


Extraction of Valuable Materials from Reverse Osmosis Concentrate

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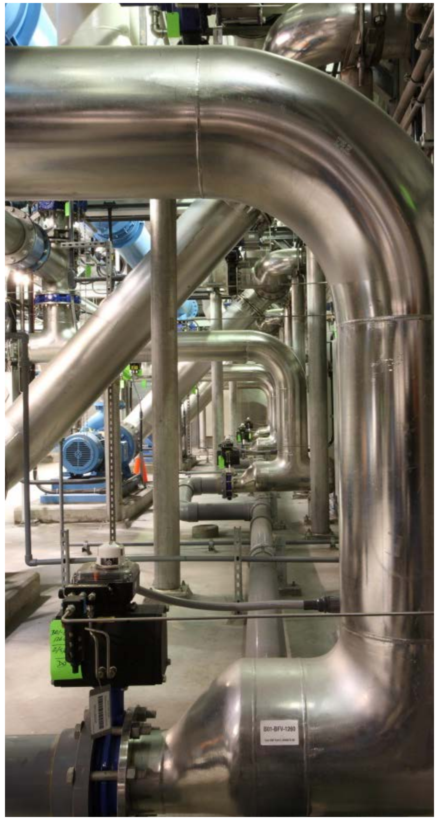


The WateReuse Research Foundation

The mission of the WateReuse Research Foundation is to conduct and promote applied research on the reclamation, recycling, reuse, and desalination of water.

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A Few Notes Before We Get Started…

- Today's webcast will be 60 minutes.
- There is 1 (one) Professional Development Hour available.
- A PDF of today's presentation can be downloaded when you complete the survey at the conclusion of this webcast.
- Links to view the recording and to download the presentation will also be emailed later.
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Today’s Moderator

Arash Shahmansouri

PhD Candidate, Clarkson University

Today's Presenter

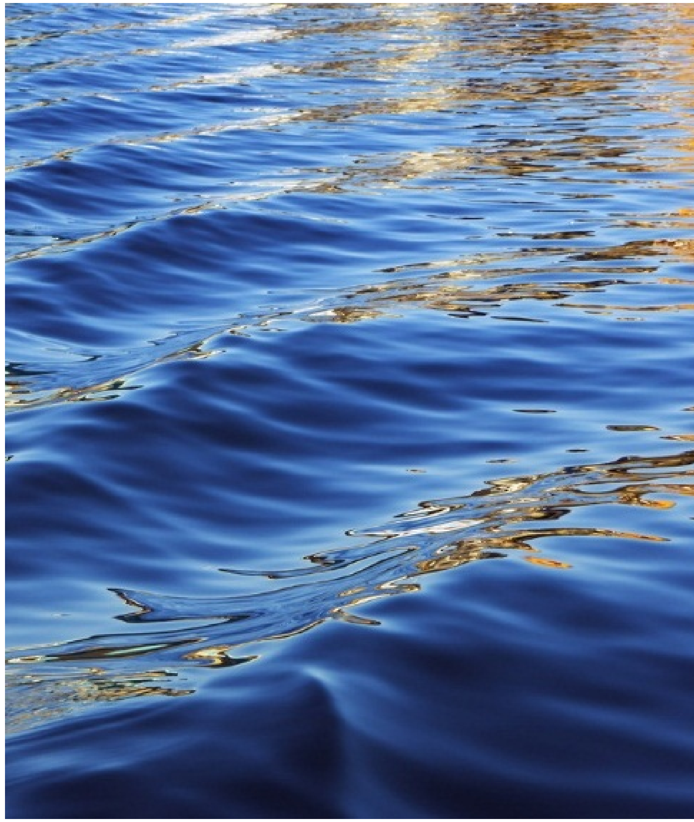
Dr. Christopher Bellona

Assistant Professor, Clarkson University

Webinar Outline

- Historical Perspective
- Project Introduction
- Economic Evaluations
- Other Options
- Conclusions

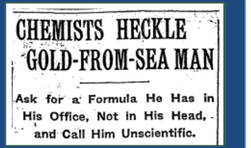
Historical Perspectives



Historical Perspective

- The ocean has long been viewed as an inexhaustible resource
- Magnesium and bromine once exclusively produced from seawater in the U.S.
- Large interest in uranium and lithium recovery from seawater
- Various minerals extracted from aqueous resources

2200 BC	Chinese extract salt from SW	11 Na, 17 Cl
ca. 600-900 BC	Mayan salt works active, Yucatan	
1872	First analysis of SW for gold	79 Au
1911	Austrian chemist laughed out of ACS meeting	
World War 1	War with Germany leads Dow to develop Mg production from brine	12 Mg
1918	Gold from SW proposed to pay German war debt	
1926	Br first produced from SW	35 Br
1933	Dow-Ethyl Br plant opens at Kure Beach, NC	
World War 2	UK develops magnesia production	
1941	Dow opens Freeport, TX, Mg plant	
1950s	UK starts uranium from SW research	92 U
1960s	Japan researches U	
1970s	Li extraction studied at Brookhaven	3 Li
1990s on	Increased interest in extracting salts from RO brine	


CHEMISTS HECKLE GOLD-FROM-SEA MAN

Ask for a Formula He Has in His Office, Not in His Head, and Call Him Unscientific.

Historical Perspective – Sodium Chloride

- Extracted from seawater in significant quantities for thousands of years
- Commonly produced in solar salt works – successive precipitation steps
- Byproducts of solar salt include bromide, iodide, potassium, nitrate and sulfate containing salts
- Japan produces food grade salt from seawater using electrodialysis followed by evaporation

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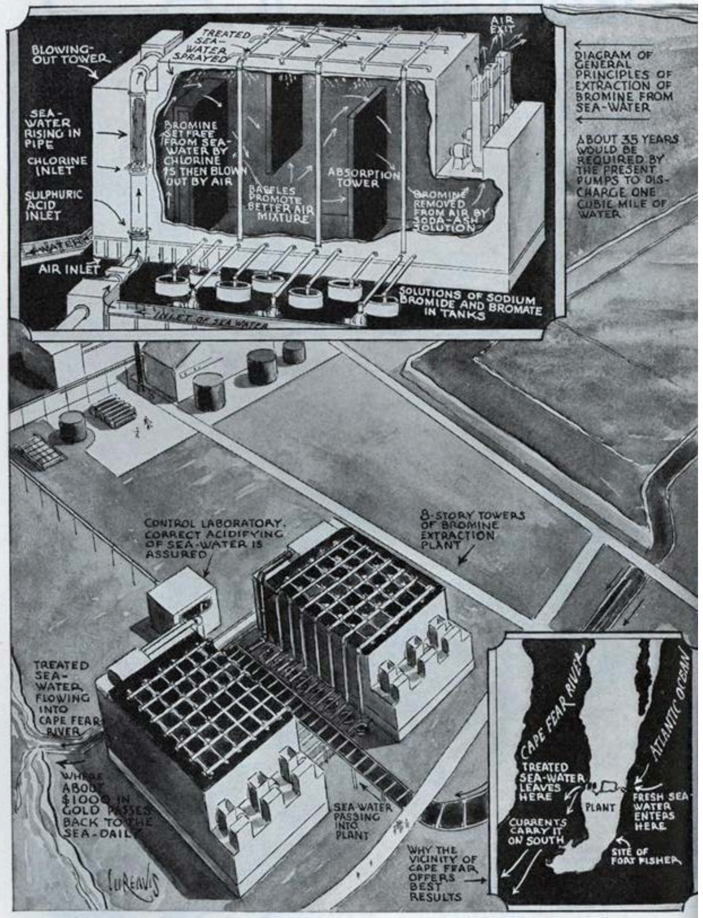
Historical Perspective – Bromine

- Ethyl Gasoline Corporation developed process for producing tribromoaniline from seawater in 1920's
- Dow Chemical Company refined process and built a large-scale bromine from seawater plant in North Carolina in 1933
- Both companies eventually turned to underground brines for a source of bromine
- Currently, a small percentage of bromine is produced from byproducts of solar salt operations

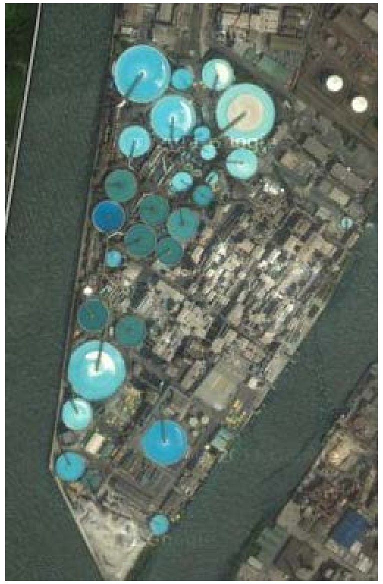
This Plant Extracts Bromine from Sea Water

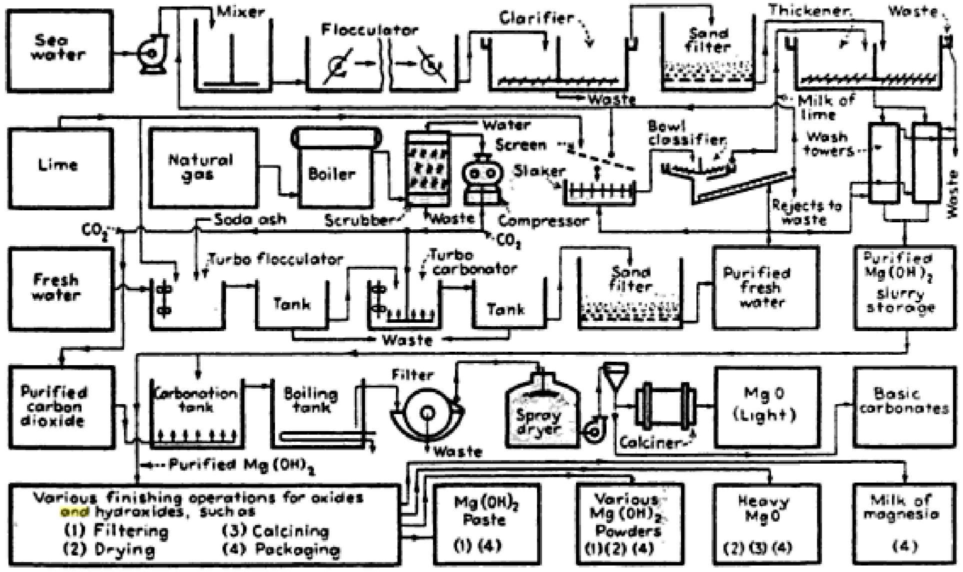


Bromine Extraction Plant; Sulphuric Acid and Chlorine Are Added to Sea Water to Release the Bromine Fumes Which Are Absorbed under a Shower of Soda-Ash Solution

Historical Perspective – Magnesium

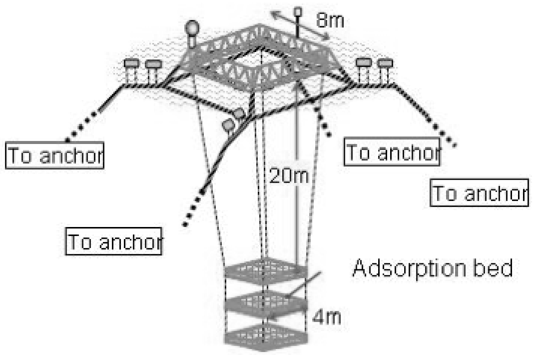
- Second most abundant cation in seawater (~1.28 g/L)
- Dow produced magnesium metal and compounds from seawater for ~50 years
- Several seawater magnesium compound ($MgOH_2$, MgO) extraction facilities in operation worldwide
- Utilize staged lime precipitation process

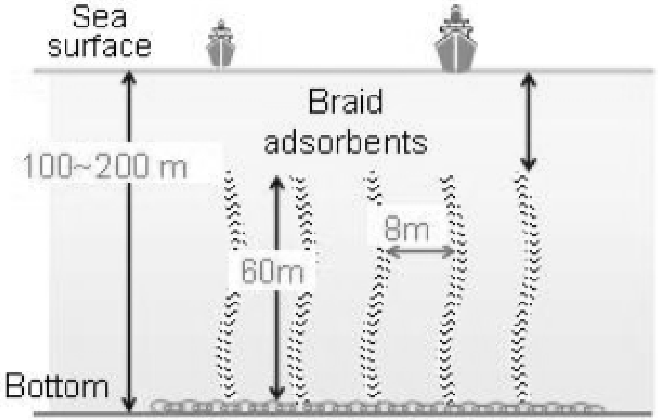




Historical Perspective – Uranium

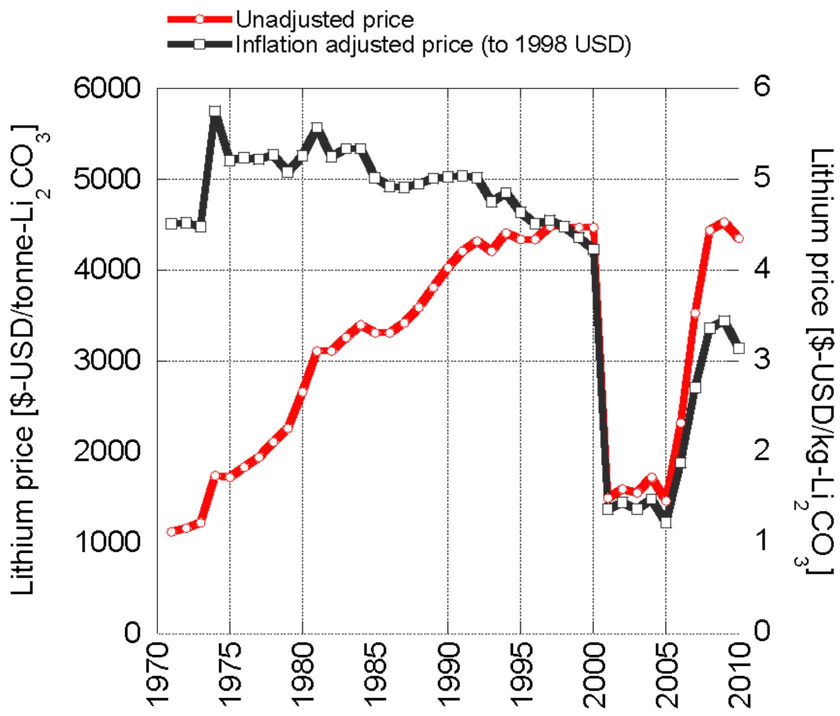
- Uranium found at ~3 ug/L in surface seawater
- Research on uranium extraction from the sea likely started in the United Kingdom in the 1950's (abandoned in 1970)
- Japan began researching uranium extraction in the 1960's and researchers have evaluated or developed a number of adsorbent materials
- Researchers at the Japanese Atomic Energy Agency and India's Bhabha Atomic Research Center have begun developing technology for large-scale uranium from sea production





Historical Perspective – Lithium

- Found in seawater at ~173.5 ug/L
- Increase in Li-ion battery (LIB) use has brought attention to lithium supply and demand
- Around 90% of lithium resources controlled by 4 major producers, which are not near LIB manufacturers
- Lithium extraction from seawater has received attention for 40-years
- Detailed cost analyses indicate the seawater lithium extraction costs are btw \$16 – 22/kg-Li_2CO_3



Historical Perspective – Desalination

- Postulated by John Mero[1] in 1964 that desalination brine would be mined in the not so distant future:

'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.'

- Others[2] have more recently raised the question:

'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?"

[1]Mero, J.L., *The mineral resources of the sea*. Vol. 1. 1965, Amsterdam: Elsevier.

[2]Petersen, U., *Mining the hydrosphere.* Geochimica et Cosmochimica Acta, 1994. **58**(10): p. 2387-2403.

Historical Perspective – Desalination

- Researchers have proposed strategies for material extraction from desalination brine

Desalination 158 (2003) 109–117

Feasibility of salt production from inland RO desalination plant reject brine: a case study

Mushtaque Ahmed[a]*, Aro Arakel[b], David Hoey[c], Muralee R. Thumarukudy[d], Mattheus F.A. Goosen[a], Mansour Al-Haddabi[a], Abdullah Al-Belushi[a]

Desalination 182 (2005) 449–460

Extraction of strategic materials from the concentrated brine rejected by integrated nuclear desalination systems

J. Le Dirach[a], S. Nisan[a]*, C. Poletiko[b]

Received 3 January 2005; accepted 21 February 2005

Desalination 270 (2011) 1–8

A review of desalting process techniques and economic analysis of the recovery of salts from retentates

Dae Hyun Kim *

Journal of Cleaner Production 17 (2009) 703–707

Metal recovery from reverse osmosis concentrate

T. Jeppesen, L. Shu, G. Keir, V. Jegatheesan*

Sustainability 2010, 2, 980-992; doi:10.3390/su2040980

Extracting Minerals from Seawater: An Energy Analysis

Ugo Bardi

RECLAMATION — Managing Water in the West

Desalination and Water Purification Research and Development Program Report No. 111

Zero Discharge Seawater Desalination: Integrating the Production of Freshwater, Salt, Magnesium, and Bromine

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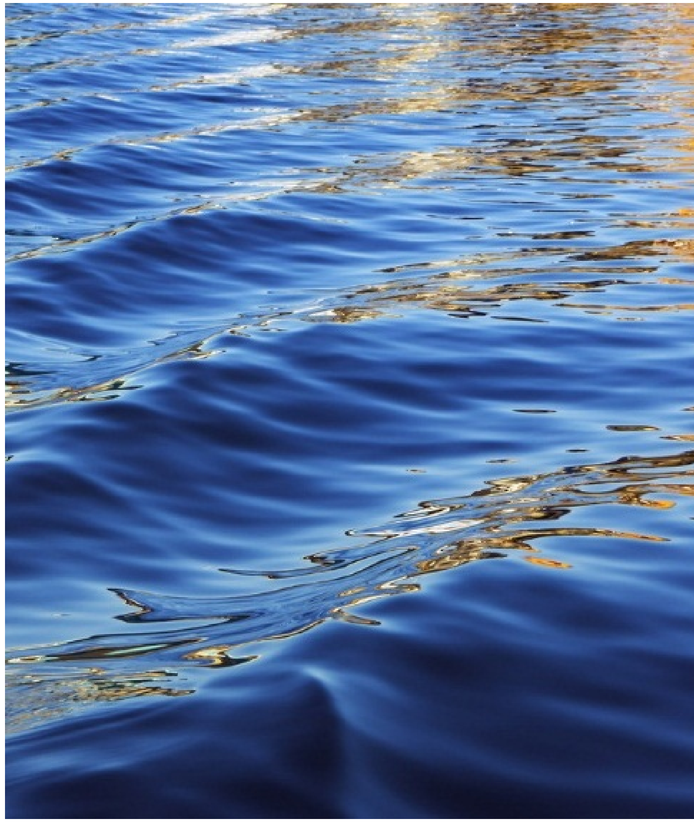
Project Introduction



Project Introduction

- Solicited project funded by the WateReuse Research Foundation
- Goal of investigating the feasibility of extracting materials for economic gain from desalination brine/concentrate
- Objective of conducting a review of past and present work focused on commodity recovery from aqueous solutions
- Final report title will be 'Guidance for Selection of Selective Salt, Metal, Radionuclide, and Other Valuable Material Recovery Approaches'

Project Introduction

- Goal: evaluate feasibility of material extraction from desalination brine/concentrate by:
  - Conducting comprehensive literature review
  - Conducting comprehensive patent review
  - Summarizing case studies
  - Performing economic analyses

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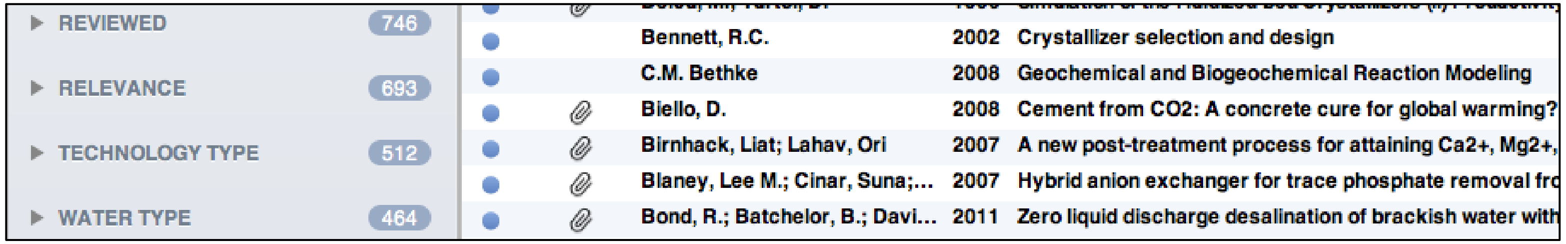
Literature Review

- A variety of literature types screened and categorized:
  - Commodity information
  - Sources of water quality information
  - Patented technologies for extraction
  - Peer-reviewed literature
  - Book chapters
  - Reports
  - Grey literature
- Significant amount of research conducted on extracting commodities from aqueous solutions over the past 100-years
- All information compiled into searchable EndNote database



Findings from Literature and Patent Reviews

- Patents were not generally useful unless associated with a published paper or report
- Commodity information often indicated that markets for extracted materials are either competitive, limited or difficult to enter
- Research has been conducted on the extraction of a wide variety of substances or elements from water using a wide range of technologies
- Most studies conducted at a very fundamental level – not near demonstration level
- Very few studies were identified that physically evaluated the technical feasibility of extracting and purifying commodities from desalination brine/concentrate

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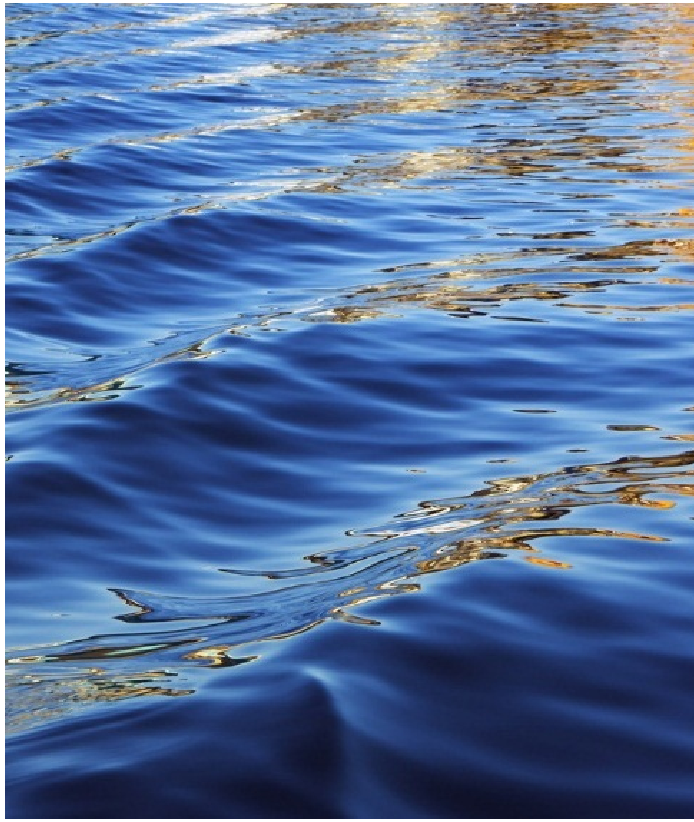
Findings from Literature and Patent Reviews

- Significant amount of research on extraction of commodities from desalination brine/concentrate streams
- Many studies conclude that extraction is feasible and would produce a profit
- Very few demonstration studies
- Very few studies that analyzed energy requirements, chemical consumption, and costs

Desal. System	Constituent(s)	Processes	Level of Investigation	Cost and Energy Requirements
SWRO	Br_2, $Mg(OH)_2$, salt	ED/EDR, precipitation, evaporation, blowout tower	Lab-scale tests conducted	Preliminary costs presented indicate potential profits
SWRO	NaCl	ED/EDR, MSF, crystallization	Lab-scale tests conducted	Cost analysis presented indicates sale of salts reduces water cost
SWRO	NaCl	ED/EDR, MED, crystallization	Simulation only	Energy analysis indicates NaCl production from SWRO brine 80% more efficient than from seawater
SWRO	$CaCO_3$, $MgSO_4$, NaCl, KCl, Li, Cl_2, NaOH	NF, RO, precipitation, evaporation, ion-exchange	Proposed only	Not evaluated
BWRO, WWRO	$CaCO_3$, $CaSO_4$, $Mg(OH)_2$, Na_2SO_4, $K_3Na(SO_4)_2$	Precipitation, RO, Evaporation	Mostly simulation, bench-scale tests conducted	Not evaluated
Thermal desal.	Na_2SO_4, Br_2, NaCl	Eutectic freezing, crystallization, blowout tower	Simulation	Not evaluated
SWRO	Cs, Rb, In, Ge, Mg, NaCl, KCl	Evaporation, IX, solvent extraction, liquid membranes	Proposed only	Not evaluated
SWRO, BWRO	NaCl, Mg, Cl_2, NaOH, $CaCO_3$	ED/EDR, MSF, MVC precipitation, NF, MCr	Proposed only	Performed cost analysis, claim that extraction is economical
Thermal desal.	NaCl, Na_2SO_4, Cl_2, NaOH	MED, electrolysis, eutectic freezing	Proposed only	Performed cost analysis: NaOH produced for $149/t, $ high capital costs
BWRO	$CaSO_4$, $Mg(OH)_2$, NaCl, $CaCl_2$, Na_2SO_4, $CaCO_3$	SAL-PROC process, precipitation, evaporation	Proposed only	Not evaluated
MSF	Mg, NaCl	MSF	Proposed only	Not evaluated
BWRO	$CaCO_3$	FBC, clarification	Demonstration	Not reported
WWRO	HCl, NaOH, Cl_2, P	Electrolysis, ED, IX	Lab-scale tests conducted	Not reported
WWRO	P, struvite	IX	Lab-scale tests conducted	Only calculated the potential revenue from struvite sales
SWRO	NaCl	Evaporation ponds	Full-scale	Not presented, produce food grade salt in a arrangement with a salt company
MED	NaCl	Solar evaporator	Simulation	Not evaluated
SWRO	Cl_2, NaOH	Precipitation, clarification, filtration, evaporation, IX, electrolysis	Simulation	Claim that production of NaOH requires 2150 kWh/t-NaOH – unclear if this is only for electrolysis
SWNF	$CaCO_3$, NaCl, $MgSO_4$	NF, precipitation, MCr	Laboratory-scale study	Not evaluated

Economic Evaluations



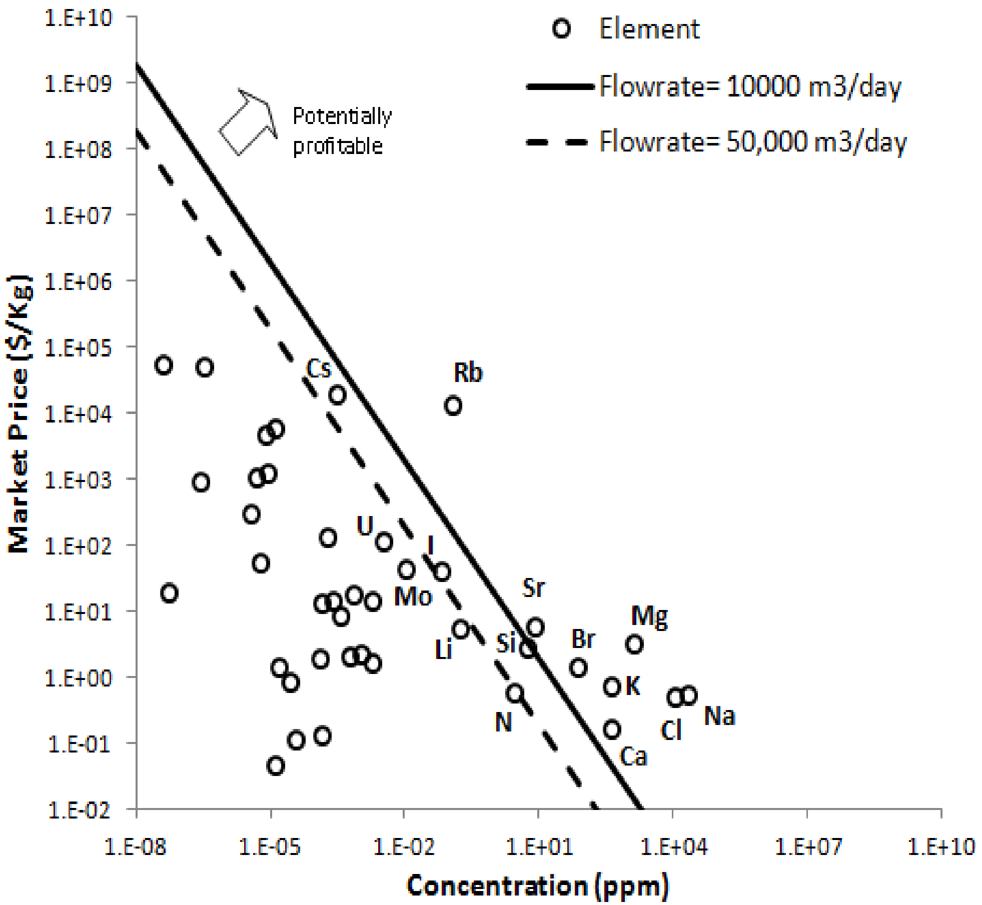
Screening for Constituents of Interest

- USGS Mineral Commodity Summaries (and other sources when necessary) used to:
  - Obtain commodity pricing
  - Understand commodity trends and potential lucrative materials
- Concentrations of ions and metals in seawater, brackish water and wastewater compiled
- Minimum operational cost ($33,000) used to identify salable constituents
- Potentially economically viable substances must meet the following criteria :

$$\boxed{Price * \text{Concentration} * \text{Flowrate} > \text{Annual Cost}}$$

Screening for Constituents of Interest

- Indicates that Br, Ca, K, Mg, NaCl, Rb, and Sr could potentially be extracted for profit
- Other researchers have concluded that Cl_2 and NaOH production feasible and lucrative
- Extraction procedures analyzed to evaluate feasibility



Economic Evaluations – Rubidium and Strontium

- Rubidium is a valuable commodity with very low demand
- Rubidium is not traded commercially in the U.S.
- Neither rubidium or strontium commodities produced in the U.S.
- Both extremely difficult to separate and purify from aqueous solutions
- Further evaluation not performed for rubidium and strontium

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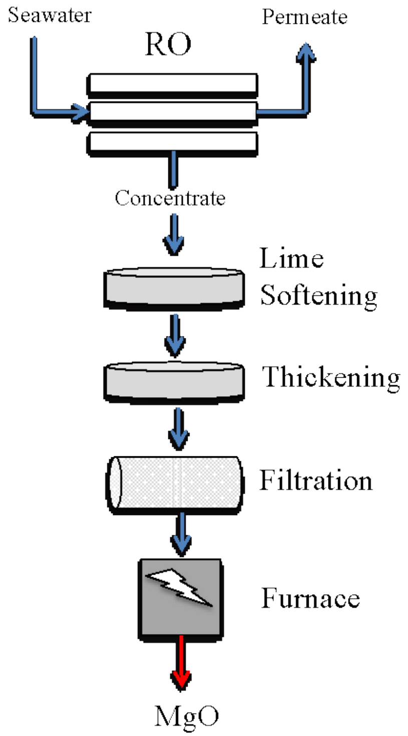
Economic Evaluations

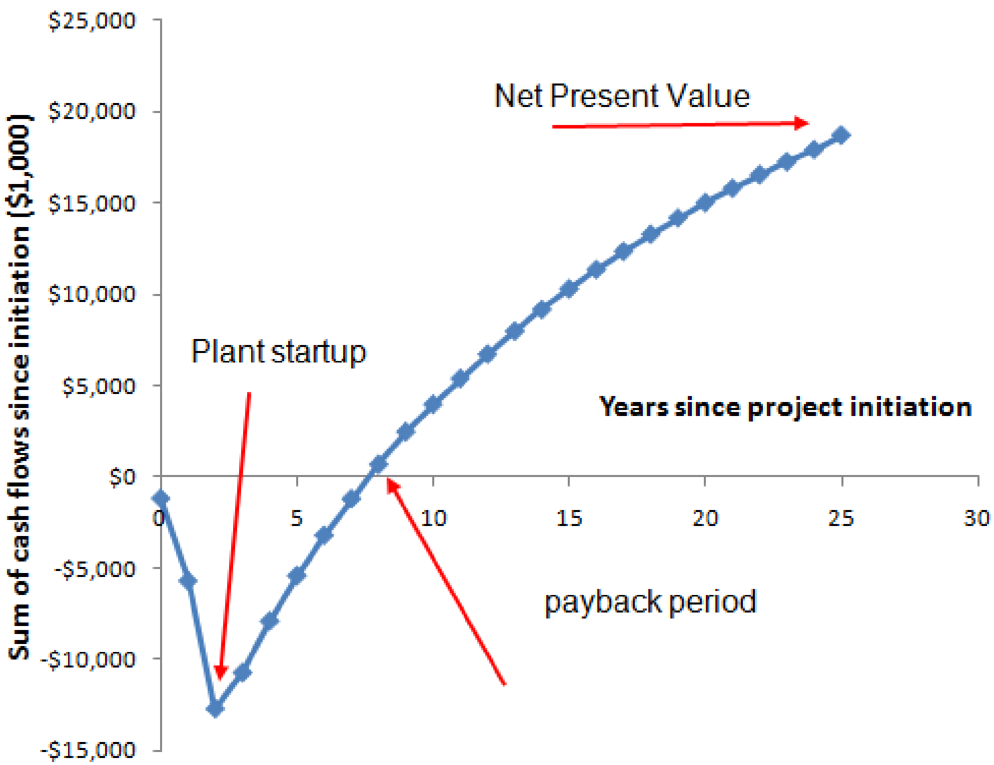
- Viable extraction schemes identified from literature
- Cost analysis performed for 20 MGD seawater desalination facility operating at 50% recovery
- Assumed 25-year facility lifespan, 6% interest rate and 80% extraction efficiency
- Approach assumes that local commodity market exists
- Payback period and net present value (NPV) calculated

Plant	Product	Plant efficiency (%)	Unit price ($/metric ton)	Revenue (M$/yr)
$Mg(OH)_2$, Br_2, NaCl	NaCl	80%	55	16.32
	Br_2	80%	1390	0.49
	$Mg(OH)_2$	80%	275	8.45
NaCl	NaCl	80%	55	16.32
MgO	MgO	80%	539	11.42
Cl_2, NaOH	Cl_2	80%	550	99.01
	NaOH	80%	500	101.56

Economic Evaluations – Magnesium Oxide

- Payback period estimated at 8-years
- Net present value of $19 million at 25-years





Economic Evaluations – Chlorine and Sodium Hydroxide

- Chlorine is produced from seawater in small quantities
- Chlorine is one of the largest production industries in the U.S.
- Chlor-alkali industry uses purified and nearly saturated sodium chloride solutions as feed stock
- Efficient electrolytic production from desalination brine would likely require significant pretreatment and concentration

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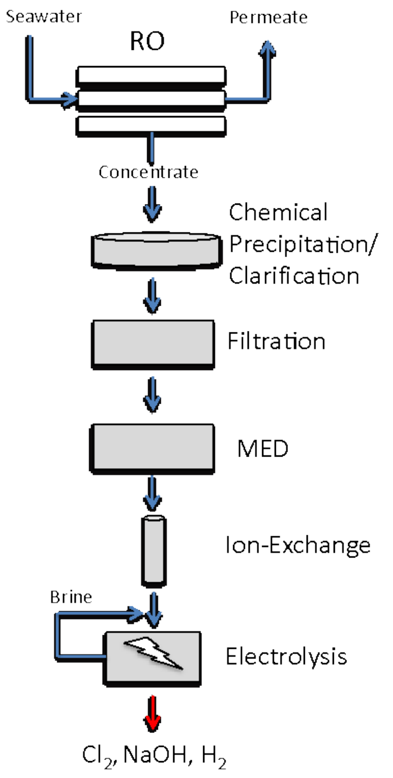
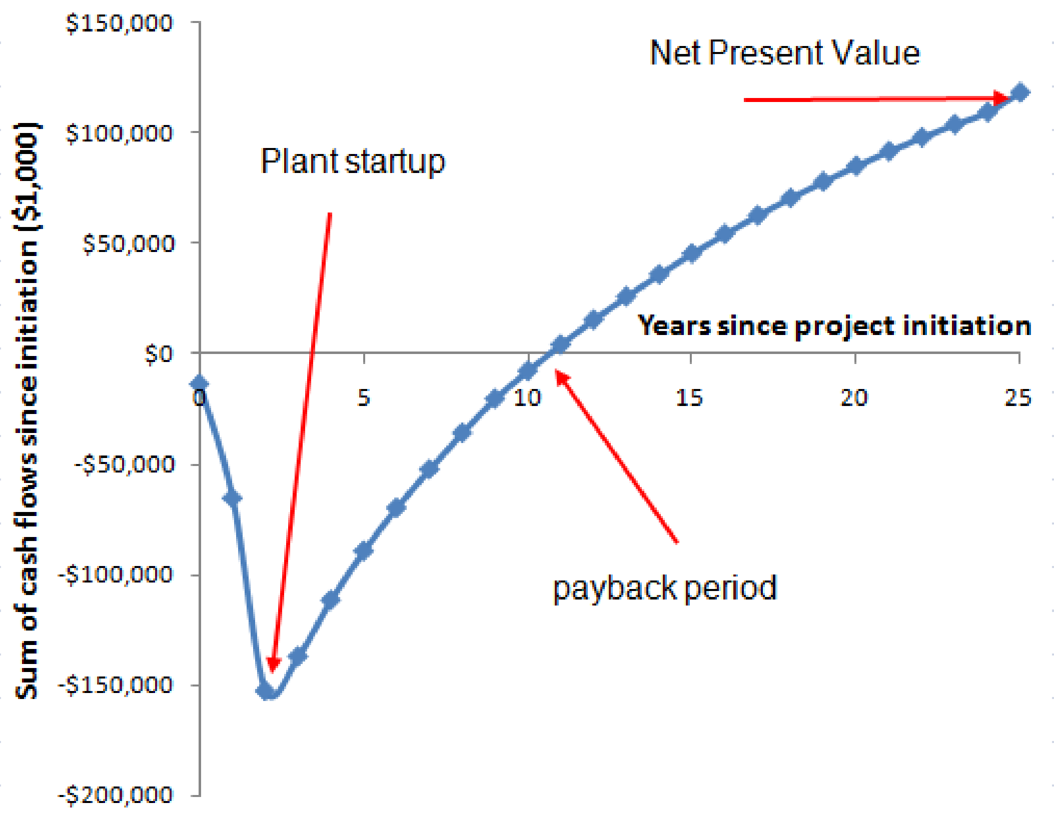
Economic Evaluations – Chlorine and Sodium Hydroxide

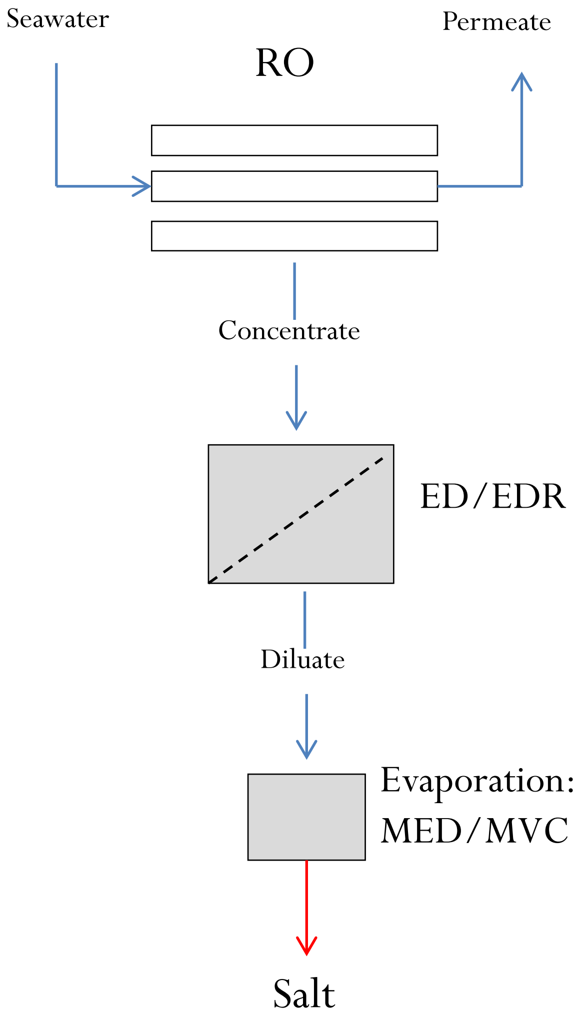
- Payback period estimated at 11-years
- Net present value of $118 million at 25-years





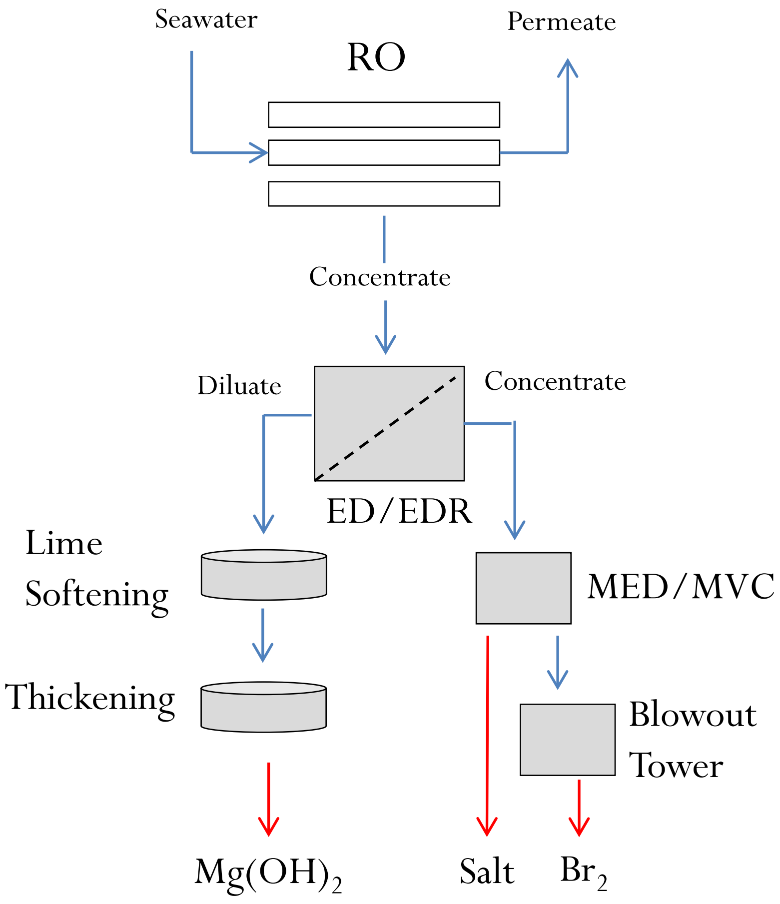
Economic Evaluations – Sodium Chloride

- Feasibility dependent on final price of salt produced
- Economically unfeasible at solar salt price of $55/ton
- Potentially profitable after 8-years for salt price of $100/ton for MED scenario



Economic Evaluations – Bromine, Magnesium, and Sodium Chloride

- Examined zero discharge desalination process developed by Thomas Davis[3] for simultaneous production of bromine, magnesium and sodium chloride
- Found cost of bromine extraction inhibited profit in developed scenario
- NPV analysis indicated that extraction would not be profitable



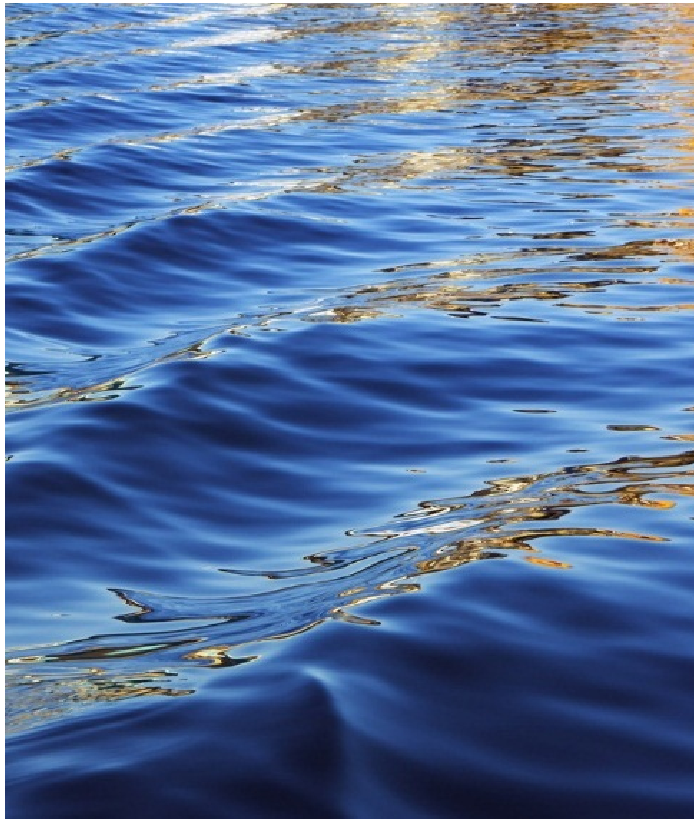
[3]Davis, T.A., *Zero discharge seawater desalination: Integrating the production of freshwater, salt, magnesium, and bromine*, in *U.S. Bureau of Reclamation Research Report No. 111*2006.

Economic Evaluations – Summary

- From a profit standpoint, it appears that only the extraction of magnesia (MgO) and NaOH-Cl_2 feasible
- Assumes that high-purity products can be produced from desalination brine and a buyer exists

Plant	Capital Cost (M$)	O&M cost (M$/yr)	NPV (M$)	Payback period (years)
Mg(OH)-Br-Salt-MED	93	18 ~ 19	-24.7	-
Mg(OH)-Br-Salt-MVC	76	21 ~ 24	-58.3	-
NaCl-MED	84 ~ 86	6 ~ 7	-14.5	-
NaCl-MVC	64 ~ 76	12 ~ 13	-40.2	-
MgO	12	7	18.7	8
NaOH-Cl_2	137	158	118.6	11

Other Options



Extraction to Alleviate Brine/Concentrate Disposal Issues

- Desalination brine/concentrate management is a highly divisive issue
- Extraction of valuable materials could offset costs associated with disposal
  - Allowing for higher system recoveries
  - Production of chemicals used within the plant
  - Potentially providing an additional revenue stream
- Two real world examples identified
- Several novel approaches identified

Example 1 – Sodium Chloride

- Mekorot Water Company entered into a partnership with the Israel Salt Company to produce high-quality NaCl from the brine of seawater and brackish water RO in Eilat, Israel
- In 2007, reportedly 150,000 tons of table and industrial grade salt was produced annually from solar salt ponds
- The two parties share the cost of seawater intake pumping and maintenance
- Challenges included preventing algal growth in evaporation ponds and producing brine with ideal chemistry

Example 2 – Calcium Carbonate

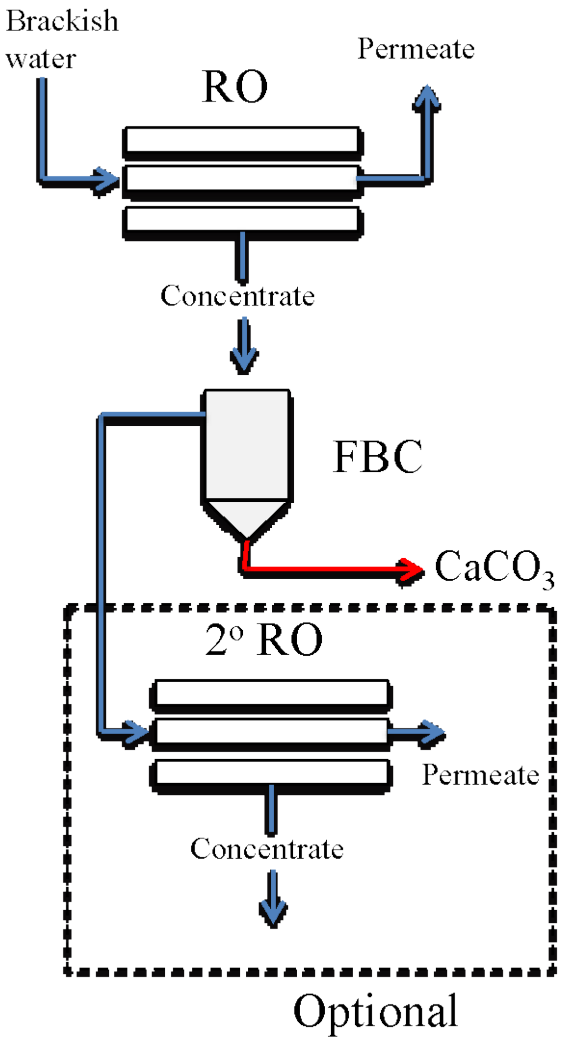
- Push towards zero liquid discharge for inland desalination benefits from production of salable materials
- Several studies evaluated secondary RO with intermediate softening[4,5]
- Recent Chino II Desalter (Southern California) expansion required concentrate minimization
- Designed to produce salable calcium carbonate material to reduce costs
- Results in increased overall system recovery and reduction of brine discharge costs

[4]Bond, R. and S. Veerapaneni, *Zero liquid discharge for inland desalination*, 2007, Black and Veatch. p. 1 - 233.

[5]Shih, W., Brandon Yallaly, Matthew Marshall, Don DeMichele, . *Chino II Desalter Concentrate Management Via Innovative Byproduct*. in *American Membrane Technology Association*. 2013. San Anotonio, Texas.

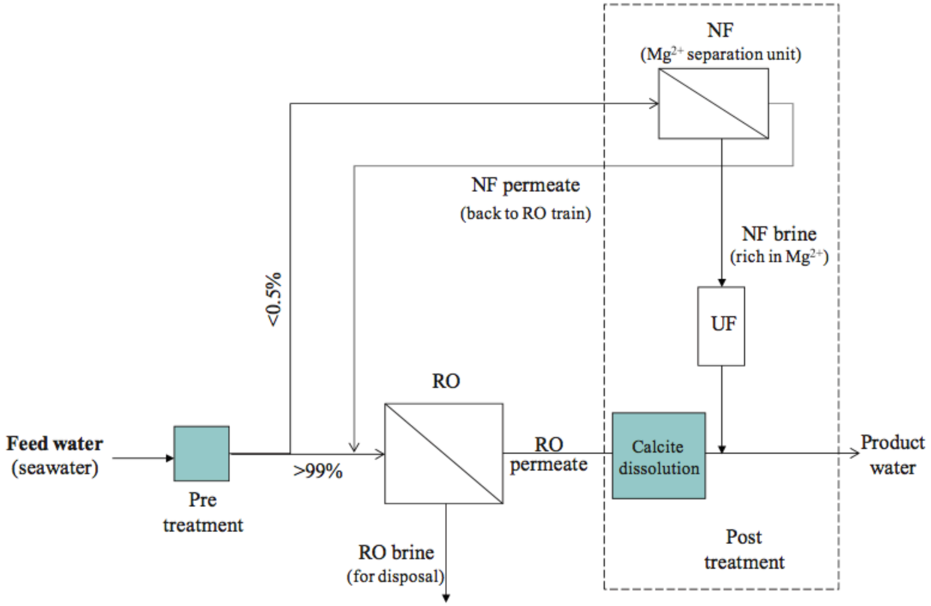
Example 2 – Calcium Carbonate

- Economics of extraction difficult to assess due to benefits from concentrate minimization
- Scenario based on 5 MGD concentrate flow rate with 800 mg/L calcium
- Assumed $CaCO_3$ price of $30/ton
- Could generate ~$130,000/yr



Other Processes – Alternative Stabilization

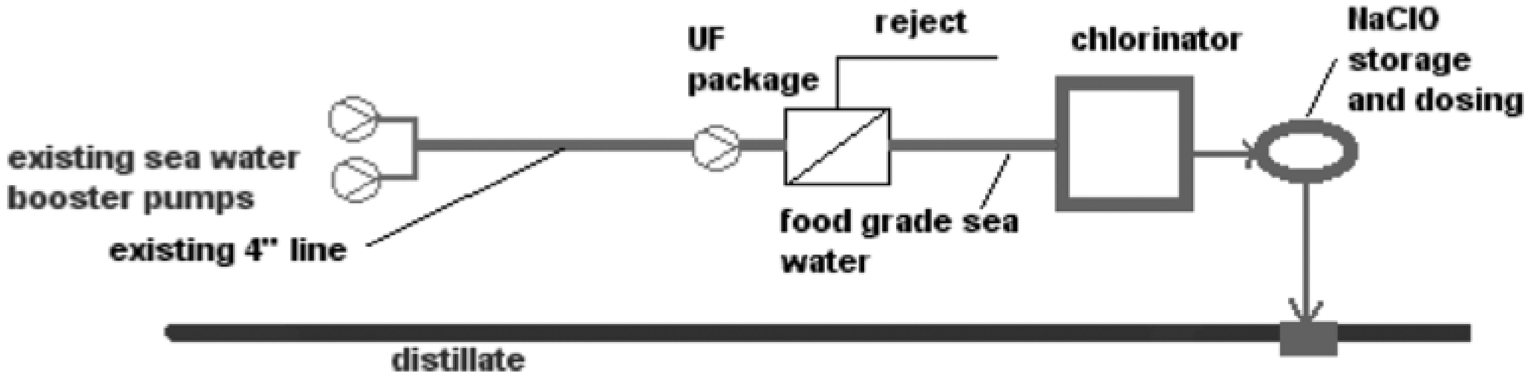
- Telzhensky et al. proposed a concept where nanofiltration would be used to separate out magnesium ions for post RO stabilization
- Alternatively, NF concentrate could be used for struvite precipitation from municipal wastewater



[6] Telzhensky, M., L. Birnhack, O. Lehmann, E. Windler and O. Lahav (2011). "Selective separation of seawater Mg2+ ions for use in downstream water treatment processes." Chemical Engineering Journal **136**: 136-143.

Other Processes – Chlorine Production

- Chlorine currently produced from seawater for a variety of industries
- Can be produced from seawater or desalination brine and used for finished water disinfection
- Desalination brine may not be the most effective feed stock for chlorine production
- Currently a need to evaluate cost effectiveness versus purchasing chlorine



Other Processes – Electrodialysis Metathesis

- Electrodialysis process that uses a mix of ion exchange membranes to achieve high recovery on moderately brackish water
- Produces two streams of mixed salts differing in composition
- Can purportedly sequentially precipitate minerals
- Not included in economic evaluations due to lack of specific information

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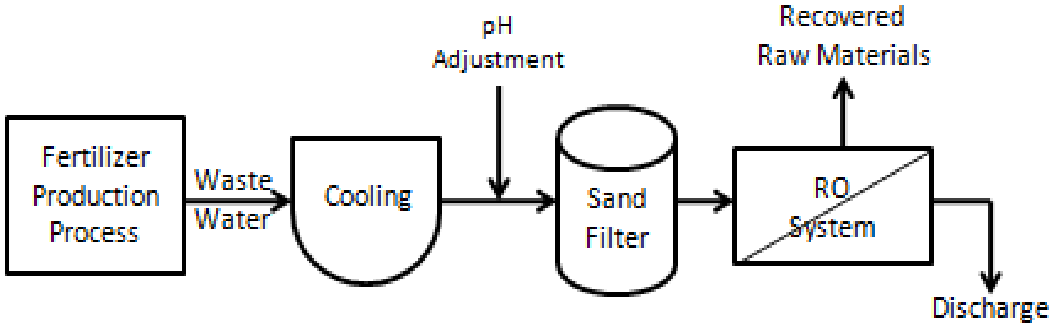
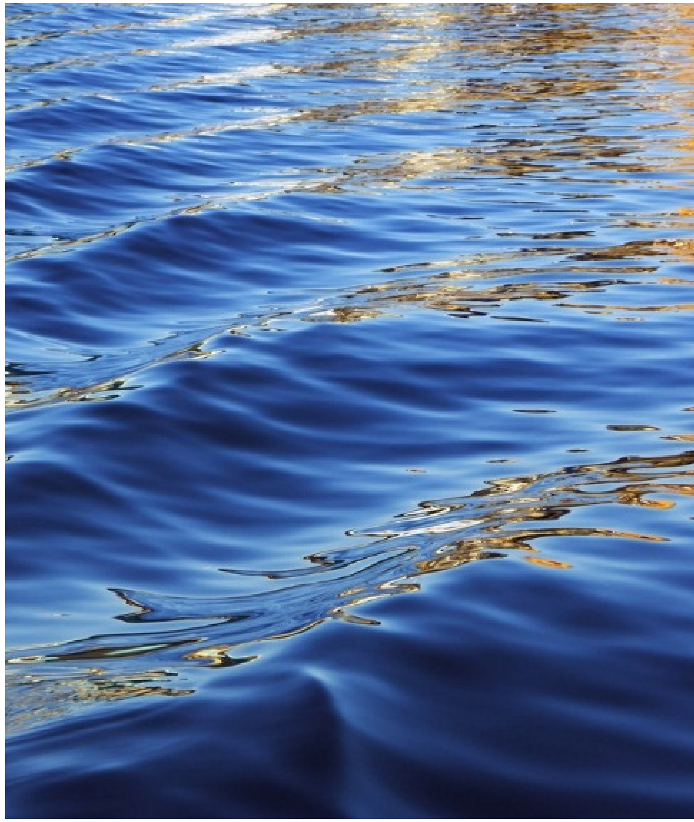
Case Studies

- Identified a number of industries where extraction is currently being or close to being implemented:
  - Nutrient recovery from municipal waste streams
  - Utilizing membranes for improving bioethanol production
  - Copper recovery from electroplating industries
  - Amino acid recovery from fermentation broth
  - Silica recovery for geothermal brines



Conclusions



Conclusions

- Extraction of many materials from desalination brine is technically feasible
- Economics of extraction currently impede material recovery from seawater desalination brine
- Other factors include facility siting, product purity, staffing, safety, material handling and storage
- Push towards inland desalination increasing research on and application of material extraction approaches and technologies

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Research Needs

- One of the main findings of this study was that although a significant amount of extraction research has been performed, very little demonstration-scale research has been performed
- There is a clear need to evaluate not only the technical and economic feasibility of extraction schemes, but also product purity, process efficiency, life cycle costs, and the real benefits of incorporating an extraction scheme into desalination

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Project Report

- This presentation provided a summary of major findings
- The final report was written to be a resource for anyone interested in the extraction of materials from aqueous solutions
- The report includes an in-depth analysis of research conducted towards the extraction of a wide variety of elements and compounds

Acknowledgements

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- Liyan Jin, PhD – BKT
- Arash Shahmansouri – Clarkson
- Ashley Waldron – Clarkson

Questions

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Upcoming Events

- November 13, 2014

  Enhancing the Soil Aquifer Treatment Process for Potable Reuse

- December 11, 2014

  Formation of Nitrosamines and Perfluorochemicals during Ozonation in Water Reuse Applications

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