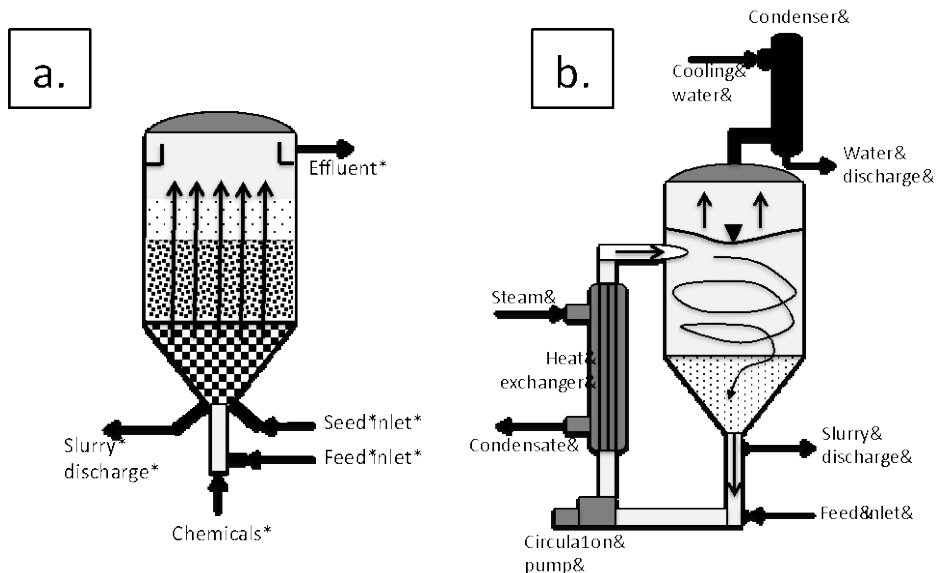
Crystallizers are used for the production of bulk and high purity compounds and materials in a variety of industries including chemical, pharmaceutical, and food applications. Industrial crystallization is well developed, and a number of different types of crystallizer designs exist [88]. The selection of one crystallizer design over another is dependent upon a number of factors, including desired product size, quality, process economics, and scale of operation [88]. Based on the available literature, FBC and forced-circulation crystallizers have been evaluated or proposed in ZLD systems and intermediate softening or chemical extraction applications for desalination [2]. Other crystallization processes proposed for brine/concentrate minimization or chemical extraction from desalination brine/concentrate include eutectic freezing crystallization [72] and MCr [38, 89, 90].

**Fluidized-Bed Crystallizer.** FBC use seeding material (e.g., sand, crystals) to promote secondary nucleation and crystal growth [91]. Depending on the ionic solid being produced, crystallization can be induced through evaporation or chemical reagents. Large seed crystal surface areas in FBCs allow for crystal growth at lower supersaturations than would be feasible in the absence of seed material [2, 91]. For example, Harms and Robinson [91] reported that calcium carbonate crystal growth occurred in FBCs when saturation indices were between 0.2 and 1.7. To produce large crystals and prevent carryover, primary nucleation is not desired; it requires intense chemical mixing and localized crystallization in the suspension or fluidized bed, recirculation of crystal-free supernatant (if recirculation is used), and avoidance of localized zones of high supersaturation.

A typical FBC operates in an upflow configuration to fluidize the seeding materials and crystals without washing them out in the process effluent (see Figure 3.4a for a schematic of typical FBC used for softening applications). Within the FBC there are two zones, the lower zone containing the fluidized bed (approximately 25% solids) and the upper zone containing fine crystals with a lower solids content [92]. For softening applications, fine silica is typically used as seeding material, and crystals produced in FBCs are reported to be between 0.3 and 10 mm in diameter [88, 91]. As crystals grow, they sink toward the bottom of the reactor, where they can be continuously or periodically removed. The drained crystals typically have high solids content (~90%) and are easily dewatered [91].

According to Bennett [88], FBCs are commonly used in industry to produce potassium chloride, ammonium sulfate, and sodium borate. Bond and Veerapaneni [2] reported that calcite crystals produced in FBC softening applications in the Netherlands are reused for various beneficial purposes. Several recent studies have evaluated FBCs for intermediate softening prior to secondary RO, and purportedly a utility in Southern California (Western Municipal Water District) is upgrading its desalination process to include intermediate softening with an FBC [93]. The municipality plans to produce calcite crystals to be sold to a construction material producer (see Case Study 13 in Chapter 5 for more detail). For this application, clarification (with coagulant addition) post-FBC was required to meet the calcium, hardness, silica, and turbidity removal goals prior to secondary RO.

**Forced-Circulation Crystallizer.** Often termed a mixed suspension, mixed product removal crystallizer, forced-circulation (FC) crystallizers use evaporation to induce crystallization. FC crystallizers consist of a main body with a recirculation loop through a heat exchanger to vaporize the liquid within the tank (Figure 3.4b). According to Bennett [88], FC crystallizers are the most widely used and least expensive type of equipment available for the production of sodium chloride, sodium sulfate, and sodium carbonate.



**Figure 3.4. Common crystallizer configurations: (a) fluidized-bed crystallizer, (b) forced-circulation crystallizer,**

**Eutectic Freezing.** A salt–water mixture has a eutectic point that defines the equilibrium condition with respect to salt, water, and ice. Because ice crystals exclude impurities, cooling a solution to its eutectic point produces ice and salt crystals simultaneously [94]. Ice and salt can be separated by utilizing density differences between the three phases present (i.e., ice, salt, and the feed solution or mother liquor). The purported advantages to eutectic freezing crystallization (EFC) include reduced energy and capital costs compared with evaporative processes, minimal pretreatment, and no chemical requirements to induce crystallization [72, 94, 95]. According to an EFC equipment company (EFC Separations, Delft, Netherlands [96]), the EFC process consumes 50% of the energy of efficient evaporation processes (e.g., MSF, MED). Nathoo et al. [97] performed a cost and energy comparison between EFC and MED for treating brines from a mining operation in South Africa and reported that EFC was 80 to 85% cheaper than MED to operate. However, capital costs for EFC were significantly higher than MED because it is not a well-developed technology.

EFC has been proposed for the recovery of minerals from seawater and brines for over 50 years [94, 98, 99]; however, it appears limited to industrial applications with relatively simple mixtures of salts [97]. Nathoo et al. [97] acknowledge that the technical and economic feasibility of EFC has yet to be ascertained for reclaiming salt products from RO brine/concentrate.

**Membrane Distillation/Crystallization.** Membrane distillation is a combined thermal evaporation–membrane separation process that relies on a vapor pressure gradient across a membrane to evaporate and transport the feed solution to the distillate side of the membrane where it condenses. Because nonvolatile solutes cannot penetrate the wetted membrane, as the feed solution becomes concentrated substances preferentially crystallize on the membrane surface (MCr). Once crystallized, solids can be removed from the membrane surface through solvent rinsing. Laboratory-scale research has demonstrated that the MCr process can operate at very high TDS concentrations and requires lower temperatures than other thermal processes.

Permeate flux is only moderately impacted by crystal growth on the membrane surface, and flux can be restored through membrane rinsing [38, 47, 48, 100]. Several researchers have claimed that integrating SWRO with MCr could lead to system recoveries of 90% or more and the recovery of precipitated salts [101]. Ji et al. [38] evaluated MCr for the treatment of RO brine and production of sodium chloride and reported that approximately 21 kg of sodium chloride could be produced from 1 m<sup>3</sup> of RO concentrate. Although MCr operation was stable over a period of 100 hours, the researchers noted that the presence of organic matter had a negative impact on sodium chloride production (crystal growth was reduced by 15–23%).

### **3.1.5 Flotation**

Air flotation or dissolved air flotation (DAF) uses gas bubbles to float dissolved and suspended materials to the water or solution surface, where they are removed. DAF is typically used in water treatment for particle removal; however, researchers have developed flotation methods for collection of ions from solution. In such methods, colloids, surfactants, or complexing agents with high affinity towards the specific metal are added to solution, and the resulting metal complex accumulates at the gas–liquid interface and is floated to the liquid surface. Flotation methods for recovering metals from water and wastewater include ion flotation, precipitate flotation, and colloid flotation. According to Zouboulis [102], such methods have been used to recover chromium, molybdenum, nickel, silver, and uranium in industrial applications. Kabil et al. developed a flotation process for recovering calcium sulfate and magnesium hydroxide from seawater and brines using oleate as a complexing agent [103].

### **3.1.6 Electrowinning**

Electrowinning or electroextraction is an electrolytic technology for metal recovery, metal purification, and reduction of metals to their metallic form. Electrowinning is an electroplating process that uses electrolysis or current (from an anode) passed through a solution to deposit metals onto the cathode. In addition to large-scale metal production facilities, electrowinning is commonly used for the recovery of metals from spent rinse waters in the metal finishing industry. Electrowinning was employed by Dow Chemical for the production of magnesium metal from magnesium salts precipitated from seawater, although production using this method is no longer used. Electrolysis is commonly used for production of chlorine from solutions concentrated in sodium chloride, including seawater. With the exception of chlorine production, very little information was identified on the use of electrowinning for the extraction of metals from RO brine/concentrate.

## *Chapter 4*

# **Materials Targeted for Extraction from Desalination Brines**

---

### **4.1 Summary of Literature and Patent Information**

From the literature and patent information compiled throughout the course of the study, summaries were developed for constituents that have received significant attention regarding their extraction from aqueous solutions. Where information was available, the summaries generally consist of commodity information and past research into methods for extraction. In addition, summary tables were developed that cover both findings from the literature and patent reviews (patent summary tables are presented in the Appendix). Because the majority of metals exist at extremely low concentrations in desalination brine/concentrate, extraction of trace metals is unlikely to be competitive with other production methods. All literature and patents identified during the course of the study are compiled in EndNote databases accompanying this report.

#### **4.1.1 Boron**

##### ***4.1.1.1 Boron Commodity Summary***

Boron in the chemical form of borates is a relatively valuable metalloid used in products such as ceramics, glasses, detergents and soaps, fiberglass, and insulation. Borates are produced from boron-containing ores, typically sodium borate, ulexite, or kernlite. In 2012, borates were produced in the United States by two companies in Southern California using borate-containing ores. The average price (for all minerals imported) of boron has been stable over the past 3 years and was reported by the United States Geological Survey (USGS) at \$360 /ton. U.S. consumption of borates is primarily for the glass and ceramics industries, and exports of boric acid and borate minerals have declined significantly over the past 5 years. Global consumption of borates is expected to increase significantly in the upcoming years, with China and South America expected to increase annual consumption. China has low-grade boron reserves and is expected to increase borate exports from the United States in the near future. The USGS indicates that most of this demand is for production of fiberglass and insulation used in building construction.

##### ***4.1.1.2 Boron Extraction Summary***

Although little work has been published on the extraction of boron to produce salable products, a significant amount of research has been performed to develop treatment technologies for the removal of boron (in the form of boric acid) from drinking water supplies. In particular, removal of boron from seawater has garnered significant attention because of the relatively poor rejection of boric acid by RO membranes used in desalination and relatively stringent limits on boron in the treated water. Several methods have been proposed or adopted for the removal of boron in a desalination treatment train; however, adsorption by ion exchange has been demonstrated as one of the most effective treatment technologies [104] and likely the only effective extraction method.

Effective boron-selective ion-exchange resins were developed in the 1970s for separation of borate from magnesium brines for ceramic production [105]. These anionic exchange resins utilized a N-methylglucamine or related functional group, which has been shown to be highly selective for boric acid [105, 106]. Exhausted ion-exchange resin can be effectively regenerated using a sulfuric acid or hydrochloric acid solution [104]. Recent studies have evaluated a variety of alternative ion-exchange materials, including polymeric ion-exchange resins, hydrogels, and inorganic materials [107–118]. However, there are several commercially available boron-selective resins with reported high selectivity, sorption capacity, and regeneration resiliency, including several products from Dow (Amberlite IRA743, Amberlite PWA10, Dowex XUS 43594).

Although a large amount of research has evaluated the removal of boric acid by ion-exchange resin, few researchers have reported on the feasibility of producing a boron product through regeneration of ion-exchange resin. Goltz et al.[119] evaluated the effectiveness of ion exchange for treatment of flue gas desulfurization wastewater from a power plant and the feasibility of reclaiming boron from hydrochloric acid regenerant solution. The researchers evaluated an ion-exclusion/ion-exchange process by which chloride can be effectively separated from the boric acid in the HCl regenerant solution, dried, and reclaimed as boric acid. Field pilot testing of the process indicated that a boric acid product could be produced at a cost of less than \$5/lb, which is approximately 30 times more than the price of boron commodities. It is also worth noting that the boron concentration in the feed water (~100 ppm) was significantly higher than in seawater (~25.7 ppm).



**Table 4.1. Boron Summary**

<b>Main form(s) in water</b>	Boric acid ( $\text{H}_3\text{BO}_3$ ); $\text{H}_2\text{BO}_3^-$ is a minor species at $\text{pH} < 9$ .
<b>Dominant commodities</b>	Sodium borate (borax), boric acid, colemanite, ulexite, kernite
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>• In 2011, borates were produced by two U.S. companies using ore and brine as feed stock [120].</li> <li>• Boron compounds are principally used in glass and ceramics, with significantly lower demand for cleaning products, agriculture, and enamels and glazes.</li> <li>• In 2012, the average value of boron minerals was approximately \$360/metric ton, similar to prices from 2009 through 2011 [121].</li> <li>• Annual U.S. boron commodity production is not available; however, global boron production was 4600 metric tons in 2012. The United States, Turkey, and several South American countries have large boron reserves.</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>• Boron consumption was negatively impacted by the recent global recession; however, increased demand is expected in Asia and South America.</li> <li>• The USGS believes that proven worldwide boron reserves will meet global demand for the foreseeable future [120].</li> </ul>
<b>Extraction technologies and processes</b>	There has been significant recent research into the removal of boron from seawater because of insufficient boric acid removal by SWRO membranes. Most of the available literature pertains to removal of boron by ion exchange or development of novel adsorbents or hybrid processes for boron removal [104, 107, 111]. Additional technologies for boron removal include electrodialysis, liquid membranes, and coprecipitation.
<b>Conclusions from literature review</b>	Extraction of boron from seawater for economic gain has attracted little interest from researchers. A significant amount of recent literature has been published on the removal of boron from seawater or SWRO permeate; however, little information exists on whether these technologies could be used to recover high purity boron compounds.

*Notes:* SWRO=seawater reverse osmosis; USGS=United States Geological Survey.

**Table 4.2. Summary of Patents Related to Boron Extraction**

Decade	Number of Patents	U.S. Patent #
prior to 1950	1	2,405,055
1950–1959	0	
1960–1969	1	3,374,081
1970–1979	1	3,839,222
1980–1989	0	
1990–1999	1	4,956,157
2000–present	2	7,520,993 B1; US 2011/0108488

## 4.1.2 Bromine

### 4.1.2.1 Bromine Commodity Summary

By 1994, the United States accounted for approximately 47% of global bromine production, down from approximately 71% in 1971 [122]. This decrease has been reported to be due to the emergence of Israel as a producer of bromine, the regulation of chemicals in the United States containing bromine (e.g., flame retardants, antiknock gasoline additives, methylbromide), and substitution of chlorine or iodine for bromine in industrial chemical reactions. However, worldwide demand for bromine is increasing. In 2006, the USGS estimated that the United States produced 243,000 metric tons of bromine while consuming 275,000 metric tons [123, 124]. In 2006, the U.S. price of bromine was \$1.39/kg of purified bromine, which is significantly higher than 2005 (\$0.79/kg) because of increased demand and costs for production. More recent data are not available on U.S. production, price, and consumption through the USGS. It appears from recent information that only Japan currently produces bromine from seawater [123, 124], with most sources now being underground brines, bitterns from potash and solar salt production, evaporitic (salt) lakes, and recycling of materials containing bromine [122–124]. The two largest producers of bromine in the United States, making up approximately one third of global bromine production, are located in Arkansas and use underground brines as a source.

### 4.1.2.2 Bromine Extraction Summary

The most common process for bromine extraction uses gaseous chlorine to liberate free bromine from acidified aqueous solutions according to the following reaction



Stripping of the solution is then used to extract free bromine from the seawater solution. Sulfur dioxide is added to the bromine-enriched airstream to produce hydrobromic acid.



The hydrobromic acid can be captured by a mist elimination process, for example, a glass fiber filter bed [125]. It has been demonstrated that the process is dependent upon the amounts of chlorine and sulfur dioxide used as chlorine competes for the sulfur dioxide.



Recently, El-Hamouz and Mann [125] developed a kinetic model to optimize this process for the extraction of bromine from seawater.

Davis [62] proposed a similar process to extract bromine from RO concentrate streams produced by desalination facilities. ED was first used to separate sodium, chloride, potassium, and bromide from the concentrate stream. The subsequent ED waste stream would then be crystallized to produce high purity NaCl crystals and the remaining KBr rich bittern further processed to produce bromine using the reactions presented herein. Although the actual production of bromine from the proposed process was not physically evaluated, it was estimated that approximately \$400,000 could be recouped annually through production of bromine, assuming a feed water flow of 6 million gpd. In 1994, Petersen [18] estimated that approximately \$190 could be gained from extracting bromine from 1 million gallons of seawater. Other methods for extracting bromine have been proposed or used in the past, including electrolytic [126], adsorption [127], and chemical methods [128].

**Table 4.3. Bromine Summary**

<b>Main form(s) in water</b>	Br <sup>-</sup>
<b>Dominant commodities</b>	Bromine (Br <sub>2</sub> ), hydrobromic acid (HBr), bromine salts, organobromides
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>• Sold as elemental bromine (Br<sub>2</sub>), organobromide fertilizers, flame retardants, gasoline additives</li> <li>• Most modern bromine production is from highly concentrated inland brines and the Dead Sea.</li> <li>• Current prices are considered proprietary company information and not published. The most recent price available from USGS reports was \$1.39/kg of purified bromine in 2006 [123].</li> <li>• The 1990 Clean Air Act classified methyl bromide, a pesticide, as a Class I zone-depleting substance.</li> </ul>
<b>Market opportunities</b>	On the basis of published price changes (which are provided without the base price), the price of bromine has been increasing since 2006.
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>• Precipitation from seawater as tribromoaniline (Dow-Ethyl Corporation, ca. 1933). Later modified to produce HBr [17].</li> <li>• Acidification of seawater, followed by steam stripping to extract free bromine, producing HBr [125]</li> <li>• Electrolysis of seawater: when optimized, liquid elemental bromine is produced, which settles to the bottom of the reaction vessel and is easily recovered [125, 126].</li> </ul>
<b>Conclusions from literature review</b>	Extraction of bromine from RO brine appears feasible, as it was once extracted from unconcentrated seawater; however, research where bromine extraction from RO brine was experimentally verified has not been identified. Of the literature reporting on the concept of bromine extraction from RO brine (and reporting potential profits), little information is given about how capital and O&M costs were calculated.

*Notes:* O&M=operation and maintenance; RO=reverse osmosis; USGS=United States Geological Survey.

**Table 4.4. Summary of Patents Related to Bromine Extraction**

Decade	Number of Patents	U.S. Patent #
prior to 1950	2	2,143,224; 2,342,666
1950–1959	0	
1960–1969	2	3,359,292; 3,374,081
1970–1979	1	4,180,547
1980–1989	1	3,374,081
1990–1999	0	
2000–present	3	US 2003/0080066; 7,083,730; 8,133,468

### **4.1.3 Calcium**

#### **4.1.3.1 Calcium Commodity Summary**

Dominant calcium commodities include calcium carbonate, lime, calcium sulfate, and calcium chloride. According to the USGS, approximately \$2.3 billion (~20 million tons) worth of lime was produced in 2012 [129]. Lime was used in a variety of industries to remove impurities in steel refining and other metal processing, recover cyanides from precious metal mining tailings, soften water, control pH in water treatment, remove acidic gases from flue gas at coal-fired power plants (producing gypsum), in the pulp and paper industry, and for filler in papers, paint, and plastics. Approximately 31 companies produce lime in the United States through mining and kilning. The price of lime has increased significantly over the past 5 years, and USGS estimates the average price of quicklime at \$116/ton and hydrate lime at \$139/ton [129].

Calcium carbonate is not reported as a commodity by the USGS, with the exception of crushed stone in the form of limestone [130]. Crushed limestone is relatively inexpensive (\$10/ton); however, relatively high purity calcium carbonate as either precipitated calcium carbonate or ground calcium carbonate used in the chemical and construction industry is priced between \$130 and \$200/ton [131].

Calcium sulfate or gypsum is primarily used in the United States for the manufacture of wallboard and plaster, and USGS estimates that 9.9 million tons was consumed in 2012 [132]. Gypsum consumption is strongly tied to the economy and the housing construction sector, and currently it is priced by the USGS at \$7/ton in crude form and \$30/ton in calcined form. Gypsum consumption is expected to increase over the next several years as countries switch to wallboard in buildings.

Calcium chloride is most commonly consumed as a brine for ice and dust suppression on roads as well as in refrigeration plants. The USGS does not monitor calcium chloride as a

commodity; however, magnesium chloride brine pricing is on the order of \$0.15 to \$0.50/gal, depending on the concentration. Jordahl [61] reported calcium chloride prices between \$132 and \$354/ton depending on purity.

#### 4.1.3.2 Calcium Extraction Summary

**Calcium carbonate.** There is increased interest in calcium removal from RO brine or concentrate to increase RO system recovery through secondary RO, as well as its extraction and sale to recoup desalination costs [2, 9, 80, 133–136]. A good review on calcium carbonate precipitation, particularly in reference to calcium removal during desalination, is presented by Bond and Veerapaneni [2]. Currently, the Western Municipal Water District in California is expanding one of its desalination facilities (Arlington Desalter) to include an FBC for calcium carbonate removal and subsequent recovery. More detail on this process is provided in a case study in Chapter 5.

Precipitated calcium carbonate (solid  $\text{CaCO}_3$ ) exists in three main forms, calcite, vaterite, and aragonite, depending on specific conditions (e.g., pH, calcium ion concentration) [137]. Although the presence of all three forms can occur, calcite is the most thermodynamically stable, and if allowed, vaterite and aragonite will transform to calcite during the ageing process. Solid calcium carbonate formation is impacted by a number of variables including temperature (solubility decreases with increasing temperature), carbonate concentration (precipitation kinetics increase with increasing  $[\text{CO}_3^{2-}]/[\text{Ca}^{2+}]$ ), carbon dioxide concentration, presence of organic matter and antiscalant chemicals, and water chemistry (e.g., pH, ionic strength and composition).

Numerous studies have documented the influence of impurities, metals, and ions on calcium carbonate crystal growth [85, 138–145]. Both phosphate and ferrous iron ( $\text{Fe}^{2+}$ ) can have strong inhibitory effects on calcium carbonate crystal growth [2]. Reaction rates for calcium carbonate precipitation were found to be only slightly impacted by the presence of sodium chloride at a concentration range of 0.5 to 1.5 M [79]. The presence of magnesium and sulfate, however, has been demonstrated to significantly influence the kinetics of calcite precipitation and the morphology of the precipitates [85, 146].

The presence of antiscalants has been shown to increase the solubility of calcium carbonate; however, increasing the solution pH can minimize the impact of antiscalants on the solubility of calcium carbonate [139]. The presence of antiscalants has been shown to change the morphology of calcium carbonate crystals and at high concentrations tends to form small particles or crystals. The rate of calcium carbonate precipitation is reduced in the presence of dissolved organic carbon (DOC) [143]. Dissolved carbon dioxide can also impact the rate of calcite precipitation, and Lebron and Suarez [144] determined that increasing the carbon dioxide partial pressure increases the rate of calcite precipitation in a pH range of 6.9 and 8.5.

The overall calcite precipitation rate can be expressed as:

$$R_T = R_{CG} + R_{HN} \quad (4.4)$$

where  $R_T$  is the total calcite precipitation rate ( $\text{mM s}^{-1}$ ),  $R_{CG}$  is the rate of crystal growth, and  $R_{HN}$  is the rate of heterogeneous nucleation. Numerous crystal growth rate equations have been proposed in the literature [147]. Compton and Daly [147] compared several calcium carbonate precipitation kinetic models and reported that, whereas the Davies and Jones rate

equation proved unsatisfactory, the Sjöberg rate equation provided excellent fits to experimental data. The Sjöberg equation is defined as

$$R_p = k_s \left( [Ca^{2+}]^{0.5} [CO_3^{2-}]^{0.5} - K_{SP}^{0.5} \right) \quad (4.5)$$

where  $R_p$  is the rate of precipitation and  $k_s$  is an empirical constant. Lebron [143] proposed a modified calcite rate equation to account for the impact of DOC on nucleation and crystal growth. These rates were expressed as:

$$R_{CG} = s k_{CG} ([Ca^{2+}] [CO_3^{2-}] - K_{SP}) f(DOC)_{CG} \quad (4.6)$$

$$R_{CG} = k_{HN} f(SA(\log[\Omega - 2.5])) f(DOC)_{HN} \quad (4.7)$$

where  $s$  is the surface area,  $k_{CG}$  and  $k_{HN}$  are kinetic coefficients of crystal growth and heterogeneous nucleation, respectively,  $\Omega$  is the saturation level,  $f(SA)$  is a term for the active sites of the particles in suspension, and  $f(DOC)$  is a function that captures the impact of DOC on the precipitation rate.

**Calcium sulfate.** Calcium sulfate can be precipitated as six different forms with calcium sulfate dihydrate, calcium sulfate hemihydrate, and anhydrous calcium sulfate (gypsum), the most commonly encountered in natural formations and scale [148]. Commercial-grade gypsum is not priced very high (\$7/ton for crude gypsum, \$30/ton for calcined gypsum), which may explain why the extraction of calcium sulfate from seawater or RO brine and concentrate has not received significant attention.

Mechanisms of precipitation and properties of calcium sulfate have been studied because of issues of calcium sulfate scaling in various industries. Bond and Veerapaneni [2] reported that calcium sulfate precipitation kinetics are relatively unaffected by temperature and increase with the state of supersaturation. In addition, it was reported that the induction time is at a minimum when the ratio of  $[Ca^{2+}]/[SO_4^{2-}]$  is close to 1 [149]. The formation of calcium nuclei is enhanced in the presence of solid substrates such as metal surfaces or crystals [148]. The kinetics of calcium sulfate crystallization can be negatively impacted by the presence of sodium chloride, phosphates, and certain organic polymers [79, 148]. Barcelona and Atwood [150], however, reported that organic matter had little influence on calcium sulfate solubility in seawater but decreased the crystal growth rate and increased the induction time.

Goldman et al. [151] performed a rather comprehensive study evaluating the use of ion-exchange to selectively extract salts from RO brine. By carefully controlling the pH of the mixture of anion and cation regeneration solution, the researchers found they could precipitate relatively pure calcium sulfate. In addition, it appeared that calcium carbonate could also be precipitated separately depending on the pH of the regenerate solution. Besides potentially producing a salable product, inter-stage softening using IX prior to secondary RO would provide the benefit of minimizing concentrate volume and lessens the negative impacts of concentrate disposal.

**Table 4.5. Calcium Overview**

<b>Main form(s) in water</b>	Ca <sup>2+</sup>
<b>Dominant commodities</b>	Calcium carbonate, lime, calcium hydroxide or slaked lime, gypsum, calcium chloride
<b>Commodity summary</b>	<p>Uses of calcium compounds</p> <ul style="list-style-type: none"> <li>• Lime is used in a variety of industries for removal of impurities and pH control. In 2013, the average price for quicklime was \$116/ton, and hydrated lime was \$139/ton.</li> <li>• Calcium carbonate is used in construction, chemical, and water treatment industries. Low purity calcium carbonate is inexpensive (\$10/ton [130]); high purity calcium carbonate is approximately \$130/ton.</li> <li>• Gypsum is used in building products, including cement, concrete, plaster, and wallboard; the 2013 average U.S. price for crude gypsum was \$7/metric ton [132].</li> <li>• CaSO<sub>4</sub>•2H<sub>2</sub>O + Mg(OH)<sub>2</sub> is used in wastewater treatment and pH buffering [61].</li> <li>• Calcium chloride is used for dust suppression and as a cement and concrete stabilizer; price is \$40–\$354/ton, depending on form and purity [61].</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>• U.S. demand for gypsum is expected to increase with residential housing construction. Production of gypsum from coal-fired power plant scrubbers is also expected to increase as more scrubbers are installed [152].</li> <li>• Possible applications for low quality calcium compounds include CaCl<sub>2</sub> use in dust suppression and CaCl<sub>2</sub> or CaSO<sub>4</sub> use in sodic soil remediation [61].</li> </ul>
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>• Calcium is generally removed during desalination in a precipitative softening step to prevent scaling rather than as an end product.</li> <li>• Several researchers have evaluated the use of FBCs to produce calcium carbonate pellets [2, 93].</li> <li>• Precipitation of CaSO<sub>4</sub> or CaCO<sub>3</sub>, depending on the composition of the brine, is most efficient above pH 10 and can be induced by adding NaOH [133]. These precipitation steps are not intended to produce high purity solids.</li> <li>• Calcium carbonate can be extracted by adding NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> to NF retentate [153].</li> </ul>
<b>Conclusions from literature review</b>	<p>High volume, low priced calcium compounds are unlikely to be economically extracted unless a local buyer is available and able to utilize a moderately impure product. In the Netherlands, however, calcium carbonate pellets produced during softening with FBCs are reportedly used for beneficial purposes [2]. There are plans to produce calcium carbonate pellets at a BWRO facility in Southern California and sell them to a local construction company [93].</p>

*Notes:* BWRO=brackish water reverse osmosis; FBC=fluidized-bed crystallizer.



**Table 4.6. Summary of Patents Related to Calcium Extraction**

Decade	Number of Patents	U.S. Patent #
prior to 1950	3	2,226,592; 2,433,458; 2,466,675
1950–1959	1	2,934,419
1960–1969	7	3,248,181; 3,119,752; 3,218,241; 3,231,340; 3,359,076; 3,345,288; 3,463,814
1970–1979	13	3,514,266; 3,627,479; 3,574,077; 3,639,231; 3,676,067; 3,725,267; 3,833,464; 3,976,569; 4,024,054; 4,036,749; 4,059,513; 4,083,781; 4,180,547
1980–1989	6	4,188,291; 4,298,577; 4,336,232; 4,423,009; 4,712,616; 4,755,303
1990–1999	6	4,973,201; 4,956,157; 5,124,012; 5,468,394; 5,587,088; 5,814,224
2000–present	23	US 6,372,143 B1; US 2006/0105082; US2006/0060532; 7,198,722; 7,392,848 B1; 7,595,001 B2; 7,520,993 B1; 7,771,684 B2; 7,744,761 B2; 7,754,169 B2; US 7,789,159; 7,829,053 B2; 7,749,476 B2; 7,815,880 B2; 7,753,618 B2; 7,993,511 B2; 7,887,694; 8,012,358 B2; 8,012,358 B2; 8,021,442; 8,158,097; 8,197,664; 8,133,468

#### 4.1.4 Cesium

##### 4.1.4.1 Cesium Commodity Summary

According to the USGS, cesium is mainly consumed as a concentrated pollucite brine for oil and gas drilling fluids [153]. Cesium is also used in atomic clocks, chemotherapy drugs for treating certain cancers, and certain metallurgical applications. Cesium commodity information, including pricing and usage data, is mostly unavailable, and the USGS estimates that, besides drilling fluids, U.S. consumption of cesium is very low [154]. One U.S. company reportedly sold 100 g ampoules for between \$684 (99.8% pure metal) and \$1876 (99.98% pure metal). Relatively inexpensive cesium is produced as a byproduct of lithium production, and known U.S. reserves are unlikely to be targeted unless cesium consumption increases significantly.

#### 4.1.4.2 Cesium Extraction Summary

Cesium is a minor component in seawater and present at a concentration of approximately 0.3 µg/L [22]. Cesium extraction from aqueous solutions has received attention for the treatment of radioactive wastes, recovery of cesium from brines, and concentration of cesium for improved analytical detection. The majority of studies have evaluated ion-exchange materials or liquid–liquid extraction processes and have not typically focused on obtaining a pure cesium product. From a study that compared various ion-exchange materials for cesium uptake, Johnson et al. [155] reported that potassium hexacyanocobalt (II) ferrate (II) provided the greatest distribution coefficient ( $K_D$ ) of the materials tested for cesium extraction from seawater matrices.

Despite the small market for cesium, several researchers have suggested that it could be extracted from SWRO brine for economic gain. Jeppesen et al. [156] and Le Dirach [157] targeted cesium because of its high commodity price and proposed a liquid–liquid extraction process using calixerenes. Gilbert et al. [158] evaluated a commercially available hexacyanoferrate-based ion-exchange resin (Cs-Treat, Fortum Engineering Ltd, Fortum, Finland) for cesium extraction from spiked SWRO brine. The researchers reported a maximum adsorption capacity of 43.7 mg Cs/g adsorbent.

**Table 4.7. Cesium Overview**

<b>Main form(s) in water</b>	Cs <sup>+</sup>
<b>Dominant commodities</b>	Cesium metal, cesium formate in brine; other cesium compounds exist, but it is not apparent that they are consumed in appreciable quantities.
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>Produced primarily from a large pegmatite deposit at Bernic Lake in Canada [160]</li> <li>Cesium formate brines are used in high temperature/high-pressure oil and gas drilling [160].</li> <li>Other uses include atomic clocks, biomedical research, and cancer treatment [160].</li> <li>Cesium is not traded, and 2009 prices ranged from \$17 to \$63/g, depending on purity and quantity [160].</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>Drilling fluid and drill pipe unsticking</li> <li>Cesium-131 brachytherapy seeds for the treatment of head, neck, and lung tumors</li> </ul>
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>Inorganic ion exchanger CsTreat® [K<sub>2</sub>CoFe(CN)<sub>6</sub>] [158]</li> <li>Liquid–liquid extraction by calixarene C5 in TPH, a process developed for purifying nuclear power plant effluent [157]</li> </ul>
<b>Conclusions from literature review</b>	Cesium extraction from RO concentrate is unlikely to be economical, as the concentration in seawater is very low, and demand is easily met by inexpensive cesium that is a byproduct of lithium extraction from ore.

Notes: RO=reverse osmosis; TPH=. tetrahydrogenated propylene

**Table 4.8. Summary of Patents Related to Cesium Extraction**

Decade	Number of Patents	U.S. Patent #
Prior to 1950	0	
1950–1959	0	
1960–1969	3	3,305,321; 3,382,034; 3,468,959
1970–1979	2	3,522,187; 3,514,266
1980–1989	3	4,313,844; 4,448,711; 4,663,052
1990–1999	0	
2000–present	2	6,402,953 B1; 6,626,860 B1

#### **4.1.5 Chlorine and Sodium Hydroxide**

##### **4.1.5.1 Commodity Summary**

Commodity information for chlorine and sodium hydroxide is not reported by the USGS. Sodium hydroxide is produced as a coproduct of chlorine production through the electrolysis of concentrated sodium chloride solutions. In 1998, approximately 14 million tons of sodium hydroxide was produced in the United States, with the majority produced by the chlor-alkali industry [161]. Average price information is difficult to obtain; however, based on several sources, sodium hydroxide prices were around \$500/ton at the end of 2012 [162]. Sodium hydroxide pricing is strongly tied to the price and demand for chlorine.

Chlorine is among the chemicals with the highest production rates in the United States; around 14 million tons is produced annually[161]. Very little chlorine is traded on the merchant market, and pricing is difficult to obtain [163]. Because sodium hydroxide and chlorine are produced through the same process, their value is often given as one unit, which is termed the electrochemical unit (ECU) netback. Information from 2012 indicates that ECU netbacks are valued around \$550/ton.

##### **4.1.5.2 Extraction Summary**

Chlorine and sodium hydroxide are primarily produced from saturated sodium chloride or brine solutions using the chlor-alkali process and either diaphragm, membrane, or mercury electrolytic cells. Chlorine can also be produced from seawater (and SWRO brine), and several companies produce on-site sodium hypochlorite generation systems. These systems typically use ion-exchange membrane electrolytic cells with activated titanium anodes and

produce sodium hydroxide and hydrogen as byproducts. The overall cell reaction for the generation of chlorine is:



Such on-site chlorine generation systems have been employed for generation of chlorine for coastal communities, oil platforms, and desalination plants. Spagnoletto [163] reported power consumption of seawater electrolysis at an Abu Dhabi desalination facility to be in the range of 2.5 to 3 kWh/kg of equivalent free chlorine gas. A maximum concentration of 2000 ppm hypochlorite can be produced from seawater.

Several researchers have proposed that chlorine produced from SWRO brine could be used for disinfection of finished drinking water [16, 164, 165]. Zaviska et al. [165] recently evaluated the efficiency of electrolytic chlorine production from concentrated seawater and reported that the most efficient chlorine production was obtained for 31 mg/L of chlorine produced at an energy consumption of 0.54 kWh/m<sup>3</sup>. Using an electrolytic cell, Adham et al. [166] produced a 0.6% hypochlorite solution from the RO concentrate of an inland desalination plant.

Recovery of sodium hydroxide from desalination facility brine has received recent attention because of its relatively high value and potential for simultaneously producing chlorine through electrolysis. Melian-Martin [167] recently described an approach to produce chlorine, hydrogen, and sodium hydroxide from SWRO brine using membrane electrolytic cells. Because the production of high purity compounds requires relatively high concentrations of sodium chloride and the absence of other solutes, the proposed process consisted of chemical precipitation and clarification, filtration, multieffect evaporation, and ion exchange prior to electrolysis for chemical production. According to the authors, the energy demand associated with membrane electrolytic cell chlorine generation from concentrated and purified sodium chloride solutions is between 2100 and 2600 kWh/t-Cl<sub>2</sub>. Energy requirements associated with the pretreatment steps were not reported.

Kim [72] performed a cost analysis on a processing scheme using MSF for desalination brine concentration and electrolysis for sodium hydroxide and chlorine production. The author concluded that sodium hydroxide and chlorine could be produced at a cost of \$166/ton, and the sale of these chemicals could pay off the capital costs of the facility (estimated at approximately \$13 million) after 10 years. However, a report prepared for the U.S. Environmental Protection Agency (EPA) in 2000 [161] indicated that average capital cost for membrane electrolytic cell-based chlor-alkali production was \$111 million (in 1990 dollars) to produce 500 tons a day. In addition, energy requirements for the chlor-alkali are significant and can account for a third of the production costs.

Estimates of the energy required for membrane electrolytic cells are between 2500 and 2900 kWh/ton/Cl<sub>2</sub>. Assuming an electricity cost of \$0.08/kWh, the cost associated with the production of 1 ton of sodium hydroxide would be between \$200 and \$232, assuming 100% efficiency. This is significantly higher than the total cost of production given by Kim [72] and does not account for the energy requirements of the MSF process used to concentrate the desalination brine. In addition, chlor-alkali processes use relatively pure and saturated sodium chloride solution as feed stock, which requires significant pretreatment prior to electrolysis. When mined salt is used for feed stock, brine purification typically involves chemical precipitation and filtration for calcium and magnesium removal (both should be significantly less than 5 ppm), and associated energy requirements are estimated to be approximately 900

kWh/t-NaOH [168]. Finally, electrolytic cell feed stocks typically have brine concentrations of 315 to 445 g/L sodium chloride for efficient operation, which may be impossible to achieve from desalination brine/concentrate. It is unlikely that schemes designed to produce sodium hydroxide and chlorine from desalination brine/concentrate would be economical, and it is worth noting that such schemes have not been demonstrated at any appreciable scale.

**Table 4.9. Chlorine and Sodium Hydroxide Overview**

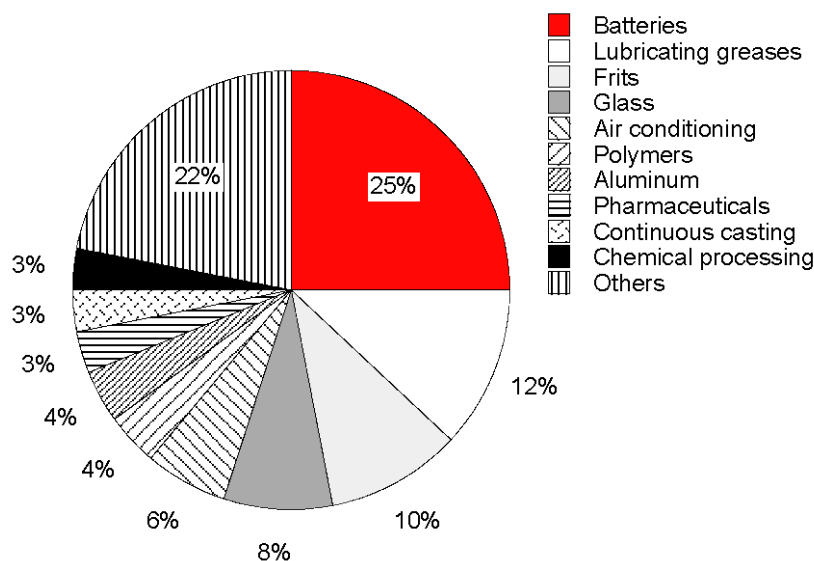
<b>Main form(s) in water</b>	Cl <sub>2</sub> is not stable in aqueous solutions; Cl <sup>-</sup> is the stable form in water. Na <sup>+</sup>
<b>Dominant commodities</b>	Chlorine gas, hypochlorous acid, solid NaOH, concentrated liquid NaOH. Electrolysis produces H <sub>2</sub> as a byproduct.
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>• Produced primarily from pure and saturated sodium chloride solutions using electrolytic cells of the mercury, diaphragm, and membrane type,</li> <li>• Obtaining current pricing for chlorine and sodium hydroxide is difficult. Because both are produced in the same process, pricing is often reported as ECU netbacks. Recent information indicates that the current ECU netback is around \$550/ton.</li> </ul> <p>The high price of electricity in many regions of the world has caused ECU netbacks to increase significantly over the past 2 years.</p>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>• Chlorine demand has decreased recently because of the global economic recession and reduced demand for PVC.</li> <li>• Demand for sodium hydroxide has increased over the past 5 years.</li> </ul>
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>• Produced by electrolysis using either diaphragm, membrane, or mercury electrolytic cells.</li> <li>• Selection of electrolytic cell type depends on environmental concerns, purity, and concentration of sodium chloride solution, desired Cl<sub>2</sub> concentration, and energy requirements.</li> <li>• Chlorine is produced in small quantities from seawater and brines for various industries and used on-site.</li> </ul>
<b>Conclusions from literature review</b>	<ul style="list-style-type: none"> <li>• Chlorine is commonly produced from seawater, chlorine, and sodium hydroxide extraction from desalination brine has been proposed and evaluated in laboratory-scale experiments. Efficient, high purity production of chlorine requires significant pretreatment and concentration steps, which are likely cost prohibitive. Chlorine production for on-site use could be viable.</li> </ul>

*Notes:* ECU=electrochemical unit; PVC=polyvinylchloride.

## 4.1.6 Lithium

### 4.1.6.1 Lithium Commodity Summary

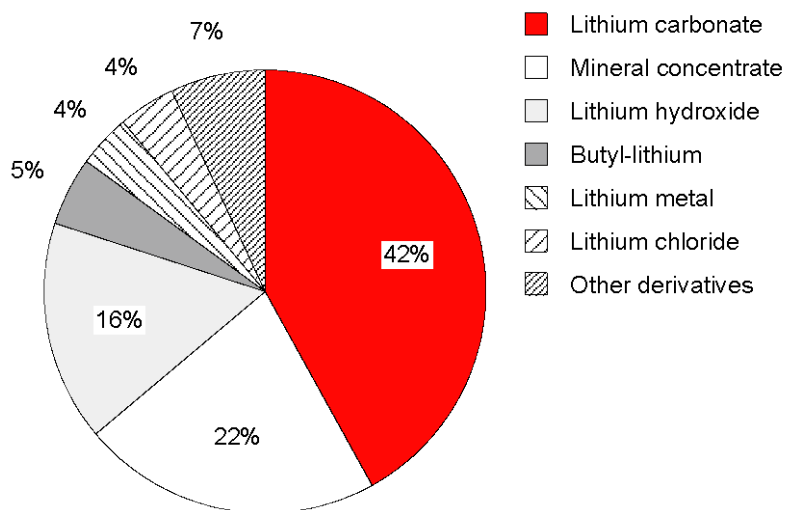
Lithium is used in a variety of end products and industrial processes (Figure 4.1) including ceramics and glass manufacturing, batteries, greases, aluminum, air treatment, rubber, thermoplastics, and pharmaceuticals [169, 170]. Lithium supply and demand has garnered past attention because of its use as a neutron absorber in the nuclear power industry as well as a potential fuel source for fusion reactors. Significant recent interest in lithium ion battery (LIB) technology, particularly for the anticipated boom of electric vehicles (EV) powered by LIB technology, has raised questions as to the short- and long-term availability of lithium resources [169, 171–173]. Because global lithium demand has been relatively stable in the past, careful assessments of lithium availability have only recently been conducted [169, 172, 174].



**Figure 4.1. Reported lithium end products in 2007.**

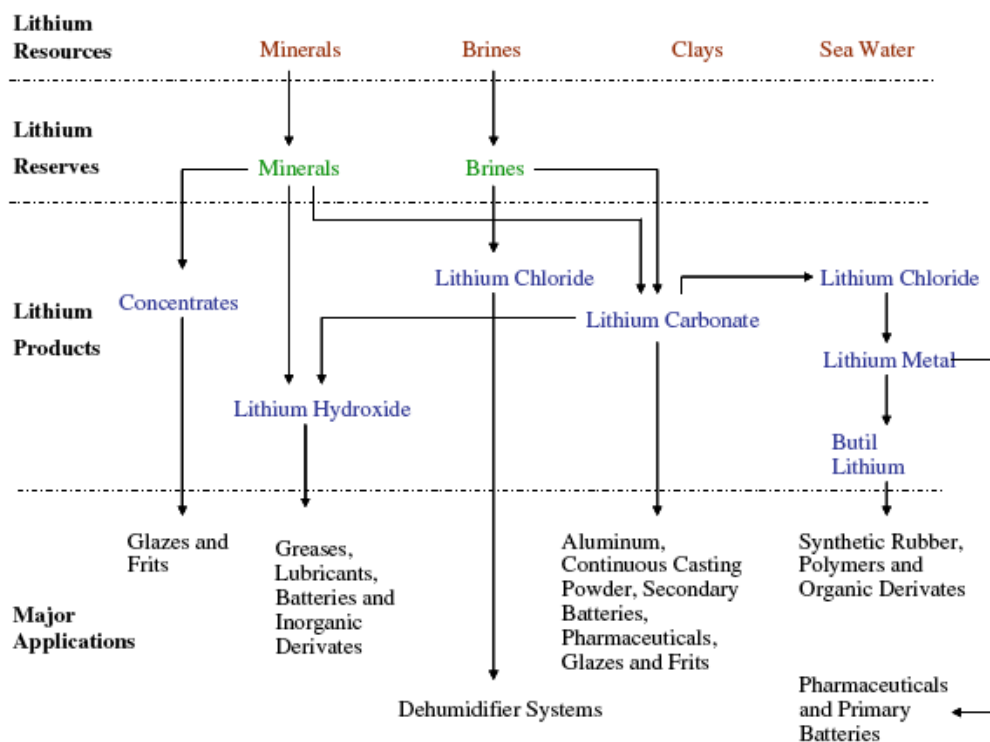
Source: Adapted from [175].

Major lithium commodities include lithium metal, lithium carbonate, lithium chloride, lithium hydroxide, organic lithium compounds (e.g., butyllithium), and concentrated lithium solutions [169, 171]. Lithium carbonate is the most commonly used lithium compound commodity, followed by lithium hydroxide and lithium chloride (Figure 4.2) [171]. Lithium commodities are currently produced from two main sources, including various terrestrial pegmatite ores (e.g., spodumene, petalite, lepidolite) and above- and underground brines; however, production from brine is significantly greater because of lower costs. A schematic showing lithium resources, reserves, products, and applications, is presented in Figure 4.3. Uncertainty regarding lithium availability has garnered interest in seawater extraction for approximately 40 years, although it has yet to be demonstrated as economical [177]. A simplified schematic of processes used to extract lithium from natural brine, ores, and seawater (proposed) is presented in Figure 4.4. Potential additional sources for lithium include certain clays, and lithium recycling is becoming more prominent as the United States and Canada increase efforts to recycle LIBs, although this has not yet been proven to be economical [172, 178].



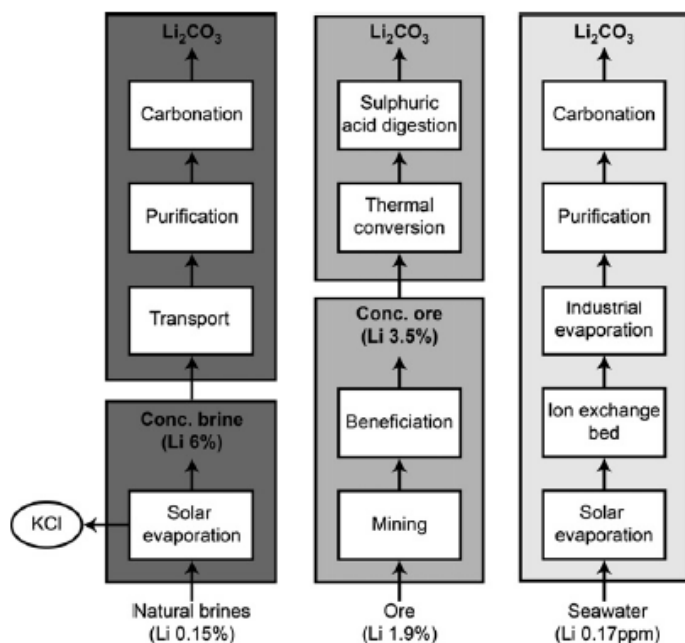
**Figure 4.2. Market shares of lithium-based commodities.**

Source: Adapted from [169].



**Figure 4.3. Types of lithium resources, reserves, products, and major end-use applications.**

Source: [175].



**Figure 4.4. Simplified process flow charts for lithium carbonate production from three resource types.**

*Source:* From [179].

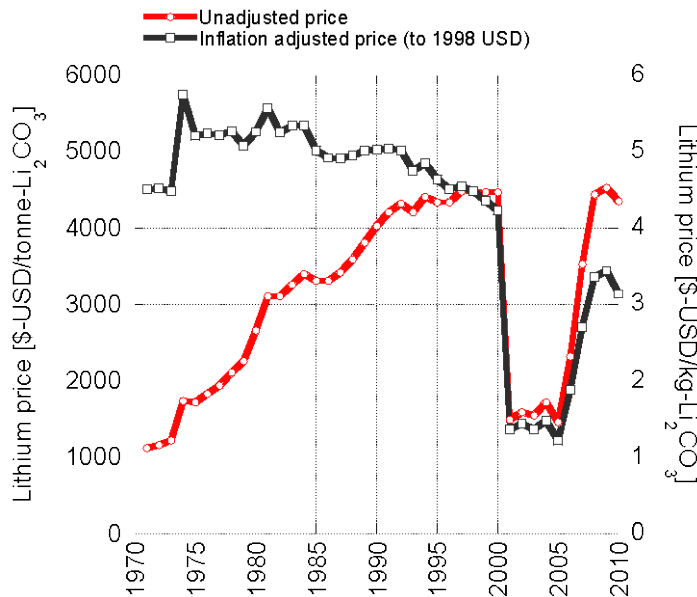
Recent lithium commodity information provided by the USGS [171, 178] indicates that the main lithium producers include Argentina, Australia, Brazil, Canada, Chile, China, Portugal, the United States, and Zimbabwe. Chile currently dominates the global lithium production market; the Chilean company SMQ is the largest producer of lithium in the world, with approximately 26% of the market [171]. Several U.S. companies extract lithium from underground brines in Nevada and produce downstream lithium commodities at facilities throughout the nation [171].

The USGS recently reported that worldwide lithium production has increased significantly in the past 2 years as Argentina, Australia, Bolivia, Canada, and China have reportedly increased production [178]. Several new facilities producing lithium from underground brine are in development in Argentina, and Australia is reportedly increasing lithium concentrate production from ores to supply China's demand for battery production and various chemical industries. The USGS reports that lithium supply security is a top priority for Asian technology companies and that strategic alliances are being established with exploration companies to assure a reliable supply of lithium for battery production [178]. Because lithium carbonate is only a small component of LIBs, however, the security issue has little to do with the cost of lithium production and is primarily a supply issue.

Lithium pricing is typically reported for lithium carbonate because it is the most commonly produced commodity and tends to represent overall trends [171]. Unadjusted and inflation-adjusted (to 1998 USD) lithium carbonate pricing provided by the USGS is presented in Figure 4.5. Lithium prices crashed in 2001 after SMQ began cheap production of large amounts of lithium from the Salar de Atacama [173]. USGS data indicate that current lithium carbonate pricing is around \$4.30/kg, although other sources indicate that it is closer to



\$5.50/kg [169]. Several sources of information [169, 175] report that lithium carbonate price reached a record high of \$6.20/kg in 2008, which is not reflected in the USGS data<sup>2</sup>. Nevertheless, with the exception of the price crash in the late 1990s, the adjusted (for inflation) lithium carbonate price has decreased over the past 30 years because of new production processes and low cost sources [175]. Based on recently published literature, there appears to be disagreement regarding how increased future demand will affect lithium commodity pricing and, to a lesser extent, whether known lithium reserves could meet anticipated future demand from electrical vehicle production.



**Figure 4.5. Unadjusted and inflation-adjusted lithium carbonate pricing.**

*Source:* USGS.

There has been some recent concern, specifically voiced by William Tahlil [35, 173, 180], that proven lithium reserves are not sufficient to meet the future demand created by electric vehicles. Estimates of both lithium resources (i.e., total inventory of lithium supplies) and reserves (i.e., economically extractable lithium supplies) vary widely based on the source of information, and recent estimates put worldwide extractable lithium reserves (not including seawater) between 4 (Tahlil's estimate) and 45 Mt, although the costs of extraction vary widely depending on the source of lithium [169, 172, 175, 179]. On the basis of more recent estimates, global lithium reserves total at least 10 Mt (USGS estimate); most analysts argue that today's known reserves are sufficient to supply the long-term electric vehicle market with LIBs at least through the 21<sup>st</sup> century [169, 172, 174–176].

Rather than a long-term supply issue, potential issues related to lithium demand have been reported to be uneven global distribution and short-term supply issues such as the time lag associated with increased production. Kushnir and Sanden [172] argued that because the top

<sup>2</sup>The USGS reports lithium carbonate pricing as an average of annual U.S. import prices, which it indicates are more representative of world prices. Other researchers use various sources for price information.

four producers of lithium represent 90% of world production, there is a supply bottleneck that could result in a significant price increase as a result of an unforeseen issue (e.g., natural disaster, nondisclosure of exhaustion, production problems, political instability) or exertion of market power due to minimal competition from other companies. Grosjean et al. [169] added that because the countries likely to produce LIBs for electric vehicles (e.g., China, France, Germany, United Kingdom) are not in close proximity to significant producers (i.e., those producing lithium from brine), trade imbalances can be expected in the near future that will raise prices until new lithium resources are exploited. In addition, current global lithium production is relatively low (estimated to be less than 25,000 tpy) compared with anticipated future demands on the order of 22,000 tpy by 2030 for electric vehicle battery production alone [176].

Although lithium producers using brine have a relatively fast response capability (reportedly 12 months [172]), bringing a new mine online is a much slower process that can take up to a decade before production begins. To meet the anticipated near-term demand for LIBs, therefore, worldwide lithium production would need to increase dramatically, which could take a significant amount of time. As a result, Grosjean et al. [169] recently estimated that a five-fold increase in lithium carbonate price will occur over the next 10 years (from ~\$5/kg–\$25/kg). However, other researchers believe that the abundance of natural brine lithium reserves and low costs of extraction will keep lithium prices relatively stable over the next 100 years [175].

The feasibility of extracting lithium from seawater (or RO brine) appears to be dependent upon several potential scenarios: (1) conventional supplies of lithium are exhausted, which seems unlikely in the near future; (2) a significant increase in lithium price occurs, making seawater extraction more attractive; or (3) a secure supply of lithium is more important than the elevated production costs associated with seawater extraction.

#### **4.1.6.2    *Lithium Extraction Summary***

Although the lithium concentration in seawater is dilute (173 µg/L [22]), the amount of lithium in the ocean (approximately 230–240 billion tons) far outweighs all other conventional lithium resources combined (current resources are estimated to be on the order of 50 Mt). In light of the previously mentioned lithium supply concerns, researchers have been continuously evaluating various aspects of seawater extraction for 40 years. Although it doesn't appear that lithium extraction has been attempted at full scale, there has been considerable recent research on developing novel adsorbent materials for lithium uptake from seawater. Several recent sources of information indicate that Japan and South Korea are in the process of developing full-scale seawater lithium extraction facilities, although specific information is difficult to obtain [179, 181, 182]. According to recent electronic articles [183], the South Korean government is co-investing approximately \$26.4 million with steel company POSCO to construct a lithium seawater extraction facility capable of producing 20 to 100 Ktpy of lithium by 2015. A South Korean seawater lithium research center was reportedly built in 2011, and an electronic article recently claimed that newly developed technology allows for high yield lithium production in a matter of months [184]. Unfortunately, no information is available on this technology.

A relatively recent (2006) publication and an undated presentation authored by Yoshizuka et al. [185, 186] provided details of a pilot-scale study evaluating the extraction of lithium from seawater using manganese oxide ion-sieve adsorbent material. The researchers continuously fed a column containing 60 kg of adsorbent with 200 L of seawater per hour for a period of

150 days. The system was operated until breakthrough was achieved (after ~3000 hours), after which the adsorbed lithium was eluted using 600 L of a 0.85 M hydrochloric acid solution. The eluate was then evaporated and dried under a vacuum to produce 791.4 g of dried precipitated salt. The precipitated salt was determined to be 33% lithium chloride, with the remainder composed of sodium, manganese, magnesium, calcium, potassium, and strontium (Table 4.10).

The energy requirements of the overall process were estimated to be 385 kWh/g/Li<sup>3</sup> (no information was given on the energy requirements of individual process components), which is extremely high considering that in the United States the cost of electricity is approximately \$0.09/kWh. The researchers indicate that future work will evaluate methods to reduce the energy demand of the process to 80 kWh/g/Li. In 2011, the research group published a paper [182] on the use of a method (from [187]) to purify the ion-exchange eluate using solvent-impregnated cation exchange resin, which allowed for greater than 99% purity lithium carbonate to be produced from seawater.

To our knowledge, the first study (and one of the most detailed) evaluating lithium extraction from seawater was undertaken in the early 1970s by Steinberg and Dang at the Brookhaven National Laboratory [177]. The authors believed that lithium use in the nuclear power industry (for both conventional and fusion reactors) would exceed conventional lithium resources (only brine is discussed as a resource) by 2030, necessitating the development of alternative supplies of lithium. The proposed process included solar evaporation for seawater concentration, ion exchange for lithium extraction, evaporation to concentrate the ion-exchange eluent, and electrolysis to produce lithium metal at a rate between 10,000 and 1 million kg/yr. Although the process was never physically evaluated, detailed energy and cost analyses were performed for three rates of lithium production (10,000, 100,000, and 1 million kg/year). Capital costs (in 1974 dollars) were calculated to be between \$1 million (~\$4.3 million in 2010 dollars) for production of 10,000 kg/year and \$100 million (~\$430 million in 2010 dollars) for production of 1 million kg/yr. Operating costs were calculated to be between \$2.10 and \$3.20/kg of lithium (\$9.10–\$14/kg in 2010 dollars). Yaksic and Tilden [175] reevaluated these operating costs, converted the reported lithium metal cost to lithium carbonate, and claimed that the cost of lithium extraction from seawater is on the order of \$16 to \$22/kg/Li<sub>2</sub>CO<sub>3</sub>, which is approximately three to four times higher than the current price of lithium carbonate. However, Grosjean et al. [169] recently put the cost of lithium carbonate production from seawater at \$80/kg, although it is unclear where this value came from. It is worth noting that Steinberg and Dang assumed 100% recovery of lithium by the ion-exchange process, which is unlikely, and also included a very large solar evaporation component (up to 155 m<sup>2</sup> of solar ponds needed to produce 1 million kg/Li/year) that would limit their process to very specific locations.

---

<sup>3</sup>This value may be a typo. Steinberg and Dang [177] estimated that energy requirements for lithium extraction from seawater are between 0.08 and 2.46 kWh/g/Li depending on the size of the extraction facility, which is much lower than what was presented in Yoshizuka et al. [186].

**Table 4.10. Metal Composition of the Dried Precipitate Salt**

Element*	30 days run [wt%]	30 days run concentration efficiency	150 days run [wt%]	150 days run concentration efficiency	Contents in seawater [wt%]
LiCl	10.35	3450	33.3	11000	$3.0 \times 10^{-3}$
NaCl	38.3	0.49	20.4	0.26	78.1
KCl	0.89	0.25	3.3	0.94	3.5
MgCl <sub>2</sub>	0.078	$5.5 \times 10^{-3}$	8.2	0.57	14.3
CaCl <sub>2</sub>	36.9	11.3	13.4	4.11	3.26
MnCl <sub>2</sub>	5.3	-	19.4	-	-
SrCl <sub>2</sub>	8.2	205	2.0	50	$4.0 \times 10^{-2}$

\* calculated as metal chlorides existing in the precipitates

Source: [185]

Natural brines used in lithium production contain 100 to 100,000 times the lithium concentration of seawater, which keeps production costs at a minimum because solar evaporation can be relied on to concentrate the lithium and precipitate out impurities such as magnesium prior to processing [188]. Yaksic and Tilden [175] estimated the cost of lithium production from a variety of brines and reported costs between \$1.60 and \$7/kg Li<sub>2</sub>CO<sub>3</sub> depending on the initial lithium concentration. Using estimates of current lithium reserves and extraction costs, the researchers developed a cumulative availability curve to assess the likelihood of lithium depletion and reported that, under the worst-case demand scenario, seawater extraction would likely become feasible sometime in the 22nd century because lithium carbonate prices would escalate as conventional sources become exhausted.

Several authors have expressed skepticism about meeting future lithium demands through extraction of lithium from seawater. Tahil [35] and Bardi [20] presented the problem in terms of the massive amounts of seawater that would require processing to meet current and future lithium demands. For example, Tahil [35] demonstrated that to supply the lithium required for 5.3 million electric vehicles built per year, a seawater flow rate five times that of the River Nile would need to be processed per year. In an electronic article by Garthwaite [183], Brian Jaskula (lithium commodity specialist at the USGS) stated that although “it theoretically is possible to extract lithium from seawater...high costs [of extraction] make it unlikely that schemes to pull lithium from seawater will succeed in the near future.”

Stamp et al. [179] recently conducted a life-cycle analysis (LCA) to evaluate the environmental impacts of different lithium supply options (natural brines, ore deposits, seawater) for lithium carbonate required for the production of LIBs. For each supply option, the LCA was performed for a favorable and an unfavorable condition dependent upon the extraction process. The seawater extraction process analysis was based on the process proposed by Steinberg and Dang [177], whereas the brine and ore options were based on information from existing lithium extraction operations. The researchers found that the environmental impacts of the seawater process were almost two and four orders of magnitude greater than brine and ore for favorable and unfavorable conditions, respectively. The environmental benefits of electric vehicles were found to outweigh the environmental impacts associated with seawater extraction for the favorable conditions only, indicating that extraction of lithium from seawater to meet the demand created by LIBs may not be an appropriate option unless process efficiencies can be improved. It is worth noting that the

LCA on seawater extraction was based on the Steinberg and Dang process, which was proposed 40 years ago. Since then, a significant amount of work has been undertaken to improve the extraction of lithium from seawater, which is summarized in the next section.

#### *4.1.6.2.1 Technologies for Lithium Extraction*

A number of different technologies have been investigated for the extraction of lithium from seawater, including adsorption, bioaccumulation, coprecipitation, flotation, ion exchange, membrane processes, and solvent extraction [74, 182, 189–191]. Recent literature suggests that adsorption using manganese oxide–based ion-exchange materials are the most promising method for the extraction of lithium from seawater.

Ion exchange has long been proposed as a method for extracting lithium from natural brines and seawater. In 1975, Steinberg and Dang [177] proposed using Dowex 50X 16 cation exchange resin to extract lithium from concentrated seawater, although the process was never evaluated. Since then, several other organic ion-exchange resins have been developed for lithium extraction, although they appear ill suited for extraction from brine or seawater because of low selectivity towards lithium [21, 76]. Khamizov et al. [192] provided a very good summary of ion-exchange materials that have been evaluated for lithium uptake since the 1980s, including charcoal impregnated with tin dioxide, chromium and zirconium oxides, thorium arsenate, aluminum hydroxide, hydrous tin (IV) oxide, manganese oxide, and hydrous titanium (IV) oxide. Although some of these adsorbents have proven efficient for lithium uptake, they are limited by low selectivity towards lithium in multicomponent solutions such as seawater.

To improve selectivity, a number of different inorganic ion-exchange materials have been evaluated or developed for extraction of lithium from brine and seawater. Early work by Mitsuo Abe led to the development of tin (IV) antimonate [189] and titanium (IV) antimonate [193] cation ion-exchange materials that were found to have high affinity for lithium in a seawater matrix, although only moderate lithium selectivity. Treated manganese oxide–based ion-sieve adsorbents have garnered significant attention over the past 30 years because they show both high sorption and selectivity towards lithium. Ion-sieve manganese oxide adsorbents are believed to exhibit high selectivity towards lithium because they have a nanoporous structure that sterically excludes other alkali metal ions [76].

Researchers at the Japanese National Institute of Advanced Industrial Science and Technology have been continuously developing treated manganese oxide ion-sieve adsorbents to maximize lithium uptake and selectivity by inserting metal ions (e.g., antimony, lithium, magnesium, tin) into a manganese-oxide matrix and performing various post-treatments (e.g., acid treatment, washing, heating) to create a lattice structure of desired spacing for lithium insertion [75, 76, 194–201].

Chitraker et al. [75, 201] developed a manganese-based ion sieve through acid treatment of  $\text{Li}_{1.6}\text{Mn}_{1.66}\text{O}_4$  to yield  $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ , which has demonstrated high lithium adsorption capacity (near 40 mg Li/g adsorbent) and lithium selectivity relative to sodium, magnesium, and potassium in a seawater matrix. The adsorption capacity of the developed ion sieve is reported to be the highest to date and significantly higher than other adsorbent materials (Figure 4.6). Shi et al. [202] recently improved the method for preparation of this ion-sieve material, produced a lithium carbonate precipitate of 99.5% purity from seawater, and obtained a final percentage yield of lithium carbonate greater than 85%.

Similar to results presented by Yoshizuka et al. [185], the ion-sieve eluate contained significant quantities of magnesium, sodium, potassium, and manganese and required post-processing (i.e., sodium hydroxide to precipitate manganese and magnesium) to yield a pure lithium carbonate precipitate. Other issues associated with ion-sieve adsorbents include loss of adsorbent capacity and manganese from the adsorbent after elution with acidic solutions. In addition, manganese-based ion sieves have been shown to be significantly more efficient at high pH (usually around 12), which indicates that pH adjustment may be necessary for lithium extraction from seawater [203, 204]. The science behind the preparation of ion-sieve materials for lithium adsorption does not appear to be completely understood, and more research is needed to identify the most promising materials and production methods for maximizing the lithium capacity of these adsorbents [205].

To reduce the energy requirements associated with pumping seawater to ion-exchange columns, several researchers [194, 206] have developed a membrane adsorbent using ion-sieve adsorbent material that could be deployed in ocean currents. Other adsorbent materials that have been evaluated for lithium extraction include various calixarenes [207], organometallic receptors [208], and aluminum hydroxides [191].

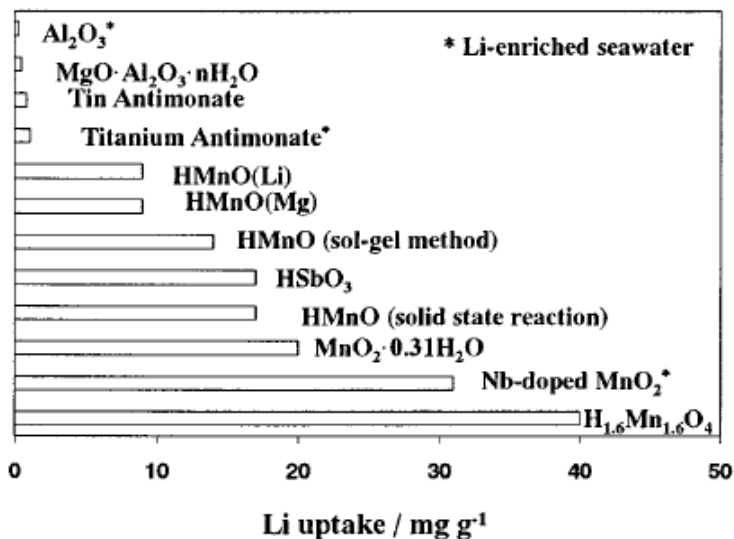


Figure 4.6. Comparison of lithium uptake from a seawater matrix for different adsorbent materials.

Source: [201]

Sakamoto et al. [209] evaluated a proton-driven liquid membrane system using crown nitrophenol ionophores for the separation and enrichment of lithium from model water solutions and reported effective separation when sodium concentrations were relatively low compared to lithium. Using a chloroform membrane and porphyrin carrier, Sun and Tabata [210] were able to separate and concentrate lithium by a factor of three from a seawater sample with comparably little transport of sodium and potassium. Ma et al. [211] evaluated a polypropylene liquid membrane system using several carriers and were able to recover 95% of the lithium from a multicomponent model water solution. Although effective extraction efficiency required high feed water pH (>12.5), the authors demonstrated that the system could be operated for over 2 days with only minimal loss of solute permeability. Tsuchiya et al. [212] used bipyridine macrocycles as lithium carriers in a dichloromethane liquid membrane system to separate and concentrate lithium from seawater and reported a lithium concentration factor of 16,000 after two separations. The authors acknowledge that other carriers may have higher selectivity for lithium, but their system did not require a lipophilic counterion (e.g.,  $\text{ClO}_4^-$ ,  $\text{SCN}^-$ ), which allows for direct separation of lithium from seawater in liquid membrane systems. A summary of technologies developed and evaluated for the extraction of lithium from aqueous solutions is presented in Table 4.11.

In light of the anticipated boom in electric vehicles, concerns regarding future lithium availability have renewed interest in the extraction of lithium from seawater. Although several technologies have been developed for extraction of lithium from aqueous solutions, ion-exchange adsorbents of ion-sieve manganese oxide type appear to be the most promising technology. Recent electronic articles indicate that South Korea and possibly Japan are planning to build large-scale seawater lithium extraction facilities based around this technology; however, several publications put the cost of seawater extraction at three to ten times the current price of lithium carbonate. Recent analysis of global lithium reserves indicates that relatively cheap production of lithium compounds can occur for a significant amount of time, which may not make seawater extraction economically viable this century unless extraction process efficiency is significantly improved. Uneven geographical distributions of lithium reserves and demands and a need to secure a stable supply may partially explain the efforts of South Korea and Japan to extract lithium from seawater. Unless lithium prices increase significantly, it does not currently appear feasible to extract lithium from SWRO brine for economic gain.

**Table 4.11. Summary of Technologies for Lithium Extraction**

Technology	Technology Specifics	Indicators of Process Efficiency Toward Lithium Extraction	Reference
Adsorption, co-precipitation	Polymeric aluminum hydroxide	Evaluated process for high lithium solutions (brine) and could achieve 87% recovery and 93% pure lithium.	[191]
Complexation	Calixarenes	Can complex lithium but does not appear to be selective relative to sodium or potassium.	[207]
	Organometallic receptor	Reported a lithium binding constant of $5.8E4\text{ M}^{-1}$ and Li-Na selectivity of 10000:1 could be obtained.	[208]
Ion-exchange	Tin(IV) antimonate (SnSbA) cation exchange material with nitric acid eluent	Maximum adsorption of 0.2 meq Li/g-adsorbent, impacted by ion strength, high selectivity towards lithium compared to sodium.	[189]
	Lithium introduced manganese oxide ion sieve (HMnO) with hydrochloric acid eluent	Maximum adsorption of 7.8 mg/g-adsorbent, high selectivity towards lithium, $K_d > 50,000\text{ mL/g}$ , up to 85% recovery of lithium from seawater, high stability to eluent.	[76]
	Titanium (IV) antimonate (TiSbA) cation exchange material with nitric acid eluent	Maximum adsorption of 0.2 meq Li/g-adsorbent, impacted by ion strength, high selectivity towards lithium compared to sodium.	[193]
	Magnesium introduced manganese oxide ion sieve (HMnO(Mg)) with dilute acid elution	Maximum adsorption of 8.5 mg/g-adsorbent, high selectivity towards lithium, moderate stability to eluent (HCl).	[196]
	Antimony introduced manganese oxide ion sieve	Maximum adsorption of 14 mg/g.	[75]
	Lithium introduced manganese oxide ion sieve ( $\text{H}_{1.6}\text{Mn}_{1.6}\text{O}_4$ ) with hydrochloric acid eluent	Maximum adsorption of 40 mg/g-adsorbent, 60% recovery of lithium from seawater, high selectivity to lithium compared with sodium and potassium.	[201]
	Nano-manganese $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$ ion-sieve	Maximum adsorption of 28.3 mg/g, good stability through 5 elution cycles.	[198]
	Nanowire lithium introduced manganese ion-sieve	Maximum adsorption of 17 mg/g, high selectivity towards lithium compared with sodium, potassium, magnesium. Relatively high uptake of calcium. Slow kinetics.	[213]
	Lithium introduced manganese oxide ( $\text{H}_{1.41}\text{Li}_{0.01}\text{Mn}_{1.65}\text{O}_4$ ) ion-sieve	Maximum adsorption of 37.6 mg/g at pH 12. Adsorption capacity decreases significantly at lower pH. Rapid (3 h) uptake of lithium. Low dissolution of	[203]



Technology	Technology Specifics	Indicators of Process Efficiency Toward Lithium Extraction	Reference
		manganese.	
	$H_{1.51}Li_{0.08}Mg_{0.24}Mn_{1.49}O_4$ manganese oxide ion-sieve	Adsorption capacity strongly dependent upon pH and lithium concentration. Achieved adsorption capacity of >35 mg/g although required pH 12 and high initial lithium concentrations. Stable after four elution cycles.	[204]
	Ion-sieve of the $LiM_{0.5}Mn_{1.5}O_4$ where M = Ni, Al, Ti	Best performing adsorbent ( $LiAl_{0.5}Mn_{1.5}O_4$ ) had the highest adsorption capacity (~20 mg/g at pH 12 and 345 mg/L Li soln.) and was stable during acid treatment.	[214]
	$H_{1.6}Mn_{1.6}O_4$ ion-sieve adsorbent with a weak acid eluent	Maximum adsorption of 27 mg/g, adsorption capacity remained above 20 mg/g after 10 adsorption/desorption cycles, high adsorption efficiency, loss of Mn reduces number of cycles to 140.	[202]
	Antimony and lithium introduced manganese oxide ion sieve	Maximum adsorption of 33 mg/g. Material with highest stability in an acidic solution had an adsorption capacity of 18 mg/g.	[215]
Ion-exchange, solvent impregnated resin	Granulated $Li_{1.5}Mn_2O_4$ ion-sieve adsorbent with HCl elution, eluate treated with solvent (TOPO) impregnated resin	Attempted to solve ion-exchange eluate purity issues using solvent impregnated resin to separate out sodium and potassium. Obtained 99.9% purity lithium carbonate at overall yield of 56%.	[182]
Liquid membrane	Polypropylene membrane, cation transport mediated by crown nitrophenol derivatives	50 times more selective for lithium than sodium, able to concentrate lithium ~5 times in 20 hours for 1:1 Na/Li solution, does not appear feasible for seawater.	[209]
	Chloroform membrane with porphyrin carrier	Selective towards lithium in seawater matrix, concentrate lithium by factor of 3, low transport of sodium and potassium.	[210]
	Polypropylene membrane, two carriers evaluated: LIX54 and TOPO	Discussed lithium separation efficiency in terms of lithium permeability coefficients, required high pH (13) for highest permeability, strip solution of 1M $H_2SO_4$ , but could recover all lithium from feed solution in batch system.	[211]
	Dichloromethane membrane, bipyridine macrocycle carrier	Concentrated lithium from seawater by a factor of 16,000. Fairly high selectivity towards lithium, 80% pure	[212]

Technology	Technology Specifics	Indicators of Process Efficiency Toward Lithium Extraction	Reference
		carrier solution after two separation cycles.	
Membrane-type adsorbent	H <sub>1.33</sub> Mn <sub>1.67</sub> O <sub>4</sub> ion-sieve powder developed into flat-sheet membranes	In membrane form could get 16 mg-Li/g-adsorbent in a seawater matrix which required more than 12-days. The idea would be to put the membrane in the ocean.	[194]

**Table 4.12. Lithium Overview**

<b>Main form(s) in water</b>	Li <sup>+</sup>
<b>Dominant commodities</b>	Lithium carbonate, lithium hydroxide, lithium chloride, organic compounds
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>• Current production from terrestrial pegmatite ores and aboveground and underground brines (preferred) [170]</li> <li>• Production has increased significantly in the past 2 years</li> <li>• Prices are generally reported for Li<sub>2</sub>CO<sub>3</sub>, the most common commodity, which tends to represent overall trends.</li> <li>• Current pricing is around \$4.30–\$5.50/kg [169, 170].</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>• Demand is expected to increase because of increasing LIB production, particularly for electric vehicles.</li> <li>• Recent literature disagrees on the extent to which increased demand will affect lithium commodity pricing and whether known reserves will meet future demand.</li> <li>• Lithium is distributed unevenly globally, and in the near term supply chain problems and trade imbalances may drive lithium prices higher.</li> <li>• Several authors are skeptical about the massive amounts of seawater necessary to extract an appreciable amount of lithium and the energy required to do so [20, 35, 173].</li> </ul>
<b>Extraction technologies and processes</b>	<p><i>Ion exchange</i></p> <ul style="list-style-type: none"> <li>• Challenging to find an adsorbent that has both high affinity and selectivity for lithium.</li> <li>• Chitraker et al. developed a manganese-based ion sieve through acid treatment of Li<sub>1.6</sub>Mn<sub>1.66</sub>O<sub>4</sub> to yield H<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>, which was demonstrated as having high lithium adsorption capacity (near 40 mg Li/g adsorbent) and lithium selectivity relative to sodium, magnesium, and potassium in a seawater matrix [75, 201].</li> <li>• This process has been improved to yield lithium carbonate precipitate of 99.5% purity, with a final yield of Li<sub>2</sub>CO<sub>3</sub> &gt;85%.</li> <li>• High energy cost of pumping water through ion-exchange columns could make extraction uneconomical.</li> </ul> <p><i>Adsorption</i></p> <p>Ion-sieve adsorbents could be deployed near ocean outfalls or in concentrate streams [185].</p> <p><i>Liquid membranes</i></p> <p>Efficient separations have been demonstrated, but issues include poor stability, low solute fluxes, and difficulty in developing large systems [67].</p>
<b>Conclusions from literature review</b>	Unless lithium prices increase significantly, it does not appear feasible to extract lithium from SWRO brine for economic gain at this time.

*Note:* SWRO=seawater reverse osmosis.

**Table 4.13. Summary of Patents Related to Lithium Extraction**

Decade	Number of Patents	U.S. Patent #
prior to 1950	0	
1950–1959	0	
1960–1969	2	3,306,700; 3,382,034
1970–1979	4	3,537,813; 3,597,340; 4,116,858; 4,116,856
1980–1989	4	4,291,001; 4,540,509; 4,665,049; 4,649,218
1990–1999	4	5,198,081; 5,389,349; 5,599,516; 5,833,844
2000–present	1	US2011/0174739 A1

#### 4.1.7 Magnesium

There are several forms of magnesium that have historically been or are currently being extracted from seawater, which include magnesium metal and various magnesium compounds (synthetic magnesia, magnesium hydroxide).

##### 4.1.7.1 Magnesium Commodity Summary

###### 4.1.7.1.1 Magnesium Metal

Although magnesium metal was predominantly produced in the United States and United Kingdom using seawater extraction facilities in the 1940s, the current worldwide production processes include [216]:

- Electrolysis of anhydrous magnesium chloride derived from carnalite from salt deposits, magnesite ore, brine or seawater
- Thermal reduction of magnesium oxide derived from magnesite or dolomite ore using the Pidgeon or Magnotherm process

According to Brown [217], electrolytic magnesium production was dominant in the past, but over the last 10 years thermal magnesium production has increased significantly and in 2011 composed 85% of the world's magnesium production, which is mostly in China.

The electrolytic process for magnesium metal production is similar to the Dow seawater process [17, 218, 219], the only significant difference being the source of the magnesium chloride (e.g., salt deposits, magnesite ore, brine, seawater). In 2000, the USGS [220] reported that a significant portion of magnesium metal produced through electrolysis using magnesium chloride is obtained from terrestrial ores occurring in Australia, Canada, and, to a

lesser extent, China. Production of magnesium from carnalite obtained from salt deposits constituted a large percentage of production and included Congo, Israel, Kazakhstan, Russia, and Ukraine. Production of magnesium from brines was much less common in 2000 and included companies in the United States (U.S. Magnesium), Norway (Norsk Hydro A/S), and the Netherlands (Antheous). The only company reportedly extracting magnesium from seawater for magnesium metal was in the United Arab Emirates (Spectrum Technology Corporation). U.S. Magnesium continues to produce magnesium metal from concentrated Great Salt Lake brine and is the sole producer of magnesium in the United States [221].

Magnesium metal production using thermal reduction generally relies on silicothermic (using ferrosilicate as the reductant) processes of either the Pidgeon or Magnotherm type, which mainly differ in the source of heat and form of magnesium produced [216, 220]. At the facilities using the silicothermic process, dolomite ore is the dominant source of magnesium. The main sources of magnesium metal obtained through silicothermic processes are Canada, China and the United States. Although production costs of magnesium metal from seawater have been reported to be lower than from brine or dolomite ore, operating costs have been reported to be significantly higher for facilities processing seawater [220].

Magnesium metal pricing in 2011 was \$2.35/lb in the United States and \$3300/metric ton in China [222]. Magnesium prices in the United States are significantly higher than in other markets because of the U.S. antidumping law on magnesium metal from Russia and China and the fact that the United States has only one producer of magnesium metal (U.S. Magnesium) [222, 223].

#### *4.1.7.1.2 Magnesium Compounds*

Economically valuable magnesium compounds include various grades of magnesium oxide (i.e., magnesia,  $\text{MgO}$ ), magnesium carbonate, magnesium chloride, magnesium hydroxide, and magnesium sulfate. Although seawater-derived magnesium chloride was commonly used for electrolytic magnesium metal production in the past, it and magnesium carbonate are now produced in the United States from underground or Great Salt Lake brines. Typical seawater magnesium facilities recover magnesium hydroxide through successive precipitation steps using lime or dolime for precipitation of magnesium hydroxide (with different methodologies employed to remove impurities such as calcium and boron) followed by washing and a filtration step to concentrate the magnesium hydroxide slurry [17, 220, 224]. This slurry can be sold or further refined to produce caustic-calcined magnesia, dead-burned or refractory magnesia, fused magnesia, or other magnesium compounds such as magnesium chloride or magnesium sulfate) [225]. There are several different patented processes for precipitating and purifying magnesium hydroxide produced from seawater, which are discussed in Section 4.1.7.2.

The USGS discontinued releasing annual magnesium compound prices in 2007, and thus recent pricing information is unavailable. The most recent year-end magnesium compound price information (for 2006) is presented in Table 4.14. The USGS conducts annual surveys of mineral commodity producers in the United States and estimated that 162,000 metric tons of caustic-calcined and various grades of magnesia were shipped and used in 2010, composing a total value of \$47 million or an average price per metric ton of \$290 [226]. Magnesium hydroxide (100%) and magnesium sulfate usage was estimated at 171,000 and 47,400 metric tons for an average price per metric ton of \$625 and \$435, respectively. Annual usage data for dead-burned magnesia was not disclosed in order to protect company proprietary data.

Production of magnesia is generally of two types, seawater and brines and magnesite ore. Synthetic magnesia (from seawater) generally contains fewer impurities than natural magnesia, containing between 92 and 99.5% magnesium oxide (see Table 4.15 [227]). In 2010, Japan, the United States, and the Netherlands accounted for 56% of worldwide magnesia production from seawater or brine [226]. In 2009, magnesium derived from seawater and natural brines accounted for 54% of magnesium compound production in the United States, with three companies producing magnesium hydroxide from seawater [228]. Magnesium hydroxide obtained from seawater can be post-processed to yield different grades of magnesia and potentially magnesium sulfate or magnesium chloride, although this does not appear to be economically viable.

Caustic-calcined magnesia is formed by thermal decomposition ( $\sim 1000^{\circ}\text{C}$ ) of magnesium hydroxide [225]. The various grades of caustic-calcined magnesia are used in different market segments, including agricultural applications (e.g., fertilizers, animal nutrition), air pollution control, cement, industrial processes, and water and wastewater treatment (e.g., pH adjustment, silica and metal removal)[220]. Caustic-calcined magnesia is also a precursor for various other products, including dead-burned magnesia, fused magnesia, magnesium oxychloride and oxysulfate cements, rayon, fuel additives, and rubber [227]. Sintered or dead-burned magnesia is produced by kilning of caustic magnesia at approximately  $2300^{\circ}\text{C}$  and used in a variety of refractory materials, including insulators for industrial furnaces. Electrofused magnesia is produced in electric furnaces from caustic magnesia and desired for certain applications because of its high stability, corrosion resistance, and uniformity of crystal size.

**Table 4.14. 2006 Year-End Prices for Various Magnesium Compounds**

Material	Unit	2006 Price
Magnesia, dead-burned	short ton	\$365 - 375
Magnesia, synthetic, technical, 98% MgO	short ton	\$490.00
Magnesium chloride, hydrous, 99%, flake	short ton	\$290.00
Magnesium chloride, anhydrous, 92%, flake or pebble	pound	\$0.128 - 0.15
Magnesium hydroxide, powder, technical	pound	\$0.45
Magnesium hydroxide slurry, technical, 100% $\text{Mg}(\text{OH})_2$	short dry ton	\$238 - 250
Magnesium sulfate, technical (epsom salts)	pound	\$0.18 - 0.22

**Table 4.15. Average Composition of Caustic-Calcined Magnesia**

Source Country	Chemical Composition, %				
	Magnesia (MgO)	Silicon Dioxide (SiO <sub>2</sub> )	Calcium Oxide (CaO)	Ferric Oxide (Fe <sub>2</sub> O <sub>3</sub> )	Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> )
Canada	96.3	0.4	2.7	0.5	0.1
Slovakia	78	1	2.5	7	0
Spain	85	3.6	7	2.5	0.4
United States (brine)	97	0.5	1	0.3	0.2
United States (seawater)	97.2	0.4	0.9	0.24	0.28

*Source:* Adapted from [227].

Overall U.S. production of magnesium compounds has declined significantly over the past 30 years, which has been attributed to both a decrease in demand and imports of low-cost dead-burned magnesia from China [220, 227]. U.S. consumption of magnesium compounds has generally declined over the past 20 years because of decreased demand by the refractory industry, which has been the largest consumer. In 2000, refractory magnesia (i.e., dead-burned and fused magnesium oxide) was the dominant magnesium compound consumed, primarily because of iron and steel industry demand [220]. By 2002, however, U.S. caustic-calcined magnesia consumption had surpassed dead-burned magnesia because of emerging markets that included the environmental sector (gas scrubbers and water and wastewater treatment, which also use magnesium hydroxide) and production of flame retardants [227].

Refractory magnesia consumption is strongly tied to the economy and steel production and thus increased significantly from 2009 to 2010 after reaching a low point in 2008 [226]. Most analysts believe that China will continue to export enough magnesia to meet demand through its abundant supplies of magnesite [226]. Recent figures for total U.S. production of refractory-grade magnesia are unavailable through the USGS; however, in 2010 the United States exported 9 ktons, compared with 323 ktons imported. The most recent numbers obtained showed that in 2002 the United States, specifically Martin Marietta, LLC (Manistee, MI), produced 123 ktons of refractory magnesia and imported 394 kt.

Compared to dead-burned magnesia, caustic-calcined magnesia and magnesium hydroxide consumption did not decrease significantly during the recent economic downturn and is expected to grow through use in industrial processes, air pollution control, and municipal water treatment. In 2010, total U.S. production of caustic-calcined magnesia (excluding that used for production of refractory magnesia) was 162 ktons, whereas imports were 127 ktons [226]. However, U.S. caustic-calcined magnesia exports decreased by 45% from 2009 to 2010 and were virtually non-existent in 2010 [226]. This is presumably due to significant production activity outside of the United States, including Canada, Brazil, Europe, Asia, and Australia [229]. Several countries including Turkey and Australia are currently constructing large facilities for production of caustic-calcined magnesia [229].

In 1990, six U.S.-based companies produced magnesium compounds from seawater in California, Delaware, Florida, and Texas, but both production and value fell drastically below the level of 1989. In 1998, the USGS indicated that four companies that extracted magnesium from seawater were operating in California, Delaware, Florida, and Texas. A web-based search was conducted to identify worldwide facilities producing magnesium from seawater in 2012. Premier Periclase (owned by RHI AG, Vienna, Austria) currently operates a magnesia from seawater facility in Ireland that reportedly produces 70,000 to 90,000 tons of sintered-

grade magnesita (dead-burned magnesita or periclase) per year [227, 230]. This appears to be one of the largest facilities currently using seawater; it also produces salable magnesium hydroxide in suspension and caustic-calcined magnesita. Yearly production data for these magnesium compounds are unavailable. The facility appears to have good access to an abundant supply of limestone and produces its own quicklime for the process of precipitating magnesium hydroxide from seawater [225]. The process requires approximately 500 tons of seawater to yield 1 ton of magnesium oxide [231].

A company in Japan (Ube Material Industries, Ltd.) continues to operate a seawater magnesita facility that produces approximately 50 ktpy of caustic-calcined magnesita and 250 ktpy of dead-burned magnesita at its plant in Ube City [227]. SMA Minerals (recently purchased by RHI AG) currently produces synthetic magnesita and magnesium hydroxide from seawater in Porsgrunn, Norway, and a calcining facility is currently being constructed to produce high-grade fused magnesita.

Two U.S. producers of synthetic magnesita and magnesium hydroxide were identified: SPI Pharma (Delaware) and Premier Chemical (Florida). SPI Pharma produces synthetic magnesium hydroxide for antacids and in 2010 had a reported annual production capacity of 5000 tpy [226]. Premier Chemical produces caustic-calcined magnesita and magnesium hydroxide for industrial and water treatment processes and in 2010 had a reported capacity of 107,000 tpy [226]. According to the USGS, however, Premier Chemical shuttered its magnesita from seawater operation in 2011. South Bay Salt Works (Chula Vista, CA) produces approximately 3000 tpy of magnesium chloride brine as a byproduct of sodium chloride production. An additional facility produces magnesita from seawater in California, according to the USGS [229], but could not be identified. Several relatively large (~85 ktpy) seawater magnesita plants were recently in operation in India and Italy but had closed by 1999 and 2003, respectively.

#### **4.1.7.2 *Magnesium Extraction Summary***

As previously mentioned, magnesium is the second most abundant metal ion (after sodium) in seawater, composing approximately 15% of the total salt. In addition, the extraction of magnesium metal and magnesium compounds from seawater has been practiced for over 70 years. Recent economic information indicates that the production of magnesium metal, sintered magnesita, magnesium chloride, magnesium sulfate, and, to a lesser extent, dead-burned magnesita from seawater may not be currently economically viable as more economical sources and technologies currently exist. Although desalination facility brine is concentrated relative to seawater (potentially greater than a concentration factor of two), there is little evidence indicating that this would improve the economics of extraction considerably; however, the economic outlook for magnesium hydroxide and caustic-calcined magnesita is positive, and the market is expected to grow in the next several years [226].

In addition, magnesium compounds could potentially be produced during ZLD processes. Several researchers have explored the concept of extracting magnesium from desalination process waste streams to both improve the recovery of desalination facilities as well as for economic gain [16, 62, 157, 232, 233]. In general, most of these studies were limited to desktop feasibility analyses and, to a lesser extent, small-scale laboratory experiments. A recent press release through *Global Water Intelligence* indicated that desalination facilities in China are implementing processes to recover potassium and magnesium from RO brine for fertilizer [234].



#### 4.1.7.2.1 *Evaporation and Crystallization*

Abdel-Aal et al. [235] proposed an MSF and separation process for recovery of water, sodium chloride, and magnesium chloride-rich bitterns from desalination facilities in Saudi Arabia. Although no cost or economic analysis was performed, the authors stressed that one major difficulty associated with the process would be handling the highly viscous and corrosive bittern solution. Ohya et al. [233] proposed a series of processes to recover salts from an integrated desalination system composed of UF and NF pretreatment followed by RO. Production of magnesium in the system would require a precipitation step to remove calcium carbonate, followed by an evaporation or crystallization step for recovery of magnesium sulfate.

Drioli et al. [48, 153] investigated several integrated processes (similar to the process proposed by Ohya et al. [233]) to extract calcium carbonate (calcite), sodium chloride, and magnesium sulfate (epsomite) from NF and RO retentate during desalination using NF pretreatment followed by RO. The integrated processes evaluated consisted of:

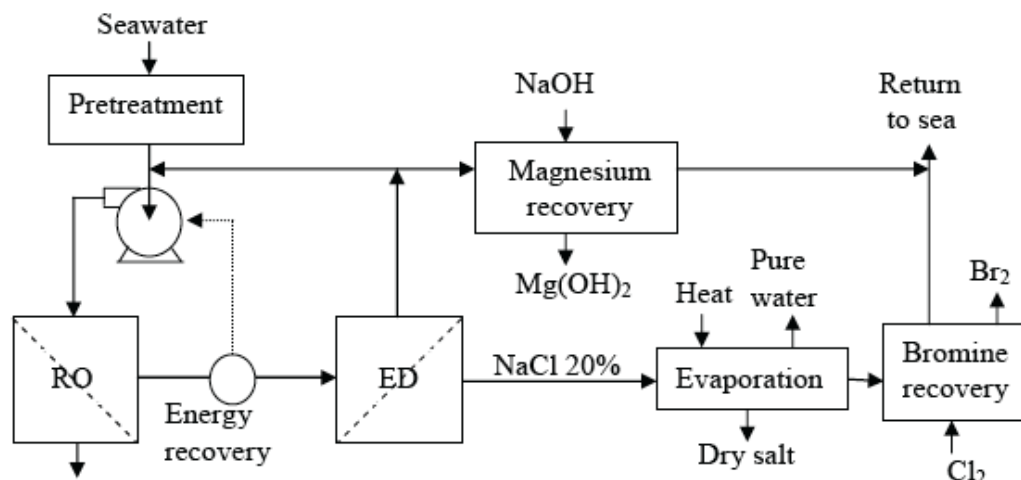
1. precipitation step fed by NF retentate followed by membrane crystallization
2. RO retentate treated by precipitation followed by membrane crystallization
3. NF retentate treated by precipitation followed by membrane crystallization and RO retentate treated by membrane distillation
4. NF and the RO retentate treated by precipitation followed by membrane crystallization

The precipitation step produced calcium carbonate, and the membrane crystallizer produced sodium chloride and magnesium sulfate. Economic analyses conducted by Drioli et al. [48] and Kim [72] indicated that several of these configurations (1, 3, and 4) could produce a profit after the sale of the extracted salts. Kim [72] indicated that the costs associated with the disposal of the final brine are significant, and the efficiencies (i.e., recovery) need to be increased to improve the overall economics of the proposed processes.

#### 4.1.7.2.2 *Precipitation*

Davis [62] recently evaluated the extraction of magnesium (as  $\text{Mg}(\text{OH})_2$ ), salt, and bromine from RO brine during a laboratory-scale study sponsored by the U.S. Bureau of Reclamation. The proposed process consisted of ED treatment of RO brine to separate monovalent and divalent ions, followed by a precipitation step using sodium hydroxide to yield magnesium from the ED diluate. The ED retentate would be treated by thermal evaporation to precipitate sodium chloride, and the remaining bittern used to produce bromine by the chlorine blowout process. A schematic of the proposed process is presented in Figure 4.7.

The researchers attempted a sequential precipitation and filtration process for magnesium production that used sodium hydroxide and sodium carbonate (soda ash,  $\text{Na}_2\text{CO}_3$ ) as a means to separate calcium from magnesium. The researchers reported that, whereas sodium carbonate addition followed by filtration could ultimately produce a magnesium precipitate without significant calcium, coprecipitation of magnesium and calcium during the first precipitation step was significant and decreased the yield of magnesium. A past research study evaluating the separation of magnesium and calcium from seawater reported that lime is more effective than soda ash [103]. A relatively simple cost analysis demonstrated that approximately \$6 million could be recouped on an annual basis through the extraction of magnesium from a 6 mgd desalination facility after capital and operating expenditures.



**Figure 4.7. Proposed process for extraction of bromine, salt, and magnesium from RO brine.**

Source: [62]

The SAL-PROC process (Geo-Processors) has been discussed [236, 237] as a technology to reclaim sodium chloride, calcium chloride, calcium sulfate, and magnesium hydroxide from desalination brine and other high salinity waste streams. SAL-PROC is an integrated process consisting of sequential chemical precipitation steps that purportedly requires no hazardous chemicals and has been demonstrated at pilot-scale for treating saline waters to produce salable byproducts and significantly reduce the volume of brine to be disposed [237].

Recently, a project cofunded by the U.S. Bureau of Reclamation on BWRO brine minimization investigated the feasibility of SAL-PROC through a desktop study (SAL-PROC was never tested) for the reclamation of magnesium hydroxide, calcium carbonate, and mixed salt product from RO brine [13]. For the study, 14 different treatment trains were evaluated for brine minimization, including estimations of capital and operating costs. The treatment trains employing SAL-PROC were estimated to be significantly more expensive than the other processes. The authors claim that these costs could be significantly reduced by improving the recovery of the RO system upstream of SAL-PROC (i.e., reducing the volume requiring treatment); however, it is unclear how this would affect salable salt production. In addition, the economic benefits from extracting salable materials were not included in the cost estimates.

Of the studies examining the recovery of magnesium or magnesia from desalination (i.e., distillation or RO) facilities using precipitation, few have discussed the difficulties of actually producing a high quality and salable magnesium product. A review of the procedures used by facilities to extract magnesium or magnesium compounds from seawater reveals that extraction is complex and involves multiple steps. Similar to what Davis [62] observed, one major difficulty in producing high purity magnesium compounds from seawater using lime or dolime arises from simultaneous precipitation of calcium carbonate, which must be separated from precipitated magnesium hydroxide prior to processing [103]. The process used by Dow to produce high purity magnesium chloride for magnesium metal production included screening, flocculation, thickening, primary filtration, chemical processing, primary evaporation, secondary filtration, and secondary evaporation [17].

To yield a magnesium chloride solution free of calcium, the concentrated magnesium hydroxide slurry produced through thickening and filtration was dissolved in hydrochloric and sulfuric acid to precipitate out calcium sulfate [17, 224]. Kim [72] performed an economic analysis of the Dow process and concluded that it was an expensive option for the recovery of magnesium, requiring annual revenues of approximately \$28 million to recoup investment, capital, and O&M costs. The process also consumes a large amount of hydrochloric acid or chlorine (although chlorine is produced during the process through electrolysis of  $\text{MgCl}_2$ ) [238]. In addition, because the process does not significantly reduce the volume of the source of magnesium (e.g., seawater, desalination brine), the costs of disposal would still be significant.

Other processes, such as those used at the Kaiser and Merck and Co. facilities and currently used in the United States, Ireland, and Japan to produce concentrated magnesium hydroxide for magnesia production (see Figures 4.8 and 4.9) rely on staged precipitation and separation. Lime softening is first used to precipitate and separate calcium and magnesium carbonate (through dolime and lime addition) and calcium sulfate (through sulfuric acid addition) followed by precipitation and settling steps to yield a 50% magnesium hydroxide solution that can be sold or further processed [224]. Production of magnesia from a concentrated magnesium hydroxide solution requires filtration, drying, and calcining at different temperatures depending on the grade of magnesium oxide desired [224]. It has been reported that, although the production costs of caustic-calcined magnesia are independent of the magnesium source, dead-burned magnesia is significantly more expensive using seawater [227].

An additional issue associated with the extraction of magnesium hydroxide is settling out the magnesium hydroxide precipitate or flocs [239]. Kinetics of magnesium hydroxide precipitation are relatively fast (compared to calcium carbonate precipitation [240]), but the rate of sedimentation is rather slow and depends on the composition of the lime (e.g., dolime, slaked lime) used in the process, completeness of the precipitation step, solution pH, and resulting density of the precipitate [239]. Researchers have reported that efficient sedimentation of magnesium hydroxide flocs requires a pH of 11 to 11.5, which is approximately the pH required for maximum precipitate formation [103, 241].

To improve separation of calcium from magnesium and remove the bottleneck created by gravity settling, several researchers evaluated alternative precipitation processes. Kabil et al. [103] investigated an ion-flotation process using sodium oleate as a collector for magnesium. In the proposed process, calcium and magnesium oleate are first floated and collected, dissolved in an acetic–nitric acid and sodium sulfate solution, and refloated to collect magnesium oleate. Combustion of the magnesium oleate yields magnesia.

According to Shreve's Chemical Process Industries [224], the successful extraction of magnesium and magnesium compounds from seawater depends on:

- Means to soften the seawater cheaply using lime or calcined dolomite
- Preparation of a purified lime or calcined dolomite slurry of proper characteristics
- Economical removal of the precipitated hydroxide from the large volume of water
- Inexpensive purification of the hydrous precipitates
- Development of means to filter the slimes

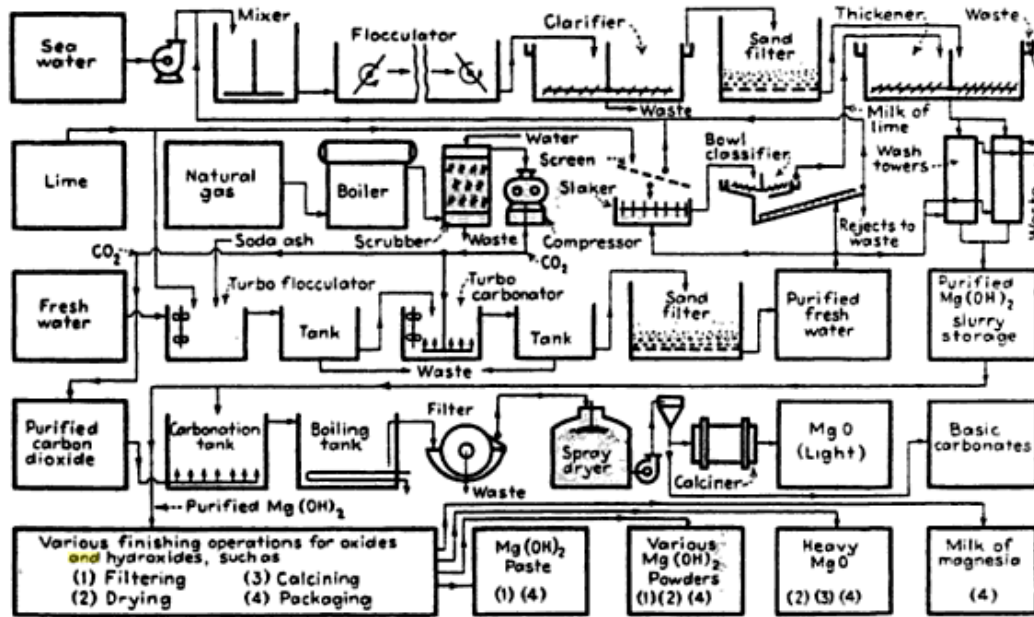
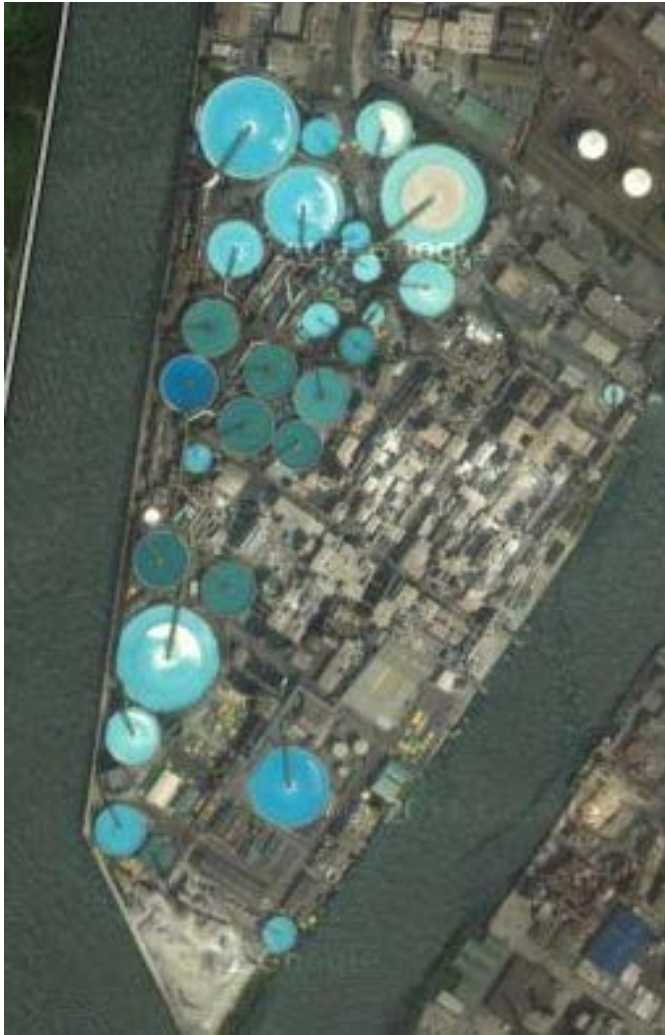


Figure 4.8. Schematic of Merck and Co.'s process for magnesium extraction from seawater.

Source: [224]





**Figure 4.10. Overhead view of Ube Material Industries' magnesium from seawater plant.**

Source: Google Maps

#### 4.1.7.2.3 Ion Exchange

In addition to thermal and precipitation processes, ion exchange has been evaluated as a method for selectively extracting magnesium from seawater. In the late 1940s, the Dow Chemical Company developed ion-exchange resin (Dowex 50 and Dowex 50W) specific for softening and demineralization [242, 243]. These resins were later included in a patented process for the recovery of magnesium from relatively dilute solutions such as seawater [21, 244]. The inventor, Bauman, proposed loading magnesium (by processing seawater) onto the resin, exchanging the magnesium using concentrated NaCl brine, extracting the magnesium using organic solvent extraction, and dissolving the magnesium into an aqueous solution [244].

Lindal [238] proposed a similar process in which precipitated  $\text{MgOH}_2$  and  $\text{CaCO}_3$  from seawater (using lime or dolime) would be dissolved in a carbonic acid solution to yield a pure solution of  $\text{Mg}(\text{HCO}_3)_2$ . The solution would be fed to ion exchange contactors to remove magnesium, yielding a concentrated solution of  $\text{NaHCO}_3$  that would be further processed to yield soda ash. The ion-exchange resin would be regenerated with a NaCl solution, yielding a

concentrated  $\text{MgCl}_2$  solution that would be further concentrated and sent to electrolytic cells for magnesium production. Because the proposed process would require several evaporation steps and a concentrated and pure  $\text{NaCl}$  solution, the author proposed co-siting the facility with a common salt production facility and a source of waste heat. Although it is unclear whether the process was actually evaluated, the author claimed that it would significantly reduce the costs associated with the production of magnesium. According to Muraviev et al. [192], however, the strong acid cationic exchange resins developed for magnesium extraction are not suitable for seawater applications because of low selectivity and capacity towards magnesium.

Researchers in Russia have evaluated weakly acidic (carboxylic) based ion-exchange resin for recovery of magnesium from seawater and reported greater selectivity and capacity towards magnesium [192, 245, 246]. In addition, the researchers demonstrated an interesting phenomenon termed ion-exchange isothermal supersaturation (IXSS) in which a metastable supersaturated solution of the target substance (e.g., amino acids, potassium, calcium, magnesium) develops in the interstitial space of an ion-exchange column during the elution procedure [192]. For magnesium, the supersaturated solution can be produced when a concentrated solution of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  is passed through an ion-exchange column with the  $\text{Mg}^{2+}$  form of the carboxylic ion-exchange resin. Exchange of  $\text{Mg}^{2+}$  by  $\text{Na}^+$  results in a supersaturated  $\text{MgCO}_3$  solution that spontaneously crystallizes to almost pure nesquegonaite ( $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ) once eluted [246]. The researchers evaluating IXSS for the extraction of magnesium claim that the process was once used at a full-scale seawater magnesium extraction facility (300 tpy) in Vladivostok, Russia (no information could be found indicating that the facility still exists) and has been considered for extracting magnesium from RO brine at a desalination facility in Russia [74, 192, 246].

#### 4.1.7.2.4 Other Processes

The remineralization of desalinated water has received attention because of difficulties and costs of stabilizing RO permeate at desalination facilities [247, 248]. Telzhensky et al. [249] recently proposed a process in which a small percentage of the seawater feed to an RO-based desalination system would be diverted to an NF system for selective recovery of a magnesium-enriched solution. The authors proposed that the reclaimed magnesium could be used to soften desalinated water or recover phosphorus as struvite from wastewater streams. Two NF membranes were evaluated for magnesium separation relative to sodium and chloride, and a cost comparison was performed to evaluate the use of NF brine to soften desalinated water compared to adding chemicals ( $\text{MgSO}_4$  and  $\text{MgCl}_2$ ). The proposed NF process was calculated to be significantly cheaper (at least two orders of magnitude) than adding chemicals for softening.

Somewhat similarly, Birnhack and Lahav [248] proposed an ion-exchange process for recovering magnesium and calcium from seawater upstream of the RO process at the Ashkelon desalination facility. Desalinated effluent would be post-treated using a sulfuric acid–calcite dissolution process and then passed through the loaded ion-exchange resin to achieve a desired magnesium–calcium ratio. Although the proposed process was estimated to be more expensive than the current process at Ashkelon for remineralization, recent regulations have mandated that the ratio of calcium to alkalinity not exceed 1:5, which has proven difficult using the current remineralization process. The proposed process would not only provide alkalinity in the form of magnesium but would use the facility’s fourth-stage brine to regenerate the ion-exchange resin.

**Table 4.16. Magnesium Overview**

<b>Main form(s) in water</b>	Mg <sup>2+</sup>
<b>Dominant commodities</b>	Magnesium metal, magnesium chloride, magnesia, magnesium hydroxide, magnesium sulfate
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>• Magnesium compounds were once primarily produced from seawater, but only magnesium hydroxide and magnesia are currently produced from seawater.</li> <li>• Magnesium metal is mainly produced from carnalite, and in 2011 the price was \$2.35/lb in the United States and \$3300/t in China.</li> <li>• Magnesium compound pricing is not disclosed by the USGS; 2006 prices are summarized in Table 4.14.</li> <li>• Magnesium chloride is used heavily for road de-icing and dust suppression.</li> <li>• Magnesium hydroxide is a precursor to caustic-calcined magnesia and used by industries including agriculture, air pollution control, and water and wastewater treatment.</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>• Production of magnesium metal from seawater is not competitive with current methods of production.</li> <li>• Demand for caustic-calcined magnesia and magnesium is expected to increase in the near future; however, the United States currently imports the majority of consumed magnesia.</li> </ul>
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>• Magnesium hydroxide is precipitated from seawater through a series of steps using lime or dolime and sodium hydroxide. Production of concentrated magnesium hydroxide requires calcium removal and a final filtration step.</li> <li>• Production of magnesia requires calcining in high temperature furnaces.</li> <li>• Researchers have proposed or developed a variety of methods to extract magnesium, including ion exchange and membrane crystallization.</li> </ul>
<b>Conclusions from literature review</b>	The extraction of magnesium from seawater for production of magnesium hydroxide and magnesia is technically and economically feasible..

*Note:* USGS=United States Geological Survey.



**Table 4.17. Summary of Patents Related to Lithium Extraction**

<b>Decade</b>	<b>Number of Patents</b>	<b>U.S. Patent #</b>
prior to 1950	6	2,226,592; 2,342,666; 2,405,055; 2,404,550; 2,433,458; 2,466,675
1950–1959	4	2,934,419; 2,703,748; 553,268; 2,793,099
1960–1969	7	3,119,752; 3,218,241; 3,262,865; 3,231,340; 3,262,877; 3,350,292; 3,463,814
1970–1979	14	3,514,266; 3,627,479; 3,627,679; 3,574,077; 3,615,181; 3,639,231; 3,676,067; 3,725,267; 3,976,569; 4,024,054; 4,036,749; 4,059,513; 4,116,857; 4,180,547
1980–1989	6	4,188,291; 2,298,577; 4,336,232; 4,521,386; 3,374,081; 4,634,533
1990–1999	4	4,973,201; 4,956,157; 5,124,012; 5,814,224
2000–present	20	6,267,854; US 6,372,143 B1; US 2003/0080066; US 2006/0105082; 7,083,730; 7,198,725; US 7,621,968 B2; 7,595,001 B2; 7,771,684 B2; 7,754,159 B2; 7,829,053 B2; 7,815,880 B2; 7,753,618 B2; US 2010/0282675; 7,993,511 B2; 7,887,694; 7,963,338 B1; 8,012,358 B2; 8,021,442; 8,197,664

## 4.1.8 Molybdenum

### 4.1.8.1 Molybdenum Commodity Summary

Molybdenum is primarily produced in the United States at four mines and recovered as a byproduct of copper mining at eight additional mines [249]. The USGS estimates the price of molybdenum was \$29/kg in 2012, down from \$63/kg in 2008 [249]. Molybdenum is mainly used in the iron and steel industry and for production of superalloys, and its consumption is strongly tied to the economy.

### 4.1.8.2 Molybdenum Extraction Summary

Molybdenum is a minor component of seawater and found at an average concentration of 9.6 µg/L [22]. Molybdenum can be extracted from aqueous solutions through sorption (e.g., sorption and flotation), complexation, and ion-exchange processes [21]. Most of the literature on molybdenum extraction concerns the development of methods of concentration for analytical chemistry or processes for heavy metal removal [251–253]. Little information exists on the potential for the extraction of molybdenum from SWRO brine, and given the relatively low concentration of molybdenum it is highly unlikely that production from SWRO would be competitive with land-based production.

**Table 4.18. Molybdenum Overview**

<b>Main form(s) in water</b>	MoO <sub>4</sub> <sup>2-</sup>
<b>Dominant commodities</b>	Molybdic oxide, MoX, ferromolybdenum
<b>Commodity summary</b>	<ul style="list-style-type: none"><li>• Molybdenum ore is mined as a primary product and byproduct from copper mining [254].</li><li>• It is used as an alloying agent in cast iron and steel [83].</li><li>• Prices ranged from \$14.50–\$17.58/lb for MoX and \$17–\$21.69/lb for FeMo [83].</li></ul>
<b>Market opportunities</b>	Demand for molybdenum has increased significantly since 2008.
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"><li>• Sorption and precipitation have been studied for the removal of molybdenum from uranium mine tailings [255].</li><li>• Most studies of molybdenum in seawater are concerned with measuring its concentration, not large-scale extraction.</li></ul>
<b>Conclusions from literature review</b>	The extraction of molybdenum from seawater has not been studied in depth, and because of its low concentration extraction is unlikely to be feasible.

## **4.1.9 Nitrogen**

### **4.1.9.1 Nitrogen Commodity Summary**

The vast majority of nitrogen-containing chemicals are produced from fixed ammonia, with 87% used in the United States as fertilizers, including ammonia for direct application, urea, ammonium nitrate, ammonium phosphates, nitric acid, and ammonium sulfate [256]. According to the USGS, ammonia was produced by 13 companies at 25 nitrogen fixing facilities in the United States in 2012 [256]. The current USGS-reported price for fixed ammonia is \$575/ton, which is significantly higher than in 2009 (\$251/ton). There has been significant recent interest in the recovery of nitrogen from wastewater streams, particularly in the form of struvite, which can be used as a slow release fertilizer. Recovery of struvite from waste streams with relatively low phosphorus (e.g., RO brine or concentrate) may require ammonia addition for precipitation. More information on struvite recovery can be found in Section 4.1.11.

### **4.1.9.2 Nitrogen Extraction Summary**

Besides the recovery of ammonia–nitrogen through struvite production, the extraction of ammonia from wastewater effluent or RO concentrate for economic gain has received limited attention. Physical–chemical processes for the removal of ammonia from wastewater streams include air stripping, electrodialysis, ion exchange, and precipitation. Various ion-exchange materials have been developed or evaluated for ammonia uptake, and significant research has been performed on the use of natural and synthetic zeolites (e.g., clinoptilolite) as sorbent materials based on their capacity and affinity for ammonium ions and low cost [257–259]. Packed tower air strippers are effective for ammonia removal; however, efficient ammonia removal requires pH adjustment above its  $pK_a$  (around 9.25) and therefore potentially significant additions of base. Both ion exchange and air stripping could potentially be used to recover ammonium sulfate as a salable product; however, the cost of nitrogen extraction by both processes is approximately six times higher than the current price of ammonium sulfate (\$451/ton) [260, 261]. Seawater or brackish waters typically have low concentrations of inorganic, nitrogen; however, RO concentrate from water reuse applications can have inorganic nitrogen concentrations greater than 40 mg N/L.

**Table 4.19. Nitrogen Overview**

<b>Dominant commodities</b>	Ammonia, urea, ammonium nitrate, ammonium phosphates, ammonium sulfate, nitric acid
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>• The vast majority of commercialized ammonia is fixed from the atmosphere and used as or to make fertilizer.</li> <li>• In 2012, the fixed ammonia price was \$575/ton.</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>• World nitrogen consumption for fertilizer is expected to increase [256].</li> <li>• Stable natural gas prices are causing nitrogen fixing production to expand.</li> </ul>
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>• Air stripping, ED, and ion exchange can be used to extract and recover ammonia.</li> <li>• Ammonia can be precipitated as struvite when ortho-phosphate concentrations are relatively high.</li> </ul>
<b>Conclusions from literature review</b>	Inorganic nitrogen is typically present in RO brine or concentrate at fairly low concentrations.

Notes: ED=electrodialysis; RO=reverse osmosis.

## 4.1.10 Phosphorus

### 4.1.10.1 Phosphorus Commodity Summary

Phosphorus commodity information is reported for phosphate rock by the USGS and as fertilizer by the U.S. Department of Agriculture. In 2012, prices reported for phosphate fertilizers were \$665/ton for super-phosphate (44–46% phosphate) and \$726/ton as diammonium phosphate. Several companies produce struvite from various waste streams to be sold as fertilizer, and, although up-to-date struvite price information is unavailable, several researchers have reported prices around \$350/ton.

The demand for traditional and unconventional sources of phosphorus is expected to increase in the near future because of population growth and increased fertilizer use in food and biofuel production [262, 263]. World consumption of phosphorus (as  $P_2O_5$ ) was estimated to be 41.9 million tons in 2012, and projected consumption is expected to be 45.3 million tons by 2016 [264]. The USGS reported significant expansion of mine-based phosphorus production in Africa, Australia, Brazil, Canada, China, New Zealand, and the United States [264].

### 4.1.10.2 Phosphorous Extraction Summary

Inorganic phosphorus concentrations in seawater are typically very low, with the exception of areas with significant anthropogenic inputs. As a result, phosphorus extraction from SWRO brine is unlikely to be feasible. Several researchers, however, have evaluated phosphorus (as ortho-phosphate) extraction from the concentrate of RO systems used for potable wastewater reuse applications. Therefore, the prospect of phosphate extraction from RO concentrate is potentially more economically feasible for wastewater reuse schemes, although little effort has been put toward this objective.

Past investigations into the extraction and recovery of phosphate have mainly focused on the use of natural and synthetic ion-exchange resins or hybrid adsorption processes. Well-studied sorbent materials for phosphate removal include commercial anion exchange resins, activated alumina, and zirconium oxide [265]. According to Zhao and SenGupta [265], such sorbents are inefficient because of poor selectivity towards phosphate, low capacity, inefficient regeneration, and gradual loss of effectiveness. More recently, polymeric ligand exchange (PLE) resins have been developed through the immobilization of transition metal cations (specifically iron or copper) onto chelating resin containing nitrogen donor atoms [265, 266]. Phosphate ions (as  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  at near-neutral pH) are retained within the resin through inner-sphere ligand reactions with the immobilized metal ions. The relatively strong affinity of phosphate for metal cations (binding constants  $[\log K]$  for phosphate, copper (II), and iron (III) are  $>16.5$ ), phosphate-specific PLE resins have high selectivity towards phosphate in the presence of other anions.

Recovery of phosphorus in the form of struvite from wastewater has been investigated for several decades, as it can serve as an effective slow-release fertilizer. For wastewater streams with low phosphate concentrations, several researchers have utilized fixed-bed sorption processes to remove the phosphate, followed by regeneration and subsequent precipitation of struvite from the regenerant solution [265, 267, 268]. Precipitation of struvite from the regenerant solution typically requires the addition of magnesium and ammonia; however, the solution volume is much smaller than that of the wastewater treated, and the solution can be reused once struvite is precipitated.

Kumar et al. [269] investigated phosphate-selective PLE resins for the extraction of phosphate from the concentrate of an RO system operating on MF wastewater effluent. Once the selective ligand exchange resins (Dow PhosX and copper [II] loaded Dow 3N, Dow Chemical Company, Midland, TX) were exhausted with respect to phosphate, they were regenerated with a sodium chloride solution from which struvite was precipitated by adding ammonium and magnesium chloride (molar ratio of  $\text{P}:\text{Mg}:\text{NH}_4$  was 1:1.5:1). The process was evaluated using concentrate samples with phosphate concentrations of 10 to 20 mg P/L and found feasible for both removing phosphate from RO concentrate with relatively high TDS and producing struvite. Based on a struvite price of \$350/ton and a concentrate stream with a flow rate of 2 mgd and phosphate concentration of 10 mg P/L, the authors claim that 200 tpy of struvite worth \$70,000 could be produced. Estimates of the capital and operating costs of the extraction process were not disclosed.

**Table 4.20. Phosphorus Overview**

<b>Main form(s) in water</b>	Phosphates
<b>Dominant commodities</b>	Phosphates and salts thereof, struvite, P <sub>2</sub> O <sub>5</sub> (used in fertilizer)
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>• 95% of the phosphate rock mined in the United States is used in fertilizers and animal feed supplements [270].</li> <li>• Phosphate rock for fertilizer production had an average value of \$78.50/metric ton in 2010 [271].</li> <li>• The average U.S. farm price for super-phosphate 44–46% phosphate fertilizer was \$665/ton in 2012 [261].</li> <li>• Struvite reportedly sells for \$100–\$400/ton depending on product purity.</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>• World phosphorus consumption for fertilizer is expected to increase [269].</li> <li>• Mined phosphorus may become insufficient for fertilizer needs in the United States in the coming decades [263].</li> </ul>
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>• Adsorption to PLE resin followed by precipitation as struvite [269]</li> <li>• Precipitation as aluminum phosphate, iron phosphate, calcium phosphate, or magnesium phosphate, followed by acid attack to produce phosphoric acid [157, 272]. Phosphorus recovered through metal salt precipitation is unrecoverable for use as fertilizer [272].</li> <li>• Up to 80% of available phosphorus can be economically recovered as struvite from municipal wastewater streams [272].</li> </ul>
<b>Conclusions from literature review</b>	Although it is technically feasible to extract phosphate from RO concentrate, the economics of doing so have not often been studied. Kumar [269] calculated that 200 tpy of struvite or other phosphorus precipitates could be produced from a 2 mgd RO concentrate stream with approximately 10 mg P/L. Assuming a struvite price of \$350/ton, the plant could gain \$70,000/year. The extraction cost of the struvite was not included in these calculations [269].

## 4.1.11 Potassium

### 4.1.11.1 Potassium Commodity Summary

Potassium commodities include a variety of different compounds, with the most significant commodity being potash in the form of either potassium chloride (muriate of potash), potassium sulfate (sulfate of potash), or potassium magnesium sulfate. Various downstream potassium compounds are produced from potash, with the most common including potassium nitrate, potassium phosphate, potassium carbonate, potassium hydroxide, and potassium thiosulfate.

According to the USGS, 37,000 metric ktons of potash were produced worldwide in 2011; the United States produced approximately 1100 metric ktons [273]. In 2011, the USGS estimated an average potassium chloride price of \$700/metric ton, which is significantly higher than 2010 values (\$605/metric ton). Of the potash produced in the United States, approximately 85% is used as fertilizer, and the remainder is used in the chemical industry. U.S. potash is produced through mining operations by various companies in Michigan, New Mexico, and Utah. Most potash operations employ conventional shaft or deep well solution

mining to produce potassium, both of which require various post-treatment processes for purification. Worldwide potash consumption is expected to increase annually by approximately 4% from population growth and increased demand for fertilizers. Known worldwide potash reserves are estimated at approximately 9.5 billion metric tons, with resources estimated at 250 billion metric tons.

#### ***4.1.11.2 Potassium Extraction Summary***

Potassium is the sixth most abundant mineral in seawater and found at a concentration of approximately 0.4‰ [22]. Potassium compounds are currently produced from seawater; however, they are generally a byproduct from solar salt operations, which makes up a very small percentage of worldwide potassium compound production. The potassium concentration in seawater is not sufficient for conventional potash production methods that use concentrated brine and sea biterms as potassium feed stock. Instead, solar salt production relies on multiple solar evaporation–precipitation steps to first precipitate out sodium and calcium and significantly concentrate the solution prior to a precipitation step to yield carnalite, which is further refined to potash.

As an alternative to solar evaporation and precipitation, several researchers have suggested that potassium could be produced from RO concentrate using an evaporation–crystallization process [134, 156, 232]. Although no physical evaluations were conducted, Mohammadesmaeili et al. [134] performed thermodynamic phase equilibrium calculations to determine the evaporation requirements to produce potassium compounds from secondary RO concentrate. After an evaporation–crystallization step to produce sodium chloride (concentration factor of approximately ten), glaserite could theoretically be produced through an additional evaporation–crystallization step by reducing the volume by 93%. The researchers indicate that a 25% glaserite/75% halite product would be produced but cautioned that evaporation experiments should be performed to verify the path used in the calculations.

According to Khamizov et al. [274], the United States, China, and Japan have attempted to develop technologies to recover potassium from seawater for fertilizers. Potassium extraction was evaluated using natural zeolite (clinoptilolites) ion-exchange resins with high capacity for potassium through a two-step, dual-temperature process. In the first step, cold seawater (<25° C) is loaded onto clinoptilolite until the resin is exhausted. In the desorption step, hot seawater (~75° C) is passed through the loaded clinoptilolite, which desorbs potassium and removes calcium and strontium. The eluent is cooled (through heat exchangers to recover the heat for a subsequent desorption step) and subsequently passed through an additional clinoptilolite column to further concentrate potassium and other microelements essential as nutrients. The loaded clinoptilolite is removed and used as a chlorine-free fertilizer. Reported advantages to this process include low costs of clinoptilolite (\$70–\$200/metric ton), simplicity of the ion-exchange process, and effectiveness of the product as a fertilizer. According to Khamizov et al. [274], a variant of this process is being pilot tested through a collaboration with the Vernadsky Institute (Moscow, Russia) and King Abdul University (Jeddah, Saudi Arabia).

**Table 4.21. Potassium Overview**

<b>Main form(s) in water</b>	K <sup>+</sup>
<b>Dominant commodities</b>	The major potassium commodity is potash, which can be in the form of either potassium chloride (MOP), potassium sulfate (sulfate of potash), or potassium magnesium sulfate [273]. A number of potassium compounds are produced from potash, including potassium nitrate, potassium phosphate, potassium carbonate, potassium hydroxide, and potassium thiosulfate.
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>• In 2011, the USGS estimated an average MOP price of \$700/metric ton, which is significantly higher than 2010 values (\$605/metric ton).</li> <li>• Approximately 85% of potash used in the United States is for fertilizer; the remainder is used in the chemical industry.</li> <li>• In the United States, potash is produced through mining operations in Michigan, New Mexico, and Utah.</li> <li>• Worldwide potash reserves are estimated at approximately 9.5 billion metric tons, with resources estimated at 250 billion metric tons.</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>• Potash consumption is expected to increase annually by approximately 4% from population growth and increased demand for fertilizers.</li> <li>• Potassium as a fertilizer has no substitutes.</li> </ul>
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>• Potassium compounds are produced as a byproduct of solar salt operations, although this represents a relatively small production method.</li> <li>• Methods to extract potassium directly from seawater have focused on ion-exchange resins and precipitation processes using insoluble potassium ligands [275, 276].</li> <li>• An approach that is reportedly being evaluated at pilot scale uses cheap, natural zeolites as a potassium adsorber during a dual-temperature ion-exchange process [274]. The zeolites can be used directly as a fertilizer.</li> </ul>
<b>Conclusions from literature review</b>	Extraction of potassium from seawater through methods other than those used at solar salt works has received limited attention. Natural zeolites are reportedly good materials for adsorption of potassium and are being investigated as a means to produce fertilizer. Evaporation and crystallization of RO brine has been proposed as a method to potentially produce potassium compounds, although it has not yet been tested [134].

*Notes:* MOP=muriate of potash; RO=reverse osmosis; USGS=United States Geological Survey,



**Table 4.22. Summary of Patents Related to Potassium Extraction**

Decade	Number of Patents	U.S. Patent #
prior to 1950	1	2,404,550
1950–1959	0	
1960–1969	6	3,231,340; 3,279,897; 3,359,076; 3,382,034; 3,437,451; 3,437,451; 3,468,959
1970–1979	3	3,497,314; 4,024,054; 4,180,547
1980–1989	2	4,313,844; 4,663,052
1990–1999	3	4,956,157; 5,066,404; 5,124,012
2000–present	7	US 6,372,143 B1; US 2003/0080066; 7,014,832; 7,198,724; US 7,621,968 B2; US 7,789,159; 8,197,664

## **4.1.12 Rubidium**

### **4.1.12.1 Rubidium Commodity Summary**

Rubidium and rubidium compounds are used in the chemical, electronic, and biomedical industries. Reported uses for rubidium include pharmaceuticals for treatment of epilepsy, rubidium-82 as a blood flow tracer, an atomic resonance frequency standard in atomic clocks and global positioning systems, in glass making, and in ceramic applications for spark plugs and electrical insulators [277]. In addition to rubidium metal, major rubidium compounds used in various applications include rubidium carbonate, rubidium chloride, rubidium hydroxide, and rubidium silver iodide.

Rubidium was once mined in small quantities in the United States; however, it is currently 100% reliant on rubidium imported from Canada, the world's leading producer [277, 278]. Although information is not readily available, the USGS estimates that U.S. rubidium consumption is on the order of a few thousand kg per year. Because rubidium is not traded, USGS pricing information is for rubidium sold by individual companies, which in 2012 was around \$72\$/g Rb and \$1321/100g Rb [277]. These prices represent a 2 to 3% increase from 2011. Past USGS rubidium commodity summaries stated that there was likely to be no new rubidium markets in the near future; however, the USGS recently indicated that there is increased interest in the use of rubidium for quantum computing, in atomic clocks and superconductors, and for biomedical uses [277].

Rubidium has historically been available as a byproduct of lithium production from pegmatite ores and can be found in several minerals such as lepidolite and pollucite. Canada produces the world's supply of rubidium from pegmatite ores enriched in lepidolite, which is

composed of approximately 3.5% rubidium oxide. Rubidium operations in Canada produce and supply a concentrated rubidium solution from which various rubidium compounds or rubidium metal are produced through further processing steps. High purity rubidium commodities are reportedly difficult to produce, as rubidium is found together with cesium and other alkali metals (e.g., potassium) that must be removed prior to rubidium commodity production. Intermediate rubidium-bearing solutions prepared through ore processing are reportedly around 23% rubidium and 3% cesium carbonate, with the remainder as potassium carbonate [279]. Rubidium producers employ ion-exchange or complexation methods to extract rubidium from these intermediate solutions to achieve a concentrated rubidium solution free of other alkali metals [279].

According to the USGS, world resources of rubidium are unknown; however, rubidium-bearing pegmatites occur in Afghanistan, Namibia, Peru, Russia, and Zambia. Other potential sources of rubidium include brines in Chile and China and evaporites in France, Germany, and the United States [280]. In 2005, the USGS reported that the supplies of rubidium-bearing ores were adequate to meet use patterns [280].

#### **4.1.12.2 Rubidium Extraction Summary**

Rubidium is a minor component in seawater and present at a concentration of approximately 120 µg/L [22]. Because of the relatively high price of rubidium, several researchers have indicated that extraction from seawater is economically viable [156, 157, 186, 281]. Rubidium is not traded in the United States, so commodity information is scarce, making it difficult to determine the feasibility of extracting rubidium from RO brine. In addition, research into technologies for extraction of rubidium from seawater and brine appears to be in its infancy compared with other metals (e.g., lithium, magnesium, uranium), and literature on the extraction of rubidium is scarce.

Several recent articles have suggested that the extraction of rubidium from RO brine could significantly improve the economics of desalination. Le Dirach et al. [156] reported that the value of rubidium extracted from the concentrate stream of a desalination plant in Tunisia producing 168,000 m<sup>3</sup>/d of potable water would be \$1.3 billion!

The authors proposed using an alkali metal-selective, cationic, ion-exchange resin (titanium silicate-based) to extract rubidium, followed by two elution steps with hydrochloric acid and a concentrated sodium chloride solution. Because the specified ion-exchange resin is only moderately selective to rubidium compared to cesium and potassium, and given the fact that all three metals have similar properties, a further purification method is needed to isolate the rubidium. The authors proposed using a crown ether carrier-liquid membrane system that is highly selective for potassium transport as a means to purify the ion-exchange eluate. Jeppesen et al. [156] further evaluated the process proposed by Le Dirach et al. [157] and proposed using phenol-formaldehyde ion-exchange resin for rubidium extraction and a liquid-liquid extraction technique using benzylphenols for rubidium purification. To improve the economics of extraction, both authors recommended implementing a thermal evaporation process to concentrate the RO brine prior to ion exchange. Jeppesen et al. [156] claimed that a desalination facility with an intake of 100,000 m<sup>3</sup>/d could generate \$56,000/day through rubidium extraction.

Of the peer-reviewed publications proposing rubidium extraction from RO brine, only one appears to have physically evaluated the efficiency of ion-exchange resins for rubidium uptake. Gilbert et al. [158] evaluated a commercially available hexacyanoferrate cation

exchange resin (CsTreat, Fortum Engineering Ltd.) for the uptake of rubidium from a seawater RO brine spiked with 20 mg/L rubidium and reported an adsorptive capacity of 238 mg Rb/g adsorbent. Although results were promising, the researchers reported that future work was needed to identify efficient elution methods (rubidium can bind strongly to ion-exchange resins, making recovery difficult) and evaluate rubidium uptake from natural RO brine. Alternative ion-exchange resins that have been studied for rubidium extraction, although not evaluated for rubidium uptake from seawater or RO brine, include phosphorylated calixarenes [206], mesoporous aluminosilicates [282], mesoporous zirconium silicates [250], and ammonium molybdophosphate-calcium alginate [283].

There are a number of apparent challenges associated with the extraction of rubidium from RO brine at a desalination facility for economic gain. Very little work has been conducted to develop adsorbent materials specifically for rubidium uptake, and those that have been developed have not been evaluated with a seawater matrix. Adsorbents and ion-exchange resins that have shown promise for rubidium uptake also tend to have moderate adsorption capacities for other alkali metals such as cesium, lithium, and potassium. Preparation of commodity-grade rubidium requires the removal of other metals which has proven difficult and requires additional technologies, including methods for isolating rubidium and concentrating the final solution (e.g., distillation). Finally, rubidium is not a traded commodity. Even though the price of rubidium is relatively high, there is little current demand. Demand may increase in the future, but it may be difficult to find purchasers for rubidium produced at a desalination facility.

**Table 4.23. Rubidium Overview**

<b>Main form(s) in water</b>	Rb <sup>+</sup>
<b>Dominant commodities</b>	Rubidium chloride, rubidium hydroxide, rubidium carbonate, rubidium oxides
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>• Not traded; USGS estimates pricing for 2012 as \$72/g Rb and \$1321/100g Rb, a 2–3% increase from 2011 [277]</li> <li>• Traditionally obtained as a byproduct of Li production from pegmatite ores</li> <li>• Canada produces sufficient Rb to meet current demand, although other sources are known.</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>• Possible increased interest in rubidium for quantum computing, atomic clocks and superconductors, and biomedical uses</li> <li>• Even though prices are high, there is little demand.</li> </ul>
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>• Rb extraction through ion exchange has been shown to be on the same order of magnitude as the potential income of the process [156].</li> <li>• Adsorbents and ion-exchange resins with an affinity for Rb also tend to absorb other alkaline metals, and purification of the final product is difficult.</li> </ul>
<b>Conclusions from literature review</b>	Detailed study of the costs of extraction has not been undertaken, but extraction itself, although complicated, is technically feasible. Rubidium is not a traded commodity, and there is relatively little worldwide demand.

**Table 4.24. Summary of Patents Related to Rubidium Extraction**

<b>Decade</b>	<b>Number of Patents</b>	<b>U.S. Patent #</b>
prior to 1950	0	
1950–1959	0	
1960–1969	3	3,305,321; 3,382,034; 3,468,959
1970–1979	2	3,522,187; 3,510,257
1980–1989	2	4,313,844; 4,663,052
1990–1999	0	
2000–present	0	

### **4.1.13 Sodium**

#### ***4.1.13.1 Sodium Commodity Summary***

Sodium is consumed as a number of different compounds and in a variety of end uses. Sodium chloride is by far the most consumed commodity, with approximately 49 million tons (valued at >\$1.6 billion) consumed in the United States annually [284]. Pricing for sodium chloride is dependent upon the production method and final product quality; in 2013, the USGS reported that the major commodities were vacuum and open pan salt (\$175/ton), solar salt (\$50/ton), rock salt (\$36/ton), and brine salt (\$8/ton) [284]. Rock salt consumption for highway de-icing accounts for approximately 41% of the sodium chloride consumed annually in the United States, followed closely by salt in brine (39%) for use in the chemical industry (to make sodium chloride and chlorine). Global sodium chloride resources are considered inexhaustible because of the oceans, and the USGS reports that almost every country in the world has salt deposits or solar evaporation operations.

Soda ash, or sodium carbonate, is used in a variety of industries and products, and approximately 5 million tons is consumed in the United States annually (valued at ~\$1.6 billion) primarily by the chemical and glass industry [285]. As of 2012, only five companies (four in Wyoming and one in California) produced soda ash in the United States, and the price has been relatively constant at approximately \$280/ton over the past 5 years, although it is expected to increase in the near future [285]. Soda ash was once exclusively produced through the Solvay process using sodium chloride, carbon dioxide (from calcium carbonate), and ammonia; however, it is now primarily produced from the evaporate mineral trona and sodium carbonate-rich brines because of the relatively high costs of the Solvay process [285]. Global soda ash production and consumption are expected to increase over the next several years.

Sodium sulfate is primarily used in soaps and detergents and by the glass, pulp, and paper industries. As of 2012, only two companies in the United States produced sodium sulfate; currently, China supplies 75% of global consumption [286]. Pricing for sodium sulfate was reported by the USGS at \$210/ton in 2013 [286]. It is mainly produced from mirabilite deposits and concentrated brines but can be produced synthetically from sodium chloride and sulfuric acid.

#### ***4.1.13.2 Sodium Extraction Summary***

Commercially available sodium chloride is primarily produced from solar salt operations (evaporation ponds), underground mining operations, or through evaporation using concentrated brine obtained through solution mining [287]. A number of researchers have proposed producing sodium chloride from desalination facility concentrate or brine, although in most cases salt production was never evaluated on an appreciable scale. Compared to conventional methods, several alternative treatment schemes and technologies have been proposed or evaluated, including evaporation technologies [235], evaporation followed by crystallization [288, 289], membrane crystallization [101, 153], ED/EDR followed by evaporation [58, 288], and evaporation ponds [71, 237].

Abdel-aal et al. [235] performed a simulation to determine the MSF system and operational requirements for producing sodium chloride and a highly concentrated sodium chloride and

magnesium chloride solution from desalination brine. The authors determined that recovering sodium chloride from seawater desalination brine required concentration using 20 MSF stages followed by cooling for crystallization and a separation step. Although such an approach would produce extra water, it is unlikely to be feasible because of high costs and scaling issues.

MCr has been investigated for sodium chloride production, and Drioli et al. [153] reportedly produced relatively pure salt crystals from a synthetic NF concentrate solution containing calcium and magnesium. MCr is a technology that is currently in the developmental stages; however, the advantages reportedly include operation at low temperatures and capability of manipulating system conditions to selectively crystallize salts from multicomponent solutions [65].

The absence of appreciable halite deposits and available land and unfavorable conditions for evaporation ponds have led Japan to commercial production of salt from seawater by employing ED for ion separation followed by evaporation using MED or vacuum pan evaporators. Reportedly, ED or EDR is used to concentrate sodium chloride in seawater up to 200 g/L prior to evaporation and crystallization using MED [287]. Tanaka et al. [58] conducted a simulation on the ED/MED process for salt production and concluded that using SWRO desalination brine would reduce energy requirements 80% compared with using seawater. Davis [62] recently proposed a similar process for ZLD systems and has developed the EDM system, which the author claims could be integrated with evaporation to yield sodium chloride. Unfortunately, no information could be acquired to demonstrate that EDM could be an effective method for the precipitation of sodium chloride.

According to several sources, the SAL-PROC process (Geo-Processors) can be used to produce sodium chloride as well as calcium sulfate, calcium chloride, and magnesium hydroxide from concentrated solutions including brackish water and seawater desalination brine [5, 11, 13, 236, 237]. According to the literature, SAL-PROC utilizes multiple evaporation and chemical conditioning steps; however, information regarding the specific processes utilized and results of demonstration testing for production of salable salts were not obtained.

Literature available on the production of sodium carbonate and sodium sulfate from desalination brines was not readily available. Both compounds can be produced from concentrated sodium chloride solutions; however, these methods are not commonly used, and production from highly concentrated brines and mined minerals are more common. Generally, discussions on the recovery of carbonate and sulfate solids are in reference to calcium carbonate and magnesium or calcium sulfate, respectively.

**Table 4.25. Sodium Overview**

<b>Sodium</b>	
<b>Main form(s) in water</b>	Na <sup>+</sup>
<b>Dominant commodities</b>	Sodium chloride, sodium sulfate, sodium hydroxide (caustic soda—see Section 4.1.5), sodium carbonate (soda ash), sodium bicarbonate
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>Commercial-grade sodium chloride pricing is dependent upon purity and production method. In 2012, it was \$175/ton for vacuum pan and open pan NaCl, \$50/ton for solar salt, and \$8/ton for salt in brine.</li> <li>Sodium sulfate is only produced by two U.S. companies and priced at \$210/ton.</li> <li>Sodium carbonate is now almost completely produced through mining operations and in 2012 was worth \$280/ton.</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>Sodium compounds are consumed in large quantities by a variety of end users and industries, and demand is relatively stable.</li> <li>It is likely that many local markets exist for sodium compounds regardless of manufacturing location.</li> </ul>
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>Solid sodium chloride is produced through the evaporation of seawater and brines. A number of researchers have proposed producing sodium chloride from desalination brine using thermal processes or ED/EDR followed by thermal processes. The latter production method is used in Japan to produce food-grade salt.</li> <li>One desalination facility in Israel reportedly produces food-grade salt from SWRO brine in evaporation ponds [71].</li> <li>Sodium sulfate and sodium carbonate can be produced from concentrated sodium chloride solutions using several chemical processes; however, these methods have been phased out.</li> </ul>
<b>Conclusions from literature review</b>	Several publications have indicated that food-grade sodium chloride could be economically produced from desalination brine using either evaporation ponds or ED/EDR followed by a thermal evaporation process.

*Notes:* ED/EDR=electrodialysis/electrodialysis reversal; SWRO=seawater reverse osmosis.

**Table 4.26. Summary of Patents Related to Sodium Extraction**

Decade	Number of Patents	U.S. Patent #
prior to 1950	1	1,435,524
1950–1959	2	2,606,870; 2,793,099
1960–1969	6	3,147,072; 3,220,941; 3,279,897; 3,359,076; 3,382,034; 3,463,814
1970–1979	2	3,676,067; 4,180,547
1980–1989	2	4,392,959; 4,755,303
1990–1999	5	5,066,404; 5,124,012; 5,221,528; 5,468,394; 5,587,088
2000–present	6	US 6,372,143 B1; 6,692,720; US 7,501,065 B1; 7,595,001 B2; US 2010/0282675; 8,197,664

#### 4.1.14 Strontium

##### 4.1.14.1 Strontium Commodity Summary

Strontium mining in the United States ceased in 1959, and the current dominant producers include China, Spain, and Mexico. Major strontium commodities include strontium metal, celestite, strontium oxide (strontia), strontium hydroxide, strontium peroxide, strontium nitrate, and strontium carbonate, which is the principal strontium compound. Most compounds are produced from celestite, which is the most abundant form of strontium in the Earth's crust. Strontium compounds are used in a number of different chemical products, including pyrotechnics, magnets, alloys, pigments and fillers in ceramics and glasses, and in the production of zinc.

According to the USGS, strontium compound consumption is expected to increase in the near future, both in traditional applications (e.g., ceramics, glasses, and magnets) and more advanced applications (e.g., pharmaceuticals). The average price of strontium mineral imports has decreased over the past 4 years and is currently around \$46/metric ton. In 2010, the USGS put the average value of imported strontium carbonate at \$0.71/kg, strontium metal at \$5.80/kg, strontium nitrate at \$1.33/kg, and celestite at around \$95/metric ton.

##### 4.1.14.2 Strontium Extraction Summary

Strontium is the fifth most abundant metal in seawater, found at a concentration of approximately 0.0079‰. Because of strontium's value, its extraction from seawater has garnered attention from researchers, although commercial seawater extraction does not currently exist. The major processes identified for strontium extraction include ion-exchange resins and liquid membrane technologies. Chemical softening has also proven to be effective



for strontium removal; however, it is likely not effective because of the high purity needed to produce salable strontium compounds.

Different liquid membrane configurations have been evaluated for the extraction of metal ions from aqueous solutions. Jeong and Ju [290] developed a liquid membrane technique using microporous hollow-fiber polyethylene films and evaluated extractants for strontium uptake that included various types of crown ethers. One extractant formulation, D<sub>2</sub>EHPA and DCH18C6 in kerosene, was able to extract approximately 80% of strontium from seawater in approximately 120 hours when the liquid membrane system was operated in batch mode. Operated in continuous mode, the flux of strontium was found to increase with increasing feed water, strontium concentration, temperature, and pH.

Khamizov et al. [74] conducted a review of ion-exchange technologies for strontium uptake from aqueous solutions. Certain mesoporous aluminosilicates have been shown to be promising for the uptake of strontium [282].

**Table 4.27. Strontium Overview**

<b>Strontium</b>	
<b>Main form(s) in water</b>	Sr <sup>2+</sup>
<b>Dominant commodities</b>	Strontium metal, strontium carbonate (dominant commodity), strontium nitrate, strontium oxide (strontia), strontium hydroxide, strontium peroxide, celestite, or strontium sulfate
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>• Strontium is not currently mined in the United States; dominant producers include China, Spain, and Mexico. Strontium compounds are mostly produced from mined celestite, which is the most abundant strontium-containing mineral in the Earth's crust [291].</li> <li>• Strontium compounds are used in various end products including pyrotechnics, magnets, alloys, pigments and fillers in ceramics and glasses, and in the production of zinc [291].</li> <li>• According to USGS, the 2012 mineral price was \$46/metric ton [291].</li> <li>• In 2010, the average price of imported strontium carbonate was \$0.71/kg, strontium metal was \$5.80/kg, strontium nitrate was \$1.33/kg, and celestite was \$95/metric ton [292].</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>• Worldwide strontium demand has decreased significantly since 1997.</li> <li>• Strontium compound consumption is expected to increase in the near future, both in traditional applications (e.g., ceramics, glasses, and magnets) and more advanced applications (e.g., pharmaceuticals) [293].</li> </ul>
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>• Several researchers have attempted to extract strontium from aqueous solutions using liquid membranes [290] or ion-exchange resins [74, 294].</li> <li>• Liquid membrane systems have been developed using microporous hollow-fiber polyethylene membranes and crown ethers as the carrier.</li> <li>• Mesoporous aluminosilicates have shown promise as adsorbers for uptake.</li> </ul>
<b>Conclusions from literature review</b>	Although strontium is the fifth most abundant element in the ocean, relatively little work has been performed to develop technologies for extraction [21]. Over the past decade, worldwide demand has decreased significantly, and market opportunities may not exist to extract it from desalination brine for profit.

*Note:* USGS=United States Geological Survey.

**Table 4.28. Summary of Patents Related to Sodium Extraction**

Decade	Number of Patents	U.S. Patent #
prior to 1990	0	
1990–1999	2	4,973,201; 5,468,394
2000–present	4	US 6,663,778 B1; US 2010/0282675; 8,012,358 B2; 8,158,097

### 4.1.15 Uranium

Past speculation that terrestrial uranium supplies may not meet future demand as well as interest by countries with limited terrestrial uranium sources have led to a significant amount of effort put into the extraction of uranium from seawater. Uranium occurs in seawater in its highest oxidation state (+6), with the dominant uranium species as the anionic tricarbonato-uranyl  $[\text{UO}_2(\text{CO}_3)_3]^{4-}$  and bicarbonate-uranyl  $[\text{UO}_2(\text{CO}_3)_3]^{2-}$  complexes [295]. Although seawater has a relatively low uranium concentration (~3 ppb), given its volume ( $\sim 1.37 \times 10^9 \text{ km}^3$ ) there is approximately 1000 times the uranium in the world's ocean (~4.5 billion tons) compared to the amount estimated in known terrestrial ores [296]. Japan, which produces approximately 30% of its electricity from nuclear reactors and has a limited terrestrial supply of uranium [297–299], has been actively researching the extraction of uranium since the 1960s. The following sections summarize uranium economics, historical attempts to extract uranium from seawater, and recent advancements in technologies for uranium extraction that could potentially be applied at desalination facilities.

#### 4.1.15.1 Uranium Commodity Summary

The major commercial use for uranium is as fuel for nuclear power plants. According to the World Nuclear Association, there are approximately 435 nuclear power reactors operating worldwide, with 60 currently being constructed [300]. Demand for uranium increased significantly from 1970 to 2000 but has fluctuated between 60 and 70 ktons U/year for the last 10 years [301, 302]. However, even in light of the recent Japanese tsunami and events at the Fukushima power plant, analysts believe that worldwide uranium demand will increase, reaching approximately 110 ktons U/year by 2030 [301].

The question of long-term terrestrial uranium availability is not easily answered. There have been several exploration booms over the past 50 years that have led to the discovery of large deposits. For example, the major exploration periods that occurred between 1970 and 1982 led to the discovery of large uranium deposits in Athabasca Basin, Canada, as well as Australia and Kazakhstan [303]. In general, these exploration booms have been in response to spikes in uranium prices. Because uranium prices bottomed out between 1980 and the early 2000s, the majority of countries actively exploring uranium deposits put little effort toward further exploration, and few additional uranium deposits were discovered. These exploration cycles have made it difficult for analysts to estimate the long-term availability of terrestrial uranium supplies; this has spurred interest in methods to extract uranium from seawater [304, 305]. Uranium prices surged between 2003 and 2007 (eventually reaching approximately \$300/kg U), resulting in significant exploration expenditures and an increase in known

uranium resources by 15%, as well as the discovery of significant unknown uranium deposits in South America, South Africa, and India [306–309].

In 2009, Australia was reported to have the largest known uranium resources (1.6 million tons U), composing 31% of known worldwide reserves (total of 5.4 million tons U) [306]. Australia was followed by Kazakhstan (12%), Canada (9%), Russia (9%), South Africa (5%), Namibia (5%), Brazil (5%), Nigeria (5%), and the United States (4%) [306]. According to the World Nuclear Association, in 2009 the total known recoverable (recoverable at a cost of <\$130/kg U) uranium resources was approximately 5.4 million metric tons. Given the number of nuclear power plants in operation and being constructed, analysts estimate that these uranium resources should last for at least 50 years (estimates vary widely) using today's reactor technology [303, 310]. Such estimates depend on electricity consumption, percentage of electricity expected to be supplied by the nuclear power industry in the future, and nuclear power plants not becoming significantly more efficient in the near future (e.g., the use of fast breeder reactors will not become significant). However, uranium exploration activities are in their infancy, and many believe that future exploration will yield significant discoveries (as it did between 2000 and 2010) that will significantly extend the reserve life of uranium [303].

The drivers for uranium prices are complex and, according to Kahouli [302], have not been well studied or understood. Uranium prices peaked in the mid-1970s as a result of the global oil crisis and spurred uranium exploration for nonmilitary uses (i.e., nuclear power plant fuel). As a result, world annual production of uranium far exceeded demand until the late 1980s, when the price of uranium declined to less than \$50/kg U [302, 303]. Although uranium demand has far exceeded primary production since 1990, uranium prices remained around \$25/kg U for a period of 15 years. This is attributed to a relatively large supply of secondary uranium (i.e., already mined) from stockpiled uranium (of both civilian and military origin) and nuclear fuel produced through reprocessing of spent reactor fuel and depleted uranium tails [302]. In addition, the Three Mile Island (1979) and Chernobyl (1986) accidents reduced the expansion of nuclear power plants and demand for primary uranium production. After a period of stagnancy, the price of uranium spiked in 2007 at an all-time high of \$300/kg U, presumably from Chinese demand and a short-term supply–demand gap. Uranium prices have declined since 2007, and the March 2012 spot price was around \$110/kg U.

The feasibility of extracting uranium from seawater largely depends on the price of uranium. Recent demonstration-scale research conducted in Japan estimated that uranium could be extracted from seawater at a cost between \$220 and \$280/kg U, which is more than double the current spot price [296, 311]. Although the current price of uranium makes seawater extraction uneconomical, analysts and uranium mine owners believe that it is likely to increase in coming years [312, 313]. Construction of new nuclear power plants in the next 10 years (estimated to increase reactor capacity by 27%) may result in a 20 to 33% increase in uranium demand by 2020 according to the World Nuclear Association [301, 314]. In 2011, the gap between primary uranium production and demand was approximately 10,000 metric tons U [313]. It is expected, although difficult to show, that secondary supplies of uranium will begin declining in availability in the near future, which would require primary uranium production to meet the demand [308, 310]. The current low uranium price indicates that a significant short-term increase in uranium production (and development of new uranium mines) is unlikely. Although uranium demand decreased in 2011 after the Fukushima incident, reactor construction and increased reliance on nuclear power by China, India, and South Korea are expected to have a large impact on demand in the near future [301, 310, 313]. As previously mentioned, the drivers for uranium pricing are complex, and prices have been

expected to rebound to 2003 to 2007 levels for the last 4 years. As will be discussed, technologies for uranium extraction from seawater need to be more efficient, or uranium has to be significantly more expensive, for seawater uranium extraction to be economically viable.

#### ***4.1.15.2 Uranium Extraction Summary***

Numerous countries have been active in the development of processes and technologies for the extraction of uranium from seawater, including China, Germany, India, Japan, the United Kingdom, and the United States [21, 296, 299]. Compared with other sources of uranium (i.e., ore), seawater is a very low grade uranium source, requiring processing of approximately 1 km<sup>3</sup> of seawater to yield 1 ton of uranium, based on an extraction efficiency of 30%. As a result, researchers have proposed various processing schemes over the years, including land-based processing facilities and adsorbent materials suspended in ocean currents. According to Schwochau [21], preliminary studies evaluated numerous processes for concentrating the uranium in seawater, including solvent extraction, ion flotation, coagulation, coprecipitation, electrolysis, and adsorption. Given the large volumes of water that need to be processed, the majority of recent research has been focused on the development of sorbent materials for uptake of uranium.

The United Kingdom started a research program in the late 1950s and evaluated a number of different adsorbents for the uptake of uranium from seawater before identifying hydrous titanium oxide (TiO) as a promising sorbent material [299, 315]. According to Kelmers [298], the researchers evaluated two scenarios for extracting 10,000 tpy of uranium from seawater. The first scenario, pumping the seawater to a land-based facility employing adsorbent beds, was found to be unfeasible because the energy required to force seawater through the adsorbent media was a significant fraction of the energy available from the uranium after recovery. As an alternative, the deployment of the sorbent material in the ocean was evaluated and ultimately found to be ill suited for the coast of Britain.

Japan began researching seawater uranium extraction in the 1960s and evaluated a number of different processes, including solvent extraction, ion exchange, biomass collection, and adsorption [296, 315]. Ultimately, it was determined that adsorbents offered the most feasible option for extraction, and various materials were developed and evaluated, including titanium oxides, titanium oxides with organic binders, acrylamidoxine, and macrocyclic hexadentates (e.g., macrocyclic hexaketone, macrocyclic hexa-carboxylic acid, polydithiocarbamate, macrocyclic triphosphonate). Early work in Japan focused on building large processing facilities using adsorbents for extraction. Kanno [298] proposed the construction of a Japanese uranium extraction facility that would treat 800 km<sup>3</sup> of seawater per year, yielding 1000 metric tons of uranium. Based on TiO<sub>2</sub> fixed adsorption beds, the facility would require 467 pumps, 15,878 adsorption beds (total of 25.2 x 10<sup>4</sup> tons TiO) and a total facility length of almost 9 km. The cost of uranium production was estimated to be \$223/lb U (1976 dollars).

Recent research activities in Japan have focused on the use of amidoxime-based adsorbents for deployment in ocean currents off the coast [281, 311]. The Japan Atomic Energy Agency developed a process for grafting amidoxime polymer chains into polyethylene fabric, resulting in sorbent material with good mechanical strength and high selectivity towards uranium. Two forms of the fabric have been developed: (1) a material that can be produced in sheets and developed into adsorbent stacks; and (2) a fiber that can be braided into adsorbent ropes [311]. Both systems have undergone long-term field testing, and the braided adsorbent system was determined to be the most effective collection system: uranium uptake was 1.5 g U/kg adsorbent after 30 days of soaking [281]. Based on the assumption that 60 days of

soaking would yield uptake of 4 g U/kg adsorbent, braided material could be deployed in 1000 km<sup>2</sup> sea area off the coast of Japan, uranium could be collected on the scale of 1200 tons U/year, and the braided system could be reused eight times, the cost of uranium was estimated to be around \$270 /kg U (in 2009 dollars). The researchers believe the costs of uranium extraction could be improved to \$210 /kg U, which is significantly higher than the current spot price of uranium. In early 2011, Rao [296] indicated that the Japanese researchers had planned the construction of a large-scale uranium farm but had not yet secured funding.

Several publications from India's Bhabha Atomic Research Centre (BARC) indicate that India is pursuing efforts to extract uranium from seawater [159, 316, 317]. Researchers are developing hydrogel-based adsorbents and porous amidoximated membranes that show high uranium uptake. The major issue appears to be the long equilibrium times needed to reach sorption saturation, although certain hydrogels are reported to have fast uranium uptake kinetics [316]. In 2006, Tewari [318] reported that an R&D program had been initiated by BARC (termed Recovery of Uranium from Sea Water pilot program [RUSWapp]) to develop a pilot-scale facility for extraction of 100 g U/year using several different amidoxime polymers. The researchers evaluated extraction at several locations and reported uptakes of 60 to 160 µg U/g adsorbent in 12 to 24 days. More recent information on the pilot facility is unavailable. A recent publication by Sodaye et al. [159] presented an overview of a partnership between BARC and France's Commissariat à l'Energie Atomique, with the goal of extracting uranium from brine generated by integrated nuclear desalination systems. The authors present three potential systems that could be used at a desalination facility, including calixarene-based adsorption columns, a magnetic particle uranium collection system, and braided amidoxime polymers immersed in a canal. The authors indicate that the concept of recovering uranium at desalination facilities is in its infancy and needs significant research efforts to be viable.

In the 1990s, researchers at Seoul National University completed a series of studies on the binding of uranyl ions with 2,2'-dihydroxyazobenzene (DHAB) for the purpose of extracting uranium from seawater. In a study by Jang et al. [319] several DHAB-containing resins were tested for uranyl uptake capacity using a 0.3 mM solution of uranium, and on a per-g of resin basis the six DHAB-containing resins absorbed between 18.6 and 24.5 mg of uranium. To extend the laboratory experiments, Jang et al. [319] built an apparatus to pass seawater through 0.10 g of resin.

Using this experimental process with 0.10 g of DHAB<sub>30</sub>-TEA-CMPS, where CMPS is partially chloromethylated cross-linked polystyrene, and TEA is triethylamine, and DHAB<sub>40</sub>-TEA-CMPS resins, experiments were performed to evaluate the effectiveness of each resin for extracting uranium [319]. Each experiment was conducted for 3 days, with a total of 6.1 µg U/g resin extracted after processing 110 L of seawater through DHAB<sub>30</sub> resin [319]. Processing 340 L of seawater through the DHAB<sub>40</sub> resin resulted in approximately 11 µg U/g resin extracted [319]. These findings indicate that approximately 10 µg of uranium is extracted for every 1 g of resin, where the concentration of uranium in seawater is 1.4E-8M at 18° C and a pH equal to 8.10 [319]. It was estimated that in order for this system to be economically feasible it needs to extract more than 500 µg U/g/day of resin from seawater [319].

A continuation study by Lee et al. [320] discovered that an increase in the cationic character of the resin led to an increased absorption capacity. The new resins, DHAP-TEA-PCD2 and

DHAB-TEA-PDC5 were able to extract 60 to 150  $\mu\text{g}$  uranium for every 1 g of resin at a seawater concentration of  $1.4\text{E-}8\text{M}$  at  $25^\circ\text{C}$  [320]. Rivas et al. [321] used radical polymerization to create two cross-linked polymers, poly(1-vinyl imidazole-co-acrylic acid) and poly(1-vinylimidazole-co-2-acrylamido-2-methyl-1-propanesulfonic acid). These polymers were developed as resins and contain weak and strong acid groups to bind with metal cations such as  $\text{UO}_2^+$  [321]. Rivas et al. [321] tested the two cross-linked polymers at pH 5 and 3, and at pH 5, the resins had the highest observed retention values.

Chauhan and Kumar [322] created a series of copolymeric hydrogels composed of acrylic acid and acrylamide and cross-linked with trimethylolpropane triacrylate (TMPTA). These hydrogels were then used as a sorbent to extract uranyl ions during laboratory experiments [322]. To determine the uranyl uptake capacity of the hydrogels, 0.15 g of dry hydrogel material was placed in 50 mL of uranyl solution at a concentration of 251 to 600 ppm [322]. An uranyl uptake of 255 mg U/g of dry hydrogel was observed. From the uranyl uptake study, it was determined that hydrogels are efficient candidates for the removal of uranyl ions from water and a simulated seawater solution [322]. Chauhan and Kumar [322] noted that the uranyl uptake of the hydrogel was temperature dependent; as the temperature increases, the adsorption capacity decreases.

The adsorptive capacity of uranium to titanium-loaded collagen fiber was researched by Cheng et al. [323] using nuclear fuel industrial wastewater. In laboratory experiments, 100 g of collagen fibers were submerged in 100 mL of 0.001 mM/L uranium solution for 24 hours [323]. The results from Cheng et al.'s [323] laboratory experiments determined that the adsorptive capacity of the titanium-loaded collagen fiber was 0.620 mmol (0.167 g) of U/g of collagen fiber. Cheng et al. [323] concluded that the tested titanium-loaded collagen fiber exhibited an "excellent adsorption selectivity and reusability to  $\text{UO}_2^+$ ."

Amidoximated macroporous membranes (AO membranes) are believed to be a more suitable method for uranium recovery than the alternative acrylonitrile (AN) membranes [317]. This is because of AO membrane selectivity towards uranium, its high loading capacity, high mechanical strength, and the fact that it can be anchored in different polymer matrices, allowing the membrane to take various shapes and sizes. Das et al. [317] found that after immersing the membrane in seawater, the average uranium uptake for a given AO membrane was 96% of the membrane's mass, where the average mass of a membrane was 0.3253 g.

In a more recent article from Gilbert et al. [158], three commercially available selective sorbents/exchangers were evaluated for the extraction of valuable metal found in RO rejected brine. The brine used in the experimental procedures performed by Gilbert et al. was collected from an RO plant in El Prat de Llobregat, Spain, where the concentration of uranium was 0.0039 mg/L [158]. The brine was then exposed to the commercial sorbent Purolite S910, after which an uptake capacity of 41.2 mg U was retained per g of resin [158]. Gilbert et al. acknowledged that the sorption capacity found in the laboratory testing is too low to be economically feasible and proposed further research to improve the kinetics of the sorption process [158]. A summary of recent sorbent material developments for extraction of uranium from aqueous solutions is presented in Table 4.29.

**Table 4.29. Summary of Sorbent Materials for Uptake of Uranium from Aqueous Solutions**

Adsorptive Material	Abbreviation	Adsorptive Capacity	Reference
Purolite S910		41.2 mg U/g resin	[158]
2,2'-dihydroxyazobenzene chloromethylated cross-linked polystyrene triethylamine	DHAB <sub>30</sub> -TEA-CMPS	6.1 µg U/g resin	[319]
2,2'-dihydroxyazobenzene chloromethylated cross-linked polystyrene triethylamine	DHAB <sub>40</sub> -TEA-CMPS	11 µg U/g resin	[319]
2,2'-Dihydroxyazobenzene polychloromethylstyrene-co-divinylbenzene	DHAP-TEA-PCD2	60 µg U/g resin	[320]
2,2'-Dihydroxyazobenzene polychloromethylstyrene-co-divinylbenzene	DHAB-TEA-PDC5	150 µg U/g resin	[320]
Acrylamide Copolymeric Hydrogels		255 mg U/g resin	[322]
Titanium loaded collagen fiber		167 mg U/g fiber	[321]
N,N'-ethylenebis (pyridoxylideneiminato)		0.05 mg U/L polymer	[324]
poly(amidoxime)/poly(hydroxamic acid) microbead resin	PAO/PHA	45 g U/g resin	[325]
Poly(N-vinyl-2-pyrrolidone) (PVP)/acrylonitrile (AN)	PVP/AN	75 g U/g resin	[326]
2,2-dihydroxyazo-benzene poly(ethylenimine)	DHAB- PEI	10 <sup>-5</sup> M	[327]
Activated carbon	AC	28.3 mg U/g AC	[328]
Poly(acrylamidoxime)	AO	670 mg U/g hydrogel	[329]
Poly(acrylamidoxime) + methacrylic acid	AO+MAA	493 mg U/g hydrogel	[329]
Amidoxime polymer synthesized with acrylonitrile and hydroxamic acid	GoPur 3000	880 mg U/g adsorbent	[330]
Polymeric amidoxime-resin	RNH-5(CH <sub>3</sub> -120)AT	705 mg U/kg resin	[331]
Glutar-imidedioxime		2 g U/g resin	[332]
Tetrafluoroethylene-ethylene copolymer fiber	AOF	80 µg U/g resin	[333]
Chloromethylated polystyrene		28 ppm	[305]
Calix[6]arene		0.120.35g U/ kg resin/day	[334]

**Table 4.30. Uranium Overview**

<b>Main form(s) in water</b>	tricarbonato-uranyl $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ ; bicarbonate-uranyl $[\text{UO}_2(\text{CO}_3)_2]^{2-}$ complexes
<b>Dominant commodities</b>	$\text{U}_3\text{O}_8$ ; other forms are sometimes sold as $\text{U}_3\text{O}_8$ equivalents.
<b>Commodity summary</b>	<ul style="list-style-type: none"> <li>• Annual demand has fluctuated from 60–70 ktons U/year for the last 10 years [302].</li> <li>• Prices hit a new 2-year low in October 2012 at \$100.86/kg [291].</li> </ul>
<b>Market opportunities</b>	<ul style="list-style-type: none"> <li>• Despite low demand since the nuclear disaster in Japan in March 2011, worldwide demand is projected to increase, reaching 110 ktons U/year by 2030 [301].</li> <li>• Recent research in Japan estimated that uranium could be extracted from seawater at \$220–\$280/kg U [296].</li> <li>• Extraction costs have been calculated to \$689–\$2850/kg U [335]. This range of costs is indicative of the complexity and uncertainty of current uranium extraction technologies.</li> </ul>
<b>Extraction technologies and processes</b>	<ul style="list-style-type: none"> <li>• Adsorption is likely the most feasible and frequently investigated method [296].</li> <li>• Amidoximine-based adsorbents are grafted onto polyethylene fabric, produced as sheets or ropes [311].</li> <li>• Other adsorbent possibilities include titanium oxides, titanium oxides with organic binders, acrylamidoxine, and macrocyclic hexadentates, which have been studied in detail.</li> </ul>
<b>Conclusions from literature review</b>	Because the extraction of uranium is not yet optimized and still expensive, feasibility is strongly dependent on price. The current price is very low compared to 2007 but is expected to increase over the next 20 years. Some analysts believe that uranium extraction from seawater and potentially desalination brine could be feasible in the foreseeable future, although uranium prices would at the very least need to be >\$300/kg U (currently ~\$100/kg U).



**Table 4.31. Summary of Patents Related to Uranium Extraction**

Decade	Number of Patents	U.S. Patent #
prior to 1950	0	
1950–1959	1	2885258
1960–1969	0	
1970–1979	4	3,522,187; 3,721,533; 3,778,498; 3,912,801
1980–1989	19	4,225,314; 4,199,470; 4,277,566; 4,285,799; 4,293,527; 4,277,345; 4,263,403; 4,283,370; 4,298,577; 4,416,860; 4,414,183; 4,565,627; 4,585,627; 4,601,889; 4,622,366; 4,678,844; 4,656,012; 4,740,359; 4,871,518
1990–1999	2	5,276,103; 5,468,394
2000–present	4	US 6,333,078; 6,402,953 B1; US 6,863,812 B2; US 2009/0075861

#### 4.1.16 Other Constituents Receiving Attention in the Literature

##### 4.1.16.1 Cobalt

Cobalt is used in a variety of end products including metal alloys (superalloys) for gas turbines and jet aircraft engines, batteries, prosthetics, and materials to improve wear resistance [336]. Cobalt is typically produced as a byproduct from copper and nickel mining activities, although production from scrap recycling is significant [336, 337]. According to the USGS, cobalt mining in the United States has not been significant since 1971, and it imports most of its supply of cobalt compounds from China, Norway, Russia, and Finland. The price of cobalt has decreased significantly over the past 5 years because of a global market surplus and decreased demand and is currently between \$13 and \$14/lb [336]. The price of cobalt is expected to decrease further as several countries continue to stockpile it.

Cobalt is generally found at extremely low concentrations in natural waters [155]. Nevertheless, methods to extract cobalt from seawater have been developed, and a summary of several approaches can be found in Schwochau [21]. More recent research into the extraction of cobalt has mostly focused on the use of adsorbent materials to remove heavy metals and radionuclides from nuclear industry wastes. Chouyyok et al. [338] compared conventional ion-exchange resin and activated carbon to a functionalized carbon for cobalt uptake from various water samples and reported relatively large solid–liquid partitioning coefficients (15,000–1.7 million). Zonoz et al. [339] evaluated a novel cation exchange resin (zirconium [IV] molybdo tungsto vanado silicate) and reported high and selective adsorption of cobalt during laboratory experiments. Additional sorbents evaluated for cobalt extraction

include mesoporous zirconium silicate [251], organosilicates [340], aluminosilicates [282], modified polymeric ion-exchange resins [343], and a variety of functionalized organic and inorganic resins [155]. A good summary of cobalt-adsorbent distribution coefficients is provided by Johnson et al. [155].

#### **4.1.16.2 Germanium**

Germanium is produced from germanium-imported compounds, recycling of germanium-containing materials, or as a byproduct of zinc mining [342]. According to the USGS, total annual U.S. consumption is around 40,000 kg for use in fiber and infrared optics and electronics. In 2011, the price of 1 kg of germanium was approximately \$1600. In seawater, germanium is considered a trace element, as it is found at a concentration of approximately 5 ng/L [22]. Nevertheless, several researchers have suggested that germanium extraction from desalination facility brine would improve the economics of desalination [156, 157, 343]. The recovery of 1 kg of germanium would require processing roughly 26.4 million gallons of SWRO brine, assuming 100% efficiency. To the best of our knowledge, the recovery of germanium from desalination brine has yet to be physically evaluated.

#### **4.1.16.3 Rare Earth Elements**

There are 17 rare earth elements typically found in natural aqueous environments at extremely low concentrations (e.g., seawater concentrations <20 ppt for most rare earth elements). Based on USGS mineral commodity summaries, rare earth element consumption is relatively low; only one company in the United States mines rare earth-containing minerals, and pricing is only available in tons of rare earth oxides (\$15–\$18/t) [344]. Although literature was identified that evaluated the separation of rare earth elements from aqueous solutions [21, 67, 345, 346], given the low concentration and level of consumption, it is unlikely that extraction of rare earth elements from desalination brine/concentrate will be feasible.

## **4.2 Summary of Proposed Extraction Schemes**

Various extraction schemes have been proposed to produce salable products from desalination brine/concentrate. In most cases, such schemes were not physically evaluated, and if they were, experiments were conducted at the laboratory scale. A summary of literature pertaining to the extraction of constituents from desalination brine/concentrate is presented in Table 4.32.

**Table 4.32. Summary of Studies Evaluating the Extraction of Dissolved Constituents from Desalination Brine/Concentrate**

Desal. System	Constituent(s)	Processes	Level of Investigation	Cost and Energy Requirements	Reference
SWRO	Br <sub>2</sub> , Mg(OH) <sub>2</sub> , salt	ED/EDR, precipitation, evaporation, blowout tower	lab-scale tests conducted	Preliminary costs presented indicate potential profits.	[62]
	NaCl	ED/EDR, MSF, crystallization	lab-scale tests conducted	Cost analysis presented indicates sale of salts reduces water cost.	[57]
	NaCl	ED/EDR, MED, crystallization	simulation only	Energy analysis indicates NaCl production from SWRO brine is 80% more efficient than from seawater.	[58]
	CaCO <sub>3</sub> , MgSO <sub>4</sub> , NaCl, KCl, Li, Cl <sub>2</sub> , NaOH	NF, RO, precipitation, evaporation, ion exchange	proposed only	not evaluated	[233]
BWRO, WWRO	CaCO <sub>3</sub> , CaSO <sub>4</sub> , Mg(OH) <sub>2</sub> , Na <sub>2</sub> SO <sub>4</sub> , K <sub>3</sub> Na(SO <sub>4</sub> ) <sub>2</sub>	precipitation, RO, evaporation	mostly simulation, bench-scale tests conducted	not evaluated	[134]
Thermal desal.	Na <sub>2</sub> SO <sub>4</sub> , Br <sub>2</sub> , NaCl	eutectic freezing, crystallization, blowout tower	simulation	not evaluated	[99]
SWRO	Cs, Rb, In, Ge, Mg, NaCl, KCl	evaporation, ion exchange, solvent extraction, liquid membranes	proposed only	not evaluated	[156, 157]
SWRO, BWRO	NaCl, Mg, Cl <sub>2</sub> , NaOH, CaCO <sub>3</sub>	ED/EDR, MSF, MVC precipitation, NF, MCr	proposed only	performed cost analysis, claim that extraction is economical	[72]
Thermal desal.	NaCl, Na <sub>2</sub> SO <sub>4</sub> , Cl <sub>2</sub> , NaOH	MED, electrolysis, eutectic freezing	proposed only	performed cost analysis: NaOH produced for \$149/ton, high capital costs	[16]
BWRO	CaSO <sub>4</sub> , Mg(OH) <sub>2</sub> , NaCl, CaCl <sub>2</sub> , Na <sub>2</sub> SO <sub>4</sub> , CaCO <sub>3</sub>	SAL-PROC, precipitation, evaporation	proposed only	not evaluated	[237]

Desal. System	Constituent(s)	Processes	Level of Investigation	Cost and Energy Requirements	Reference
MSF	Mg, NaCl	MSF	proposed only	not evaluated	[235]
BWRO	CaCO <sub>3</sub>	FBC, clarification	demonstration	not reported	[93]
WWRO	HCl, NaOH, Cl <sub>2</sub> , P	electrolysis, ED, ion exchange	lab-scale tests conducted	not reported	[166]
	P, struvite	ion exchange	lab-scale tests conducted	only calculated the potential revenue from struvite sales	[269]
SWRO	NaCl	evaporation ponds	full scale	not presented, produce food-grade salt in arrangement with a salt company	[71]
MED	NaCl	solar evaporator	simulation	not evaluated	[347]
SWRO	Cl <sub>2</sub> , NaOH	precipitation, clarification, filtration, evaporation, ion exchange, electrolysis	simulation	claim that production of NaOH requires 2150 kWh/t NaOH—unclear if this is only for electrolysis	[167]
SWNF	CaCO <sub>3</sub> , NaCl, MgSO <sub>4</sub>	NF, precipitation, MCr	lab-scale study	not evaluated	[153]
<b>BWRO</b>	CaCO <sub>3</sub> , CaSO <sub>4</sub>	IX, precipitation	Demonstration	Market study performed	[151]

*Notes:* BWRO=brackish water reverse osmosis; ED/EDR=electrodialysis/electrodialysis reversal; FBC=fluidized-bed crystallization; MCr=membrane crystallization; MED=multiple-effect distillation; MSF=multistage flash; MVC=mechanical vapor compression; NF=nanofiltration; RO=reverse osmosis; SWNF=seawater nanofiltration; SWRO=seawater reverse osmosis; WWRO=wastewater reverse osmosis

### **4.3 General Considerations Toward Material Extraction**

The feasibility of producing commodities from desalination brine/concentrate is dependent on numerous factors that require careful consideration on a case-by-case basis. Several of these considerations are discussed in this section.

#### **4.3.1 Economic Considerations**

Economic factors that weigh heavily on the feasibility of material extraction include commodity demand and pricing, energy consumption and cost, labor requirements, and the overall costs of production. Although the overall processing costs can be estimated, there are a number of costs that are often overlooked or underestimated when evaluating the feasibility of extracting materials from brine/concentrate for economic gain. Such costs include, but are not limited to, overhead, sales, customer service, commodity packaging, shipping, and storage [223]. The overall cost of commodity production cannot be fully determined until a plant is in operation.

The chemical processing industry is in a constant state of flux regarding processing technologies, commodity sources and raw materials, and commodity production volumes. Changes in the chemical processing industry arise from fluctuations in commodity demand and pricing, emergence of competing production methods and suppliers, identification of lower cost commodity sources, and development of new technologies. As a result, there are numerous examples of commodity sources and production methods that have been or are currently being phased out. It is worth noting that, although the concept of extracting materials from desalination brine/concentrate has been discussed for over 40 years, only one real-world example could be identified where extraction was implemented on a large scale [71]. As previously mentioned, only sodium chloride and magnesium compounds are extracted from seawater, which strongly indicates that the production of commodities from desalination brine/concentrate is not competitive with alternative production methods.

#### **4.3.2 Product Considerations**

Product purity, condition, and uniformity greatly influence the marketability of a commodity. Although high purity commodities typically have greater value, byproduct reduction can be costly. Important physical conditions for solids include crystal structure, particle size, shape, and color. Purity and physical condition will ultimately dictate the final marketplace, and both are influenced by numerous factors including the commodity source, raw materials used in processing, process design and operation, level of instrumentation, skilled labor, and careful plant supervision [224]. Studies evaluating the extraction of desalination brine/concentrate typically do not evaluate final product purity and uniformity, although these issues are sometimes discussed.

#### **4.3.3 Facility Considerations**

The location of chemical manufacturing facilities is generally determined by proximity to and availability of required raw materials, energy, transportation, and markets. Other considerations include environmental factors, availability of labor, land costs, water supply, and waste disposal [224]. Obviously, siting of a desalination brine/concentrate extraction facility is inflexible (unless constructed with a complementary facility), and the facility siting

requirements for profitable commodity production should be carefully evaluated. In addition to facility location, safety is a major consideration in the chemical processing industry, which requires significant planning and effort and a specialized labor force. Finally, handling and processing of concentrated brine requires corrosion-resistant materials, which may add significant capital costs to extraction equipment.

Of the studies discussing material extraction from desalination brine/concentrate, little analysis has been performed on the feasibility of transforming a water treatment facility into a chemical processing facility. Such an arrangement would likely require major changes in how a desalination facility is operated, including facility management, labor requirements, training, safety requirements, and research and development activities.

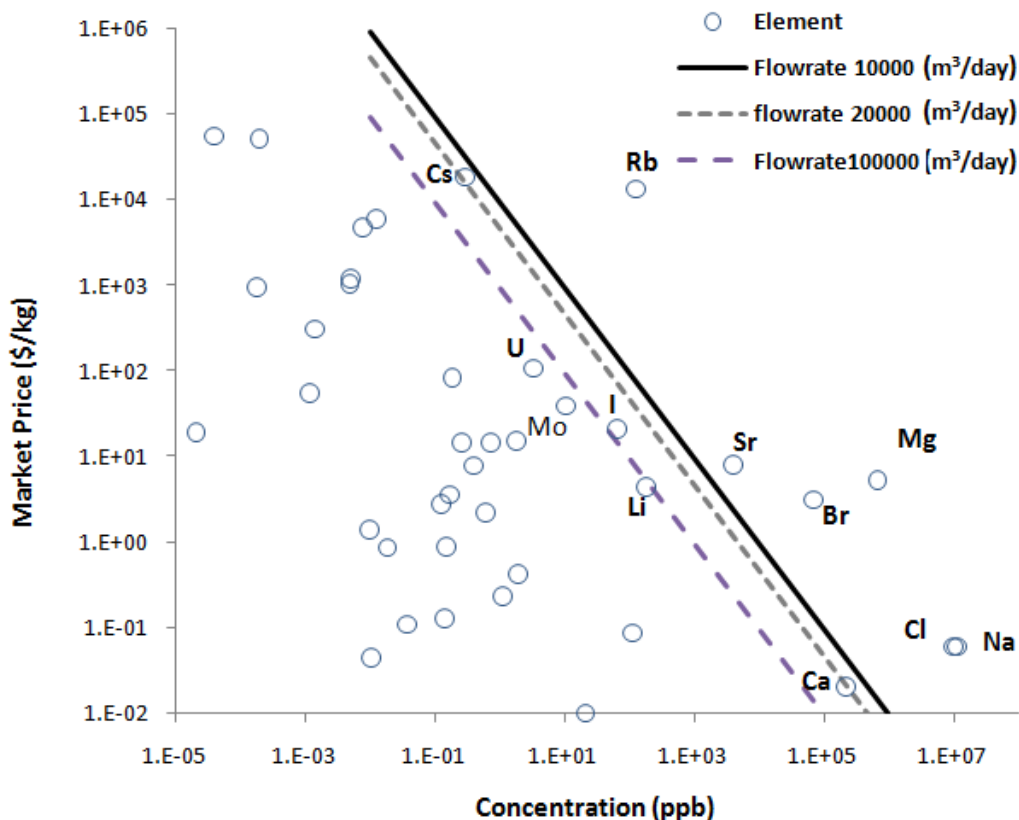
## **4.4 Assessment of Material Extraction**

### **4.4.1 Seawater Desalination**

The feasibility of extracting minerals from desalination facility brine was evaluated in several steps. As a preliminary assessment to screen out compounds that could not be extracted for profit, the current highest average market price (derived from USGS Mineral Commodity Summaries) for any constituent was plotted as a function of its concentration in seawater. The annual profit of extraction of each mineral from seawater is calculated without considering capital costs. The annual profit for each mineral was then estimated based on the concentration of the element in RO concentrate, profit made from selling the extracted compound (revenue), and basic maintenance costs. A mineral's concentration in RO concentrate was estimated for RO plants with influent flow rates of 10,000 to 100,000 m<sup>3</sup>/day for expected concentrations of the element in seawater (based on Pilson [22]). A basic minimal O&M cost was estimated as the average salary for a utilities maintenance worker in the United States (\$33,000/year [1]). Potentially profitable compounds need to fulfill the following inequality:

$$P \cdot C \cdot Q_c > P_m \quad (4.9)$$

Where, P is market price of the element, C is concentration of the element in RO concentrate, Q<sub>c</sub> is flow rate of concentrate, and P<sub>m</sub> is basic maintenance costs. Figure 4.11 demonstrates potentially profitable compounds (those with positive annual profit) based on the previous assumptions. The results demonstrate that extraction of bromine, magnesium, rubidium, sodium, and strontium are potentially profitable for plants with flow rates greater than 10,000 m<sup>3</sup>/day. By increasing flow rate to 20,000 m<sup>3</sup>/day, extraction of cesium could also be profitable. Extraction of iodine is potentially profitable for flow rate greater than 100,000 m<sup>3</sup>/day, and extraction of lithium (and to a lesser extent molybdenum and uranium) are marginally profitable for plants with this flow rate.



**Figure 4.11. Preliminary screening of profitable elements in RO concentrate for plants with different brine flow rates.**

*Note:* Potentially profitable elements are located at the right side of each flow rate line.

From a technical and economic perspective based on reviewed literature, the extraction of rubidium and cesium for profit are likely to be unfeasible because they are not traded in appreciable quantities, have very low current demand, and technologies for extraction from seawater are not well developed. Similarly, strontium extraction is unlikely to be feasible due to the lack of technologies for its extraction, the fact that it is no longer produced in the United States, and the dominance of China and Spain in the strontium market.

As previously discussed, magnesium metal was once produced from seawater by extracting magnesium chloride and through further processing using electrowinning. Magnesium metal is no longer produced through this method because of the associated high costs and energy requirements and development of alternative processes that are significantly more efficient. Therefore, the feasibility of magnesium metal production was not evaluated further. Kim et al. [72] performed a cost analysis that put the cost of magnesium metal production from SWRO brine at \$14,146/ton, which is approximately five times higher than the current spot price.

On the basis of the analysis presented as Figure 4.11 and the literature review, the following compounds could potentially be produced from seawater desalination brine:

- sodium chloride
- magnesium hydroxide or caustic-calcined magnesia

- bromine
- chlorine and sodium hydroxide

It is worth noting that the list of extractable compounds is composed of compounds that are currently being or have been extracted from seawater.

#### **4.4.1.1 Preliminary Cost Assessments of Selected Extraction Methods**

Based on literature and common methods for industrial production of these chemicals, processing schemes were developed that include the required technologies for pretreatment, concentration, purification, and chemical production (Figures 4.14 and 4.15). Preliminary cost analyses were performed on each of the schemes to evaluate the profitability of extracting these compounds. For comparison purposes and unless otherwise noted, the cost analyses were performed for a brine flow rate of 10 mgd with ion concentrations twice that of seawater (50% recovery of SWRO system). Summarized commodity prices and potential revenues are presented in Table 4.33. All facilities were assumed to have a 25-year lifetime, and the evaluation was performed for an interest rate of 6%. To be conservative, unit extraction process efficiency was assumed to be 80%. In addition, the cost of generated waste disposal was not included in the cost analysis, which is likely to add significant additional costs.

**Table 4.33. Summarized Commodity Prices and Potential Revenue from Commodity Sales**

<b>Plant</b>	<b>Product</b>	<b>Plant Efficiency (%)</b>	<b>Unit Price (\$/metric ton)</b>	<b>Revenue (\$M/yr)</b>
Mg(OH) <sub>2</sub> , Br <sub>2</sub> , NaCl	NaCl	80	55	16.32
	Br <sub>2</sub>	80	1390	0.49
	Mg(OH) <sub>2</sub>	80	275	8.45
NaCl	NaCl	80	55	16.32
MgO	MgO	80	539	11.42
Cl <sub>2</sub> , NaOH	Cl <sub>2</sub>	80	550	99.01
	NaOH	80	500	101.56



#### 4.4.1.1.1 Magnesia Production

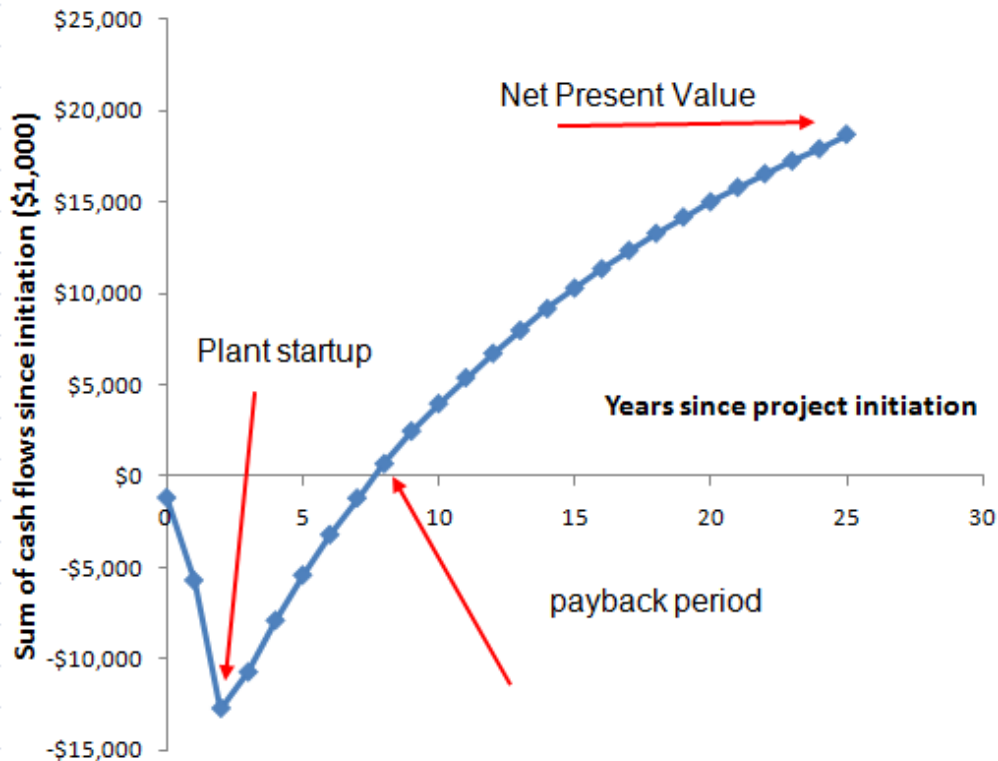
As opposed to magnesium metal, magnesia is still produced from seawater, and the magnesia market is expected to grow in the near future. A cost analysis was performed to evaluate the feasibility of extracting MgO from SWRO concentrate through the scheme presented in Figure 4.14a for an RO plant with a capacity of 38,000 m<sup>3</sup>/d (10 mgd). Capital and O&M costs were estimated based on the current magnesia seawater production process used by Premier Periclase at its Ireland facility (Tables 4.34 and 4.35). Capital and O&M costs for unit processes were obtained from McGivney and Kawamura [348], and raw material costs were based on commodity information (e.g., lime, natural gas). Assuming a MgO price of \$539/ton, the sum of cash flow since facility initialization is presented in Figure 4.12, and net present value (NPV) and payback period for magnesia extraction are summarized in Table 4.45. Results of the preliminary cost analysis indicate a payback period of approximately 8 years and an NPV of approximately \$19M.

**Table 4.34. Calculated Cost for Different Units of MgO Extraction Plant**

Item	Number of units	Total cost (M\$)	Reference
Thickeners	2	2.73	[350]
Secondary tanks	2	0.90	
Filter press	2	3.61	
Centrifuge facility	2	2.73	
Furnace	2	2.00	Estimated
Total		11.97	

**Table 4.35. Calculated O&M for MgO Extraction Plant**

Item	Unit cost (\$/ton)	Cost (\$M/yr)	Reference	Description
Lime	110	4.18	[129]	
Gas	3	0.71	assumed	
Fresh water	0.6	0.21	[62]	
Maintenance		0.71	[350]	assumed maintenance costs for a conventional water treatment plant
Other costs		1.16	-	20% of all O&M costs
<b>Total</b>	113.6	6.97		



**Figure 4.12. Cash flow diagram for the MgO plant**

#### 4.4.1.1.2 Chlorine, Sodium Hydroxide, and Hydrogen Production

Although chlorine can be generated in small quantities from seawater, several processes have been proposed for large-scale electrolytic production of chlorine and sodium hydroxide from desalination brine. Major caveats associated with production include the necessity to remove any impurities and the fact that the chlor-alkali industry produces near saturated and high purity sodium chloride solutions for feed stock and still employs pretreatment to remove ions that can interfere with the electrolysis process. Therefore, the proposed process illustrated in Figure 4.14b assumes that brine pretreatment using chemical precipitation and filtration, concentration using thermal processes (i.e., MED, MVC), and purification using ion exchange yields an effluent sufficient for efficient chlorine and sodium hydroxide production using membrane electrolysis.

Capital and O&M costs for the scenario illustrated in Figure 4.14b were derived from several sources (Tables 4.36 and 4.37). Costs of brine pretreatment (i.e., precipitation, clarification and filtration) were estimated from McGivney and Kawamura [348], and ion-exchange costs were estimated from Sorg [349]. The capital and O&M costs for membrane electrolytic cells were difficult to obtain, and conservative values were obtained from Mansfield et al. [161]. In addition, it was assumed that hydrogen production would not yield economic benefits, although past researchers have purported that the hydrogen produced could be used to generate electricity.

The profitability of producing chlorine and sodium hydroxide from desalination brine was found to be strongly dependent upon the process efficiency assumed for the membrane electrolytic cell. Assuming a membrane electrolytic cell efficiency of 70% yielded an unprofitable scenario over the lifetime of the facility; however, 80% efficiency yielded a potentially profitable extraction process with a payback period of approximately 11 years. The sum of cash flow since facility initialization assuming 80% efficiency of the membrane electrolysis process is presented in Figure 4.13, and NPV and payback period are summarized in Table 4.45. As previously discussed, there is little information available to indicate that desalination brine is appropriate feed stock for the production of chlorine and sodium hydroxide, and more research is required to evaluate electrolysis process efficiencies using pretreated desalination brine.

**Table 4.36. Calculated Cost for Different Units of Cl<sub>2</sub> and NaOH Extraction Plant**

Item	Number of units	Total cost (\$M)	Reference
Pretreatment	-	1.07	[348]
MED	2	108.57	
Ion exchange	2	2.23	EPA report [161]
Electrolysis	1	25.00	Cl <sub>2</sub> report [161]
Backwash pumps	-	0.38	[348]
<b>Total</b>	<b>5</b>	<b>137.25</b>	

*Notes:* EPA=United States Environmental Protection Agency; MED=multiple-effect distillation

**Table 4.37. Calculated O&M Cost for Cl<sub>2</sub> and NaOH Extraction Plant**

Item	Unit Cost	Cost (\$M/yr)	Reference	Description
Na <sub>2</sub> CO <sub>3</sub>	147 (\$/ton)	14.19	USGS [285]	
BaCl <sub>2</sub>	550 (\$/ton)	24.60	Alibaba—average price	
NaOH	500 (\$/ton)	28.88	report [161]	
Electricity	0.1 (\$/kWh)	52.21	assumed	
Maintenance (pretreatment)	-	0.68	[348]	assuming maintenance costs for a softening plant
Maintenance (for MED)	-	6.87	[348]	
Maintenance (for ion exchange and electrolysis)	-	5.45	-	assumed to be 20% of capital cost of equipment
Other costs		26.37	-	20% of all O&M costs
<b>Total</b>		159.25		

Notes: MED=multiple-effect distillation; USGS=United States Geological Survey.

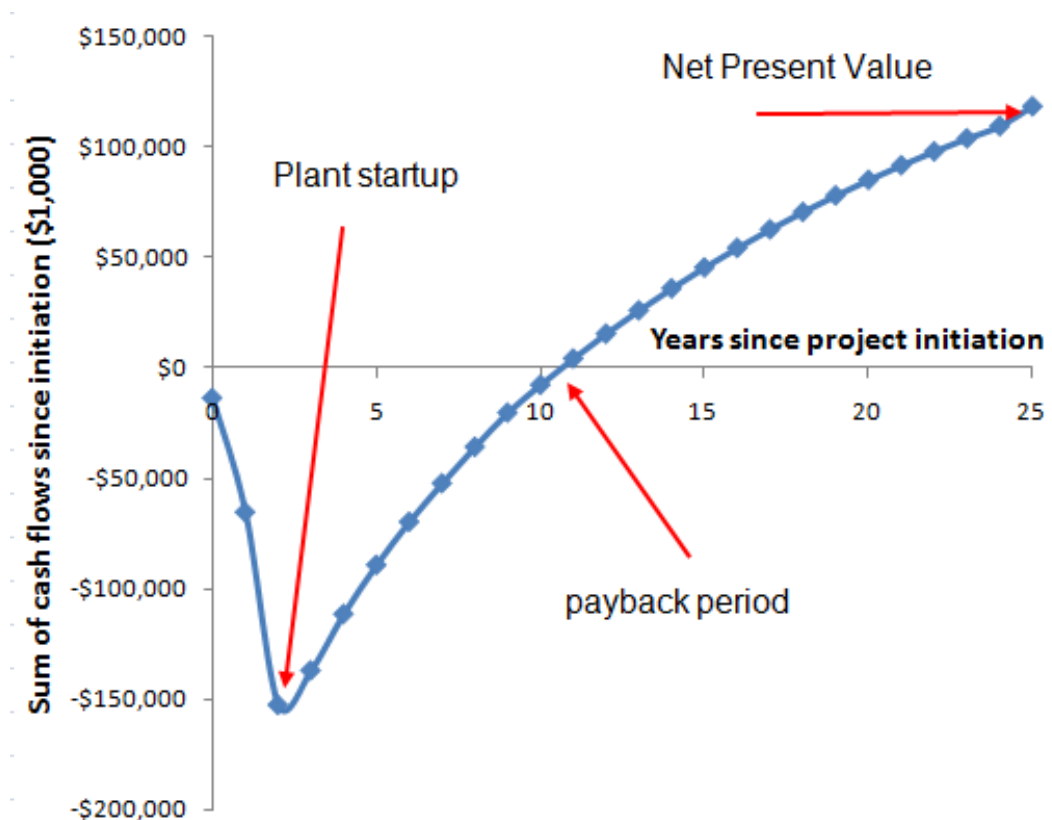


Figure 4.13. Cash flow diagram for the  $\text{Cl}_2$ -NaOH plant.

#### 4.4.1.1.3 Sodium Chloride Production

Sodium chloride is produced in Japan from seawater using ED or EDR to separate monovalent ions from multivalent ions, followed by evaporation by thermal processes and crystallization (Figure 4.15a). Recently, Tanaka [58] performed an energy analysis of such an approach for salt generation from SWRO brine and reported an 80% reduction in energy requirements compared to extraction from seawater. Reportedly, the ED/EDR step is sufficient to separate out impurities so the salt produced is fit for human consumption; however, there is little information available on final product purity using this approach.

A cost analysis was performed on the scenario illustrated in Figure 4.15a assuming that EDR would be employed for sodium chloride separation and concentration. Two scenarios were evaluated, which included using either MED or MVC for evaporation and concentration of the EDR concentrate stream. Capital and maintenance costs for EDR, MVC, and forced-circulation crystallization were obtained from Juby et al. [13], and costs for MED were obtained from McGinley and Kawamura [348] (Tables 4.38–4.41). The feasibility of sodium chloride extraction was found to depend on the price that could be obtained for it. The USGS reported that in 2012 sodium chloride produced through evaporation (vacuum or open pan) was worth \$175/ton, whereas the average price of solar salt was only \$55/ton. At a cost of \$55/ton, the extraction of sodium chloride through the proposed process using MED or MVC for evaporation would not be economically viable (see Table 4.45 for the NPV). However, at

a price of \$100/ton, the payback period for both alternatives is roughly 8 years with the MVC alternative being marginally more advantageous from a profitability perspective. Typically, high value vacuum pan salt (produced with multiple-effect evaporators) is produced with brines obtained through solution mining after significant pretreatment to achieve a 99.9% sodium chloride solution [227]. It is unlikely that sodium chloride produced through the process scheme illustrated in Figure 4.15a would yield high value salt, and at \$55/ton, sodium chloride production would likely be unprofitable at a desalination facility.

**Table 4.38. Calculated Cost for Different Units of NaCl Extraction Plant Using MED**

Item	Number of Units	Total Cost (\$M)	Reference
EDR	1	16.7	[13]
MED	2	46.6	[348]
Forced circulation crystallizer	1	20.8–22.6	[13]
<b>Total</b>		84.1–85.9	

*Notes:* EDR=electrodialysis reversal; MED=multiple-effect distillation.

**Table 4.39. Calculated Cost for Different Units of NaCl Extraction Plant Using MVC**

Item	Number of Units	Total Cost (\$M)	Reference
EDR	1	16.7	[13]
MVC	2	26.9–37.05	[348]
Forced circulation crystallizer	1	20.8–22.6	[13]
<b>Total</b>		64.4–76.35	

*Notes:* EDR=electrodialysis reversal; MVC=mechanical vapor compression.

**Table 4.40. Calculated O&M Cost of NaCl Extraction Plant Using MED**

Item	O&M Costs (\$M)	Reference/Other
EDR	2.4	[13]
MED	0.9–1.1	[348]
Forced circulation crystallizer	1.9–2.6	[13]
Other costs	1.05–1.22	20% of all O&M costs
<b>Total</b>	6.25–7.32	

*Notes:* EDR=electrodialysis reversal; MED=multiple-effect distillation; O&M=operation and maintenance.

**Table 4.41. Calculated O&M Cost for Different Units of NaCl Extraction Plant Using MVC**

Item	O&M Costs (\$M)	Reference/Other
EDR	2.4	[13]
MVC	5.8–6.0	[348, 13]
Forced-circulation crystallizer	1.9–2.6	[13]
Other costs	2.02–2.2	20% of all O&M costs
<b>Total</b>	12.12–13.2	

*Notes:* EDR=electrodialysis reversal; MVC=mechanical vapor compression; O&M=operation and maintenance.

#### 4.4.1.1.4 Bromine, Magnesium Hydroxide, and Sodium Chloride Production

Davis [62] recently proposed an integrated desalination system for the production of bromine, magnesium hydroxide, and sodium chloride (Figure 4.15b) and through a preliminary cost analysis estimated annualized yearly profits of \$6.6 million for a brine flow rate of 3 mgd. A preliminary cost analysis was performed to reexamine the feasibility at a brine flow rate of 10 mgd. Two scenarios were evaluated that included using either MED or MVC for evaporation and concentration of the EDR concentrate stream. Capital costs for EDR and MVC were obtained from Juby et al. [13], the bromine blowout tower was based on Davis [62], and those for magnesium hydroxide production were obtained from the same sources as in Section 4.4.1.1.1 (Tables 4.42–4.44).

For both scenarios evaluated, the costs of extraction cannot be recouped through the sale of bromine, magnesium hydroxide, and salt over the 25-year lifetime of the facility. Because the bromine concentration in seawater is relatively low, the costs of production are nearly equal to the total revenue gained from bromine production (assuming 80% efficiency of the bromine production process), and its extraction is not advantageous. It should be noted that Davis [62] assumed a capital investment of \$1 million for bromine production, whereas a value of \$3 million was used for the cost analysis (the flow rate used in this analysis is roughly three times greater). The NPV of the proposed extraction process is presented in Table 4.45.

**Table 4.42. Calculated Cost for Different Units of Mg(OH)<sub>2</sub> Br<sub>2</sub> Salt Extraction Plant Using MED**

Item	Number of Units	Total Cost (\$M)	Reference
EDR	2	17.6	[13]
Softening	2	12.6	[348]
Thickening	2	0.9	
MED	2	40.7	
Crystallizer	1	17.9	[13]
Blowout tower	1	3.0	Estimated
<b>Total</b>		92.7	

*Notes:* EDR=electrodialysis reversal; MED=multiple-effect distillation.

**Table 4.43. Calculated Cost for Different Units of Mg(OH)<sub>2</sub> Br<sub>2</sub> Salt Extraction Plant Using MVC**

Item	Number of Units	Total Cost (\$M)	Reference
EDR	2	17.6	[13]
Softening	2	12.6	[348]
Thickening	2	0.9	
MVC	2	22.0	
Crystallizer	1	17.9	[13]
Blowout tower	1	3.0	Estimated
<b>Total</b>		74.0	

*Notes:* EDR=electrodialysis reversal; MVC=mechanical vapor compression.



**Table 4.44. O&M Costs for Mg(OH), Br, Salt Extraction Plant Using MED and MVC**

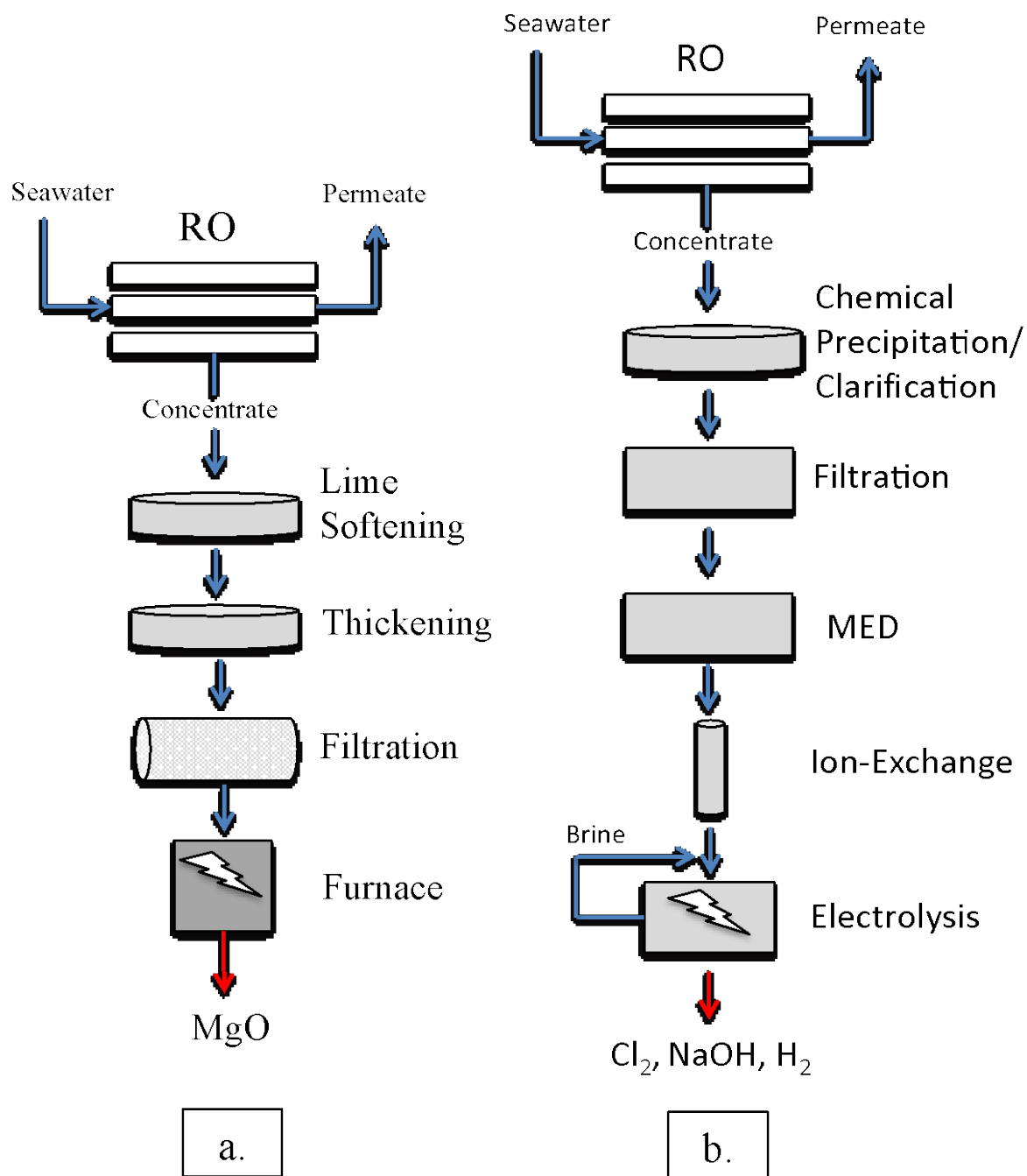
Item	Maximum Cost (\$M/yr)	Reference	Description
EDR	2.4	[13]	
Softening	9.8	[13]	
Thickening	0.4	Assumed	
MED	0.9–1.2	[348]	
MVC	3.3–5.1	[348, 13]	
Crystallizer	1.3–1.8	[13]	
Blowout tower	0.5	Assumed	15% of capital cost
Other costs (MED)	3.1–3.2		20% of O&M costs
Other costs (MVC)	3.4–4.0		20% of O&M costs
<b>Total (if using MED)</b>	18.4–19.3		
<b>Total (if using MVC)</b>	21.2–24.0		

*Notes:* MED=multiple-effect distillation; MVC=mechanical vapor compression; O&M=operation and maintenance.

**Table 4.45. Net Present Value and Payback Period for Different Extraction Plants**

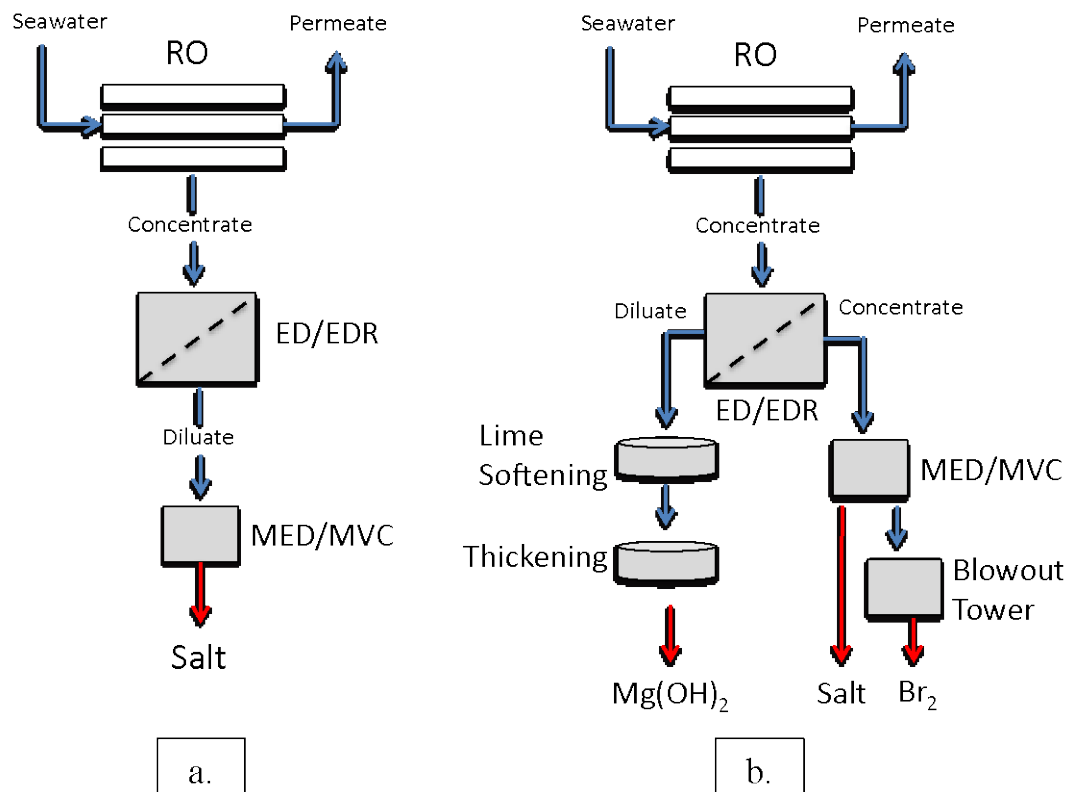
Plant	NPV (\$M)	Payback Period (yrs)
Mg(OH)-Br-Salt MED	- 24.73	-
Mg(OH)-Br-Salt MVC	-58.33	-
NaCl MED	- 17.61	-
NaCl MVC	- 40.90	-
MgO	18.72	8
NaOH-Cl <sub>2</sub>	118.58	11

*Notes:* Payback period includes the construction period. MED=multiple-effect distillation; MVC=mechanical vapor compression.



**Figure 4.14. Proposed schemes for extraction of constituents from RO brine/concentrate.**

*Notes:* Scenario (a) is the common production method for producing magnesia from seawater, based on literature by Melian-Martel et al.[167]. Scenario (b) is the proposed process for chlorine, sodium hydroxide, and hydrogen production.



**Figure 4.15. Additional proposed schemes for extraction of constituents from RO brine/concentrate.**

*Sources:* Scenario (a) is from literature by Tanaka et al. [58] and Turek [57]. Scenario (b) is from literature by Davis [62].

#### 4.4.2 Brackish Water Desalination

Several examples exist in the literature that demonstrate that extraction of salts from desalination brines is technically viable, including calcium carbonate and potentially magnesium hydroxide, sodium sulfate, and mixed salts [2, 93, 134]. The production of calcium carbonate crystals in water treatment facilities using FBCs for softening applications is relatively common in the Netherlands, and the Eastern Municipal Water District in Southern California is reportedly planning on employing an FBC for intermediate softening and selling produced calcium carbonate crystals to a local construction company [93].

On the basis of water quality data presented by Brady et al. [42] for brackish water sources in the United States, it is unlikely that extraction of valuable compounds from desalination brine/concentrate would be profitable because of the relatively low concentrations of ions in most cases. However, several studies have recently evaluated the use of FBCs for intermediate softening (Figure 4.16) to maximize the recovery of brackish water reverse osmosis (BWRO) systems and the subsequent recovery of salable calcium carbonate crystals. Evaluating the benefits of selling calcium carbonate for BWRO systems is difficult as brine/concentrate water quality can have a significant impact on O&M costs because of the potential requirement for pretreatment to remove ions that interfere with calcium carbonate crystal growth. A preliminary cost assessment of scenarios presented in Bond and Veerapaneni ([2], data not presented) indicated that the sale of calcium carbonate would have

minimal impact on the total costs of desalination because of its relatively low market price (\$10–20/ton). The major advantage of such an approach is achieving high desalination system recoveries and minimizing brine disposal costs. An additional example of such an approach is provided in Section 5.3.1.

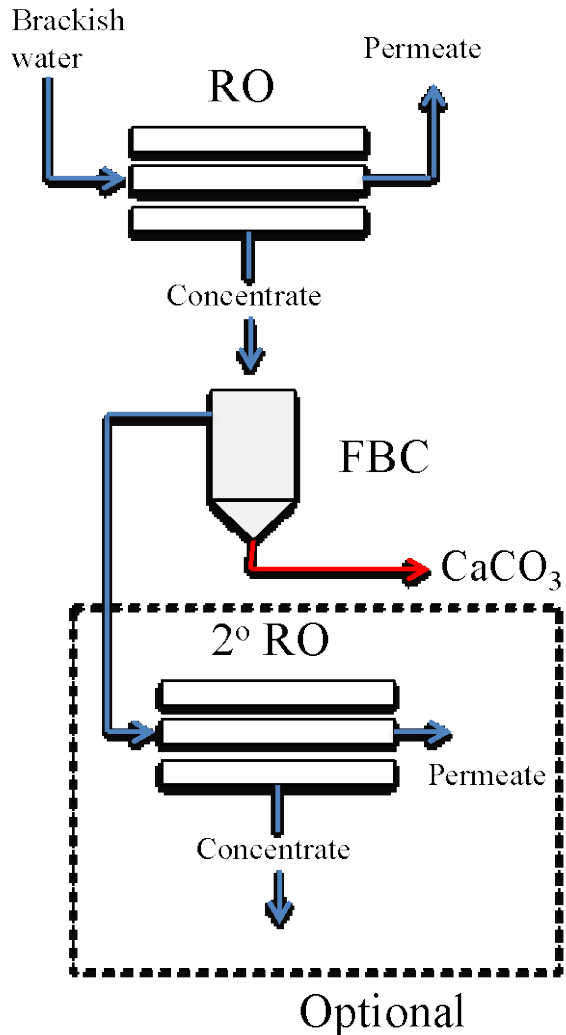


Figure 4.16. Proposed process for recovery of calcium carbonate from BWRO desalination brine.

## Chapter 5

# Extraction Case Studies

---

The following 13 case studies were developed to describe real-world examples from different industries where valuable material recovery from a production line or waste stream was achieved or attempted. Based on the topic relevance and available information, eight cases were developed to full case studies with more detailed information, such as the market value of the recovered product; and five cases are presented as short synopses. The case studies were also divided into two categories based on project goal. The first category includes three case studies that intentionally recover or concentrate product to increase the value of the product or production. In the second category of cases, the primary goal was the treatment of wastewater, but the use of the introduced technology provided the additional benefit of recovery of raw materials or salable product or reduced treatment costs. The following table outlines the topics of the case studies presented in this report.

### 5.1 Intentional Material Recovery from Production Lines

#### 5.1.1 Case Study 1—Colloidal Silica Recovery from Chemical Production Plant

Goals:

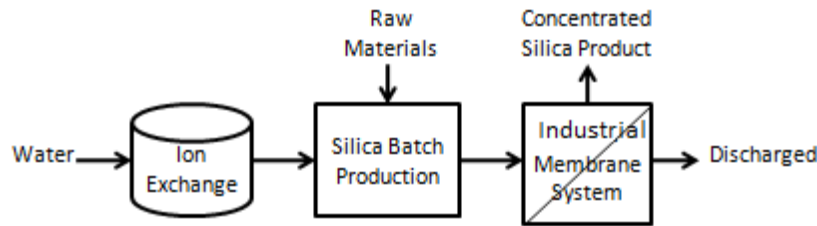
- Reduce O&M costs by maximizing membrane separation.
- Recover more than 40% of colloidal silica.

##### 5.1.1.1 Application Details

A large chemical manufacturer was using tubular UF membranes to concentrate colloidal silica ; however, the conventional tubular system was experiencing limitations of flux and recovery rate because of high concentrations of colloidal silica gels. Because of this gelling effect, an evaporator was being used to achieve total solids (TS) concentrations greater than 40%, but the use of evaporators results in high operating costs because of energy requirements. Nonetheless, a higher concentration of silica was desired because it results in a higher market value for the final product.

**Table 5.1. Overview of Case Studies**

Case	Topic	Technology	Case Study Type
<b>5.1 Intentional Material Recovery from Production Line</b>			
1	Colloidal silica recovery	UF	short synopsis
2	Orange juice pulp concentration	UF	short synopsis
3	Maple sap concentration	RO/NF	short synopsis
4	Silica recovery from Geothermal Fluids	UF&RO	full case study
<b>5.2 Unintentional Material Recovery During Waste Stream Management</b>			
<b>5.2.1 Material Recovery from Industrial Waste and Wastewater</b>			
5	Lysine recovery from production wastewater	UF	short synopsis
6	Ammonium nitrate recovery from fertilizer production wastewater	RO	short synopsis
7	Syrup recovery from ethanol wastewater	RO	short synopsis
8	Copper recovery in a copper casting plant	electrowinning	full case study
9	Nutrient recovery from digestate	UF&RO	full case study
10	Carbon source recovery from production wastewater	UF	full case study
11	Grain recovery from brewery wastewater	UF	full case study
<b>5.2.2 Material Recovery from Brines</b>			
12	Mineral recovery from brackish water RO concentrate	isothermal evaporation	full case study
13	Calcium recovery from desalination brine	pellet softening	Full case study



**Figure 5.1. Process flow diagram for colloidal silica concentration.**

A vortex-enhanced industrial membrane system with UF membrane was tested to evaluate its performance versus the current method, combined tubular membranes and evaporation. Testing with the membrane system achieved 42% recovery without the use of an evaporation process [350]. Also, the unique design of the system allowed it to be operated at a feed temperature of 95° C, resulting in a flux increase of 50%. As a result, the recovered silica product could be sold to customers at a higher value with lower operating costs. Pilot testing has been completed, and full-scale installation is expected in 2013.

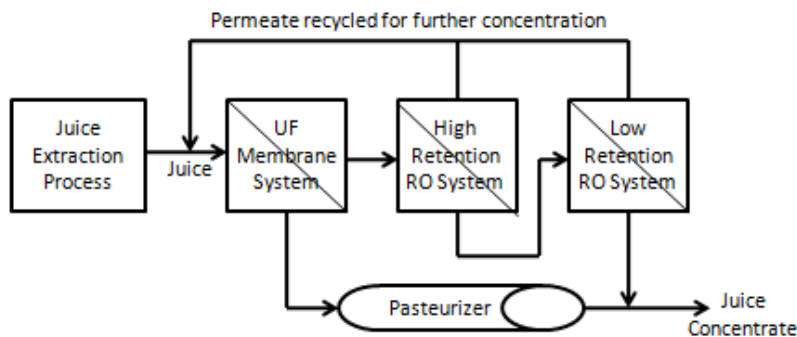
## **5.1.2 Case Study 2—Orange Juice Pulp Concentration for Use in Industrial Applications**

Goal:

- Recover pulp from an orange juicing concentration process.

### **5.1.2.1 Application Details**

The juicing process for oranges is very simple but results in byproducts such as rind and pulp. The recovered rind and pulp are of value because they can be sold as a raw material for other production processes [351]. Pulp and rind from the juicing process can be dehydrated for use as feed for livestock, pectin for making jellies, citric acid, essential oils, molasses, candied peel, and industrial cleaners.



**Figure 5.2. Process flow diagram for the recovery and concentration of orange juice pulp.**

The solid orange rind is removed during the juicing step, and both the pulp and juice are sent to the membrane systems. By using a hollow-fiber UF membrane system prior to RO, nearly 100% of the pulp can be removed and concentrated, adding a further revenue source to orange juice production. The pulp that is concentrated via membranes can be added to the other solids separated during juicing, such as the rind, which both reduces waste disposal fees and generates a secondary revenue stream for the facility.

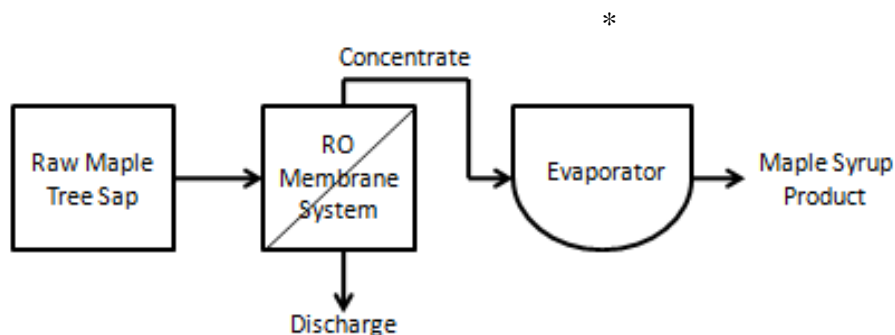
### 5.1.3 Case Study 3—Maple Tree Sap Concentration for Maple Syrup Production

Goal:

- Recover sugar from maple syrup sap to decrease evaporator costs.

#### 5.1.3.1 Application Details

The process of maple syrup production begins with the collection of sap from maple trees. It takes roughly 40 to 50 gallons of sap to produce 1 gallon of maple syrup. Conventional maple syrup production uses a cloth filter (to remove large solids) followed by an evaporator to concentrate the sap to create syrup; however, evaporation has very high operating costs when compared to a conventional RO system. To mitigate the high costs associated with evaporation, RO membranes are used to concentrate the sap first, thus reducing the amount of energy required to evaporate the smaller volume of sap.



**Figure 5.3. Process flow diagram for the concentration of maple sap prior to evaporation.**



A total of nine membranes (two RO and seven NF) were tested by Robaire and Arzate [352] to evaluate their ability to concentrate the sap while retaining flavoring and coloring compounds. The RO membranes tested produced filtrates that met the quality standards of 0.1 Brix and 50  $\mu\text{S}/\text{cm}$  conductivity for maple syrup sale. Only two of the seven NF membranes produced filtrates that could meet the basic quality standards. The pilot test results showed a 95% retention rate of sucrose [352].

#### 5.1.4 Case Study 4—Silica Recovery from Geothermal Fluids

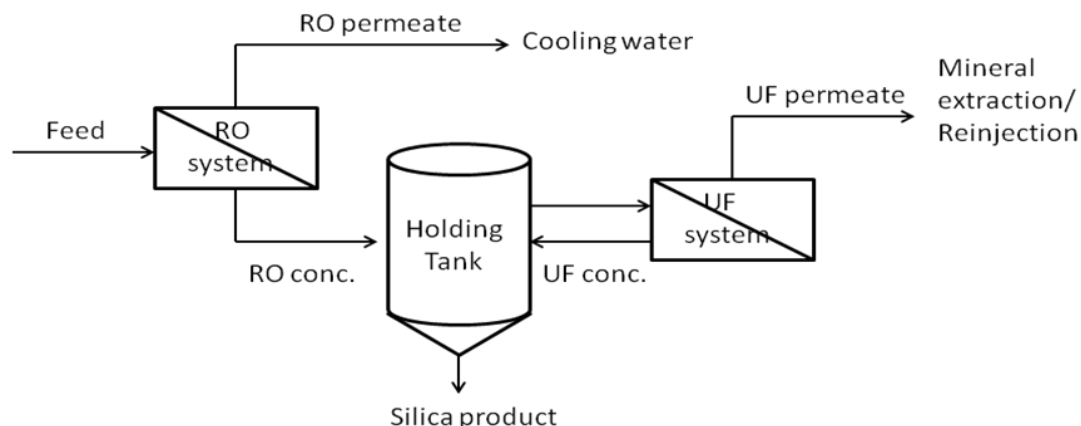
Goals:

- Recover high grade silica from geothermal fluid before reinjection.
- Reduce silica scaling in pipelines and reinjection wells.

##### 5.1.4.1 Introduction

Silica scaling in pipelines and reinjection wells is one of the most serious problems in geothermal plants, affecting reinjection capacity and heat exchanger performance. Several methods have been applied to prevent silica scaling, such as hot brine reinjection, pH adjustment, and silica seeding methods; however, these methods have not been commercialized because of their high cost or limited efficiency [353]. RO can be used to remove silica from geothermal waste to resolve scaling issues in pipelines. Recovering marketable silica from RO brine can offset the cost of the RO process and further reduce the cost of geothermal power [354]. Geothermal fluid is rich in valuable minerals such as lithium and tungsten. Once the silica has been removed, mining other metals from the geothermal fluid becomes more feasible, both economically and technically. Another benefit to silica extraction is the production of freshwater that can be used as a heat exchanger coolant in geothermal power plants.

Lawrence Livermore National Laboratory has developed a technology for extracting silica from geothermal fluids. A pilot-scale silica recovery project has been conducted at the geothermal power plant in Mammoth Lakes, CA to demonstrate the technical and economic feasibility of metal and mineral coproduction from geothermal fluids [356]. Additional details provided below are based on the Public Interest Energy Research Project report prepared by Lawrence Livermore National Laboratory [354].



**Figure 5.4. Process of silica recovery from geothermal fluid.**

#### 5.1.4.2 Recovery Process

The extraction process involves an RO separation process to create freshwater and concentrated brine, as shown in Figure 5.4. The freshwater is used for evaporative cooling, and the concentrated brine is pumped into a stirred reactor in which silica is polymerized and aggregates to form colloids. The silica particles are separated from the brine in a filtration process. Then, other metals can be extracted from the silica-free brine before it is reinjected into the subsurface. Limited information about the extraction process is currently available, however.

The geothermal fluid used in this project was obtained downstream of a heat exchanger with a feed rate of 18 to 25 gpm. The fluid was sent to a series of three modular RO vessels with a 120 to 150 psi system pressure. Because high fluid temperatures (43–52° C) can result in lower salt and silica rejection in RO than in other brackish water, a tighter (smaller pore size) seawater RO element from Toray Group USA was selected for this process. The concentrated silica from the RO unit was then introduced into a holding tank. The silica was further concentrated from the RO concentrate using a cross-flow UF system. The UF system consisted of a 5 hp pump and twin set of ITT-PCI B1 tubular UF modules. The membranes and pressure vessels used in this project were obtained from PCI. The membrane was hydrophobic, with a pore size of 100 nm; cross-flow fluid velocities were maintained around 11 ft/sec with a cross-membrane pressure of 80 to 100 psi.

#### 5.1.4.3 Results

Typical silica levels in the feed, permeate, and concentrate from the RO system are summarized in Table 5.2. Silica concentration in the feed fluid was around 250 ppm. Less than 10 ppm of silica was detected in the RO permeate. Silica concentrations in the RO concentrate were between 500 and 1500 ppm, which corresponds to 50 to 85% fluid recovery. Based on the flux and pressure, no significant membrane fouling occurred up to 80% fluid recovery. In contrast, a rapid decrease in permeate flux was detected in the second housing when the fluid recoveries reached 83% and higher. The permeate flux dropped from approximately 5 gpm to values of less than 1 gpm over a few hours, and repeated rinsing and flushing did not restore the flux. Thus, recoveries greater than 80% are not feasible on a continuous basis in the RO system.

**Table 5.2. Performance and Mass Balance of RO System**

	Feed	Permeate	Concentrate
pH	5.8–6.2	5.2–5.8	6.3–6.7
Conductivity (ms)	2.5–2.8	0.3–0.6	5.0–12.0
Temperature (° C)	43–52	43–52	43–52
Silica (mg/kg)	245–255	6–18	500–1500

Once the silica has been concentrated from the thermal fluid by RO, it begins to polymerize to form larger molecules (silica polymers). Based on the pilot test, polymerization was rapid over the first few minutes, which is advantageous for the commercial production of silica colloids. The silica in solution stops polymerizing when the concentration reaches a value of about 160 to 200 mg/kg monomeric silica, which corresponds to saturation with amorphous silica.

In order to produce concentrated silica colloids, the RO concentrate was connected to a UF system fed by a holding tank. The silica colloids can be concentrated in a batch mode in the feed tank, or, alternatively, it could be run in continuous mode by matching the RO concentrate feed with UF permeate discharge. In order to get a commercial-grade silica colloid (20% w/w) from 0.1% silica, the solution needs to be concentrated up to 200 times. During a 6-month period of interval operation, approximately 350,000 gallons of plant feed was processed.

#### **5.1.4.4 *Economic Analysis***

Silica extracted from geothermal fluid can be used to produce various types of products such as precipitated silica, silica gel, and silica colloids (silica solution) because of its relatively high purity. In this case study, the market analysis was focused on silica colloids production because the value is higher than other products and no post processing or chemical addition is required. The current market price of dry silica ranges from \$0.78 to \$1.41/lb; however, high quality silica solutions for silicon wafer polishing applications command a higher price, up to \$3.20/lb. In this study, a conservative value of \$0.79/lb of 30wt.% solution, taken from a market report by the Freedonia Group, was used [355]. Economic analysis has been conducted for a silica recovery facility from a geothermal fluid feed of 18 mgd, which is close to the average total fluid flux at the Mammoth Lakes power plant. Input parameters used in this estimation are summarized in Table 5.3 [355].

**Table 5.3. Economic Analysis of Silica Recovery at Mammoth Lakes**

<b>Total Production</b>	
Recovered product	colloidal silica (30wt% solution)
Feed flow	18 mgd
Silica in feed	250 ppm
Silica recovery rate	70%
Daily production rate	38 tons (84,000 lb)
Yearly production rate	13,780 tons (30 M lb)
<b>Marketability</b>	
Market value	\$790/1000 lb (\$1750/ton)
Potential income	\$ 24,115,000/yr
<b>Operational cost savings</b>	<b>NA</b>
<b>Total benefit</b>	<b>\$ 24,115,000/yr</b>

The size of the geothermal energy production offset by the coproduction of silica can be determined using cost data. This analysis assumes the plant obtains a no-risk royalty stream of 6% of gross sales from a separate silica production company. A power production of 350M kWh/y was also assumed. The estimated gross income is \$24,115,000, 6% of which is \$1,446,900. After dividing the royalty stream (\$1,446,900/ year) by the energy production (kWh), an offset of \$0.04/kWh was calculated.

#### **5.1.4.5 Conclusions**

Silica extraction from geothermal fluids was found to be feasible using a pilot-scale facility at the Mammoth Lakes geothermal plant. The simple technology can be readily applied to full-scale geothermal systems. It can be a potential solution for current subeconomic geothermal sites. The results of the economic analysis suggest that the rates of return are favorable, with cost offsets of about \$0.01/kWh.

## **5.2 Material Recovery from Industrial Waste and Wastewater**

### **5.2.1 Case Study 5—Lysine Recovery from Production Wastewater**

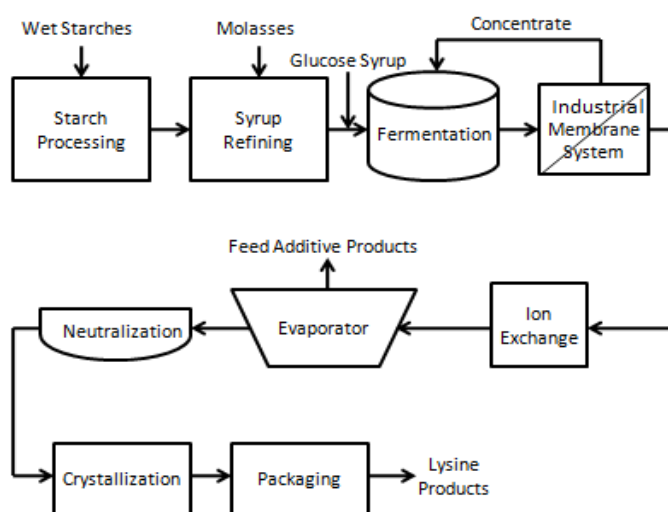
Goal:

- Recover bacteria from lysine production to recycle into fermentation process.

### 5.2.1.1 Application Details

Lysine is an alpha amino acid that is essential because animals cannot synthesize it. It is produced on an industrial scale by microbial fermentation from a base of mainly sugar. In lysine production, a membrane system is used to separate the lysine solution from fermentation effluent. The high bacterial and other solid concentrations in the fermenter effluent require dilution before conventional membrane separation. A specially designed industrial membrane system was tested to extract lysine without dilution.

The tested membrane system was able to achieve 90% average recovery rate for the fermentation effluent without dilution. The permeate stream, which has the lysine product, then passes through an ion-exchange system for further purification. Because of the higher lysine concentration in the permeate, the post-processing fee can be saved. In addition, the concentrate produced from this process, which contains most of the fermentation bacteria, can be recirculated into the fermentation tank to save production cost. By recycling the bacteria back to the fermentation tanks, there is no longer a need to “seed” the next batch to be fermented. By reducing the seeding required, production costs can be further reduced [356].



**Figure 5.5. Process flow diagram for lysine extraction and fermentation bacterial recovery from production wastewater.**

The tested membrane system was able to achieve a 90% average recovery rate for the fermentation effluent without dilution. The permeate stream that has the lysine product then passes through an ion exchange system for further purification. Because of the higher lysine concentration in the permeate, the post processing fee can be saved. In addition, the concentrate produced from this process, which contains most of the fermentation bacteria, can be recirculated back into the fermentation tank to save production cost. By recycling the bacteria back to the fermentation tanks there is no longer a need to “seed” the next batch to be fermented. By reducing the seeding required, production costs can be further reduced [356].

## 5.2.2 Case Study 6—Ammonium Nitrate Recovery from Fertilizer Production Wastewater

Goals:

- Recover and concentrate ammonium nitrate from fertilizer effluent streams.
- Reuse ammonium nitrate in production process and achieve close to 90% recovery via RO membrane systems.

### 5.2.2.1 Application Details

A study was conducted to investigate the technical and economic feasibility of concentrating valuable compounds from an industrial fertilizer production process. Wastewater streams from the fertilizer plant contain essential plant nutrients such as ammonium nitrate, which is typically not recovered prior to discharge. By recovering the ammonium nitrate, it can be recycled back into the production process, saving raw material costs and increasing yield.

Four different membranes were tested on both bench- and pilot-scale systems [357]. Two of the membranes were common low-pressure spiral RO membranes, with similar characteristics but different manufacturers. The other two membranes had higher published rejection values and acid resistance that was suitable for the waste stream. The pH of the feed was raised by the addition of ammonia so the common low-pressure RO membranes could be used [358]. The starting concentration of ammonium nitrate was 182 mg/L, which was concentrated to 300 mg/L.

The test result demonstrated that it was feasible to achieve approximately 90% recovery by using RO membranes. By recovering the ammonium nitrate from the waste stream, the fertilizer production facility can reduce the raw material cost for production while simultaneously treating the wastewater prior to discharge, thus saving the wastewater management cost.

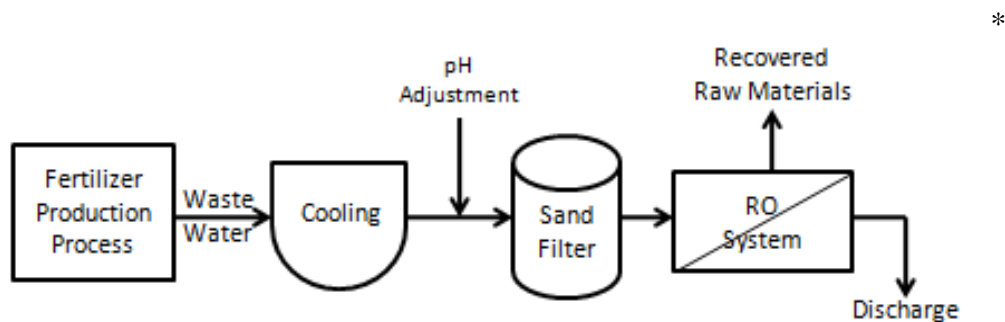


Figure 5.6. Process flow diagram for ammonium nitrate recovery and concentration.

### 5.2.3 Case Study 7—Ethanol Wastewater Treatment

Goal:

- Separate and dewater suspended solids from thin stillage via an RO membrane as a pretreatment to an evaporator to reduce operational costs and improve resource recovery.

#### 5.2.3.1 Application Details

The production of ethanol begins with the grinding of a feed stock such as corn or sugar cane. The ground-up feed stock is then boiled in water to remove sugars and other desired compounds needed to produce ethanol. The boiled liquid is then sent to a fermentation tank, where yeast is added to convert the sugars into ethanol. The ethanol must now be separated from the water–ethanol slurry by distillation. Once the ethanol has been separated, the bulk slurry is sent to a centrifuge to remove the bulk solids (grains), resulting in both distillers grains, which can be dried and sold, and thin stillage. Thin stillage ranges from 1 to 2% TS and requires further treatment.

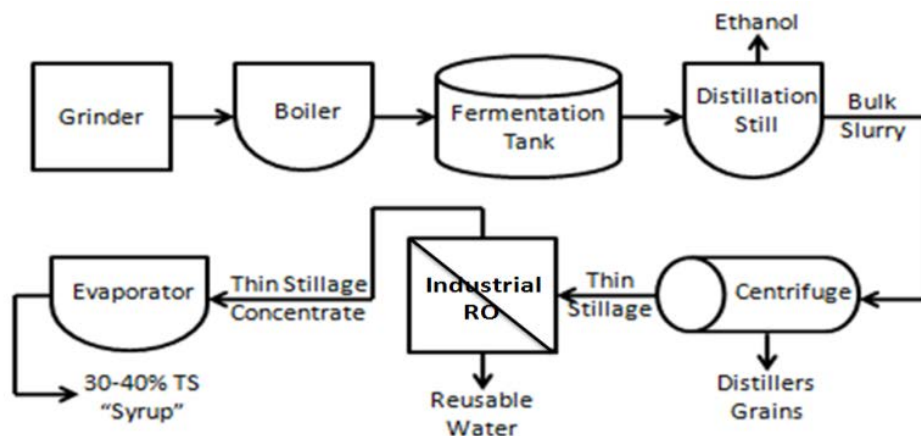


Figure 5.7. Process flow diagram for the recovery of solids from ethanol wastewater.

The conventional treatment method for thin stillage is evaporation, which results in reuse-quality water and a nutrient-rich syrup. The syrup can be added to the dried distillers grains to create dried distillers grains with solubles, simultaneously disposing of the syrup and increasing the value of the grains. However, evaporation requires large amounts of energy, resulting in high operating costs. A vibratory enhanced membrane system utilizing RO membranes was used to concentrate the thin stillage prior to evaporation. Using RO membranes provided high quality permeate, which could be reused on-site, and concentrated solids, which would be sent to the evaporator. The membrane system was able to concentrate 2% TS in the feed to approximately 10% TS in the concentrate. With RO membranes, the membrane system averaged a flux of 25 GFD while achieving a recovery rate of 80% [361].

Utilizing membrane filtration in ethanol production to dewater thin stillage can improve the solids recovery and the energy of production to energy of ethanol ratio. By reducing the starting volume of water by 80%, the evaporator operating costs can be drastically reduced while maintaining the production of the high quality, nutrient-rich syrup.

## 5.2.4 Case Study 8—Copper Recovery from a Waste Stream in a Casting Plant Using Electrowinning Technology

Goals:

- Replace existing copper sulfate plant to manage spent wash solution produced in a copper casting plant.
- Recover copper and sulfuric acid from waste stream.

### 5.2.4.1 Introduction

In copper casting plants, a chemical cleaning process is usually required to remove undesirable oxides and mill scale from the products. Although most of the chemical solutions can be recycled in “bleed and feed” mode, the process still produces a significant amount of spent wash solution containing a high level of copper. A copper casting plant that produces approximately 2.4 million lb/day of copper rod generates 38,000 to 53,000 L/day of spent cleaning solution. The spent solution consists of 35 g/L copper sulfate, 200 g/L sulfuric acid, 0.50% hydrogen peroxide, and a small amount of propylene glycol [360].

Historically, the spent cleaning solution from the plant was sent to an associated refinery copper sulfate plant to produce copper sulfate penthydrate by reacting with additional copper chips. In order to handle continuously produced spent cleaning solution, the copper sulfate plant had to operate continuously. However, because of the high energy consumption in the copper sulfate crystallization process, operating the plant regardless of market conditions may cause a deficit.

A commercialized electrowinning process was selected to replace the existing process of making crystalline copper sulfate from spent cleaning solution at the copper casting plant. The electrowinning process was able to recover high purity copper from the spent cleaning solution, which can be returned to the casting furnace directly. In addition, the process regenerates a chemical solution that contains 5 g/L copper sulfate and 245 g/L sulfuric acid, which can be returned to the chemical cleaning process.

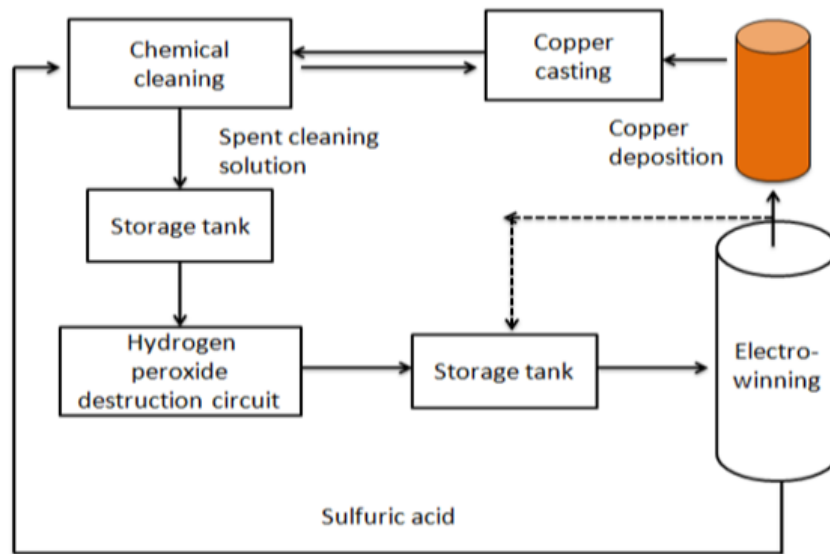
### 5.2.4.2 Process Description

As shown in Table 5.4, the recovery system in the copper casting plant has a 1700 kg/day copper capacity with 270 cells in total. The cells are divided into three electrically and mechanically independent modules for maintenance. Each cell is able to produce 23 kg of copper cathode per batch. A schematic of copper recovery process is shown in Figure 5.8. The spent cleaning solution from the product cleaning process is stored in a storage tank first. The presence of excess hydrogen peroxide in the feed solution will lower the current efficiency of the recovery system and also the copper quality. Thus, the solution is routed to a thermal destruction circuit to reduce the hydrogen peroxide level before copper recovery. In the circuit, the incoming spent cleaning solution is heated to 75° C and agitated until the peroxide concentration is below 0.03%. The solution is then cooled to 54° C or less and stored for processing in the electrowinning cells.



**Table 5.4. Specifications of Copper Electrowinning System**

Capacity	1700 kg/day of cathode copper
Cathodes	90 cells * 3 modules
Copper harvest	23 kg/cathode
Energy consumption rate	2.1 kWh/kg copper deposited
Average current efficiency	85%

**Figure 5.8. A schematic of copper recovery from waste cleaning solution.**

The spent cleaning solution from the hydrogen peroxide destruction circuit will be stored in another tank. The electrowinning copper recovery system, which consists of tubular plating cells, a cathode, and an inert anode in each cell, is designed for batch processing. The cathode, a thin rolled stainless steel sleeve (a starter sheet) is inserted into the cell. The anode is a small-diameter rod located at the center of the plating cell. The spent cleaning solution (electrolyte) in the storage tank is pumped through the cell from the bottom. Power is applied to the cell between the anode and cathode. Copper begins to plate on the cathode. The effluent from electrowinning cells returns to the storage tank until the copper concentration in the solution reaches a desirable level. The copper concentration is monitored using a continuous copper detection device. When the concentration reaches the desired copper concentration (5 g/L), the batch will be automatically finished.

After a batch electrowinning, the top of the cell is removed, and the copper cathode along with the split sleeve is extracted from the top of each cell. The split sleeve easily separates from the copper cathode and is inserted back into the cell for service again. The copper cathodes are used in copper casting to increase production. The copper-depleted solution (regenerated acid) from the electrowinning process contains 5 g/L copper sulfate, 245 g/L

sulfuric acid, and some organic compounds. The regenerated acid can be returned to the chemical cleaning system to reduce sulfuric acid feed in the copper casting plant.

The accumulation of impurities, such as organics from the decomposition of propylene glycol in the recycling acid, was a great concern in this approach. In a simulated batch test, samples were periodically taken for analyses of the constituents to determine the rate of impurities accumulation; however, no excessive organics accumulations were detected, even in a severe test with no withdrawal or dilution of the circulating acid.

#### 5.2.4.3 Economic Analysis

On the basis of the design capacity, the electrowinning units can produce 1.3 M lb of copper cathodes from the spent cleaning solution. It has been reported that the casting plant saved 1460 tpy of sulfuric acid by recycling spent cleaning solution recovered from the copper recovery system. The market price of the recovered products and potential income are summarized in Table 5.5 [360]. Considering the potential market value of the recovered copper, savings in sulfuric acid, and operating costs of the copper recovery plant, cost savings from the implementation of the system are estimated to be \$1.7 million/year. Capital cost of the project was \$3.43 million. Estimated payback time is approximately 2 years.

**Table 5.5. Economic Analysis of Copper Electrowinning System**

<b>Total production</b>		
Recovered product	Copper	sulfuric acid
Production rate per day	3740 lb (1.7 tons)	8800 lb (4 tons)
Production rate per year	1.3 M lb (620 tons)	3.2 M lb (1460 tons)
<b>Marketability</b>		
Market value	\$1.25/lb	\$50/ton
Potential income	\$4660 /d (\$1.7 M/yr)	\$200/d (\$73 K/yr)
Total potential income	\$4860/d (\$1.7 M/yr)	
<b>Operational cost</b>		
Electric consumption	2.1 kWh/kg copper	
Electricity price applied	\$0.06/kWh	
Electricity cost	\$214/day	
<b>Total potential profit</b>	<b>\$4660/d (\$1.70 M/yr)</b>	
<b>System capital cost</b>	<b>\$3.43 M</b>	

The implementation of the copper recovery system allowed the copper casting plant to recover metallic copper and eliminate a high cost copper sulfate plant. The recovered copper can be used in a casting process directly to increase the profit of the plant. Regenerated sulfuric acid from the electrowinning process can be recycled as a cleaning solution to save further cost. The recovery system is operating at design capacity and has contributed to significant cost savings for the plant. In combination with a copper-selective ion-exchange unit, this recovery system can be applied to a copper-containing waste stream as low as 1 ppm.

## 5.2.5 Case Study 9—Nutrient Recovery from Digestate in a Biogas Plant

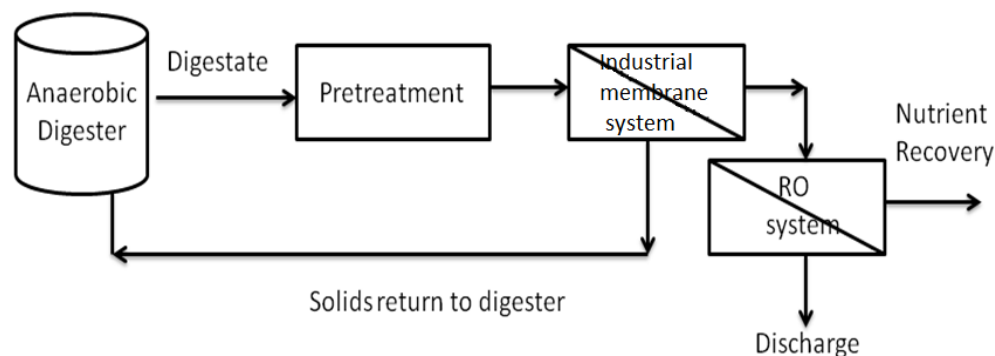
Goals:

- Treat digestate using conventional RO system.
- Recover nutrient from digestate for liquid fertilizer, and improve the gas production in the digester.

### 5.2.5.1 Introduction

Anaerobic digesters have been used to treat waste source materials and create methane in biogas plants; however, the wastewater (digestate) produced by anaerobic digesters has become an increasing problem. It has a high concentration of ammonia relative to organic carbon, rendering common biological nitrogen removal processes impossible. Many studies suggest membrane separation would be a good technology for digestate treatment [361–364]; however, conventional membrane filtration is challenged by the high solid content in the digestate, which is known to contribute significantly to membrane fouling, lower filtration efficiency, and higher operating costs. Although fats, oils, and grease offer enhanced biogas production from the digester, their elevation of water viscosity serves to further inhibit the filtration process [363].

In order to better manage the waste stream, a biogas plant in the Netherlands applied a vortex-enhanced membrane system followed by RO to treat digestate and recover valuable nutrients (shown in Figure 5.9). The membrane system has been able to effectively treat digestate without frequent maintenance or replacements. The UF-grade membrane system removes suspended solids so the RO can recover the nutrients [363, 365].



**Figure 5.9. Schematic of digestate treatment using a vortex-enhanced membrane system and conventional RO.**

Sources: [365, 366]

### 5.2.5.2 Process and Performance

The biogas plant produces 48,000 gpd of digestate from five anaerobic digesters. Most of the large particles in the digestate are first removed in a pretreatment process, and then the supernatant is sent to the membrane system. The membrane system utilizes a flat UF membrane with 150 kDa. The industrial membrane system uses rotating vortex generators between membrane surfaces to reduce membrane fouling during filtration. As a result, the

system makes it possible to apply membrane filtration to digestate with high solids and viscosity. Operating conditions are summarized in Table 5.6. The membrane system has a single-stage recovery rate of 65 to 72%. A three-stage conventional RO system recovers the nutrients. The single-stage recovery rate of the RO system is 48 to 55%, as shown in Table 5.6.

**Table 5.6. Operating Conditions of UF and RO Membranes**

Item	Unit	UF Membrane	RO Membrane
Operation		batch	three-pass
Membrane		UF 150 kDa	brackish water
Membrane type		flat plate	spiral wound
Feed temperature	F	113–150	95–122
Pressure	1st	psi	70
	2nd	psi	420–640
	3rd	psi	140–210
			14–40
Single-stage recovery rate	%	65–72	48–55
Feed TS conc.	%	3.0–6.0	1.2–1.8
Permeate TS conc.	%	1.2–1.8	0.02–0.05

Because the UF concentrate contains high levels of small organics and bacteria that are beneficial to the biogas performance, the concentrate is sent back to the anaerobic digester. It has been reported that methane production in the biogas plant has increased up to 20% as a result of this recycling of organics and bacteria from the digestate [365, 367]. The concentrate from the RO system, which is high in nutrients, can be sold as liquid fertilizer. The mass balances for nitrogen, potassium, and phosphorus are listed in Table 5.7. Based on the data in Table 5.7, most of the phosphorus is rejected by UF, whereas a significant amount of potassium and nitrogen stay in the UF filtrate. These nutrients are further concentrated in the RO system, resulting in a final concentration of nitrogen (0.8%), phosphorus (0.2%), and potassium (0.3%).

**Table 5.7. Mass Balance of Nutrients from UF and RO Membranes**

Parameter	Unit	UF Feed	UF Filtrate	UF Concentrate	RO Permeate	RO Concentrate
Flow rate	gpd	44,600	30,400	14,300	16,700	13,700
Potassium	mg/L	780	620	960	7.9	3100
Total nitrogen	mg/L	3878	3837	3304	31	8370
Total phosphorus	mg/L	179	105	335	0.02	232

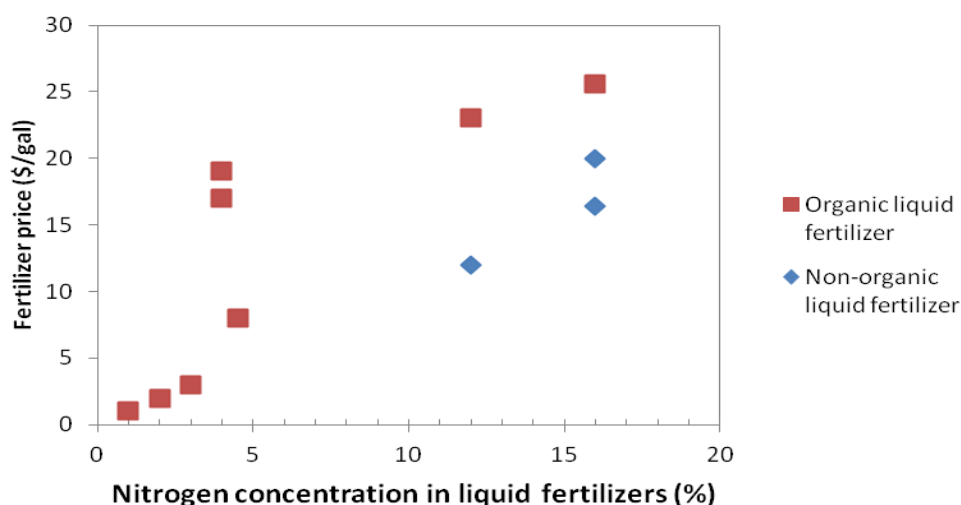
*Notes:* RO=reverse osmosis; UF=ultrafiltration.

**Table 5.8. Factors That Affect Liquid Fertilizer Market Value**

Nutrient concentration	Low concentration liquid fertilizers (nitrogen concentration <3%) have relatively low market price (Figure 5.10). Most of the products available from retailers have nitrogen concentration higher than 4%.
Composition	Fertilizer prices are affected by different nutrient ratios, micronutrient levels, and bioactive compounds such as soluble humates. As non-point source phosphorus pollution has become an international concern, low phosphorus liquid fertilizer is preferred.
Targeting market	Nationwide marketing and selling may not be feasible for low concentration fertilizers because of expensive packaging and transportation.
Organic certification	Organic certified fertilizers are two to three times higher in cost than conventional fertilizers with similar composition and nutrient level (Figure 5.10).

### **5.2.5.3 Economic Analysis**

As shown in Table 5.7, the digestate treatment process can produce 13,700 gpd of RO concentrate, which can be sold as organic liquid fertilizer directly or after further concentration. The N:P:K ratio in the concentrate is close to 4:1:2, which is a common nutrient ratio in liquid fertilizers. In addition, soluble humates and trace elements in the concentrate resulting from anaerobic digestion make the concentrate more attractive as liquid fertilizer. Current market prices of the liquid fertilizer are affected by many factors, such as nutrient concentrations, micronutrients, targeting market, and geographical locations, which have been summarized in Table 5.8.



**Figure 5.10. Market prices of different fertilizers with different nitrogen levels**

*Note:* Data and resources presented in this figure are summarized in Table 5.9.

**Table 5.9. Market Analysis of Fertilizers Used**

Fertilizer	Price*	References
Organic anaerobic digestate fertilizer (1%, 2%, and 3% N)	approximately \$1/gal, \$2/gal, \$3/gal, respectively	personal communication [368]
Organic liquid fertilizer** (4% N)	\$17.50/gal (>275 gal)	aggrand.com
Organic liquid fertilizer (4% N)	\$19.10/gal	woodcreekfarm.com
Organic fish fertilizer (4.5% N)	\$8/gal (>180 gal)	groworganic.com
Organic liquid fertilizer (12% N)	\$30/gal	shop.fifthseasongardening.com
Liquid fertilizer (12%N)	\$11.30/gal	outsidepride.com
Liquid fertilizer (16% N)	\$16.40/gal	store.interstateproducts.com
Liquid fertilizer (16% N)	\$20/gal (>20 gal)	store.interstateproducts.com
Nature Liquid fertilizer (16% N)	\$25.60/gal	greenergreengrass.com

*Notes:* N=nitrogen. \*Prices listed here are the published retail price of liquid fertilizers. The variation in prices of similar products may also be caused by marginal cost and other related costs such as packaging and transportation.

An economic analysis was conducted for the biogas plant considering two scenarios. In the first (actual) scenario, RO concentrate from the treatment process is sold to local buyers as a

low concentration bulk fertilizer to eliminate packaging and long-distance transportation. This scenario assumes that significant and sustained long-term demand of the fertilizer exists locally. Potential buyers of the RO concentrate include local farmers, lawn care service providers, and other commercial fertilizer applicators such as the sport turf and golf industries. In the second (conceptual) scenario, the RO concentrate will be further processed to increase the nitrogen level to 4% for higher market price per lb/N. In both scenarios, the final products will be certified as organic soil conditioner or organic fertilizer. Based on the current market price of different liquid fertilizers (see Figure 5.10), the market price of liquid fertilizer has been estimated as \$0.83/gal and \$12/gal in the first and second scenarios. As listed in Table 5.10, the potential value of the fertilizers is \$4.14 million and \$12 million/year, respectively. However, the concentration process, packaging, marketing and shipping will offset part of the fertilizer value in the second scenario. In addition, 16,700 gpd of water recovered from RO can also be reused in the process.

**Table 5.10. Potential Value of RO Concentrate as Organic Liquid Fertilizer**

	<b>Scenario 1 (Actual)</b>	<b>Scenario 2 (Conceptual)</b>
<b>Total production</b>		
Recovered product	liquid fertilizer (0.83% N)	liquid fertilizer (4% N)
Production rate	13,700 gpd	2740 gpd
<b>Marketability</b>		
Market value	\$0.83/gal	\$12/gal
Potential income	\$11,370/day (\$4.14 M/yr)	\$32,000/day (\$12 M/yr)
<b>Disposal savings</b>		
	NA	NA
<b>Total benefit</b>	<b>\$4.14 M/yr</b>	<b>\$12 M/yr</b>

Note: NA=not available.

#### **5.2.5.4 Conclusions**

This biogas plant successfully treats digestate from its anaerobic digesters using a combination of UF and RO membrane systems. By applying a vortex-enhanced membrane system, the biogas plant has simplified the digestate treatment process while saving operating costs. At the same time, this treatment process also provides economic benefits by recovering nutrients previously being disposed of. The treatment process can produce 1 to 5 million gallons of liquid fertilizer per year, which has a potential value of \$4.14 to \$12 million/year.

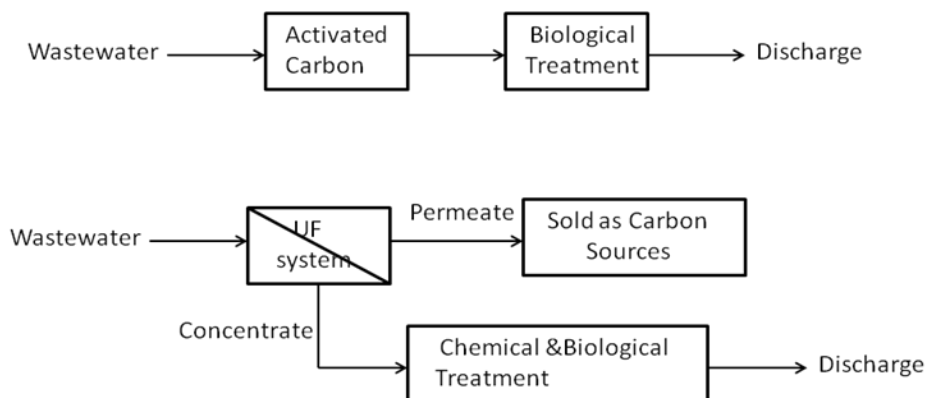
## 5.2.6 Case Study 10—Polymer Production Wastewater Treatment and Alternative Carbon Source

Goals:

- Reduce the treatment cost of the methylcellulose wastewater.
- Concentrate methylcellulose from wastewater and recover easily degradable organics as alternative carbon source.

### 5.2.6.1 Introduction

Methylcellulose, a chemical compound derived from cellulose, is used as a thickener and emulsifier in multiple applications. The wastewater generated from the washing step of methylcellulose production is very difficult to treat using biological treatment because of the significant amount of non-biodegradable substances. Thus, activated carbon is often used first to treat the wastewater before it is sent to conventional biological treatment. As discharge restrictions have become more stringent, it has become more difficult and costly to treat the methylcellulose wastewater using conventional methods. To reduce wastewater treatment costs and recover useful material from methylcellulose wastewater, a large chemical company in Korea has applied a membrane system to its wastewater treatment process [361, 369]. Schematics of the conventional wastewater treatment process and membrane treatment process are shown in Figure 5.11.



**Figure 5.11. Comparison of conventional treatment process and membrane treatment process.**

By applying the membrane system, the chemical company has been able to reduce its volume of wastewater from 100 to 35 tpd [370]. Permeate from the membrane system contains readily biodegradable organic carbon such as methanol. Thus, it can be sold or hauled away as a carbon source to a municipal wastewater treatment plant. The remaining concentrate can be further treated in a process that includes powder-activated carbon and biological nutrient removal.

### 5.2.6.2 Process and Performance

Although membrane technology is a good candidate to remove insoluble and non-biodegradable substrates from wastewater, conventional membrane systems have proved to be not feasible in this application because of the high solids content and viscosity of the wastewater. To control this fouling issue, the membrane system used in this project has a



vortex generator between the membrane surfaces. The operating conditions of the filtration process are summarized in Table 5.11.

**Table 5.11. Operating Conditions for the Membrane System Used in Methylcellulose Wastewater Treatment**

Membrane	UF (5000 MWCO)
Operating pressure	70–110 psi
Average flux	20 GFD
Single-stage recovery rate	65%
Wastewater temperature	80° C
pH level	10–12
Cleaning method	20-minute hot water flush every 4 hours

*Note:* MWCO=molecular weight cut-off.

Once the wastewater is prescreened for large particles, it can be pumped to the membrane system without other complicated pretreatments. The system uses a 5000 molecular weight cut-off (MWCO) UF membrane to remove particles. A 20-minute hot water flushing is performed after every 4 hours of operation, and no other type of chemical cleaning is needed. The flux is maintained at an average of 20 GFD.

#### **5.2.6.3 Source of Alternative Carbon**

In municipal wastewater treatment plants, carbon sources are needed for the denitrification process when the carbon to nitrogen ratio in the wastewater is low. Methanol is one of the preferred external carbon sources because of its lower cost, simple chemical structure, and highly biodegradable nature; however, as the price of methanol is greatly affected by the price of oil, which has been steadily increasing, the operational costs of wastewater treatment facilities have also been increasing, and alternative carbon sources are needed.

A potential alternative carbon source from the membrane process to replace methanol should meet the following criteria.

- low in nitrogen and phosphate
- low in or have no non-biodegradable substrates
- consistent water quality
- no toxic materials in the carbon source

The membrane system, by removing non-biodegradable components, increases the proportion of readily biodegradable chemical oxygen demand (COD) in the UF permeate to higher than 99%. Analytical results to identify the structure of the material, conducted by the Korea Testing & Research Institute, indicated the substance had less than four carbon elements with a straight line structure. It had high hydrophilic properties with high biological reactivity from the presence of acetate and hydroxyl groups. The concentration of heavy metals was very low, and nitrogen and phosphorus were not found in the UF permeate. In addition, it has been confirmed that using the methylcellulose wastewater permeate produced by the system

as a carbon source results in a nitrogen removal rate as high as that with methanol in a full-scale wastewater treatment facility. Therefore, permeate from the UF system has a market value as an alternative carbon source for wastewater treatment facilities.

#### 5.2.6.4 *Economic Analysis*

Treating methylcellulose wastewater with the membrane process can significantly reduce the cost of treatment by reducing the volume of wastewater that needs to be subsequently treated. Because the wastewater volume needing subsequent treatment by a conventional system is significantly reduced, operating costs can also be reduced. Although the market value of permeate from the membrane system has not yet been determined, it has a potential value, or at least it can be readily given away as an alternative carbon source without further treatment. Based on the estimations summarized in Table 5.12, the total savings resulting from implementation of the membrane system are \$94,100/year.

**Table 5.12. Operational Cost–Benefit Analysis of Membrane Methylcellulose Recovery Process Versus Conventional Process**

<b>Total Production</b>	
Recovered product	alternative carbon source
Daily production rate	65 tons (143,000lb)
Yearly production rate	131,000 tons (289 M lb)
<b>Marketability</b>	
Market value	NA
Potential income	NA
<b>Operational Cost Savings</b>	
Savings on reduced activated carbon cost	\$455/day (\$166,000/yr)
Savings on biological treatment cost reduction due to the lower wastewater production	\$23/day (\$8395/yr)
Amortized membrane system cost	-\$220/day (-\$80,300/yr)
Total savings on operational cost	\$94,100 /yr
<b>Total Benefit</b>	<b>\$ 94,100 /yr</b>

*Note:* NA=not available.

#### 5.2.6.5 *Conclusions*

The membrane system used in this project is able to treat wastewater from methylcellulose production with high solids and viscosity. Permeate from the filtration process has potential value to wastewater treatment facilities as a desirable alternative carbon source. The filtration process delivered a single-stage recovery of 65%, which can reduce the wastewater volume by 35%. As a result, the company can save \$95,000/year in operating costs of its wastewater treatment.

### **5.2.7. Case Study 11—Grain Recovery from High Strength Brewery Wastewater**

Goals:

- Recover suspended solids from trub wastewater to reduce operational issues experienced in downstream wastewater treatment facility.
- Concentrate the recovered TS to 15% to be sold as an animal food additive.

#### **5.2.7.1 Introduction**

During the brewing process, large quantities of wastewater are produced; typically, 3 to 4 L of water is used to produce 1 L of beer [361, 371]. One component of this waste stream is known as trub, which is separated from the grain boiling process and has high TS concentrations. Most of the solids (spent grains) in the trub are usually separated by a conventional grit screen and sold as a feed additive to local farmers. The remaining waste stream, containing approximately 3 to 5% TS, is typically sent to a conventional wastewater treatment system; however, on-site operation of a conventional wastewater treatment system is difficult and expensive because of the high solid content in the trub waste. Relatively small breweries discharge the wastewater to the sewer system and pay a wastewater surcharge fee or haul away the waste because they are not able to afford conventional wastewater treatment systems [361].

A commercial brewery in California was interested in examining the possibility of further recovery of grain from the waste stream using a membrane system so the liquid portion could be discharged without surcharges and recovered grain could be sold as liquid animal feed together with the spent grains. In order to have a market value as animal feed, the solid content in the recovered grain should be around 15 to 20%. Conventional membrane systems have limited performance and applicability in brewery wastewater because of fouling and the associated maintenance cost of frequent membrane cleaning and replacement. In this case study, a specially designed vortex membrane system was used to evaluate the feasibility of grain recovery from high strength brewery wastewater.

#### **5.2.7.2 Process and Performance**

A pilot test has been conducted with a vortex membrane system to evaluate this approach for the brewery. As shown in Figure 5.12, the brewing process begins by boiling malted grains, barley, and hops in water to produce what is known as a mash. The mash separates into wort (liquid) and trub (high solid part). The wort is sent to the fermentation tank for beer production with the addition of yeast. Trub is considered a waste stream in the process. The bulk solids (spent grains) in the trub are removed using a conventional grit screen or cyclone-type system. The remaining trub will be introduced to the vortex membrane system for solid concentration. The permeate from the membrane system can be discharged to the conventional wastewater treatment facility without surcharge.

Operating conditions of the vortex membrane system are summarized in Table 5.13. The wastewater (trub) from the grit screen had TS of approximately 4%. The pH and conductivity of the trub were 8.3 and 1400  $\mu\text{S}$ . The temperature of the trub directly from the process line is approximately 176 to 200° F (80–95° C). Although the membrane system can take feed water up to 200° F, it was difficult to maintain a feed temperature this high in the pilot setup. The

pilot test was conducted between 86 and 118° F (30–48° C). A higher feed temperature will result in a higher flux, which means an increased throughput from the system. After testing various membranes, a UF membrane was selected as the most suitable for this application. The membrane was made from polyethersulfone with an MWCO of 150,000 Da. Filtration was conducted at 5 kg/cm<sup>2</sup> (73 psi).

The membrane recovered 77.2% of the water from the original process wastewater. That is, from an initial value of 4.1%, the TS of the final concentrated material was 13%. In the brewery line, the vortex membrane system will be able to concentrate the process waste to 15% TS, meeting the requirement for animal feed stock, because the feed temperature is much higher than during the pilot test. At the same time, the membrane system can remove more than 99% of total suspended solids (TSS) from the wastewater to reduce TSS loading in conventional treatment.

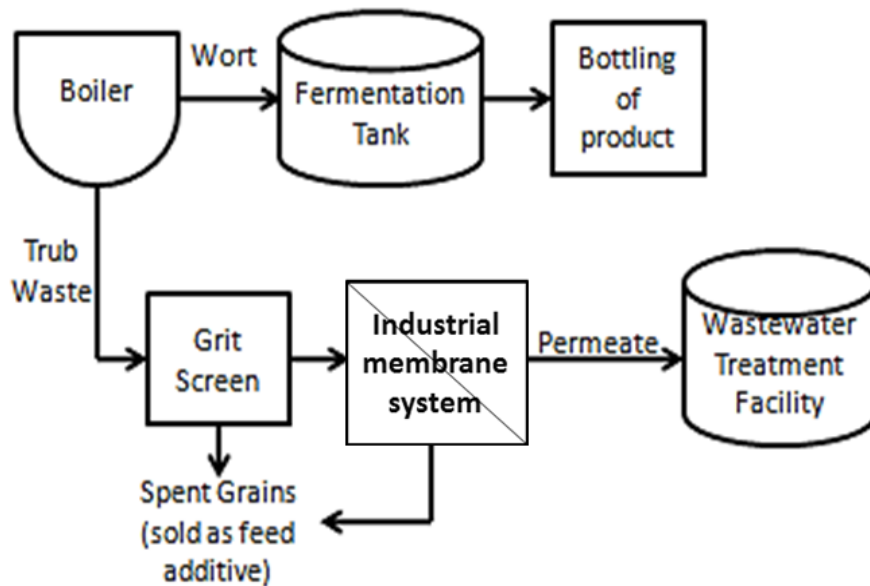


Figure 5.12. Process flow diagram in brewery wastewater treatment.

**Table 5.13. Operating Conditions of Vortex Membrane System**

Parameter	Unit	Value
pH	-	8.3
Turbidity	NTU	N/A
Total Solids	%	~ 4
Electrical conductivity	mS	~ 1400
Test temperature range	° F	86–118 (30–48° C)
Optimum operating pressure	kg/cm <sup>2</sup> /psi	5
Membrane	-	UF 150,000 Da
Flux	GFD	73
Recovery rate	%	77.2

Notes: NA=not applicable; NTU=nephelometric turbidity units; UF=ultrafiltration.

#### **5.2.7.3 Economic Analysis**

The brewery produces 13,000 to 15,000 gallons of wastewater per day containing 3 to 5% TS. An average flow rate of 14,000 gallons/day and TS value of 4% will be used in the following economic analysis (see Table 5.14). Based on the recovery rate and final TS expected, the brewery will produce 53 tpd additional spent grain by applying the vortex membrane system. Typically, the spent grain from the brewery is used to feed cattle because its high protein content and dietary fiber make it a valuable supplement to existing feed. It has been reported that spent grain in some breweries was sold to farmers for livestock feed at a price of \$6.50 to \$7/wet ton [372]. A value of \$6.50/wet ton was selected as the market price of the spent grain in this study. Economic analysis assumes the brewery discharges the wastewater to the sewage system with surcharge penalties. Based on a surcharge survey conducted in U.S. EPA Region 4 [373], the average discharge limit of TSS was 300 mg/L; TSS over the discharge limits is subject to surcharge penalties. The average TSS surcharge fee is \$0.186/lb. Biochemical oxygen demand (BOD) and COD surcharges were not considered in the analysis because of the limited water quality data. Thus, actual surcharge cost savings may be higher than estimated here.

**Table 5.14. Economic Analysis for Grain Recovery from Brewery Wastewater**

<b>Total Production</b>	
Recovered product	spent grain (TS 15%)
Total flow rate	14,000 gallons/day (53 tpd)
Initial TS concentration	4%
Daily production rate	2800 gallons (10.6 ton)
Yearly production rate	1 M gallons (3860 ton)
<b>Marketability</b>	
Market value	\$6.50/ton
Potential income	\$ 25,000/yr
<b>Sewage Surcharge Savings</b>	
Discharge limit	300 mg/L
Daily TSS discharge over the limit	4630 lb/day
TSS surcharge cost	\$0.186/lb
Daily saving in surcharge cost	\$861
Yearly saving in surcharge cost	\$314,300
<b>Total Benefit</b>	<b>\$339,300 /yr</b>

Notes: TS=total solids; TSS=total suspended solids.

As presented in Table 5.14, the recovered spent grain will bring a potential income of \$25,000/year and additionally can save \$314,300/year in sewage surcharge cost. The total benefit of implementing the recovery system will be \$339,300/year.

#### **5.2.7.4 Conclusions**

The significantly high levels of TSS and BOD in brewery waste require many breweries to pay penalties or haul away the waste at high cost. Typical membranes not only have significant fouling issues with these high solid wastes but also a reduction in temperature is needed to protect the membrane elements. The vortex membrane system enables the brewery to process total solids of 1 to 10% or more at temperatures of up to 200° F, all while removing greater than 99% of TSS. By removing greater than 99% TSS, the solid loading to the wastewater treatment facility can be greatly reduced, significantly decreasing treatment, surcharge penalty, and haul-away costs. In addition, the membrane system will be able to concentrate the process waste to 15% TS, meeting the requirement for animal feed stock, so it can be sold to provide added revenue to help offset the cost of treatment. Based on the economic analysis conducted for a commercial brewery, the recovery system can produce \$339,300/year net benefit to the brewery.

## 5.3 Material Recovery from Brines

### 5.3.1 Case Study 12—Mineral Recovery from RO Concentrate Using Isothermal Evaporation

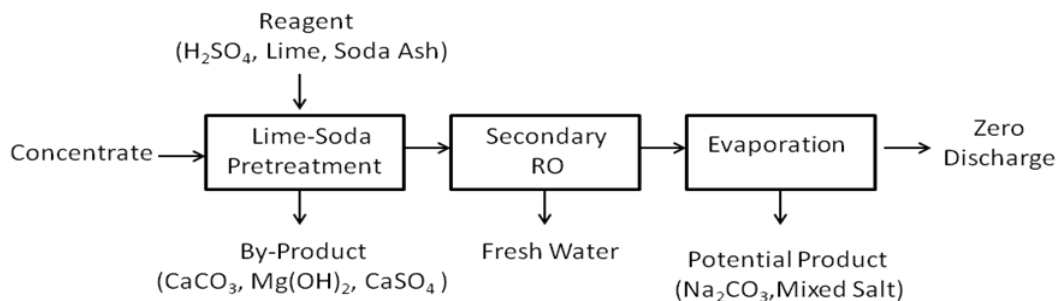
Goals:

- Manage RO concentrate from a desalination plant where ZLD is required.
- Recover minerals during RO concentrate treatment process.

#### 5.3.1.1 Introduction

Disposal of RO concentrate is one of the constraints to implementing RO to treat brackish water. In inland areas, concentrate disposal is especially challenging and expensive. One attractive solution to the concentrate disposal issue is to turn this disposal problem into a natural resource by finding beneficial uses for the waste stream.

To reduce the volume of the waste stream, the concentrate from a desalination system can be further concentrated using a seawater-type RO system. In order to maximize water recovery from the RO system, potential scalants should be removed in a pretreatment process [374]. The selective precipitation and recovery of useful salts also has the potential to reduce the costs of solid waste disposal, process operation, and chemical consumption. The objective of this study was to treat RO concentrate with byproduct recovery using a three-step process, shown in Figure 5.13.



**Figure 5.13. Process schematic for desalination effluent management.**

Source: [376]

#### 5.3.1.2 Recovery Process

RO concentrate used in this study was obtained from the city of Goodyear's drinking water RO system and the city of Scottsdale's reclaimed water RO system. Goodyear treats brackish groundwater to produce potable water and produces over 0.5 mgd of concentrate with a TDS of approximately 6500 mg/L. Scottsdale Water Campus purifies reclaimed water from municipal wastewater for indirect potable reuse and produces over 2 mgd of concentrate with a TDS concentration of approximately 7800 mg/L.

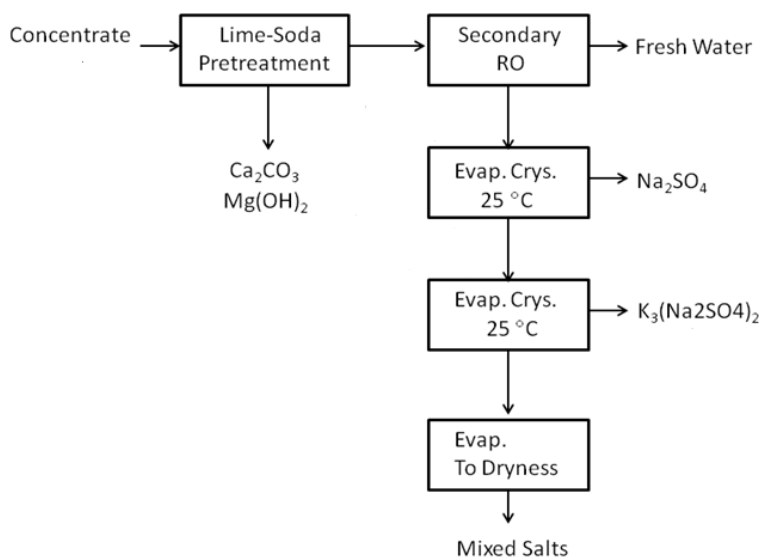
The first process converts soluble calcium and magnesium to insoluble calcium carbonate and magnesium hydroxide. A modified lime–soda treatment is used to improve the efficiency of magnesium and calcium removal and enhance the quality of solid byproducts. In this method,

the addition of concentrated sulfuric acid lowers the pH to below 4.3 to remove alkalinity as carbon dioxide. In the next step, the concentrate pH is increased to 11 by lime addition to precipitate magnesium hydroxide with limited calcium products. In the last step, the addition of soda ash precipitates calcium carbonate as a byproduct of the reaction. After the completion of each reaction, precipitates are separated by filtration.

After removing the major foulants in the lime–soda treatment, the concentrate can be fed into a secondary RO process to recover 80 to 90% of the freshwater [375] and reduce the concentrate volume. The remaining concentrate can be further reduced in volume by evaporation with the selective precipitation of sodium sulfate as a potential byproduct.

### 5.3.1.3 Practical Application

Possible product recoveries from the Scottsdale concentrate and process requirements are shown in Figure 5.14, based on the pilot test. The lime–soda pretreatment can produce 8.7 tpd calcium carbonate and 4.3 tpd magnesium hydroxide mixture from 1 mgd RO concentrate. Assuming 90% recovery by secondary RO, 0.1 mgd concentrate and 0.9 mgd freshwater can be produced in the secondary RO treatment. After evaporation, 13.1 tpd sodium sulfate can be recovered from the secondary RO concentrate. The volume of concentrate after the precipitation of sodium sulfate will be approximately 1% of the original concentrate volume. Further evaporation to reach a concentration factor of 171 [374] may allow for the production of potassium salts. The volume of the final concentrate after the complete precipitation of potassium salts will be approximately 0.07% of the initial concentrate volume.



**Figure 5.14. Products recoverable from evaporation/crystallization of Scottsdale concentrate at 25° C.**

Source: [374]

### 5.3.1.3 Economic Analysis

The major compositions of the byproducts from the pretreatment and secondary RO system are calcium carbonate and sodium sulfate, as presented in Table 5.15.



**Table 5.15. Main Composition of the Byproducts in Different Steps of Mineral Recovery from RO Concentrates**

Goodyear Concentrate Sample	Mass of Solid (tpd)	Compositions
Lime stage byproduct	4.3	50.8% $\text{Mg}(\text{OH})_2$ , 19.5% $\text{CaCO}_3$ , 7.8% $\text{CaSO}_4$
Soda stage byproduct	8.7	95% $\text{CaCO}_3$ , 4.1% $\text{CaSO}_4$
RO stage byproduct	11.5	80.2% $\text{Na}_2\text{SO}_4$ , 12.6% $\text{NaCl}$

*Note:* RO=reverse osmosis.

The purity of magnesium hydroxide obtained during the lime stage was 51%. One of the main applications of magnesium hydroxide is as a neutralizer in wastewater treatment or waste gas treatment. Although the purity seems low, the main impurities in the byproducts (calcium carbonate and calcium sulfate) do not affect the neutralizing ability of the byproduct. The price of magnesium hydroxide used in an environmental application such as an acidic wastewater neutralizer is \$350 to \$500/dry ton [376, 377]. Although the market value of this byproduct is uncertain because of the low purity, there is a potential demand for it; at a minimum, it can be readily given away to reduce the sludge disposal fee in the plant.

Calcium carbonate recovered from the soda stage has relatively high purity compared to the other byproducts. The main uses of calcium carbonate include pulp and paper, rubber and plastic, and construction-related products. Most of these uses require purities higher than 96%, whereas construction-related products such as steel, bricks, and paint can use lower quality calcium carbonate. The market price of calcium carbonate ranges from \$130 to \$300/ton [131, 378, 379]. The market value of the calcium carbonate is estimated to be \$130/ton.

Sodium sulfate from the secondary RO stage has 80% purity. The average price of sodium sulfate in 2011 was \$140/ton; major applications such as detergent, glass, and pulp and paper, require high purity (>99%) [378, 379]. Without further purification or modification of the recovery process, it is difficult to determine the market value of recovered sodium sulfate.

The major costs associated with using RO concentrate are estimated to be the chemical cost and sludge disposal for the pretreatment process. As summarized in Table 5.16, recovering valuable minerals from the RO concentrate can significantly reduce sludge disposal fees, and the potential income of \$413,000/year can further offset treatment costs and make the process more economical and potentially more sustainable. The major challenge in commercializing these mineral byproducts is limited application as a result of low purity. Modification or optimization of the recovery process to produce higher quality byproduct is desirable.

**Table 5.16. Economic Analysis of Mineral Recovery from Scottsdale’s Reclaimed Water RO System**

<b>Total Production</b>			
Recovered product	Magnesium hydroxide	Calcium carbonate	Sodium sulfate
Production rate	4.3 tpd (1570 tpy)	8.7 tpd (3475 tpy)	13.1 tpd (4781 tpy)
<b>Marketability</b>			
Market value	NA	\$130 tpd	NA
Potential income	NA	\$413,000/yr	NA
<b>Disposal Savings</b>			
Disposal cost	\$62.50/ton (based on average trucking and tipping fees for hauling and land filling in California) [24]		
Saving in disposal cost	\$98,100/yr	\$217,200/yr	NA
<b>Total Benefit</b>	<b>\$728,300/yr</b>		

#### 5.3.1.4 Conclusions

The methods outlined in this study may be applicable for treating RO concentrate and producing sodium sulfate minerals, sodium chloride, or potassium salts. After the three steps of RO concentrate treatment, the volume of final concentrate will be approximately 1% of the original concentrate volume. The recovery of byproducts from the concentrate may have \$728,300 benefit per year, which may lower the costs of the desalination processes.

### 5.3.2 Case Study 13—Calcium Recovery from RO Concentrate Using a Fluidized-Bed Crystallizer

Goals:

- Remove major scalant from RO concentrate to increase recovery rate in a desalination plant.
- Recover calcium product during RO concentrate treatment process.

#### 5.3.2.1 Introduction

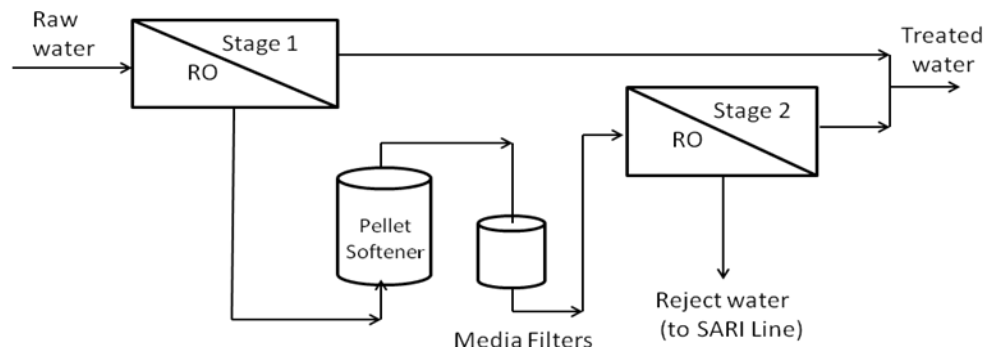
RO can be used to convert reclaimed and brackish water to potable water; however, high cost and technological constraints limit the implementation of desalination plants. One of the constraints is the production of a significant volume of RO wastewater containing concentrated salts [380]. To reduce the volume of this waste stream, the reject from a desalination system can be further concentrated using a secondary RO system that utilizes

seawater membranes. In order to maximize the recovery of the RO system, potential scalants such as calcium, magnesium, and silica should be removed in a pretreatment process; however, the costs of pretreatment and sludge disposal are significant. One attractive solution to this issue is to turn this disposal problem into a revenue-producing natural resource by finding beneficial uses for the waste product [374].

Chino Desalters in Chino, CA produce drinking water from brackish groundwater basins. In an effort to reduce the brine concentrate discharge and scale formation in the Santa Ana River Interceptor (SARI) line, the Chino Basin Desalter Authority (CBDA) has worked with the Western Municipal Water District to pilot test pellet softening, a precipitative softening process using seeding nuclei to remove hardness and produce pellets as byproduct, at the Arlington Desalter [93]. Additional details provided are based on the market survey report prepared by Water Quality Treatment Solutions Inc. (WQTS). The CBDA is considering implementing this technology with the expansion of the Chino II Desalter, which will produce an additional 10.5 mgd of RO-treated water. CBDA conducted a market survey to determine the possible market value of the softening pellets to be generated at the Chino II Desalter.

### 5.3.2.2 Process and Performance

With the current brackish water quality, RO recovery in the Chino II Desalter is approximately 82%, with the remaining 18% disposed into the SARI line as concentrate waste. Removing mineral content from the RO brine can increase the total RO recovery up to 97%. The technology being considered by CBDA is a pellet softening process. A schematic of the brine management process is shown in Figure 5.15. The concentrate from the first-stage RO is introduced into a pellet softener to precipitate minerals. The supernatant from the softener can be sent to the second-stage RO to recover more water. Concentrate from the secondary RO can be discharged to the SARI line.



**Figure 5.15. Schematic of brackish water treatment and mineral recovery.**

Source: [93]

The pellet softening is achieved in an upflow reactor with fluidized particles introduced at the reactor bottom. The particles act as seeding nuclei onto which calcium carbonate and other minerals will precipitate. In order to promote the precipitation, caustic soda or lime is added to the feed concentrate. As precipitates build up on the nuclei, pellets in the fluidized reactor grow and eventually reach a size that can no longer remain fluidized. Thus, large pellets can be removed from the vessel bottom at a certain frequency. This process can produce hard, durable pellets that are relatively easy to handle and transport, compared to the wet sludge

produced by conventional softening processes. Although the chemical composition of the pellet depends on the water quality, the primary components of the pellets have been analyzed to be calcium carbonate (83%) and sand (8%). It has been estimated that 40 tons of pellets will be produced per day in the Chino II Desalter after its planned expansion.

### **5.3.2.3 Economic Analysis**

A market survey of potential pellet users was conducted by CBDA, focusing on the Riverside–San Bernardino region to minimize transportation costs. The survey covered a diverse set of industries, and construction material manufactures and limestone mining companies have been identified as the most likely potential users based on the following criteria:

1. proximity to the water treatment plants, which affects transportation costs
2. ability to use up to 40 tons of pellets per day because of the limited pellet storage capacity at the Chino II Desalter
3. sustained, long-term demand for pellets
4. high tolerance for variability in pellet properties because the pellets are derived from source water that is subject to variability
5. willingness to pay for the pellets; the financial viability of the pellet softening treatment depends on the ability to partially recover operational costs.

A local construction material manufacturer has considered receiving the material and is conducting an internal evaluation of the pellets to determine the specific application. This company can be a large and reliable user of the pellets. The pellets can be used as additives to increase the strength or change the appearance of the blocks in block manufacturing processes. For this application, the hardness and roundness of the pellets are important physical characteristics because they affect the structural properties of the block.

Limestone mining provides calcium carbonate for various applications. A limestone mining company has considered the softening pellets to replace limestone. Limestone miners are interested in the pellets because they have unique chemical and physical properties (hardness, roundness, and consistent chemical composition compared to limestone) that may be beneficial in particular applications. In addition, the pellets can extend the life of the limestone quarry for the company. Because limestone buyers require low moisture content in the product to reduce transportation costs, pellet drying may be required for this application. The Lucerne Valley company is approximately 85 miles northeast of Chino, so the distance could be a negative factor.

On the basis of this southern California market survey, the unit sale price of the pellets may range from \$10 to \$20/ton. Economic analysis of the pellets is summarized in Table 5.17. Considering a 40 tpd production rate, operating 90% of the year, the potential income from the pellets is \$131,000 to \$263,000/year. In a conventional softening process, the produced sludge requires disposal and tipping fees; however, such disposal costs will be eliminated by the potential beneficial use of the pellets. The current disposal cost is \$35/ton at the two local landfills. Considering the additional transportation cost, the total cost to dispose of these pellets is estimated to be between \$660,000 and \$1.25 million/year. Thus, the Chino II Desalter can achieve potential net savings in the range of \$790,000 to \$1.5 million/year by selling the pellets.

**Table 5.17. Economic Analysis of Mineral (Pellet) Recovery from Chino II Desalter**

<b>Total Production</b>	
Recovered product	Calcium carbonate pellets (83% purity)
Production rate	40 tpd (131,000 tpy)
<b>Marketability</b>	
Market value	\$10–\$20 /ton
Potential income	\$131,000–\$263,000/yr
<b>Disposal Savings</b>	
Disposal cost savings (including landfill and transportation costs reduction)	\$50–\$95/ton
Saving in disposal cost	\$0.66 M–\$1.25 M/yr
<b>Total Benefit</b>	<b>\$0.79 M–\$1.5 M/yr</b>

#### **5.3.2.4 Conclusions**

By applying a pellet softener system, Chino II Desalter can increase its RO recovery from 82% to 97%. As a further consequence, the discharge of concentrate waste to the SARI line and scaling problems in the line can be significantly reduced. This process can also produce a marketable byproduct, 40 tpd of calcium carbonate pellets. The market survey suggests a clear market demand for the pellets. The construction material manufacturer and the limestone mining company are excellent candidate pellet users. Either of these companies can handle the entire 40 tpd pellet production from the Chino II Desalter; however, further testing of the actual Chino pellets will be necessary to determine their suitability for each application. Chino II Desalter can achieve potential net savings in the range of \$790,000 to \$1.5 million/year by implementing the pellet softener process.



## Chapter 6

### Conclusions

---

Because of increasing demands on conventional water sources, communities in the United States and abroad are turning toward unconventional water resources such as brackish groundwater, wastewater effluent, irrigation return water, and seawater to meet current and future water demands [1–4]. The issues associated with concentrate management and disposal have created increased interest in developing methods and technologies for the minimization of RO concentrate volumes, with the ultimate goal of ZLD from desalination facilities. Unfortunately, the obvious benefits of concentrate minimization and ZLD practices are often offset by their high O&M costs and energy requirements [1, 2, 13, 14]. One possible strategy to recover costs from ZLD implementation is through the selective recovery of valuable constituents in RO concentrate streams. Potentially, these constituents could be marketed to increase the profitability of desalination facilities, which could in turn increase private investment in the desalination sector.

The major goal of this project was to examine current and past efforts aimed at recovering materials from aqueous solutions with the aim of recovering valuable compounds from desalination brine/concentrate streams. To this end, a comprehensive review was undertaken to summarize the literature pertaining to the extraction of metals, salts, and other valuable constituents from aqueous solutions. Based on the literature review, the feasibility of extracting materials in desalination brine/concentrate was evaluated, and a preliminary cost assessment was performed to evaluate the economics of extracting potentially viable compounds. Finally, various case studies on extraction in a variety of applications were compiled and summarized. A summary of potentially profitable compounds is provided in Table 6.1.

Currently, sodium chloride and magnesium compounds (magnesium hydroxide and magnesia) are the only compounds extracted from seawater at any appreciable extent; however, a significant amount of effort and research has been put into the development of processing schemes for the extraction of valuable constituents from desalination brine/concentrate over the past 40 years. With the exception of a planned process to produce calcium carbonate at a desalination facility in Southern California, only one documented case of valuable material extraction from desalination brine for economic gain was identified at full scale: sodium chloride is produced from SWRO brine in evaporation ponds in Israel.

Because the ocean is viewed as an inexhaustible resource, a significant amount of research has been performed to develop methods for extracting relatively high value trace metals. Particularly, technologies for the extraction of lithium, rubidium, and uranium have been continually refined over the past 30 years to improve extraction efficiency. Currently, such methods of extraction are inhibited by a number of factors, including poor selectivity, low commodity pricing (with the exception of rubidium), relatively low aqueous concentrations, low demand (particularly for rubidium), and complex post-processing necessary to yield pure products. Many analysts believe that the extraction of constituents with concentrations less than boron (~26 mg/L in seawater) will likely never be feasible unless alternative resources become exhausted. Although a number of publications have proposed the extraction of trace

metals from desalination brine/concentrate, very few report on the feasibility of extraction at an appreciable scale.

From a technical standpoint, the extraction of most major ions in desalination brine/concentrate is currently viable; however, the feasibility of producing commodities at profit from desalination brine/concentrate is dependent on numerous factors that require careful consideration. Economic factors that weigh heavily on the feasibility of material extraction include commodity demand and pricing, energy consumption and cost, labor requirements, and the overall costs of production. Other major considerations include facility siting (e.g., availability of raw materials, transportation, and cheap energy; close proximity to consumers), product purity and uniformity, safety, material handling, storage, and transport. In the studies discussing material extraction from desalination brine/concentrate, little analysis has been performed on the feasibility of transforming a water treatment facility into a chemical processing facility. Such an arrangement would likely require major changes in how a desalination facility is operated, including facility management, labor requirements, training, safety requirements, and research and development activities.

Besides the previously discussed trace metals, preliminary screening of the major commodities in seawater desalination brine indicated that bromine, magnesium, and sodium chloride could potentially be extracted for economic gain. In addition, several researchers have concluded that chlorine and sodium hydroxide could also be produced from desalination brine for a profit. Preliminary cost analyses performed on several reported schemes for the production of these commodities were developed to evaluate the economics of extraction. Preliminary cost analyses indicate that it is likely only economically feasible to produce magnesia (and potentially magnesium hydroxide) and potentially chlorine and sodium hydroxide from seawater desalination brine. The profitability of extracting chlorine and sodium hydroxide is strongly dependent upon the efficiency of the electrolytic cell, and more research is required to evaluate the efficiency of chlorine and sodium hydroxide production using purified desalination brine as feed stock.

Developed case studies of industrial and water treatment applications indicate that numerous industries are currently applying or considering the integration of material extraction into current operations. Depending on the industry, significant benefits can be realized that extend beyond maximizing profits (e.g., waste minimization).



**Table 6.1. Summary of Extraction of Potentially Profitable Compounds from Seawater and RO Concentrate**

Element	Price	Main Commodities	Literature on Mineral Extraction	Market Opportunities	Likelihood of Commercial Use
<b>Bromine</b>	\$1390/ton* [123]	elemental bromine, organobromide fertilizers, flame retardants, gasoline additives	[18, 62, 123–128]	<ul style="list-style-type: none"> <li>negatively impacted by the recent recession</li> <li>increased demand expected in Asia and South America</li> <li>proven worldwide boron reserves will meet global demand for the foreseeable future</li> </ul>	likely
<b>Calcium</b>	Crushed limestone: \$10/ton [381]	calcium carbonate, lime, calcium sulfate, calcium chloride	[2, 9, 80, 93, 133–136, 151]	<ul style="list-style-type: none"> <li>U.S. demand for gypsum is expected to increase.</li> <li>Production of gypsum from coal-fired power plant scrubbers is expected to increase [152].</li> <li>Possible applications for low quality commodities: dust suppression; sodic soil remediation [61].</li> </ul>	unlikely
	High purity CaCO <sub>3</sub> : \$165/ton [131]			-	
	Quicklime: \$116/ton [382]			-	
	Hydrate: \$139/ton [382]			-	
	Gypsum: \$30/ton [383]			-	
	CaCl <sub>2</sub> : \$132–\$354/ton [61]			-	
<b>Cesium</b>	Metal basis: \$1876/100 g [384]	cesium metal	[155–158]	Small market as drilling fluid, drill pipe unsticking, and treatment of some tumors.	unlikely
<b>Chlorine and Sodium Hydroxide</b>	Electrochemical unit netback: \$550/ton	chlorine gas, hypochlorous acid, solid NaOH, concentrated liquid NaOH	[16, 72, 161, 164–167]	<ul style="list-style-type: none"> <li>Demand for sodium hydroxide has increased over the past 5 years.</li> <li>Chlorine demand has decreased recently because of the global economic recession.</li> </ul>	likely, dependent on process efficiency

<b>Magnesium</b>	Magnesia, dead-burned: \$365–\$375/short ton [385]	magnesium metal, magnesia, $\text{Mg}(\text{SO}_4)$ , $\text{Mg}(\text{OH})_2$ , $\text{MgCl}_2$ , $\text{MgO}$ synthetic	[13, 16, 48, 62, 72, 74, 103, 153, 157, 192, 220, 224, 226, 227, 229, 230, 232–238, 245, 246, 248, 249]	<ul style="list-style-type: none"> <li>• Production of magnesium metal from seawater is not competitive with current methods of production.</li> <li>• Caustic-calcined magnesia and magnesium hydroxide demand is expected to increase in the near future.</li> <li>• United States currently imports the majority of consumed magnesia.</li> </ul>	likely
	Magnesia, synthetic: \$490/short ton [385]			-	
	Magnesium chloride, hydrous: \$290/short ton [385]			-	
	Magnesium chloride, anhydrous: \$0.128–\$0.15/lb [385]			-	
	Magnesium hydroxide, powder: \$0.45/lb [385]			-	
	Magnesium hydroxide, slurry: \$238–\$250/short dry ton [385]			-	
	Magnesium sulfate: \$0.18–\$0.22/lb [385]			-	
	Mg metal: \$2.20/lb [385]			-	
	Mg metal (China free market): \$3250/ton [385]			-	
<b>Nitrogen</b>	Fixed ammonia: \$540/ton [386] Ammonium nitrate: \$395–\$400/ton [387] Ammonium sulfate: \$365–\$375/ton [387] Anhydrous ammonia: \$612–\$710/ton [387] Diammonium phosphate: \$540–\$575/ton [387]	ammonia, urea, ammonium nitrate, ammonium phosphates, ammonium sulfate, nitric acid,	[257–261]	<ul style="list-style-type: none"> <li>• World nitrogen consumption for fertilizer is expected to increase [256].</li> <li>• Stable natural gas prices are creating expanding nitrogen fixing production.</li> </ul>	unlikely
<b>Potassium</b>	$\text{K}_2\text{O}$ : \$740/ton [388] as muriate of potash	potash: potassium chloride, potassium sulfate, potassium magnesium sulfate	[134, 156, 232, 274]	<ul style="list-style-type: none"> <li>• Worldwide potash consumption is expected to increase annually by approximately 4% from population growth and increased demand for fertilizers.</li> </ul>	likely

				<ul style="list-style-type: none"> <li>Potassium as a fertilizer has no substitutes.</li> </ul>	
<b>Rubidium</b>	Rubidium metal: Not commercially traded but around \$1400/100 g-Rb [389]	rubidium metal, rubidium carbonate, rubidium chloride, rubidium hydroxide, rubidium silver iodide	[156–158, 186, 281]	<ul style="list-style-type: none"> <li>possible increased interest for quantum computing, atomic clocks and superconductors, biomedical uses</li> <li>little demand</li> </ul>	unlikely, little demand
<b>Sodium</b>	Solar salt: \$70/ton [390]	salt, sodium hydroxide	[5, 11, 13, 58, 62, 71, 101, 153, 235–237, 288, 289]	<ul style="list-style-type: none"> <li>Sodium compounds are consumed in large quantities by a variety of end users and industries; demand is relatively stable.</li> <li>Many local markets likely exist regardless of manufacturing location.</li> </ul>	likely
	Rock salt: \$37/ton [390]			-	
	Salt in brine: \$8.50/ton [390]			-	
	Sodium hydroxide: \$500/ton [162]			-	
	Sodium carbonate (soda ash): \$280/ton [285]			-	
	Sodium sulfate: \$140/ton [391]			-	
<b>Strontium</b>	Strontium carbonate : \$0.71/kg [392]	strontium metal, strontium carbonate, strontium nitrate, strontium oxide (strontia), strontium hydroxide, strontium peroxide, celestite (strontium sulfate)	[74, 282, 290]	<ul style="list-style-type: none"> <li>Worldwide strontium demand has decreased significantly since 1997.</li> <li>Strontium compound consumption is expected to increase in the near future, both in traditional (ceramics, glasses, magnets) and more advanced applications (pharmaceuticals) [293].</li> </ul>	unlikely
	strontium metal: \$5.8/kg [392]			-	
	strontium nitrate: \$1.33/kg [392]			-	
	celestite : \$95/metric ton [392]			-	

<b>Lithium</b>	Lithium carbonate: \$4.22/kg (imported); \$6.25/kg (exported) [393] Lithium hydroxide: \$6.45/kg (imported); \$7.85/kg (exported) [393]	lithium carbonate, lithium hydroxide, lithium chloride	[20, 169, 175, 177, 179, 181, 182, 185–187]	<ul style="list-style-type: none"> <li>•Demand is expected to increase due to increasing lithium ion battery production.</li> <li>•Recent literature disagrees on the extent to which increased demand will affect lithium commodity pricing, and whether known reserves will be able to meet future demand.</li> <li>•Lithium is distributed unevenly globally.</li> </ul>	unlikely
<b>Molybdenum</b>	MoX: \$12.60–\$12.85/lb [394] <hr/> FeMo: \$14.58–\$14.85/lb [394]	ferro molybdenum, molybdenum trioxide	little information exists	Demand for molybdenum has increased significantly since 2008. <hr/> -	highly unlikely
<b>Uranium</b>	\$100.86/kg [290]	triuranium octoxide	[21, 158, 159, 281, 296, 298, 299, 304, 305, 311, 315–323]	Despite low demand since the nuclear disaster in Japan, worldwide demand is projected to increase, reaching 110 ktpy by 2030 [301]. Uranium could be extracted from seawater: cost \$220–\$280/kg [295]; also reported to fall between \$689–\$2850/kg [335].	likely if price >\$300/kg

*Note:* \*ton=metric ton.

## References

---

1. Martinetti, C. R.; Childress, A. E.; Cath, T. Y. High recovery of concentrated RO brines using forward osmosis and membrane distillation. *J. Membrane Sci.* **2009**, *331*(1–2), 31–39.
2. Bond, R.; Veerapaneni, S. *Zero liquid discharge for inland desalination*. Black and Veatch: Overland Park, KS, 2007; pp 1–233.
3. U.S. Bureau of Reclamation and Sandia National Laboratories. Desalination and water purification technology roadmap. A report of the executive committee, Water Treatment Engineering & Research Group, Denver, CO, 2003.
4. Lattemann, S.; Hopner, T. Environmental impact and impact assessment of seawater desalination. *Desalination* **2008**, *220* (1–3), 1–15.
5. Khan, S. J.; Murchland, D.; Rhodes, M.; Waite, T.D. Management of Concentrated Waste Streams from High-Pressure Membrane Water Treatment Systems. *Crit. Rev. Env. Sci. Technol.* **2009**, *39* (5), 367–415.
6. National Research Council. *Desalination: A national perspective*. National Academy Press: Washington, DC, 2008.
7. Greenlee, L. F.; Lawler, D. F.; Freeman, B. D.; Marrot, B.; Moulin, P. Reverse osmosis desalination: water sources, technology, and today's challenges. *Water Res.* **2009**, *43* (9), 2317–2348.
8. Gabelich, C. J.; Xu, P.; Cohen, Y. Chapter 10: Concentrate Treatment for Inland Desalting. In *Sustainability Science and Engineering*; Isabel, C. E.; Andrea, L. S. F., Eds; Elsevier: Amsterdam, The Netherlands, 2010; pp 295–326.
9. Sethi, S.; Walker, S.; Drewes, J. E.; Xu, P. Existing & Emerging Concentrate Minimization & Disposal Practices for Membrane Systems. *FLA Water Resour. J.* **2006**, 38–48.
10. Mickley, M. C. *Membrane concentrate disposal: practices and regulation*. U.S. Department of the Interior, Bureau of Reclamation, 2006, p 298.
11. Mickley, M. *Treatment of concentrate*. U.S. Bureau of Reclamation, 2008.
12. Mickley, M. *Brackish Groundwater Concentrate Management*. Mickley & Associates: Boulder, CO, 2010, pp 1–39.
13. Juby, G. J. G.; Zacheis, A.; Shih, W.; Ravishankar, P.; Mortazavi, B.; Nusser, M. D. *Evaluation and Selection of Available Processes for a Zero-Liquid Discharge System for the Perris, California, Ground Water Basin*. U.S. Department of the Interior, Desalination and Water Purification Research and Development Program: Denver, CO, 2008.
14. Koppol, A. P. R.; Bagajewicz, M. J.; Dericks, B. J.; Saveleski, M. J. On zero water discharge solutions in the process industry. *Adv. Env. Res.* **2004**, *8* (2), 151–171.
15. Dytnersky, Y.; Hojainov, Y. Extraction and utilization of valuable components from ocean water. *Desalination* **1991**, *81* (1–3), 261–264.

16. Al-mutaz, I. S.; Wagialla, K. M. Techno-economic feasibility of extracting minerals from desalination brines. *Desalination* **1988**, 69 (3), 297–307.
17. Mero, J. L. *The mineral resources of the sea*. Vol. 1. Elsevier: Amsterdam, The Netherlands, 1965.
18. Petersen, U. Mining the hydrosphere. *Geochim. Cosmochim. Ac.* **1994**, 58 (10), 2387–2403.
19. Cloud, P. Mineral resources from the sea. In *Resources and man: a study and recommendations*; Freeman, W. H., Ed.; W. H. Freeman: San Francisco, CA, 1969.
20. Bardi, U. Extracting minerals from seawater: An energy analysis. *Sustainability* **2010**, 2, 980–992.
21. Schwochau, K. Extraction of metals from sea water. In *Topics in Current Chemistry*. Springer: Berlin, Heidelberg, Germany, 1984, pp 91–133.
22. Pilson, M. E. Q. An Introduction to the Chemistry of the Sea. In *An Introduction to the Chemistry of the Sea*; McConnin, R. A., Ed.; Prentice-Hall: Upper Saddle River, NJ, 1998, 207–232, 341–350.
23. McHugh, J. B. Concentration of gold in natural waters. *J. Geochem. Explor.* **1988**, 30, 85–94.
24. Lieberman, M. B. The magnesium industry in transition. *Rev. Ind. Organ.* **2001**, 19.1, 71–80.
25. Stewart, L. C. Commercial extraction of bromine from sea water. *Ind. Eng. Chem.* **1934**, 26 (4), 361–369.
26. Stine, C. M. A. Recovery of bromine from sea water. *Ind. Eng. Chem.* **1929**, 21 (5), 434–442.
27. Ball, C. J. P. The History of Magnesium. *Journal of the American Society for Naval Engineers.* **1957**, 69 (1), 81–94.
28. Thorp, H. W.; Gilpin, W. C. Magnesia from sea water. In *Society of Chemical Industry*. London, 1949.
29. Kleiner, D. J. Magnesium industry. Handbook of Texas online (<http://www.tshaonline.org/handbook/online/articles/dkm01>) (accessed March 5, 2012). Published by the Texas State Historical Association.
30. Biello, D. Cement from CO<sub>2</sub>: A concrete cure for global warming? *Scientific American*, August 7, 2008.
31. Murray, J. *Major ions of seawater*. 2004. pp. 1–13.  
[http://www.ocean.washington.edu/courses/oc421/Lecture\\_Notes/CHPT4.pdf](http://www.ocean.washington.edu/courses/oc421/Lecture_Notes/CHPT4.pdf)
32. Riley, J. P.; Tongudai, M. The major cation/chlorinity ratios in sea water. *Chem. Geol.* **1967**, 2, 263–269.
33. Morris, A.W.; Riley, J. P. The bromide/chlorinity and sulphate/chlorinity ratio in sea water. *Deep Sea Research and Oceanographic Abstracts* **1966**, 13 (4), 699–705.
34. Culkin, F.; Cox, R. A. Sodium, potassium, magnesium, calcium and strontium in sea water. *Deep Sea Research and Oceanographic Abstracts* **1966**, 13 (5), 789–804.
35. Tahil, W. *The trouble with lithium 2: under the microscope*. Meridian International Research: Martainville, France, 2008, p. 54.

36. Ahmed, M.; Shayya, W. H.; Hoey, D.; Al-Handaly, J. Brine disposal from reverse osmosis desalination plants in Oman and the United Arab Emirates. *Desalination* **2001**, *133* (2), 135–147.
37. Zhou, J.; Chang, V. W. C.; Fane, A. G. An improved life cycle impact assessment (LCIA) approach for assessing aquatic eco-toxic impact of brine disposal from seawater desalination plants. *Desalination* **2013**, *308*, 233–241.
38. Ji, X.; Curcio, E.; Al Obaidani, S.; Di Profio, G.; Fontananova, E.; Drioli, E. Membrane distillation-crystallization of seawater reverse osmosis brines. *Sep. Purif. Technol.* **2010**, *71* (1), 76–82.
39. Millero, F. J. The conductivity-density-salinity-chlorinity relationships for estuarine waters. *Limnol. Oceanogr.* **1984**, *29* (6), 1317–1321.
40. Moore, W. S. The subterranean estuary: a reaction zone of ground water and sea water. *Mar. Chem.* **1999**, *65* (1–2), 111–125.
41. Hannigan, R.; Dorval, E.; Jones, C. The rare earth element chemistry of estuarine surface sediments in the Chesapeake Bay. *Chem. Geol.* **2010**, *272* (1–4), 20–30.
42. Brady, P. V.; Kottenstette, Richard J.; Mayer, T. M.; Hightower, M. M. Inland desalination: Challenges and research needs. *J. Contemp. Water Res. Educ.* **2005**, *132* (1), 46–51.
43. Hassan, A. M.; Al-Sofi, M. A. K.; Al-Amoudi, A. S.; Jamaluddin, A. T. M.; Farooque, A. M.; Rowaili, A.; Dalvi, A. G. I.; Kither, N. M.; Mustafa, G. M.; Al-Tisan, I. A. R. A new approach to membrane and thermal seawater desalination processes using nanofiltration membranes (Part 1). *Desalination* **1998**, *118*(1–3), 35–51.
44. Al-Sofi, M. A. K.; Hassan, A. M.; Hamed, O. A.; Dalvi, A. G. I.; Kither, M. N. M.; Mustafa, G. M.; Bamardouf, K. Optimization of hybridized seawater desalination process. *Desalination* **2000**, *131*(1–3), 147–156.
45. Al-Amoudi, A. S.; Farooque, A. M. Performance restoration and autopsy of NF membranes used in seawater pretreatment. *Desalination* **2005**, *178* (1–3), 261–271.
46. Macedonio, F.; Curcio, E.; Drioli, E. Integrated membrane systems for seawater desalination: energetic and exergetic analysis, economic evaluation, experimental study. *Desalination* **2007**, *203* (1–3), 260–276.
47. Creusen, R., van Medevoort, J., Roelands, M., van Renesse van Duivenbode, A., Hanemaaijer, J. H., van Leerdam, R. Integrated membrane distillation-crystallization: Process design and cost estimations for seawater treatment and fluxes of single salt solutions. *Desalination* **2013**, *323*, 8–16.
48. Drioli, E.; Curcio, E.; Di Profio, G.; Macedonio, F.; Criscuoli, A. Integrating membrane contactors technology and pressure-driven membrane operations for seawater desalination. Energy, Exergy and Costs Analysis. *Chem. Eng. Res. Des.* **2006**, *82*, 209–220.
49. Guler, E.; Kabay, N.; Yuksel, M.; Yigit, N. ñ.; Kitis, M.; Bryjak, M.. Integrated solution for boron removal from seawater using RO process and sorption-membrane filtration hybrid method. *J. Membrane Sci.* **2011**, *375*(1–2), 249–257.

50. Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: A review. *J. Environ. Manage.* **2011**, *92* (3), 407–418.
51. Volchek, K.; Krentsel, E.; Zhilin, Y.; Shtereva, G.; Dytnersky, Y.. Polymer binding/ultrafiltration as a method for concentration and separation of metals. *J. Membrane Sci.* **1993**, *79* (2–3), 253–272.
52. Wang, Q.; Lenhart, J. J.; Walker, H. W. Recovery of metal cations from lime softening sludge using Donnan dialysis. *J. Membrane Sci.* **2010**, *360* (1–2), 469–475.
53. Rozanska, A.; Wisniewski, J.; Winnicki, T. Donnan dialysis with anion-exchange membranes in a water desalination system. *Desalination* **2006**, *198*(1–3), 236–246.
54. Rozanska, A.; Wisniewski, J. Modification of brackish water composition by means of Donnan dialysis as pretreatment before desalination. *Desalination* **2009**, *240* (1–3), 326–332.
55. Reahl, E. R. *Half a century of desalination with electrodialysis*. Technical paper, G.E. Water and Process Technologies: Trevose, PA, 2006.
56. Jurenka, B. *Electrodialysis (ED) and electrodialysis reversal (EDR)*. Bureau of Reclamation: Denver, CO, 2010, pp. 1–4.
57. Turek, M. Dual-purpose desalination-salt production electrodialysis. *Desalination* **2003**, *153* (1–3), 377–381.
58. Tanaka, Y.; Ehara, R.; Itoi, S.; Goto, T. Ion-exchange membrane electrodialytic salt production using brine discharged from a reverse osmosis seawater desalination plant. *J. Membrane Sci.* **2003**, *222* (1–2), 71–86.
59. Seigworth, A.; Ludlum, R.; Reahl, E. Case study: Integrating membrane processes with evaporation to achieve economical zero liquid discharge at the Doswell Combined Cycle Facility. *Desalination* **1995**, *102* (1–3), 81–86.
60. Oren, Y.; Korngold, E.; Daltrophe, N.; Messalem, R.; Volkman, Y.; Aronov, L.; Weismann, M.; Bouriakov, N.; Glueckstern, P.; Gilron, J. Pilot studies on high recovery BWRO-EDR for near zero liquid discharge approach. *Desalination* **2010**, *261* (3), 321–330.
61. Jordahl, J. *Beneficial and Nontraditional Uses of Concentrate*. Report No. WRRF-06-002b; WateReuse Research Foundation: Alexandria, VA, 2006, p. 217.
62. Davis, T. A. Zero discharge seawater desalination: Integrating the production of freshwater, salt, magnesium, and bromine. Report No. 1112006; U.S. Bureau of Reclamation Research: Denver, CO, 2006.
63. Bond, R.; Batchelor, B.; Davis, T.; Klayman, B. Zero liquid discharge desalination of brackish water with an innovative form of electrodialysis: Electrodialysis metathesis. *FLA Water Res. J.* **2011**, 36–44.
64. Veolia Water. ZDD: Zero discharge desalination. Product Brochure: [http://veoliawatertechnologies.com/vwst/ressources/files/1/18771,ZDD\\_brochure-download-version.pdf](http://veoliawatertechnologies.com/vwst/ressources/files/1/18771,ZDD_brochure-download-version.pdf)
65. Veerapaneni, V.; Bond, R.; Dacheille, F.; Hays, B. Emerging desalination technologies—An overview. In *WateReuse Symposium*; Phoenix, AZ, 2011, p. 34.
66. Drioli, E.; Curcio, E.; di Profio, G. State of the art and recent progresses in membrane contactors. *Chem. Eng. Res. Des.* **2005**, *83* (3), 223–233.



67. de Gyves, J.; Rodriguez de San Miguel, E. Metal ion separations by supported liquid membranes. *Ind. Eng. Chem. Res.* **1999**, 38 (6), 2182–2202.
68. Nghiem, L. D.; Mornane, P.; Potter, I. D.; Perera, J. M.; Cattrall, R. W.; Kolev, S. D. Extraction and transport of metal ions and small organic compounds using polymer inclusion membranes (PIMs). *J. Membrane Sci.* **2006**, 281 (1–2), 7–41.
69. U.S. Bureau of Reclamation. *Evaluation of two concentrate disposal alternatives for the Phoenix metropolitan area: Evaporation ponds and discharge to the Gulf of California*; U.S. Bureau of Reclamation: Denver, CO, 2000.
70. Ahmed, M.; Shayya, W. H.; Hoey, D.; Mahendran, A.; Morris, R.; Al-Handaly, J. Use of evaporation ponds for brine disposal in desalination plants. *Desalination* **2000**, 130 (2), 155–168.
71. Ravizky, A.; Nadav, N. Salt production by the evaporation of SWRO brine in Eilat: A success story. *Desalination* **2007**, 205 (1–3), 374–379.
72. Kim, D. H. A review of desalting process techniques and economic analysis of the recovery of salts from retentates. *Desalination* **2011**, 270(1–3), 1–8.
73. Alexandratos, S. D. Ion-exchange resins: A retrospective from industrial and engineering chemistry research. *Ind. Eng. Chem. Res.* **2008**, 48 (1), 388–398.
74. Khamizov, R. K.; Muraviev, D.; Warshawsky, A. Recovery of valuable mineral components from seawater by ion exchange and sorption methods. In *Ion exchange and solvent extraction. A series of advances*; Marinsky, J.; Marcus, Y., Eds; Marcel Dekker: New York, 1995.
75. Chitrakar, R.; Kanoh, H.; Makita, Y.; Miyai, Y.; Ooi, K. Synthesis of spinel-type lithium antimony manganese oxides and their Li extraction/ion insertion reactions. *J. Mater. Chem.* **2000**, 10 (10), 2325–2329.
76. Ooi, K.; Miyai, Y.; Katoh, S. Recovery of lithium from seawater by manganese oxide adsorbent. *Separ. Sci. Technol.* **1986**, 21 (8), 755–766.
77. Randtke, S. J. Precipitation, coprecipitation, and precipitative softening. In *Water quality and treatment: A handbook on drinking water*; Edzwald, J. K., Ed.; AWWA: Denver, CO, 2011, pp. 13.1–13.82.
78. Zhang, Y.; Dawe, R. The kinetics of calcite precipitation from a high salinity water. *Appl. Geochem.* **1998**, 13 (2), 177–184.
79. Sheikholeslami, R.; Ong, H. W. K. Kinetics and thermodynamics of calcium carbonate and calcium sulfate at salinities up to 1.5 M. *Desalination* **2003**, 157 (1–3), 217–234.
80. Juby, G. J. G.; Wen-Yi [Shih](#), G.; [Zacheis](#), A.; [James](#), W.; [Nusser](#), M. D.; [Mortazavi](#), B.; [Ravishanker](#), P. Optimize brackish groundwater: Treating RO brine to increase recovery and reduce disposal volume. *IDA Journal of Desalination and Water Reuse* **2008**, 1 (1), 64–73.
81. Juby, G. *Reverse osmosis recovery maximization*; Report No. 119; U. S. Department of the Interior, Bureau of Reclamation: Denver, CO , 2008.
82. Swift, A. H. P.; Lu, H.; Becerra, H. *Zero discharge waste brine management for desalination plants*; Report No. 89; U. S. Department of the Interior, Bureau of Reclamation: Denver, CO, 2002.

83. Jarvenin, G. *Precipitation and crystallization processes*. Technical paper; Los Alamos National Laboratory: Los Alamos, NM, 2008.
84. Stumm, W.; Morgan, J. J. *Aquatic chemistry*, 3rd ed. John Wiley: New York, 1996.
85. Chong, T. H.; Sheikholeslami, R. Thermodynamics and kinetics for mixed calcium carbonate and calcium sulfate precipitation. *Chem. Eng. Sci.* **2001**, *56* (18), 5391–5400.
86. Mullin, J. W. *Crystallisation*. Butterworth & Co. Ltd.: London, UK, 1972.
87. Myerson, A. S., Ed. *Handbook of industrial crystallization*, 2nd ed. Butterworth-Heinemann: Oxford, UK, 2002.
88. Bennett, R. C. Crystallizer selection and design. In *Handbook of industrial crystallization*; Myerson, A. S., Ed.; Butterworth-Heinemann: Oxford, UK, 2002.
89. Gryta, M. Concentration of NaCl Solution by membrane distillation integrated with crystallization. *Separ. Sci. Technol.* **2002**, *37* (15), 3535–3558.
90. Macedonio, F.; Katzir, L.; Geisma, N.; Simone, S.; Drioli, E.; Gilron, J. Wind-Aided Intensified Evaporation (WAIV) and Membrane Crystallizer (MCR) integrated brackish water desalination process: Advantages and drawbacks. *Desalination* **2010**, *273* (1), 127–135.
91. Harms, W.; Robinson, R. B. Softening by fluidized bed crystallizers. *J. Environ. Eng.* **1992**, *118* (4), 513–529.
92. Belcu, M.; Turtoi, D. Simulation of the fluidized-bed crystallizers (II) productivity related aspects. *Cryst. Res. Technol.* **1996**, *31* (8), 1025–1031.
93. Shih, W.; Yallaly, B.; Marshall, M.; DeMichele, D. Chino II desalter concentrate management via innovative byproduct. In *American Membrane Technology Association*, San Antonio, TX, 2013.
94. Stepakoff, G. L.; Siegelman, D.; Johnson, R.; Gibson, W. Development of a eutectic freezing process for brine disposal. *Desalination* **1974**, *15* (1), 25–38.
95. van der Ham, F.; Witkamp, G. J.; de Graauw, J.; van Rosmalen, G. M. Eutectic freeze crystallization simultaneous formation and separation of two solid phases. *J. Cryst. Growth* **1999**, *198-199*, Part 1, 744–748.
96. EFC Separations. *The EFC process*. 2013. <http://efc.nl/the-efc-process/> (accessed May 10, 2013).
97. Nathoo, J.; Jivanji, R.; Lewis, A. E. Freezing your brines off: Eutectic freeze crystallization for brine treatment. In *International Mine Water Conference*, Pretoria, South Africa, 2009, 431–437.
98. Tallmadge, J. A.; Butt, J. B.; Solomon, H. J. Minerals from sea salt. *Ind. Eng. Chem.* **1964**, *56* (7), 44–65.
99. Madani, A. A. Zero-discharge direct-contact freezing/solar evaporator desalination complex. *Desalination* **1992**, *85* (2), 179–195.
100. Jean-Pierre Mericq, S. L.; Cabassud, C. Vacuum membrane distillation of seawater reverse osmosis brines. *Water Res.* **2010**, *44* (2010), 5260–5273.
101. Drioli, E.; Di Profio, G.; Curcio, E. Progress in membrane crystallization. *Curr. Opin. Chem. Eng.* **2012**, *1* (2), 178–182.

102. Zouboulis, A. I. Silver recovery from aqueous streams using ion flotation. *Miner. Eng.* **1995**, 8 (12), 1477–1488.
103. Kabil, M. A.; Ghazy, S. E.; Abeidu, A. M.; El-Metwaly, N. M. Comparative study of selective separation of magnesium from brine and seawater. *Separ. Sci. Technol.* **1995**, 30 (20), 3787–3799.
104. Kabay, N.; Guler, E.; Bryjak, M. Boron in seawater and methods for its separation—A review. *Desalination* **2010**, 261 (3), 212–217.
105. Jacob, C. Seawater desalination: Boron removal by ion exchange technology. *Desalination* **2007**, 205 (1–3), 47–52.
106. Simonnot, M.-O.; Castel, C.; Nicolaè, M.; Rosin, C.; Sardin, M.; Jauffret, H. Boron removal from drinking water with a boron selective resin: Is the treatment really selective? *Water Res.* **2000**, 34 (1), 109–116.
107. Liu, H.; Ye, X.; Li, Q.; Kim, T.; Qing, B.; Guo, M.; Ge, F.; Wu, Z.; Lee, K. Boron adsorption using a new boron-selective hybrid gel and the commercial resin D564. *Colloid Surface A* **2009**, 341 (1–3), 118–126.
108. Gazi, M.; Bicak, N. Selective boron extraction by polymer supported 2-hydroxyethylamino propylene glycol functions. *React. Funct. Polym.* **2007**, 67 (10), 936–942.
109. Wei, Y.-T.; Zheng, Y.-M.; Chen, J. P. Design and fabrication of an innovative and environmental friendly adsorbent for boron removal. *Water Res.* **2011**, 45 (6), 2297–2305.
110. Polat, H.; Vengosh, A.; Pankratov, I.; Polat, M. A new methodology for removal of boron from water by coal and fly ash. *Desalination* **2004**, 164 (2), 173–188.
111. Morisada, S.; Rin, T.; Ogata, T.; Kim, Y.-H.; Nakano, Y. Adsorption removal of boron in aqueous solutions by amine-modified tannin gel. *Water Res.* **2011**, 45 (13), 4028–4034.
112. Kir, E.; Gurler, B.; Gulec, A. Boron removal from aqueous solution by using plasma-modified and unmodified anion-exchange membranes. *Desalination* **2011**, 267 (1), 114–117.
113. Kabay, N.; Sarp, S.; Yuksel, M.; Arar, N.; Bryjak, M. Removal of boron from seawater by selective ion exchange resins. *React. Funct. Polym.* **2007**, 67 (12), 1643–1650.
114. Goh, K.-H.; Lim, T.-T.; Dong, Z. Application of layered double hydroxides for removal of oxyanions: A review. *Water Res.* **2008**, 42 (6–7), 1343–1368.
115. Seki, Y. ü.; Seyhan, S.; Yurdakoc, M. r. v. Removal of boron from aqueous solution by adsorption on Al<sub>2</sub>O<sub>3</sub> based materials using full factorial design. *J. Hazard. Mater.* **2006**, 138 (1), 60–66.
116. Ozturk, N.; Kose, T. E. Boron removal from aqueous solutions by ion-exchange resin: Batch studies. *Desalination* **2008**, 227 (1–3), 233–240.
117. Kose, T. E.; Ozturk, N. Boron removal from aqueous solutions by ion-exchange resin: Column sorption–elution studies. *J. Hazard. Mater.* **2008**, 152 (2), 744–749.

118. Cengeloglu, Y.; Tor, A.; Arslan, G.; Ersoz, M.; Gezgin, S. Removal of boron from aqueous solution by using neutralized red mud. *J. Hazard. Mater.* **2007**, *142* (1–2), 412–417.
119. Goltz, H. R.; Eicher, C.; Levy, N. A zero liquid discharge process for boron recovery from FGD wastewater. In *International Water Conference (IWC-09-49)*, 2009, p. 13. [http://www.degremont-technologies.com/IMG/pdf/cs\\_Infilco\\_BoronRecoveryfromFGDWastewater.pdf](http://www.degremont-technologies.com/IMG/pdf/cs_Infilco_BoronRecoveryfromFGDWastewater.pdf)
120. Angulo, M. A. *Boron*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2012, pp. 32–33.
121. Crangle, R. D. *Boron*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013.
122. Lyday, P. A. *Bromine*; U.S. Geological Survey Mineral Commodity Report, Department of the Interior: Reston, VA, 1994.
123. Ober, J. A. *Bromine*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2011, pp. 34–35.
124. Apodaca, L. E. *Bromine*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2010, pp. 34–35.
125. El-Hamouz, A. M.; Mann, R. Chemical reaction engineering analysis of the blowout process for bromine manufacture from seawater. *Ind. Eng. Chem. Res.* **2006**, *46* (10), 3008–3015.
126. Yalcin, H.; Koc, T.; Pamuk, V. Hydrogen and bromine production from concentrated sea-water. *Int. J. Hydrogen Energ.* **1997**, *22* (10–11), 967–970.
127. Chitrakar, R.; Tezuka, S.; Sonoda, A.; Sakane, K.; Hirotsu, T. A new method for synthesis of Mg-Al, Mg-Fe, and Zn-Al layered double hydroxides and their uptake properties of bromide ion. *Ind. Eng. Chem. Res.* **2008**, *47* (14), 4905–4908.
128. Qi, Z.; Cussler, E. L. Bromine recovery with hollow fiber gas membranes. *J. Membrane Sci.* **1985**, *24* (1), 43–57.
129. Miller, M. M. *Lime*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013.
130. Willett, J. C. *Stone (crushed)*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013.
131. Railroad Industries, Inc. Market Analysis Lime & CaCO<sub>3</sub> Report, 2011. <http://ebookbrowse.com/imc-market-analysis-lime-caco3-04-27-11-pdf-d350740416> (accessed January 15, 2013).
132. Crangle, R. D. *Gypsum*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013.
133. Gabelich, C. J.; Williams, M. D.; Rahardianto, A.; Franklin, J. C.; Cohen, Y. High-recovery reverse osmosis desalination using intermediate chemical demineralization. *J. Membrane Sci.* **2007**, *301* (1–2), 131–141.
134. Mohammadesmaeili, F.; Badr, M. K.; Abbaszadegan, M.; Fox, P. Mineral recovery from inland reverse osmosis concentrate using isothermal evaporation. *Water Res.* **2010**, *44* (20), 6021–6030.

135. Rahardianto, A.; Gao, J.; Gabelich, C. J.; Williams, M. D.; Cohen, Y. High recovery membrane desalting of low-salinity brackish water: Integration of accelerated precipitation softening with membrane RO. *J. Membrane Sci.* **2007**, 289 (1–2), 123–137.
136. Gabelich, C. J.; Rahardianto, A.; Northrup, C. R.; Yun, T. I.; Cohen, Y. Process evaluation of intermediate chemical demineralization for water recovery enhancement in production-scale brackish water desalting. *Desalination*. **2011**, 272 (1–3), 36–45.
137. Al Nasser, W. N.; Shaikh, A.; Morriss, C.; Hounslow, M. J.; Salman, A. D. Determining kinetics of calcium carbonate precipitation by inline technique. *Chem. Eng. Sci.* **2008**, 63 (5), 1381–1389.
138. Al Nasser, W. N.; Al-Salhi, F. H.; Hounslow, M. J.; Salman, A. D. Inline monitoring the effect of chemical inhibitor on the calcium carbonate precipitation and agglomeration. *Chem. Eng. Res. Des.* **2011**, 89 (5), 500–511.
139. Greenlee, L. F.; Testa, F.; Lawler, D. F.; Freeman, B. D.; Moulin, P. Effect of antiscalant degradation on salt precipitation and solid/liquid separation of RO concentrate. *J. Membrane Sci.* **2011**, 366 (1–2), 48–61.
140. He, S.; Kan, A. T.; Tomson, M. B. Inhibition of calcium carbonate precipitation in NaCl brines from 25 to 90°C. *Appl. Geochem.* **1999**, 14 (1), 17–25.
141. Chave, K. E.; Suess, E. Calcium carbonate saturation in seawater: Effects of dissolved organic matter. *Limnol. Oceanogr.* **1970**, 15 (4), 633–637.
142. Kralj, D.; Vdović, N. The influence of some naturally occurring minerals on the precipitation of calcium carbonate polymorphs. *Water Res.* **2000**, 34 (1), 179–184.
143. Lebron, I.; Suarez, D. L. Calcite nucleation and precipitation kinetics as affected by dissolved organic matter at 25°C and pH 7.5. *Geochim. Cosmochim. Ac.* **1996**, 60 (15), 2765–2776.
144. Lebron, I.; Suarez, D. L. Kinetics and mechanisms of precipitation of calcite as affected by PCO<sub>2</sub> and organic ligands at 25°C. *Geochim. Cosmochim. Ac.* **1998**, 62 (3), 405–416.
145. Zhang, Y.; Dawe, R. A. Influence of Mg<sup>2+</sup> on the kinetics of calcite precipitation and calcite crystal morphology. *Chem. Geol.* **2000**, 163 (1–4), 129–138.
146. Pokrovsky, O. S. Precipitation of calcium and magnesium carbonates from homogeneous supersaturated solutions. *J. Cryst. Growth* **1998**, 186 (1–2), 233–239.
147. Compton, R. G.; Daly, P. J. The dissolution/precipitation kinetics of calcium carbonate: An assessment of various kinetic equations using a rotating disk method. *J. Colloid Interface Sci.* **1987**, 115 (2), 493–498.
148. Lioliou, M. G.; Paraskeva, C. A.; Koutsoukos, P. G.; Payatakes, A. C. Calcium sulfate precipitation in the presence of water-soluble polymers. *J. Colloid Interface Sci.* **2006**, 303 (1), 164–170.
149. Alimi, F.; Elfil, H.; Gadri, A. Kinetics of the precipitation of calcium sulfate dihydrate in a desalination unit. *Desalination* **2003**, 158 (1–3), 9–16.

150. Barcelona, M. J.; Atwood, D. K. Gypsum-organic interactions in natural seawater: Effect of organics on precipitation kinetics and crystal morphology. *Mar. Chem.* **1978**, 6 (2), 99–115.
151. Goldman, J. E.; Howe, K. J.; Thomson, B. M.; Fowlie, R. A.; Howe, K.; Goldman, J. *Selective salt recovery from reverse osmosis concentrate*. WateReuse Research Association: Alexandria, VA, 2013, p 212.
152. Crangle, R. D. *Gypsum*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2011, pp. 70–71.
153. Drioli, E. E.; Curcio, E.; Criscuoli, A.; di Profio, G. Integrated system for recovery of CaCO<sub>3</sub>, NaCl and MgSO<sub>4</sub>·7H<sub>2</sub>O from nanofiltration retentate. *J. Membrane Sci.* **2004**, 239, 27–38.
154. Tuck, C. A. *Cesium*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013, pp. 40–41.
155. Johnson, B. E.; Santschi, P. H.; Shane Addleman, R.; Douglas, M.; Davidson, J. D.; Fryxell, G. E.; Schwantes, J. M. Collection of fission and activation product elements from fresh and ocean waters: A comparison of traditional and novel sorbents. *Appl. Radiat. Isotopes* **2011**, 69 (1), 205–216.
156. Jeppesen, T.; Shu, L.; Keir, G.; Jegatheesan, V. Metal recovery from reverse osmosis concentrate. *J. Cleaner Prod.* **2009**, 17 (7), 703–707.
157. Le Dirach, J.; Nisan, S.; Poletiko, C. Extraction of strategic materials from the concentrated brine rejected by integrated nuclear desalination systems. *Desalination* **2005**, 182, 449–460.
158. Gilbert, O.; Valderrama, C.; Peterkova, M.; Cortina, J. L. Evaluation of selective sorbents for the extraction of valuable metal ions (Cs, Rb, Li, U) from reverse osmosis rejected brine. *Solvent Extr. Ion Exc.* **2010**, 28 (2010), 543–562.
159. Sodaye, H.; Nisan, S.; Poletiko, C.; Prabhakar, S.; Tewari, P. K. Extraction of uranium from the concentrated brine rejected by integrated nuclear desalination plants. *Desalination*, **2008**, 235, 9–32.
160. Angulo, M. A. *Cesium*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2010, pp. 40–41.
161. Mansfield, C. A.; Depro, B. M.; Perry, V. A. The chlorine industry: a profile. U.S. EPA: Washington, DC, 2000, p. 47.
162. Fountain, K. E. N; Kamalick, J. US chlor-alkali outlook uncertain. *ICIS Chem. Bus.* **2012**, 282 (9), 14.
163. Abreu, A; Burrridge, E. Chlorine. *ICIS Chem. Bus.* **2012**, 281 (12), 42.
164. Spagnoletto, G. Innovation in food grade hypochlorination generation and injection plant at Al Taweelah site. *Desalination* **2005**, 182 (1–3), 259–265.
165. Zaviska, F.; Drogui, P.; Pablo, G. Statistical optimization of active chlorine production from a synthetic saline effluent by electrolysis. *Desalination* **2012**, 296, 16–23.
166. Adham, S.; Oppenheimer, J.; Kumar, M.; Webb, L.; Kottenstette, R. Innovative approaches to RO concentrate management: Beneficial reuse and concentrate minimization. In *WEFTEC*, October 21–25, 2006, Dallas, TX.

167. Melian-Martel, N.; Sadhwani, J. J.; Ovidio Perez Baez, S. Saline waste disposal reuse for desalination plants for the chlor-alkali industry: The particular case of pozo izquierdo SWRO desalination plant. *Desalination* **2011**, *281*, 35–41.
168. Pellegrino, J. Energy and environmental profile of the U.S. chemical industry; Chapter 6: The chlor-alkali industry. U.S. Department of Energy: Washington, DC, 2000.
169. Grosjean, C.; Miranda, P. H.; Perrin, M.; Poggi, P. Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry. *Renew. Sust. Energ. Rev.* **2012**, *16* (3), 1735–1744.
170. Jaskula, B. W. *Lithium*; U.S. Geological Survey Mineral Commodity Survey, Department of the Interior: Reston, VA, 2011, pp. 94–95.
171. Jaskula, B. W. *2010 Minerals Yearbook—Lithium*, U.S. Geological Survey: Reston, VA, 2010.
172. Kushnir, D.; Sanden, B. A. The time dimension and lithium resource constraints for electric vehicles. *Resour. Policy* **2012**, *37* (1), 93–103.
173. Tahil, W. *The trouble with lithium 1: Implications of future PHEV production for lithium demand*. Meridian International Research: Martainville, France, 2007, p. 22.
174. Kesler, S. E.; Gruber, P. W.; Medina, P. A.; Keoleian, G. A.; Everson, M. P.; Wallington, T. J. Global lithium resources: Relative importance of pegmatite, brine and other deposits. *Ore Geol. Rev.* **2013**, *50*, 171–183.
175. Yaksic, A. S.; Tilton, J. E. Using the cumulative availability curve to assess the threat of mineral depletion: The case of lithium. *Resour. Policy* **2009**, *34* (4), 185–194.
176. Goonan, T. G. *Lithium use in batteries*; Circular 1371; Department of the Interior, U.S. Geological Survey: Reston, VA, 2012, p. 14.
177. Steinberg, M.; Dang, V.-D. Preliminary design and analysis of a process for the extraction of lithium from seawater. In *A Symposium on U.S. Lithium Resources and Requirements*. U.S. Geological Survey, Denver, CO, 1975.
178. Jaskula, B. W. *Lithium*; Mineral Commodity Summary; Department of the Interior, U.S. Geological Survey: Reston, VA, 2012.
179. Stamp, A.; Lang, D. J.; Wager, P. A. Environmental impacts of a transition toward e-mobility: The present and future role of lithium carbonate production. *J. Cleaner Prod.* **2012**, *23* (1), 104–112.
180. Bradbury, D. What is going to power our cars? *The Guardian*, July 30, 2008.
181. South Korea commercialization lithium-extraction from seawater. 2011. <http://nextbigfuture.com/2011/01/south-korea-commercialization-lithium.html>.
182. Nishihama, S.; Onishi, K.; Yoshizuka, K. Selective recovery process of lithium from seawater using integrated ion exchange methods. *Solvent Extr. Ion Exc.* **2011**, *29* (3), 421–431.
183. Garthwaite, J. Why seawater isn't the answer to the lithium squeeze, 2010. <http://gigaom.com/cleantech/will-seawater-stave-off-a-lithium-squeeze>.

184. So-hyun, K. POSCO develops lithium extraction technology. *The Korea Herald*, February 23, 2012.
185. Yoshizuka, K.; Kitajou, A.; Holba, M. Selective recovery of lithium from seawater using a novel MnO<sub>2</sub> type adsorbent III—Benchmark evaluation. *Ars Separatoria Ac.* **2006**, *4*, 78–85.
186. Yoshizuka, K.; Holba, M.; Yasunaga, N.; Ikegami, Y. Performance analysis of benchmark plant for selective lithium recovery from seawater; Institute of Ocean Energy and The University of Kitakyush, Japan, p. 22.
187. Onishi, K.; Holba, M.; Yasunaga, N.; Ikegami, Y. Synergistic solvent impregnated resin for adsorptive separation of lithium ion. *Ind. Eng. Chem. Res.* **2010**, *49* (14), 6554–6558.
188. An, J. W.; Kang, D. J.; Tran, K. T.; Kim, M. J.; Lim, T.; Tran, T. Recovery of lithium from Uyuni salar brine. *Hydrometallurgy* **2012**, *117–118*, 64–70.
189. Abe, M.; Hayashi, K. Synthetic inorganic ion-exchange materials: Part XXXIV. Selective separation of lithium from seawater by tin(IV) antimonate cation exchanger. *Hydrometallurgy* **1984**, *12* (1), 83–93.
190. Tsuruta, T. Removal and recovery of lithium using various microorganisms. *J. Biosci. Bioeng.* **2005**, *100* (5), 562–566.
191. Hawash, S.; Abd El Kader, E.; El Diwani, G. Methodology for selective adsorption of lithium ions onto polymeric aluminum (III) hydroxide. *J. Am. Sci.* **2010**, *6* (11), 301–309.
192. Muraviev, D.; Khamizov, R.; Tikhonov, N. A. Ion-Exchange Isothermal Supersaturation. *Solvent Extr. Ion Exc.* **1998**, *16* (1), 151–221.
193. Abe, M.; Chitrakar, R. Synthetic inorganic ion-exchange materials. XLV. Recovery of lithium from seawater and hydrothermal water by titanium (iv) antimonate cation exchanger. *Hydrometallurgy*, **1987**, *19* (1), 117–128.
194. Umeno, A.; Miyai, Y.; Takagi, N.; Chitrakar, R.; Sakane, K.; Ooi, K. Preparation and adsorptive properties of membrane-type adsorbents for lithium recovery from seawater. *Ind. Eng. Chem. Res.* **2002**, *41* (17), 4281–4287.
195. Ooi, K.; Feng, Q.; Kanoh, H.; Hirotsu, T.; Oi, T. Lithium isotope fractionations on inorganic ion-exchangers with different ion-sieve properties. *Separ. Sci. Technol.* **1995**, *30* (20), 3761–3770.
196. Miyai, Y.; Ooi, K.; Katoh, S. Recovery of lithium from seawater using a new type of ion-sieve adsorbent based on MgMn<sub>2</sub>O<sub>4</sub>. *Separ. Sci. Technol.* **1988**, *23* (1–3), 179–191.
197. Miyai, Y.; Ooi, K.; Katoh, S. Preparation and ion-exchange properties of ion-sieve manganese oxide based on Mg<sub>2</sub>MnO<sub>4</sub>. *J. Colloid Interf. Sci.* **1989**, *130* (2), 535–541.
198. Chung, K.-S.; Lee, J.; Jeong, J.; Kim, T.; Kim, E.; Kim, Y. Recovery of lithium from seawater using nano-manganese oxide adsorbents prepared by gel process. *Mater. Sci. Forum* **2004**, *449–452*, 277–280.
199. Chitrakar, R.; Kanoh, H.; Miyai, Y.; Ooi, K. Recovery of lithium from seawater using manganese oxide adsorbent (H<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>) derived from Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>. *Ind. Eng. Chem. Res.* **2001**, *40* (9), 2054–2058.



200. Ariza, M. J.; Jones, D. J.; Roziere, J.; Chitrakar, R.; Ooi, K. Probing the local structure and the role of protons in lithium sorption processes of a new lithium-rich manganese oxide. *Chem. Mater.* **2006**, *18* (7), 1885–1890.
201. Chitrakar, R.; Kanoh, H.; Miyai, Y.; Ooi, K. Recovery of lithium from seawater using manganese oxide adsorbent (H<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>) derived from Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub>. *Ind. Eng. Chem. Res.* **2001**, *40* (9), 2054–2058.
202. Shi, X.; Zhou, D.; Zhang, Z.; Yu, L.; Xu, H.; Chen, B.; Yang, X. Synthesis and properties of Li<sub>1.6</sub>Mn<sub>1.6</sub>O<sub>4</sub> and its adsorption application. *Hydrometallurgy* **2011**, *110* (1–4), 99–106.
203. Wang, L.; Meng, C. G.; Ma, W. Study on Li<sup>+</sup> uptake by lithium ion-sieve via the pH technique. *Colloid Surface A* **2009**, *334* (1–3), 34–39.
204. Tian, L.; Ma, W.; Han, M. Adsorption behavior of Li<sup>+</sup> onto nano-lithium ion sieve from hybrid magnesium/lithium manganese oxide. *Chem. Eng. J.* **2010**, *156* (1), 134–140.
205. Wang, L.; Ma, W.; Liu, R.; Li, H. Y.; Meng, C. G. Correlation between Li<sup>+</sup> adsorption capacity and the preparation conditions of spinel lithium manganese precursor. *Solid State Ionics* **2006**, *177*, (17–18), 1421–1428.
206. Chung, K.-S.; Lee, J.-C.; Kim, W.-K.; Kim, S. B.; Cho, K. Y. Inorganic adsorbent containing polymeric membrane reservoir for the recovery of lithium from seawater. *J. Membrane Sci.* **2008**, *325* (2), 503–508.
207. Alexandratos, S. D.; Natesan, S. Coordination chemistry of phosphorylated calixarenes and their application to separations science. *Ind. Eng. Chem. Res.* **2000**, *39* (11), 3998–4010.
208. Grote, Z.; Scopelliti, R.; Severin, K. pH-triggered assembly of organometallic receptors for lithium ions. *J. Am. Chem. Soc.* **2004**, *126*, 16959–16972.
209. Sakamoto, H.; Kimura, K.; Shono, T. Lithium separation and enrichment by proton-driven cation transport through liquid membranes of lipophilic crown nitrophenols. *Anal. Chem.* **1987**, *59* (11), 1513–1517.
210. Sun, H.; Tabata, M. Separation and transport of lithium of 10<sup>-5</sup> M in the presence of sodium chloride higher than 0.1 M by 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin. *Talanta* **1999**, *49* (3), 603–610.
211. Ma, P.; Chen, X. D.; Hossain, M. M. Lithium extraction from a multicomponent mixture using supported liquid membranes. *Separ. Sci. Technol.* **2000**, *35* (15), 2513–2533.
212. Tsuchiya, S.; Nakatani, Y.; Ibrahim, R.; Ogawa, S. Highly efficient separation of lithium chloride from seawater. *J. Am. Chem. Soc.* **2002**, *124* (18), 4936–4937.
213. Zhang, Q.-H.; Sun, S.; Li, S.; Jiang, H.; Yu, J.-G. Adsorption of lithium ions on novel nanocrystal MnO<sub>2</sub>. *Chem. Eng. Sci.* **2007**, *62* (18–20), 4869–4874.
214. Ma, L.-W.; Chen, B.-Z.; Shi, X.-C.; Zhang, W.; Zhang, K. Stability and Li<sup>+</sup> extraction/adsorption properties of Li<sub>Mx</sub>Mn<sub>2-x</sub>O<sub>4</sub> (M=Ni, Al, Ti; 0 < x < 1) in aqueous solution. *Colloid and Surface A* **2010**, *369* (1–3), 88–94.

215. Ma, L.-W.; Chen, B.-z.; Shi, X.-c.; Zhang, K. Li<sup>+</sup> extraction/adsorption properties of Li-Sb-Mn composite oxides in aqueous medium. *T. Nonferr. Metal. Soc. China* **2011**, *21* (7), 1660–1664.
216. ASM International Handbook Committee. Magnesium and magnesium alloys. Avedesian, M. M.; Baker, H. Eds.; ASM International: Materials Park, OH, 1999, p. 314.
217. Brown, R. E. Environmental challenges for the magnesium industry. In *TMS (The Minerals, Metals & Materials Society)*; Sillekens, W. H.; Agnew, S. R.; Neelameggham, N. R.; Mathaudhu, S. N., Eds.; Wiley: San Diego, CA, 2011, pp. 7–10.
218. Heath, S. B.; Minger, F. R. Recovering magnesium salts. Dow Chemical Company: Midland, MI, 1944,
219. Robinson, H. A.; Friedrich, R. E.; Spencer, R. S. Magnesium hydroxide from seawater. Dow Chemical Company: Midland, MI, 1946.
220. Kramer, D. A. *Magnesium, its alloys and compounds*. U.S. Geological Survey Open-File Report 01-341. Department of the Interior: Reston, VA, 2001.
221. Kramer, D. A. *Magnesium metal*. U. S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2011.
222. Kramer, D. A. *Magnesium metal*. U. S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2012.
223. Ikenson, D. Death by antidumping. *Forbes*, January 3, 2011.
224. Austin, G. T.; Basta, N. *Shreves chemical process industries handbook*. 5th ed. McGraw-Hill Professional: New York, 1998.
225. *Premier Periclase Process*. Online product brochure.  
<http://www.premierpericlase.com/process.html>
226. Kramer, D. A. *Magnesium Compounds - 2010 Minerals Yearbook*, U.S. Geological Survey, Department of the Interior: Reston, VA, 2011.
227. Kogel, J. E.; Trivedi, N. C.; Barker, J. M.; Krukowski, S. T. *Industrial Minerals & Rocks: Commodities, Markets and Uses*, 7th ed. Society for Mining, Metallurgy, and Exploration: Littleton, CO, 2006.
228. Kramer, D. A. *Magnesium compounds*. U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2011, pp. 94–95.
229. Kramer, D. A. *Magnesium compounds*. U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2012, pp. 96–97.
230. RHI Group increased revenues and profit in the first nine months. Online article, 2011. [http://www.rhi.at/internet\\_en/investor\\_relations\\_en/19822/03.11.11\\_-\\_Q3.html](http://www.rhi.at/internet_en/investor_relations_en/19822/03.11.11_-_Q3.html)
231. Manufacture of magnesium oxide from sea water by Premier Periclase in Drogheda, Co. Louth, Ireland. <http://www.premierpericlase.ie/>.
232. Al-Mutaz, I. S. By-product recovery from Saudi desalination plants. *Desalination* **1987**, *64*, 97–110.

233. Ohya, H.; Suzuki, T.; Nakao, S. Integrated system from complete usage of components in seawater. A proposal of inorganic chemical combinat on seawater *Desalination*. **2001**, *134*, 29–36.
234. Chinese desal turns green. *Global Water Intelligence* **2007**, *8* (4).
235. Abdel-aal, H. K.; Ba-lubaid, K. M.; Shaikh, A. A.; Al-harbi, D. K. Recovery of mineral salts and potable water from desalting plant effluents by evaporation. Part II. Proposed simulation system for salt recovery. *Separ. Sci. Technol.* **1990**, *25* (4), 437–461.
236. Ahmed, M.; Arakel, A.; Hoey, D.; Coleman, M. Integrated power, water and salt generation: A discussion paper. *Desalination* **2001**, *134* (1–3), 37–45.
237. Ahmed, M.; Arakel, A.; Hoey, D.; Thumarukudy, M. R.; Goosen, M. F. A.; Al-Haddabi, M.; Al-Belushi, A. Feasibility of salt production from inland RO desalination plant reject brine: A case study. *Desalination* **2003**, *158* (1–3), 109–117.
238. Lindal, B. The production of chemicals from brine and seawater using geothermal energy. *Geothermics* **1970**, *2*, Part 1, 910–917.
239. Petric, B.; Petric, N. Investigations of the rate of sedimentation of magnesium hydroxide obtained from seawater. *Ind. Eng. Chem. Proc. Des. Dev.* **1980**, *19*, 329–335.
240. Kapp, E. M. The precipitation of calcium and magnesium from sea water by sodium hydroxide. *Biol. Bull.* **1928**, *55* (6), 453–458.
241. Semerjian, L.; Ayoub, G. M. High-pH-magnesium coagulation-flocculation in wastewater treatment. *Adv. Environ. Res.* **2003**, *7* (2), 389–403.
242. Bauman, W. C.; Skidmore, J. R.; Osmun, R. H. Dowex 50. *Ind. Eng. Chem.* **1948**, *40* (8), 1350–1355.
243. Bauman, W. C. Production of sulfonated resin ion exchange agents in stable granular form. The Dow Chemical Company: Midland, KS, Patent No.. 2,466,675, 1949.
244. Bauman, W. C. Process for producing solutions of magnesium values. The Dow Chemical Company: Midland, KS, Patent No. 3,615,181, 1971.
245. Khamizov, R. K.; Mironova, L. I.; Tikhonov, N. A.; Bychkov, A. V.; Poezd, A. D. Recovery of pure magnesium compounds from seawater by the use of the effect of isothermal supersaturation in the ion-exchange process. *Separ. Sci. Technol.* **1996**, *31*(1), 1–20.
246. Khamizov, R. K.; Muraviev, D.; Tikhonov, N. A.; Krachak, A. N.; Zhiguleva, T. I.; Fokina, O. V. Clean ion-exchange technologies. 2. Recovery of high-purity magnesium compounds from seawater by an ion-exchange isothermal supersaturation technique. *Ind. Eng. Chem. Res.* **1998**, *37* (6), 2496–2501.
247. Delion, N.; Mauguin, G.; Corsin, P. Importance and impact of post treatments on design and operation of SWRO plants. *Desalination* **2004**, *165*, 323–334.
248. Birnhack, L.; Lahav, O. A new post-treatment process for attaining Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and alkalinity criteria in desalinated water. *Water Res.* **2007**, *41* (17), 3989–3997.

249. Telzhensky, M.; Birnhack, L.; Lehmann, O.; Windler, E.; Lahav, O. Selective separation of seawater  $Mg^{2+}$  ions for use in downstream water treatment processes. *Chem. Eng. J.* **2011**, *136*, 136–143.
250. Polyak, D. E. *Molybdenum*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013.
251. Sepehrian, H.; Yavari, R.; Waqif-Husain, S.; Ghannadi-Maragheh, M. Separation of radionuclides on mesoporous zirconium silicate: A novel sorbent. *Separ. Sci. Technol.* **2008**, *43* (11–12), 3269–3285.
252. Hakim, L.; Sabarudin, A.; Oshita, K.; Oshima, M.; Motomizu, S. Synthesis of cross-linked chitosan functionalized with threonine moiety and its application to on-line collection/concentration and determination of Mo, V and Cu. *Talanta* **2007**, *74* (2008), 997–985.
253. Haratake, M.; Yasumoto, K.; Ono, M.; Akashi, M.; Nakayama, M. Synthesis of hydrophilic macroporous chelating polymers and their versatility in the preconcentration of metals in seawater samples. *Anal. Chim. Acta* **2006**, *561* (1–2), 183–190.
254. Polyak, D. E. *Molybdenum*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2010, pp. 106–107.
255. De Yoreo, J. J.; Vekilov, P. *Principles of crystal nucleation and growth*, in *Biom mineralization*; Dove, P. M.; De Yoreo, J. J.; Weiner, S., Eds.; Mineralogical Society of America: Washington, DC, 2003, pp. 57–93.
256. Apodaca, L. E. *Nitrogen (fixed)—ammonia*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013, pp. 112–113.
257. Zhang, M.; Zhang, H.; Xu, D.; Han, L.; Niu, D.; Zhang, L.; Wu, W.; Tian, B. Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes. *Desalination* **2011**, *277* (1–3), 46–53.
258. Zhang, M.; Zhang, H.; Xu, D.; Han, L.; Niu, D.; Tian, B.; Zhang, J.; Zhang, L.; Wu, W. Removal of ammonium from aqueous solutions using zeolite synthesized from fly ash by a fusion method. *Desalination* **2011**, *271* (1–3), 111–121.
259. Abd El-Hady, H. M.; Grunwald, A.; Vlckova, K.; Zeithammerova, J. Clinoptilolite in drinking water treatment for ammonia removal. *Acta Polytech.* **2001**, *41*(1), 41–45.
260. Muster, T. Ammonia stripping for N recovery. *CSIRO Mater. Sci. Eng.* **2012**, *10*.
261. United States Department of Agriculture. *Fertilizer use and price*. USDA: Washington, DC, 2012.
262. Sverdrup, H. U.; Ragnarsdottir, K. V. Challenging the planetary boundaries II: Assessing the sustainable global population and phosphate supply, using a systems dynamics assessment model. *Appl. Geochem.* **2011**, *26*, Supplement, S307–S310.
263. Vaccari, D. A. Phosphorus famine: The threat to our food supply. *Scientific American*, June 2, 2009.
264. Jasinski, S. M. *Phosphorus*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013.
265. Zhao, D.; Sengupta, A. K. Ultimate removal of phosphate from wastewater using a new class of polymeric ion exchangers. *Water Res.* **1998**, *32* (5), 1613–1625.

266. Blaney, L. M.; Cinar, S.; SenGupta, A. K. Hybrid anion exchanger for trace phosphate removal from water and wastewater. *Water Res.* **2007**, *41*(7), 1603–1613.
267. Liberti, L.; Boari, G.; Passino, R. Phosphates and ammonia recovery from secondary effluents by selective ion exchange with production of a slow-release fertilizer. *Water Res.* **1978**, *13*, 65–73.
268. Sengupta, S.; Pandit, A. Selective removal of phosphorus from wastewater combined with its recovery as a solid-phase fertilizer. *Water Res.* **2011**, *45* (11), 3318–3330.
269. Kumar, M.; Badruzzaman, M.; Adham, S.; Oppenheimer, J. Beneficial phosphate recovery from reverse osmosis (RO) concentrate of an integrated membrane system using polymeric ligand exchanger (PLE). *Water Res.* **2007**, *41* (10), 2211–2219.
270. Jasinski, S. M. *Phosphate; phosphate rock*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2011, pp. 118–119.
271. Ali, S. M.; Maity, D. K.; De, S.; Shenoi, M. R. K. Ligands for selective metal ion extraction: A molecular modeling approach. *Desalination* **2008**, *232* (1–3), 181–190.
272. de-Bashan, L. E.; Bashan, Y. Recent advances in removing phosphorus from wastewater and its future use as fertilizer (1997–2003). *Water Res.* **2004**, *38*, 4222–4246.
273. Jasinski, S. M. *Potash*; U.S. Geological Survey Mineral Commodity Summary Department of the Interior: Reston, VA, 2012, pp. 122–123.
274. Khamizov, R. K.; Ivanovand, N. A.; Tikhonov, N. A. Dual temperature methods of separation and concentration of elements in ion exchange columns. In *Ion exchange and solvent extraction*; SenGupta, A. K., Ed.; CRC Press: Boca Raton FL, 2011, pp. 171–231.
275. Cao, J.-I.; Liu, X.-W.; Fu, R.; Tan, Z.-Y. Magnetic P zeolites: Synthesis, characterization and the behavior in potassium extraction from seawater. *Sep. Purif. Technol.* **2008**, *63* (1), 92–100.
276. Epstein, J. A.; Altaras, D.; Feist, E. M.; Rosenzweig, J. The recovery of potassium chloride from Dead Sea brines by precipitation and solvent extraction. *Hydrometallurgy* **1975**, *1* (1), 39–50.
277. Angulo, M. A. *Rubidium*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2012. pp. 132–133.
278. Reese, R. G. *Rubidium*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 1998.
279. *Encyclopaedia Britannica*. rubidium (Rb); 2012.  
<http://www.britannica.com/EBchecked/topic/511956/rubidium-Rb>
280. Brooks, W. E. *Rubidium*; U.S. Geological Survey Mineral Commodity Summaries, Department of the Interior: Reston, VA, 2005.
281. Tamada, M. Current status of technology for collection of uranium from seawater. In *NA 2009*. Environment and Industrial Materials Research Division: Japan Atomic Energy Agency, Gunma, Japan, 2009, pp. 1–9.

282. Sepehrian, H.; Ahmadi, S. J.; Waqif-Husain, S.; Faghihian, H.; Alighanbari, H. Adsorption studies of heavy metal ions on mesoporous aluminosilicate: Novel cation exchanger. *J. Hazard. Mater.* **2010**, *176* (1–3), 252–256.
283. Ye, X.; Wu, Z.; Li, W.; Liu, H.; Li, Q.; Qing, B.; Guo, M.; Ge, F. Rubidium and cesium ion adsorption by an ammonium molybdophosphate, calcium alginate composite adsorbent. *Colloid and Surface A* **2009**, *342* (1–3), 76–83.
284. Kostick, D. S. *Salt*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013.
285. Kostick, D. S. *Soda ash*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013, pp. 148–149.
286. Kostick, D. S. Sodium sulfate; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013.
287. Kasedde, H.; Kirabira, J. B.; Babler, M. U.; Tilliander, A.; Jonsson, S. A state of the art paper on improving salt extraction from Lake Katwe raw materials in Uganda, KTH Royal Institute of Technology, Stockholm, Sweden, 2012, p. 28.
288. Turek, M.; Dydo, P.; Klimek, R. Salt production from coal-mine brine in ED - evaporation - crystallization system. *Desalination* **2005**, *184* (1–3), 439–446.
289. Turek, M.; Dydo, P.; Klimek, R. Salt production from coal-mine brine in NF – evaporation—Crystallization system. *Desalination* **2008**, *221* (1–3), 238–243.
290. Jeong, S.-K.; Ju, C.-S. Extraction of strontium ion from sea water by contained liquid membrane permeator. *Korean J. Chem. Eng.* **2002**, *19* (1), 93–98.
291. Angulo, M. A. *Strontium*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2012, pp. 156–157.
292. Angulo, M. A. *2010 Minerals Yearbook: Strontium*, U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2010, pp. 73.1–73.7.
293. Angulo, M. A. *Strontium*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2011, pp. 156–157.
294. Nikolaev, N. P.; Ivanov, V. A.; Gorshkov, V. I.; Nikashina, V. A.; Ferapontov, N. B. Counter-current ion-exchange separation of strontium from brines with acrylic-type cation-exchange resins. *React. Polym.* **1992**, *18* (1), 25–33.
295. Konstantinou, M.; Pashalidis, I. Speciation and spectrophotometric determination of uranium in seawater. *Mediterr. Mar. Sci.* **2004**, *5* (1), 55–60.
296. Rao, L. Recent international R&D activities in the extraction of uranium from seawater. Lawrence Berkeley National Laboratory: Berkeley, CA, 2011, pp. 1–20.
297. World Nuclear Association. What is uranium? How does it work? Web page, 2011. <http://www.world-nuclear.org/education/uran.htm> (accessed March 29, 2012).
298. Kanno, M. Design and cost studies on the extraction of uranium from seawater. *Separ. Sci. Technol.* **1981**, *16* (9), 999–1018.
299. Kelmers, A. D. Status of technology for the recovery of uranium from seawater. *Separ. Sci. Technol.* **1981**, *16* (9), 1019–1035.
300. World Nuclear Association. Plans for new reactors worldwide. Web page, February 2012. <http://www.world-nuclear.org/info/inf17.html> (accessed March 30, 2012).

301. *World Nuclear News*. WNA reports world market post Fukushima, September 15, 2011.
302. Kahouli, S. Re-examining uranium supply and demand: New insights. *Energ. Policy* **2011**, 39 (1), 358–376.
303. MacDonald, C. Uranium: Sustainable Resource or Limit to Growth? In *World Nuclear Association Annual Symposium*, London, 2003.
304. Schenk, H. J.; Astheimer, L.; Witte, E. G.; Schwochau, K. Development of sorbers for the recovery of uranium from seawater. 1. Assessment of key parameters and screening studies of sorber materials. *Separ. Sci. Technol.* **1982**, 17 (11), 1293–1308.
305. Astheimer, L.; Schenk, H. J.; Witte, E. G.; Schwochau, K. Development of sorbers for the recovery of uranium from seawater. Part 2. The accumulation of uranium from seawater by resins containing amidoxime and imidoxime functional groups. *Separ. Sci. Technol.* **1983**, 18 (4), 307–339.
306. World Nuclear Association. Supply of Uranium. Web page, 2011. <http://www.world-nuclear.org/info/inf75.html> (accessed March 30, 2012).
307. *BBC News India*. 'Massive' uranium find in Andhra Pradesh. July 19, 2011.
308. International Atomic Energy Agency. *Uranium 2007: Resources, production and demand*, OECD Publishing: Paris, France, 2008.
309. McKenzie, J. Uranium supply gap expected by the time Husab starts production. *Creamer Media's Mining Weekly*, February 8, 2012.
310. Guang, Y.; Wenjie, H. The status quo of China's nuclear power and the uranium gap solution. *Energ. Policy* **2010**, 38 (2), 966–975.
311. Tamada, M. Collection of uranium from seawater. Japan Atomic Energy Agency, Gunma, Japan, 2009, pp. 1–20.
312. Kiladze, T. Uranium miners still waiting on that rebound. *The Globe and Mail*, January 24, 2012.
313. *Winnipeg Free Press*. Cameco CEO warns of squeeze in uranium supplies in 'very near future,' February 29, 2012.
314. World Nuclear Association. Uranium Markets, Web page, 2010. <http://www.world-nuclear.org/info/inf22.html> (accessed March 30, 2011).
315. Kanno, M. Present status of study on extraction of uranium from sea water. *J. Nucl. Sci. Technol.* **1984**, 21 (1), 1–9.
316. Das, S.; Pandey, A. K.; Vasudevan, T.; Athawale, A. A.; Manchanda, V. K. Adsorptive preconcentration of uranium in hydrogels from seawater and aqueous solutions. *Ind. Eng. Chem. Res.* **2009**, 48 (14), 6789–6796.
317. Das, S.; Pandey, A. K.; Athawale, A.; Kumar, V.; Bhardwaj, Y. K.; Sabharwal, S.; Manchanda, V. K. Chemical aspects of uranium recovery from seawater by amidoximated electron-beam-grafted polypropylene membranes. *Desalination* **2008**, 232 (1–3), 243–253.
318. Tewari, P. K. Recovery of uranium from seawater. *Chem. Sci. Eng.* **2006–2007**, BARC Highlights, Bhabha Atomic Research Center, Trombay, India, p. 53.

319. Jang, B.-B.; Lee, K.; Kwon, W. J.; Suh, J. Binding of uranyl ion by 2,2'-Dihydroxyazobenzene attached to a partially chloromethylated polystyrene. *J. Appl. Polym. Sci. A* **1999**, *37*, 3169–3177.
320. Lee, K.; Jang, B.-B.; Kwon, W. J.; Suh, J. Binding of uranyl ion by 2,2'-Dihydroxyazobenzene attached to crosslinked polystyrenes covered with highly populated quaternary ammonium cations. *J. Polym. Sci. A* **1999**, *37*, 4117–4125.
321. Rivas, B. L.; Pereira, E.; Jara, M.; Esparza, C. Resins with the ability to bind copper and uranyl ions. *J. Appl. Polym. Sci.* **2005**, *99* (2006), 706–711.
322. Chauhan, G. S.; Kumar, A. A Study in the uranyl ions uptake on acrylic acid and acrylamide copolymeric hydrogels. *J. Appl. Polym. Sci.* **2007**, *110*, 3795–3803.
323. Cheng, Y.; Sun, X.; Liao, X.; Shi, B. Adsorptive recovery of uranium from nuclear fuel industrial wastewater by titanium loaded collagen fiber. *Chinese J. Chem. Eng.* **2011**, *19* (4), 592–597.
324. Ahmadi, S. J.; Noori-Kalkhoran, O.; Shirvani-Arani, S. Synthesis and characterization of new ion-imprinted polymer for separation and preconcentration of uranyl (UO<sub>2</sub><sup>2+</sup>) ions. *J. Hazard. Mater.* **2010**, *175* (1–3), 193–197.
325. F. Vernon, Shah, T. The extraction of uranium from seawater by poly(amidoxime)/poly(hydroxamic acid) resins and fibre. *React. Polym.* **1983**, *1*, 301–308.
326. Pekel, N.; Sahiner, N.; Guven, O. Use of amidozimated Acrylonitrile/N-Vinyl 2-Pyrrolidone interpenetrating polymer networks for uranyl ion adsorption from aqueous systems. *J. Appl. Polym. Sci.* **2000**, *81* (2001), 2324–2329.
327. Lee, K.; Jang, B.-B.; Kwon, W. J.; Suh, J. Binding of uranyl ion by poly(ethylenimine) containing a salicylate derivative. *J. of Polymer Science: Part A: Polymer Chemistry*, **1997**, *35*, 2935–2942.
328. Mellah, A.; Chegrouche, S.; Barkat, M. The removal of uranium(VI) from aqueous solutions onto activated carbon: Kinetic and thermodynamic investigations. *J. Colloid Interf. Sci.* **2006**, *296* (2), 434–441.
329. Das, S.; Pandey, A. K.; Vasudevan, T.; Athawale, A. A.; Manchanda, V. K. Adsorptive preconcentration of uranium in hydrogels from seawater and aqueous solutions. *Ind. Eng. Chem. Res.* **2009**, *48* (14), 6789–6796.
330. Hulya Guler, N. S.; Aycik, G. A.; Guven, O. Development of novel adsorbent materials for recovery and enrichment of uranium from aqueous media. *J. Appl. Polym. Sci.* **1997**, *66*, 2475–2480.
331. Kabay, N.; Egawa, H. Chelating polymers for recovery of uranium from seawater. *Separ. Sci. Technol.* **1994**, *29* (1), 135–150.
332. Kusakabe, K.; Goto, A.; Morooka, S. Kinetics of uranium adsorption from seawater with imidedioxime adsorbent. *Separ. Sci. Technol.* **1994**, *29* (12), 1567–1577.
333. Omichi, H.; Katakai, A.; Sugo, T.; Okamoto, J. A new type of amidoxime-group-containing adsorbent for the recovery of uranium from seawater. *Separ. Sci. Technol.* **1985**, *20* (2–3), 163–178.
334. Aihara, T.; Goto, A.; Kago, T.; Kusakabe, K.; Morooka, S. Rate of adsorption of uranium from seawater with a Calix[6]arene adsorbent. *Separ. Sci. Technol.* **1992**, *27* (12), 1655–1667.



335. Sachde, D. J. *Uranium extraction from seawater: An assessment of cost, uncertainty and policy implications*. University of Texas at Austin, 2011, p. 241.
336. Shedd, K. B. *Cobalt*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2010, pp. 46–47.
337. Shedd, K. B. *Cobalt*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013, pp. 46–47.
338. Chouyyok, W.; Yantasee, W.; Shin, Y.; Grudzien, R. M.; Fryxell, G. E. Transition metal ion capture using functional mesoporous carbon made with 1,10-phenanthroline. *Inorg. Chem. Commun.* **2009**, 12 (11), 1099–1103.
339. Zono, F. M.; Ahmadi, S. J.; Nosrati, S. A.; Maragheh, M. G. Preparation and characterization of zirconium (IV) molybdo tungsto vanado silicate as a novel inorganic ion exchanger in sorption of radionuclides. *J. Hazard. Mater.* **2009**, 169 (1–3), 808–812.
340. Voronkov, M. G.; Vlasova, N. N.; Pozhidaev, Y. N. Organosilicon ion-exchange and complexing adsorbents. *Appl. Organomet. Chem.* **2000**, 14 (6), 287–303.
341. Alexandratos, S. D.; Crick, D. W. Polymer-supported reagents: Application to separation science. *Ind. Eng. Chem. Res.* **1996**, 35 (3), 635–644.
342. Guberman, D. E. *Germanium*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2011, pp. 64–65.
343. Le Dirach, J.; Nisan, S.; Poletiko, C. Extraction of strategic materials from the concentrated brine rejected by integrated nuclear desalination systems. *Desalination* **2005**, 182, 449–460.
344. Gambogi, J. *Rare earths*; U.S. Geological Survey Mineral Commodity Summary, Department of the Interior: Reston, VA, 2013.
345. Sakamoto, N.; Kano, N.; Imaizumi, H. Biosorption of uranium and rare earth elements using biomass of algae. *Bioinorg. Chem. Appl.* **2008**, 1–8.
346. Inoue, K.; Baba, Y. Chitosan: A versatile biopolymer for separation, purification, and concentration of metal ions. In *Ion Exchange and Solvent Extraction: A Series of Advances*, Volume 18; SenGupta, A. K., Ed.; CRC Press: Boca Raton, FL, 2007, pp. 339–372.
347. Pereira, M. C.; Mendes, J. F.; Horta, P.; Korovessis, N. Final design of an advanced solar dryer for salt recovery from brine effluent of an MED desalination plant. *Desalination* **2007**, 211 (1–3), 222–231.
348. McGivney, W.; Kawamura, S. *Cost estimating manual for water treatment facilities*, John Wiley: Hoboken, NJ, 2008.
349. Sorg, T. Cost estimation program for arsenic removal from drinking water supplies by adsorptive media and anion exchange processes. U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Cincinnati, OH, 2004.
350. *Colloidal silica dewatering*. Confidential client, 2012.
351. O’Phelan, A. M. Fruit’s pulp, seeds, oil all involved in making a number of products. *The Tampa Tribune*, September 19, 2012.

352. Robaire, S.; Arzate, A. Recent advances in membrane concentration of maple sap and factors affecting membrane performance. In *Annual meeting of the international maple syrup institute and the North American maple syrup council*, Stratford, ON, October 2010.
353. Ueda, A.; Kato, K.; Mogi, K.; Mroczek, E.; Thain, I. A. Silica removal from Mokai, New Zealand, geothermal brine by treatment with lime and a cationic precipitant. *Geothermics* **2003**, 32 (1), 47–61.
354. Roberts, S.; Viani, B.; Conley, S.; Martin, S. Co-production of silica from geothermal fluids, PIER Renewables Research Technologies Program, California Energy Commission, 2009.
355. The Freedonia Group, *World Specialty Silicas – Industry market research, market share, market size, sales, demand forecast, market leaders, company profiles, industry trends*. The Freedonia Group: Cleveland, OH, 2004.
356. The Biology Project. Website.  
[http://www.biology.arizona.edu/biochemistry/problem\\_sets/aa/Lysine.html](http://www.biology.arizona.edu/biochemistry/problem_sets/aa/Lysine.html) (accessed June 13, 2012).
357. Karabelas, A. J.; Yiantsios, S. G.; Metaxiotou, Z.; Andritsos, N.; Akiskalos, A.; Vlachopoulos, G.; Stavroulias, S. Water and materials recovery from fertilizer industry acidic effluents by membrane processes. *Desalination* **2001**, 138(1–3), 93–102.
358. Karabelas, A. J.; Yiantsios, S. G.; Metaxiotou, Z.; Andritsos, N.; Akiskalos, A.; Vlachopoulos, G.; Stavroulias, S. Water and materials recovery from fertilizer industry acidic effluents by membrane processes. *Desalination* **2001**, 138 (1–3), 93–102.
359. Millero, F. J.; Feistel, R.; Wright, D. G.; McDougall, T. J. The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. *Deep-Sea Res. Pt I* **2007**, 50–72.
360. Electrometals Technologies Limited. Operating experience recovering acid and copper at the Phelps Dodge El Paso rod mill using emew® technology. [Web page]. <http://www.electrowinning.com/sites/default/files/brochures/Phelps Dodge Rod Mill.pdf> (accessed May 30, 2013).
361. Min, J. H.; Kim, D. I.; Eum, Y. J.; Park, G. T.; Kim, S. U.; Kim, J. K.; Rhu, D. H. *Anti-fouling membrane system for industrial wastewater treatment and recovery*. International Water Conference, Orlando, FL, November 2011.
362. Gebrezgabher, S. A.; Meuwissen, M. P. M.; Prins, B. A. M.; Lansink, A. G. J. M. O. Economic analysis of anaerobic digestion case of Green power biogas plant in The Netherlands. *NJAS—Wageningen J. Life Sci.* **2010**, 57 (2), 109–115.
363. Wardle, C. J.; Min, J. H.; Kim, S. U.; Eum, Y. J.; Park, G. T.; Kim, J. K.; Suk, H.; Lee, J. W. Nutrient recovery and energy enhancement from an anaerobic digester 5 using anti-fouling FMX membrane system. WEFTEC, New Orleans, LA, 2012.
364. Eum, Y. J.; Min, J. H.; Chan, A. C.; Rhu, D. H.; Kim, J. K.; Hwang, H. J.; Recovery and treatment of anaerobic digester effluent and hog manure with high solid using vortex generating membrane system. In WEFTEC, New Orleans, LA, 2012.

365. Kang, S. J.; Olmstead, K.; Schraa, O.; Rhu, D. H.; Eum, Y. J.; Kim, J. K.; Min, J. H.; Enhanced biogas generation in an activated anaerobic digestion with membrane filtration system. In *International Water Association*, Busan, Korea, 2012.
366. Kang, S. J.; Olmstead, K.; Schraa, O.; Rhu, D. H.; Eum, Y. J.; Kim, J. K.; Min, J. H.; Activated anaerobic digestion with a membrane filtration system. In *WEFTEC*, Los Angeles, CA, 2011.
367. Min, J. H.; Eum, Y. J.; Limke, J. C. Biogas wastewater digestate treatment. In *Biogas West Conference*, San Francisco, CA, 2011.
368. Torello, W. A. Chief Agronomist at NEO Energy, CTO at NewGro Fertilizer. Personal communication, January 17, 2013.
369. Eum, Y. J.; Min, J. H.; Lee, J. W. Anti-fouling membrane system in industrial applications. In *UKC*, Garden Grove, CA, 2012.
370. Min, J. H.; Eum, Y. J.; Chen, A. C.; Limke, J. C.; Park, G. T.; Kim, S. W.; Kim, J. K.; Rhu, D. H. Industrial water treatment and resource recovery using anti-fouling membrane system. In *WEFTEC*, New Orleans, LA, 2012.
371. Ben-Hamed, U.; Seddighi, H.; Thomas, K. Economic returns of using brewery's spent grain in animal feed. *World Academy of Science, Engineering and Technology* **2011**, 50.
372. Murphy, N.; Rosa, B.; Seymour, J. North Carolina Division of Pollution Prevention and Environmental Assistance, Site Visit Summary, 2003.
373. California Regional Water Quality Board, *Pretreatment Program Economics-Cost, Fees, Surcharges*. April 2010.
374. Mohammadesmaeili, F.; Badr, M.; Abbaszadegan, M.; Fox, P. Mineral recovery from inland reverse osmosis concentrate using isothermal evaporation. *Water Res.* **2010**, 44 (20), 6021–6030.
375. Water Research Foundation, *Inland membrane concentrate treatment strategies for water reclamation systems*. Water Research Foundation: Denver, CO, 2009.
376. Leykauf, S. *Industrial wastewater neutralization using magnesium hydroxide*. Ohio Water Environment Association Annual Conference, May, 15, 2012.
377. Martin Marietta Magnesia Specialties. [Website]. <http://www.magnesiaspecialties.com/> (accessed January 11, 2013).
378. U.S. Geological Survey. Commodity Statistics and Information. <http://minerals.usgs.gov/minerals/pubs/commodity/> (accessed January 11, 2013).
379. Fowlie, R.A.; Howe, K.; Goldman, J. Marketability and selective recovery of salts from brackish water desalination. In *NMWRRI Conference New Water New Energy*, Alamogordo, NM, December 2011.
380. Jeppesen, T.; Shu, L.; Keir, G.; Jegatheesan, V. Metal recovery from reverse osmosis concentrate. *J. Cleaner Prod.* **2009**, 17 (7), 703–707.
381. Willett, J. C. *Stone (crushed)*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2014.
382. Miller, M. M. *Lime*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2014.

383. Crangle, R. D. *Gypsum*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2014.
384. Tuck, C. A. *Cesium*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2014; pp. 40–41.
385. Kramer, D. A. *2006 Minerals Yearbook: Magnesium Compounds*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2007.
386. Apodaca, L. E. *Nitrogen (fixed)—Ammonia*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2014; pp 112–113.
387. Apodaca, L. E. *2012 Minerals Yearbook: Nitrogen*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2012.
388. Jasinski, S. M. *Potash*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2014; pp. 122–123.
389. Tuck, C. A. *Rubidium*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2014.
390. Bolen, W. P. *Salt*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2014.
391. Kostick, D. S. *Sodium sulfate*. In Department of the Interior: Reston, VA: Department of the Interior: Reston, VA, 2013.
392. Angulo, M. A. *2010 Minerals Yearbook Strontium*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2010; pp. 73.1–73.7.
393. Jaskula, B. W. *2012 Minerals Yearbook - Lithium*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2012.
394. Polyak, D. E. *2012 Minerals Yearbook - Molybdenum*. In U.S. Geological Survey Mineral Commodity Summary, Ed. Department of the Interior: Reston, VA, 2012.

## Appendix

### Patent Summary Tables

---

**Table A.1. Patents on Boron Extraction or Removal**

Year	Title	Technology	US Patent #
1946	Magnesium Hydroxide from Seawater	Electrolysis; Precipitation	2,405,055
1968	Precipitation of Minerals from Brines	Lignin Compounds; Precipitation; Proteinaceous Compounds; Tannins; Waste Pulp Digester Liquors	3,374,081
1973	Extraction of Boron from Aqueous Solutions with Salicylic Acid Derivatives and Isoamyl Alcohol	Liquid Extraction	3,839,222
1990	Process for Separating Salts in Seawater	Precipitation	4,956,157
2009	Water Treatment Process for Oilfield Produced Water	Lime Softening; Microfiltration; Precipitation; Reverse Osmosis	7,520,993 B1
2011	Boron-Selective Resins	Ion Exchanger; Glucamide Structures; Specific Precipitate Formation	US 2011/0108488

**Table A.2. Patents on Bromine Extraction or Removal**

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patent #</b>
1939	Halogen Extraction	Blowing Out Process; Chlorinating or Electrolyzing Free Constituent; Oxidizing Acidified Brine; Scrubbing with Alkali Solution; Voluminous Current of Air	2,143,224
1944	Recovering Magnesium Salts	Blow Out; Evaporation; Precipitation	2,342,666
1967	Utilization of Saline Water	Blow-out; Electrolysis; Evaporation; Filtration; Ion exchange; Precipitation;	3,350,292
1968	Precipitation of Minerals from Brines	Lignin Compounds; Precipitation; Proteinaceous Compounds; Tannins; Waste Pulp Digester Liquors	3,374,081
1979	Process for Recovery of Chemicals from Saline Water	Crystallization	4,180,547
1986	Precipitation of Minerals from Brines	Precipitation	3,374,081
2003	Recovery of Common Salt and Marine Chemicals from Brine	Bromine; Magnesium; Potassium; Salt;	US 2003/0080066
2006	Production of Purified Water and High Value Chemicals from Salt Water	Electrodialysis; Nanofiltration; Reverse Osmosis	7,083,730
2012	Processes for Conjointly Producing Bromine, Calcium Chloride, and Chlorine	Air Stripping	8,133,468

**Table A.3. Patents on Calcium Extraction or Removal**

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patient #</b>
1940	Prevention of Scale Deposits in Steam Generating Plants	Boiler Feed; Precipitation; Preparatory Treatment	2,226,592
1947	Treatment of Pickle Liquor	Filtration; Neutralization; Precipitation	2,433,458
1949	Production of Sulfonated Resin Ion Exchange Agents in Stable Granular Form	Ion-exchange; Ion Exchange	2,466,675
1955	Method of Treating Sea Water	Precipitation	2,934,419
1962	Process of Concentrating Salt-Water by Double Salt Precipitation	Double Precipitation; Evaporation; Precipitation	3,248,181
1964	Recovery of Fresh Water from Sea Water	Distillation; Electrolysis; Evaporation	3,119,752
1965	Inhibiting Scale Formation in Fresh Water Recovery	Ion Exchange; pH Adjustment	3,218,241
1966	Recovery of Potassium Halides from Brine	Evaporation; Ore Flotation; Precipitation; Separation	3,231,340
1967	Precipitation of Potassium Halides from Mixed Brines Using Organic Solvents	Precipitation	3,359,076
1967	Process for Dewatering Organic Sludges from Waste Water Treatment	Calcination; Dewatering; Neutralizing; Thickening	3,345,288
1969	Chemical Cycle for Evaporative Water Desalination Plant	Chemical Treatment; Condensation; Electrolysis; Evaporation; Precipitation	3,463,814
1970	Separation of Aluminum, Calcium, and Magnesium from the Alkali Metals by Solvent Extraction	Precipitation, Solvent Extraction, Scrub	3,514,266
1971	Chemical-Electro-Chemical Cycle for Desalination of Water	Evaporator; Precipitation	3,627,479
1971	Evaporation-Electrodialysis Process for Producing Fresh Water from Brine	Electrodialyzer; Evaporator; Ion Exchange membranes;	3,574,077

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patient #</b>
		Ion Exchanger	
1972	Desalination Process	Ion Exchange; Reverse Osmosis	3,639,231
1972	Production of Fresh Water, Brine and Magnesium Hydroxide	Evaporation; Precipitation; Seeded Precipitation;	3,676,067
1973	Softening of Sea Water by Addition of Barium Carbonate and CO <sub>2</sub>	In situ; Precipitation	3,725,267
1974	Method of Decolorizing Paper Mill Effluent Liquid	Chemical Reaction; Color Imparting Reaction; Mixing; Pressure	3,833,464
1976	Water Softening Process	Cross Flow Filtration; Filtering; Hard Water Softening; Precipitation	3,976,569
1977	Method of Separating Ionized Substances from an Aqueous Solution	Bioaccumulation; Bioextraction	4,024,054
1977	Purification of Saline Water	Distillation; Electrodialysis; Evaporation, Flocculation; Preconcentration; Precipitation; Reverse Osmosis	4,036,749
1977	Treatment of Water to Remove Certain Ions Therefrom	Precipitation; Softening	4,059,513
1978	Desalination Process System and By-product Recovery	Brine Concentration; Flash Evaporation; Reverse Osmosis	4,083,781
1979	Process for Recovery of Chemicals from Saline Water	Crystalization	4,180,547
1980	Treatment of Industrial Waste Water	Precipitation	4,188,291
1981	Process for Recovery of Uranium from Sea Water	Granulated Lignite Coal Filtration Matrix	4,298,577
1982	Production of Purified Brine	Flocculation; Precipitation	4,336,232



<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patient #</b>
1983	Carbonate, Sulphate and Hydroxide or Hydrogen Carbonate	Flocculation; Precipitation	4,423,009
1987	Method for Scale Reduction in Off-Shore Platform	Precipitation	4,712,616
1988	Method of Converting Brines to Useful Products	Precipitation; Filtration	4,755,303
1990	Method for Removing Scale and Radioactive Material from Earth	Precipitation	4,973,201
1990	Process for Separating Salts in Seawater	Precipitation	4,956,157
1992	Process for the Desalination of Sea and for Obtaining Energy and the Raw Materials Contained in Sea Water	Electrolysis	5,124,012
1995	Precipitation and Separation of Salts, Scale Salts, and Norm Contaminant Salts from Saline Waters and Saline Solutions	Precipitation; Vaporization	5,468,394
1996	Precipitation and Separation of Inorganic Species from Aqueous Solutions	Condensation; Ion Exchange; Miscible Organic Solvent; Precipitation	5,587,088
1998	Method for Complex Processing of Sea-Water	Mechanical Filtration; Modified Zeolite; Weak-acid Cation Exchanger	5,814,224
2002	Purification of Produced Water from Coal Seam Natural Gas Wells Using Ion Exchange and Reverse Osmosis	Ion Exchange; Reverse Osmosis	US 6,372.143 B1
2006	Method of Producing Useful Products from Seawater and Similar Brines	Co-precipitation; Coprecipitation	US 2006/0105082
2006	Water Desalination Process and Apparatus	Electrodialysis Device; Ion Exchange	US2006/0060532
2007	Process for Pre-treating and Desalinating Sea Water	Precipitation	7,198,722

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patient #</b>
2008	Methods to Produce Sulfate-free Saline Water and Gypsum	Membrane Filtration; Compressed-phase Precipitation; Solvent Aided Precipitation	7,392,848 B1
2009	Process for the Treatment of Saline Water	Crystallization; Dewatering; Evaporation; Precipitation	7,595,001 B2
2009	Water Treatment Process for Oilfield Produced Water	Lime Softening; Microfiltration; Precipitation; Reverse Osmosis	7,520,993 B1
2010	CO2-sequestering Formed Building Materials	Carbon Dioxide Sequestration; Precipitation	7,771,684 B2
2010	Desalination Methods and Systems that Include Carbonate Compound Precipitation	Precipitation; Separation	7,744,761 B2
2010	Methods and Systems for Utilizing Waste Sources of Metal Oxides	Carbon Dioxide Sequestration; Precipitation	7,754,169 B2
2010	Methods to De-Sulfate Saline Streams	De-sulfate Saline Streams; Multi-stage Flash; Multi-effect Distillation; Reverse Osmosis	US 7,789,159
2010	Non-cementitious Compositions Comprising CO2 Sequestering Additives	Precipitation	7,829,053 B2
2010	Production of Carbonate-containing Compositions from Material Comprising Metal Silicates	Filtration; Precipitation	7,749,476 B2
2010	Reduced-carbon Footprint Concrete Compositions	Precipitation	7,815,880 B2
2010	Rocks and aggregate, and methods of making and using the same	Carbon Dioxide Sequestration; Precipitation	7,753,618 B2
2011	Electrochemical Production of an Alkaline Solution Using CO2	Electrolysis; Membrane; Nanofiltration; Precipitation; Reverse Osmosis	7,993,511 B2
2011	Methods of Sequestering CO2	Electrolysis; Precipitation	7,887,694

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patient #</b>
2011	Mobile Systems and Methods of Sufficiently Treating Water so that the Treated Water may be Utilized in Well-treatment Operations	Precipitation	8,012,358 B2
2011	Mobile Systems and Methods of Sufficiently Treating Water so that the Treated Water may be Utilized in Well-treatment Operations	Precipitation	8,012,358 B2
2011	Process for the Preparation of Common Salt of High Purity from Brines in Solar Salt Pans	Precipitation	8,021,442
2012	Method of Making Pure Salt from FRAC-water/wastewater	Crystallization; Filtration	8,158,097
2012	Onsite Integrated Production Factory	Electrolysis; Ion Exchange; Ion-exchange; Marine Wind and Tidal Power; Reverse Osmosis	8,197,664
2012	Processes for Conjointly Producing Bromine, Calcium Chloride, and Chlorine	Air Stripping	8,133,468

**Table A.4. Patents on Cesium Extraction or Removal**

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patent #</b>
1967	Recovery and Separation of Cesium and Rubidium Fluorides Using Alcohols	Evaporation; Filtration; Liquid Extraction	3,305,321
1968	Process for Separating Inorganic Cations from Solution with Hydrous Oxide Cation Exchangers	Adsorption; Ion exchange; Ion-exchange	3,382,034
1969	Separation of Cesium from Potassium and Rubidium	Precipitation	3,468,959
1970	Hydrous Oxides Cation Exchangers	Adsorption; Ion exchange; Ion-exchange	3,522,187
1970	Separation of Aluminum, Calcium, and Magnesium from the Alkali Metals by Solvent Extraction	Precipitation, Solvent Extraction, Scrub	3,514,266
1982	Inorganic Ion Exchanger	Adsorption; Ion-exchange; Ion Exchange	4,313,844
1984	Process for Producing Zeolite Adsorbent and Process for Treating Radioactive Liquid Waste with the Zeolite Adsorbent	Adsorption; Adsorbent; Impregnated Zeolite; Ion-exchange; Ion Exchange; Sorbent; Sorption; Zeolite	4,448,711
1987	Drying Process Using Chabazite-type Adsorbents	Adsorption	4,663,052
2002	Adsorption Means for Radionuclides	Adsorption; Adsorbent; Chitin; Chitosan; Sorption; Sorbent	6,402,953 B1
2003	Biopolymer Composite Ion-exchanger with High Cesium Selectivity and its Manufacturing Method	Ion Exchange; Ion-exchange; Biopolymer; Calcium Alginate	6,626,860 B1

**Table A.5. Patents on Lithium Extraction or Removal**

Year	Title	Technology	US Patent #
1967	Method of Lithium Recovery	Adsorption; Precipitation	3,306,700
1968	Process for Separating Inorganic Cations from Solution with Hydrous Oxide Cation Exchangers	Adsorption; Ion exchange; Ion-exchange	3,382,034
1970	Recovery of Lithium from Bitterns	Addition of Metal Halide; Extraction	3,537,813
1971	Recovery of Lithium as LiOH.H <sub>2</sub> O from Aqueous Chloride Brines Containing Lithium Chloride and Sodium Chloride	Electrolysis	3,597,340
1978	Recovery of Lithium from Brines	Ion-exchange; Ion Exchange	4,116,858
1978	Recovery of Lithium from Brines	Ion-exchange; Ion Exchange	4,116,856
1981	Recovery of Lithium from Brines	Ion-exchange; Ion Exchange	4,291,001
1985	Crystalline 3-layer Lithium Aluminates	Adsorption; Ion Exchange; Ion-exchange	4,540,509
1987	Adsorbent for Lithium and a Method for the Preparation Thereof	Adsorption; Ion-sieve; Ion Sieve	4,665,049
1987	Lipophilic Lithium Ionophores	Ionophores; Ion-exchange	4,649,218
1993	Method and Electrode for Electrochemical Recovery of Lithium Value from Aqueous Solution	Adsorption; Electrochemical Adsorption	5,198,081
1995	Recovery of Lithium Values from Brine	Adsorption; Ion exchange; Ion-exchange	5,389,349
1997	Recovery of Lithium Values from Brine	Adsorption; Ion exchange; Ion-exchange	5,599,516
1998	Thermally-driven Ion-exchange Process for Lithium Recovery	Ion-exchange; ion exchange; zeolites	5,833,844
2011	Lithium Recovery Device Using Separator Reservoir, Lithium Recovery Method and Lithium Adsorption/Desorption System Using the Same	Lithium adsorption/desorption; Lithium Recovery Device; Membrane; Polymer; Separator Reservoir	US2011/0174739 A1

**Table A.6. Patents on Magnesium Extraction or Removal**

	<b>Title</b>	<b>Technology</b>	<b>US Patie nt #</b>
1940	Prevention of Scale Deposits in Steam Generating Plants	Boiler Feed; Precipitation; Preparatory Treatment	2,226,592
1944	Recovering Magnesium Salts	Blow Out; Evaporation; Precipitation	2,342,666
1946	Magnesium Hydroxide from Seawater	Electrolysis; Precipitation	2,405,055
1946	Method of Obtaining Magnesia and Potash from the Waters of The Great Salt Lake	Precipitation	2,404,550
1947	Treatment of Pickle Liquor	Filtration; Nuetralization; Precipitation	2,433,458
1949	Production of Sulfonated Resin Ion Exchange Agents in Stable Granular Form	Ion-exchange; Ion Exchange	2,466,675
1955	Method of Treating Sea Water	Precipitation	2,934,419
1955	Process for the Manufacture of Magnesium Products	Precipitation	2,703,748
1955	Production of Magnesium Compound	Precipitation	553,268
1957	Processes for the Manufacture of Various Chemicals from Sea Water	Blow-out; Evaporation; Filtration; Precipitation	2,793,099
1964	Recovery of Fresh Water from Sea Water	Distillation; Electrolysis; Evaporation	3,119,752
1965	Inhibiting Scale Formation in Fresh Water Recovery	Ion Exchange; pH Adjustment	3,218,241
1966	Chemical Treatment and Distillation	Distillation; Precipitation; Tubular Heat Exchange	3,262,865
1966	Recovery of Potassium Halides from Brine	Evaporation; Ore Flotation; Precipitation; Separation	3,231,340

	<b>Title</b>	<b>Technology</b>	<b>US Patie nt #</b>
1966	Water Treatment Process	Coagulant; Sedimentation;	3,262,877
1967	Utilization of Saline Water	Blow-out; Electrolysis; Evaporation; Filtration; Ion exchange; Precipitation;	3,350,292
1969	Chemical Cycle for Evaporative Water Desalination Plant	Chemical Treatment; Condensation; Electrolysis; Evaporation; Precipitation	3,463,814
1970	Seperation of Aluminum, Calcium, and Magnesium from the Alkali Metals by Solvent Extraction	Precipitation, Solvent Extraction, Scrub	3,514,266
1971	Chemical-Electro-Chemical Cycle for Desalination of Water	Evaporator; Precipitation	3,627,479
1971	Effluent Treatment Process	Precipitation	3,627,679
1971	Evaporation-Electrodialysis Process for Producing Fresh Water from Brine	Electrodialyzer; Evaporator; Ion Exchange membranes; Ion Exchanger	3,574,077
1971	Process for Producing Solutions of Magnesium Values	Ion-exchange; Ion Exchange; Liquid Extraction	3,615,181
1972	Desalination Process	Ion Exchange; Reverse Osmosis	3,639,231
1972	Production of Fresh Water, Brine and Magnesium Hydroxide	Evaporation; Precipitation; Seeded Precipitation;	3,676,067
1973	Softening of Sea Water by Addition of Barium Carbonate and CO <sub>2</sub>	In situ; Precipitation	3,725,267
1976	Water Softening Process	Cross Flow Filtration; Filtering; Hard Water Softening; Precipitation	3,976,569
1977	Method of Seperating Ionized Substances from an Aqueous Solution	Bioaccumulation; Bioextraction	4,024,054
1977	Purification of Saline Water	Distillation; Electrodialysis; Evaporation, Flocculation; Preconcentration; Precipitation;	4,036,749

	<b>Title</b>	<b>Technology</b>	<b>US Patie nt #</b>
		Reverse Osmosis	
1977	Treatment of Water to Remove Certain Ions Therefrom	Precipitation; Softening	4,059,513
1978	Recovery of Mg++ from Brines	Ion-exchange; Ion Exchange	4,116,857
1979	Process for Recovery of Chemicals from Saline Water	Crystalization	4,180,547
1980	Treatment of Industrial Waste Water	Precipitation	4,188,291
1981	Process for Recovery of Uranium from Sea Water	Granulated Lignite Coal Filtration Matrix	4,298,577
1982	Production of Purified Brine	Flocculation; Precipitation	4,336,232
1985	Procedure for Obtaining High Purity Magnesium Salts or their Concentrate Solutions from Sea Water, Brine or Impure Magnesium Salt Solutions	Liquid Extraction; Precipitation; Solvent Extraction	4,521,386
1986	Precipitation of Minerals from Brines	Precipitation	3,374,081
1987	Method of Converting Brines to Useful Products	Precipitation	4,634,533
1990	Method for Removing Scale and Radioactive Material from Earth	Precipitation	4,973,201
1990	Process for Separating Salts in Seawater	Precipitation	4,956,157
1992	Process for the Desalination of Sea and for Obtaining Energy and the Raw Materials Contained in Sea Water	Electrolysis	5,124,012



	<b>Title</b>	<b>Technology</b>	<b>US Patent #</b>
1998	Method for Complex Processing of Sea-Water	Mechanical Filtration; Modified Zeolite; Weak-acid Cation Exchanger	5,814,224
2001	Apparatus and Method for Producing Magnesium from Seawater	Electrolysis	6,267,854
2002	Purification of Produced Water from Coal Seam Natural Gas Wells Using Ion Exchange and Reverse Osmosis	Ion Exchange; Reverse Osmosis	US 6,372,143 B1
2003	Recovery of Common Salt and Marine Chemicals from Brine	Bromine; Magnesium; Potassium; Salt;	US 2003/008006 6
2006	Method of Producing Useful Products from Seawater and Similar Brines	Co-precipitation; Coprecipitation	US 2006/010508 2
2006	Production of Purified Water and High Value Chemicals from Salt Water	Electrodialysis; Nanofiltration; Reverse Osmosis	7,083,730
2007	Process for Pre-treating and Desalinating Sea Water	Precipitation	7,198,725
2009	Process for Producing Low Sodium Sea Salt from Sea Water	Crystallization	US 7,621,968 B2
2009	Process for the Treatment of Saline Water	Crystallization; Dewatering; Evaporation; Precipitation	7,595,001 B2
2010	CO <sub>2</sub> -sequestering Formed Building Materials	Carbon Dioxide Sequestration; Precipitation	7,771,684 B2
2010	Methods and Systems for Utilizing Waste Sources of Metal Oxides	Carbon Dioxide Sequestration; Precipitation	7,754,169 B2
2010	Non-cementitious Compositions Comprising CO <sub>2</sub> Sequestering Additives	Precipitation	7,829,053 B2
2010	Reduced-carbon Footprint Concrete Compositions	Precipitation	7,815,880 B2
2010	Rocks and aggregate, and methods of making and using the same	Carbon Dioxide Sequestration; Precipitation	7,753,618 B2

	<b>Title</b>	<b>Technology</b>	<b>US Patie nt #</b>
2010	System and Method for Reversible Cation-Exchange Desalination	Cation Exchanger; Pressure Driven Membrane	US 2010/028267 5
2011	Electrochemical Production of an Alkaline Solution Using CO <sub>2</sub>	Electrolysis; Membrane; Nanofiltration; Precipitation; Reverse Osmosis	7,993,511 B2
2011	Methods of Sequestering CO <sub>2</sub>	Electrolysis; Precipitation	7,887,694
2011	Methods to Treat Produced Water	Precipitation	7,963,338 B1
2011	Mobile Systems and Methods of Sufficiently Treating Water so that the Treated Water may be Utilized in Well-treatment Operations	Precipitation	8,012,358 B2
2011	Process for the Preparation of Common Salt of High Purity from Brines in Solar Salt Pans	Precipitation	8,021,442
2012	Onsite Integrated Production Factory	Electrolysis; Ion Exchange; Ion-exchange; Marine Wind and Tidal Power; Reverse Osmosis	8,197,664

**Table A.7. Patents on Potassium Extraction or Removal**

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patie nt #</b>
1946	Method of Obtaining Magnesia and Potash from the Waters of The Great Salt Lake	Precipitation	2,404,550
1966	Recovery of Potassium Halides from Brine	Evaporation; Ore Flotation; Precipitation; Separation	3,231,340
1966	Recovery of Potassium Halides from Brine	Evaporation; Ore Flotation; Precipitation; Separation	3,231,340
1966	Selective Precipitation of Potassium Chloride by Addition of Ammonia	Ammoniating; Filtration; Separation	3,279,897
1967	Precipitation of Potassium Halides from Mixed Brines Using Organic Solvents	Precipitation	3,359,076
1968	Process for Separating Inorganic Cations from Solution with Hydrous Oxide Cation Exchangers	Adsorption; Ion exchange; Ion-exchange	3,382,034
1969	Selective Precipitation of Potassium Chloride from Brine Using Organoamines	Precipitation	3,437,451
1969	Separation of Cesium from Potassium and Rubidium	Precipitation	3,468,959
1970	Recovery of Potassium from Sea Water	Adsorbition with Zeolite	3,497,314
1977	Method of Seperating Ionized Substances from an Aqueous Solution	Bioaccumulation; Bioextraction	4,024,054
1979	Process for Recovery of Chemicals from Saline Water	Crystalization	4,180,547
1982	Inorganic Ion Exchanger	Adsorption; Ion-exchange; Ion Exchange	4,313,844
1987	Drying Process Using Chabazite-type Adsorbents	Adsorption	4,663,052
1990	Process for Separating Salts in Seawater	Precipitation	4,956,157

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patie nt #</b>
1991	Method for Separating Sodium and Potassium by Ion Exchange	Ion exchange; Ion-exchange	5,066,404
1992	Process for the Desalination of Sea and for Obtaining Energy and the Raw Materials Contained in Sea Water	Electrolysis	5,124,012
2002	Purification of Produced Water from Coal Seam Natural Gas Wells Using Ion Exchange and Reverse Osmosis	Ion Exchange; Reverse Osmosis	US 6,372.143 B1
2003	Recovery of Common Salt and Marine Chemicals from Brine	Bromine; Magnesium; Potassium; Salt;	US 2003/008006 6
2006	Simultaneous Recovery of Potassium Chloride and KCL Enriched Edible Salt	Evaporation	7,014,832
2007	Process for Pre-treating and Desalinating Sea Water	Precipitation	7,198,724
2009	Process for Producing Low Sodium Sea Salt from Sea Water	Crystallization	US 7,621,968 B2
2010	Methods to De-Sulfate Saline Streams	De-sulfate Saline Streams; Multi-stage Flash; Multi-effect Distillation; Reverse Osmosis	US 7,789,159
2012	Onsite Integrated Production Factory	Electrolysis; Ion Exchange; Ion-exchange; Marine Wind and Tidal Power; Reverse Osmosis	8,197,664

**Table A.8. Patents on Rubidium Extraction or Removal**

Year	Title	Technology	US Patent #
1967	Recovery and Separation of Cesium and Rubidium Fluorides Using Alcohols	Evaporation; Filtration; Liquid Extraction	3,305,321
1968	Process for Separating Inorganic Cations from Solution with Hydrous Oxide Cation Exchangers	Adsorption; Ion exchange; Ion-exchange	3,382,034
1969	Separation of Cesium from Potassium and Rubidium	Precipitation	3,468,959
1970	Hydrous Oxides Cation Exchangers	Adsorption; Ion exchange; Ion-exchange	3,522,187
1970	Process of Separating Rubidium from Alkali Metal Impurities	Acidification; Evaporation; Precipitation	3,510,257
1982	Inorganic Ion Exchanger	Adsorption; Ion-exchange; Ion Exchange	4,313,844
1987	Drying Process Using Chabazite-type Adsorbents	Adsorption	4,663,052

**Table A.9. Patents on Salt Extraction or Removal**

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patent #</b>
1922	Process of Treating Salt Mixtures	Precipitation; Saturation	1,435,524
1952	Method and Apparatus for Conditioning Liquids	Anion Exchange Materials; Filtration	2,606,870
1957	Processes for the Manufacture of Various Chemicals from Sea Water	Blow-out; Evaporation; Filtration; Precipitation	2,793,099
1964	Method of Processing Sea Water	Crystalization; Evaporation; Electrolysis; Precipitation	3,147,072
1972	Production of Fresh Water, Brine and Magnesium Hydroxide	Evaporation; Precipitation; Seeded Precipitation;	3,676,067
1965	Method for Electrolysis	Electrolytic Decomposition; Electrolysis	3,220,941
1978	Desalination Process System and By-product Recovery	Brine Concentration; Flash Evaporation; Reverse Osmosis	4,083,781
1966	Selective Precipitation of Potassium Chloride by Addition of Ammonia	Ammoniating; Filtration; Separation	3,279,897
1967	Precipitation of Potassium Halides from Mixed Brines Using Organic Solvents	Precipitation	3,359,076
1993	Process for the Preparation of Sodium Chloride	Crystallization; Evaporation; Precipitation	5,221,528
1968	Process for Separating Inorganic Cations from Solution with Hydrous Oxide Cation Exchangers	Adsorption; Ion exchange; Ion-exchange	3,382,034
1969	Chemical Cycle for Evaporative Water Desalination Plant	Chemical Treatment; Condensation; Electrolysis; Evaporation; Precipitation	3,463,814
2003	Recovery of Common Salt and Marine Chemicals from Brine	Bromine; Magnesium; Potassium; Salt;	US 2003/0080066
2004	Method for Producing Sodium Chloride Crystals	Evaporation; Filtration; Precipitation	6,692,720
2006	Production of Purified Water and High Value Chemicals from Salt Water	Electrodialysis; Nanofiltration; Reverse Osmosis	7,083,730
2006	Production of Ultra Pure Salt	Evaporation	7,037,481

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patie nt #</b>
2006	Simultaneous Recovery of Potassium Chloride and KCL Enriched Edible Salt	Evaporation	7,014,832
1972	Production of Fresh Water, Brine and Magnesium Hydroxide	Evaporation; Precipitation; Seeded Precipitation;	3,676,067
1979	Process for Recovery of Chemicals from Saline Water	Crystallization	4,180,547
2012	Method of Making Pure Salt from FRAC-water/wastewater	Crystallization; Filtration	8,158,097
1983	Process for Sterilization and Removal of Inorganic Salts From a Water Stream	Electrolysis; Filtration; Precipitation	4,392,959
1988	Method of Converting Brines to Useful Products	Precipitation; Filtration	4,755,303
1991	Method for Separating Sodium and Potassium by Ion Exchange	Ion exchange; Ion- exchange	5,066,404
1992	Process for the Desalination of Sea and for Obtaining Energy and the Raw Materials Contained in Sea Water	Electrolysis	5,124,012
1993	Process for the Preparation of Sodium Chloride	Crystallization; Evaporation; Precipitation	5,221,528
1995	Precipitation and Separation of Salts, Scale Salts, and Norm Contaminant Salts from Saline Waters and Saline Solutions	Precipitation; Vaporization	5,468,394
1996	Precipitation and Separation of Inorganic Species from Aqueous Solutions	Condensation; Ion Exchange; Miscible Organic Solvent; Precipitation	5,587,088
2002	Purification of Produced Water from Coal Seam Natural Gas Wells Using Ion Exchange and Reverse Osmosis	Ion Exchange; Reverse Osmosis	US 6,372.143 B1
2004	Method for Producing Sodium Chloride Crystals	Evaporation; Filtration; Precipitation	6,692,720
2009	Methods for Treating Agricultural Drainage Water and the Like	Agricultural Drainage Water System; IFDM; Integrated on Farm Drainage Management	US 7,501,065 B1
2009	Process for the Treatment of Saline Water	Crystallization; Dewatering; Evaporation; Precipitation	7,595,001 B2

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patient #</b>
2010	System and Method for Reversible Cation-Exchange Desalination	Cation Exchanger; Pressure Driven Membrane	US 2010/0282675
2012	Onsite Integrated Production Factory	Electrolysis; Ion Exchange; Ion-exchange; Marine Wind and Tidal Power; Reverse Osmosis	8,197,664

**Table A.10. Patents on Strontium Extraction or Removal**

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patient #</b>
1990	Method for Removing Scale and Radioactive Material from Earth	Precipitation	4,973,201
1995	Precipitation and Separation of Salts, Scale Salts, and Non Contaminant Salts from Saline Waters and Saline Solutions	Precipitation; Vaporization	5,468,394
2003	Process for the Treatment of Aqueous Streams Containing Inorganics	Cation Formation; Concentrating; Distilling; Precipitation; Vacuum Membrane Distillation	US 6,663,778 B1
2010	System and Method for Reversible Cation-Exchange Desalination	Cation Exchanger; Pressure Driven Membrane	US 2010/0282675
2011	Mobile Systems and Methods of Sufficiently Treating Water so that the Treated Water may be Utilized in Well-treatment Operations	Precipitation	8,012,358 B2
2012	Method of Making Pure Salt from FRAC-water/wastewater	Crystallization; Filtration	8,158,097



**Table A.11. Patents on Uranium Extraction or Removal**

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patent #</b>
1959	Recovery of Uranium from Dilute Uranium-Containing Solutions	Filtration; Precipitation; Sedimentation	2,885,258
1970	Hydrous Oxides Cation Exchangers	Adsorption; Ion exchange; Ion-exchange	3,522,187
1973	Method of Extraction Uranium from Seawater	Tri-carbonate Complexes; Acidification; Alkali Carbonate Solution	3,721,533
1973	Process for Recovering Uranium	Battings; Fabrics; Fibers; Filaments; Filtration; Flakes; Films; Particles; Polyvinyl Alcohol;	3,778,498
1975	Solvent Extraction of Metals with a Cyclic Alkylene Carbonate	Cyclical Organic Carbonates; Extraction	3,912,801
1980	Chemical Analysis and Mineral Prospecting	Inert Carrier Gas	4,225,314
1980	Material for Recovering a Uranium Solution of High Purity and High Concentration, Using the Same	Distillation; Ion Exchange; Precipitation	4,199,470
1981	Chelate Resin Prepared by Aftertreatment of Aminated Resin with Polyfunctional Compound and Amine	Chelation	4,277,566
1981	Electrodes for Electrolytic Processes, Especially Metal Electrowinning	Electrodes; Electrolytic Processes; Manganese Oxide anodes	4,285,799
1981	Metals Extraction from Sea Water	Adsorber Sheets; Eluting Metals	4,293,527
1981	Method for the Recovery of Uranium Dissolved in Sea Water	Absorbentatrix; Adsorption; Black Peat Adsorbant Matrix	4,277,345
1981	Method for the Recovery of Uranium Dissolved in Sea Water	Adsorption; Counter-current-extraction; Humic acids	4,277,345
1981	Method of Extracting Uranium from Sea Water	Inoculation; Microorganism Extraction; X-ray exposure	4,263,403
1981	Method of Quantitatively Separating Uranium from Specimens of Natural Water by Sorption on Silica	Adsorption; Granular Silica; Silica Gel;	4,283,370
1981	Process for Recovery of Uranium from Sea Water	Granulated Lignite Coal Filtration Matrix	4,298,577
1983	Method and Apparatus for Recovering Raw Material,	Carrier Bodies; Carrier Body Discharge; Filtration; Inert	4,416,860

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patie nt #</b>
	Especially Uranium, from Natural Waters, Especially from the Sea	Material	
1983	Phenolic Chelate Resin, Process for Producing the Same, and Method of Recovering Heavy Metal Ions with the Same	Alkylamino Group Introduced to Phenol Nucleus; Chelate Resin	4,414,183
1986	Apparatus for Gathering Valuable Floating, Dissolved and Suspended Substances from Sea Water	Bioactive Mass; Filtration; Hydrostatic Pressure; Ion Exchanging; Sorbing	4,565,627
1986	Process for the Concentration of Uranium from Sea Water	Chemical Accumulation; Elution; Solid Adsorption Medium; Titanium Oxide Hydrate	4,585,627
1986	Process for the Recovery of Heavy Metal	Heavy Metal Recovery; Polymer Adsorbtion	4,601,889
1986	Uranium Adsorbing Material and Process for Preparing the Same	Graft Polymer; Adsorbing Material;	4,622,366
1987	Chelate, Crosslinked Polyethyleneimine Resin Having 2-Hydroxy Benzoyl Group	Adsorption; Hydroxybenzoic acid; 2-hydroxybenzoyl group;	4,678,844
1987	Process for the Recovery of Uranium from Phosphoric Acid Solutions	Filtration; Flotation; Organophosphorus Complexing Agent; Sedimentation;	4,656,012
1988	Process for the Recovery of Uranium Values in an Extractive Reprocessing	Fission Material; Ion Exchanger; Organic Extraction Phase	4,740,359
1989	Recovery or Removal of Uranium by the Utilization of Acorns	Co-precipitation; Coprecipitation	4,871,518
1994	Uranium Adsorbent	Precipitate Formation; Uranium Adsorbent	5,276,103
1995	Precipitation and Separation of Salts, Scale Salts, and Norm Contaminant Salts from Saline Waters and Saline Solutions	Precipitation; Vaporization	5,468,394
2001	Collector of Dissolved Metal from Sea Water Having an Amidoxime Group and a Hydrophilic Group, A Method for Production Thereof	Polyolefin Fiber; Radiation-Initiated Graft Polymerization	US 6,333,078
2002	Adsorption Means for Radionuclides	Adsorption; Adsorbent; Chitin; Chitosan; Sorption; Sorbent	6,402,953 B1
2005	Collector for Adsorptive Recovery of Dissolved Metal from Sea Water	Polyolefin Fiber; Radiation-Initiated Graft Polymerization	US 6,863,812 B2

<b>Year</b>	<b>Title</b>	<b>Technology</b>	<b>US Patie nt #</b>
2009	Systems and Methods of Removing and Managing Heavy Metals	Constituents Before Absorption on Organism; Heavy Metal Binding; Ligand Extract	US 2009/0075861







**1199 North Fairfax Street, Suite 410**  
**Alexandria, VA 22314 USA**  
**703.548.0880**  
**703,548.5085 (fax)**  
**[foundation@watereuse.org](mailto:foundation@watereuse.org)**  
**[www.WateReuse.org](http://www.WateReuse.org)**