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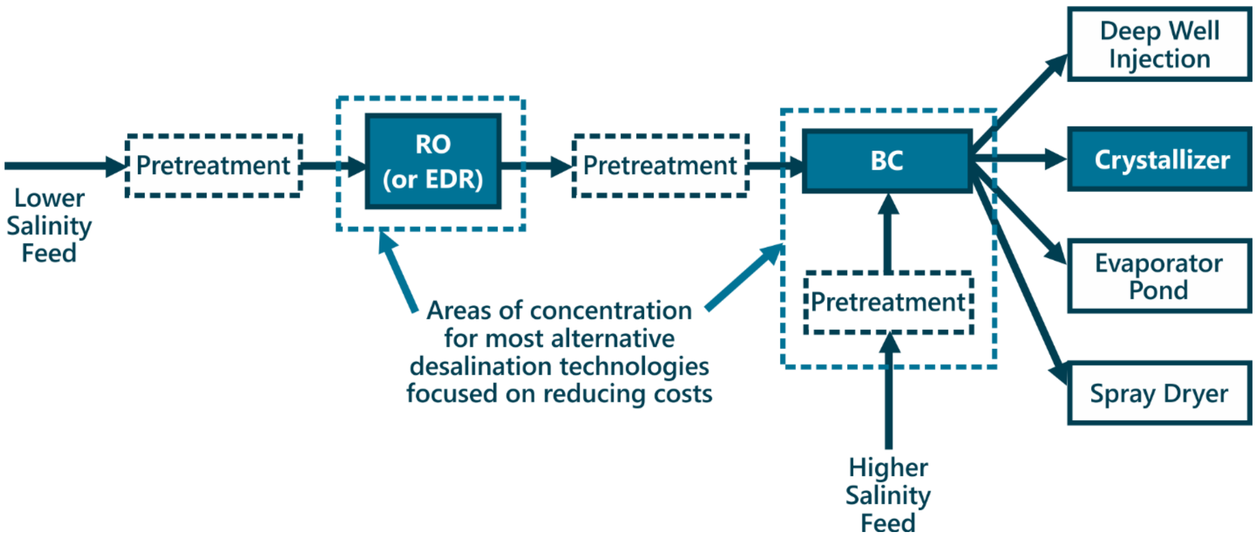
Desalination and Water Purification Research and Development Program Report No. 208

Emerging Technologies for High Recovery Processing



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14. ABSTRACT

The history of high recovery processing is one of high costs and limited markets. Beginning in about 2008, perceptions were that the marketplace could significantly increase due to new applications in the unconventional oil and gas industry. In addition, markets could grow due to increased interest in industrial water reuse and increased regulation of wastewater disposal. As a result, many companies began looking at ways to lower costs through development of alternative technologies or modification of existing technologies.

The purpose of the project was to assess the status and potential of the technologies to impact high recovery processing. To do this, information was gathered about both the technologies and the companies involved in their development. The assessment was done twice over a period of two years in order to observe and document progress and changes.

While various technical innovations have been made resulting reducing costs, there has been little impact on the marketplace. The perceptions of 2008 have not been realized and along with other reasons, the markets are still limited. The largest potential impact technology was reasoned to be high recovery RO systems

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Emerging Technologies for High Recovery Processing

Prepared for the Bureau of Reclamation Under Agreement No. R16AC00120

by

Mickley and Associates

U.S. Department of the Interior January 2021

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The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

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Acronyms and Abbreviations

AARO	Advanced Recovery Reverse Osmosis
ACD	accelerated chemical demineralization
ACP	accelerated chemical precipitation
AD	adsorption desalination
AEM	anion exchange membrane
AGMD	air gap membrane distillation
APS	accelerated precipitation softening
ARROW	Advanced Reject Recovery of Water
AVMD	Advanced Vacuum MD
BC	brine concentrator
BGNDRF	Brackish Groundwater National Desalination Research Facility
CapDi	capacitive deionization
CAPEX	capital expenses
CAOW	closed air, open water
CC	cooling crystallization
CCRO	Closed Circuit Reverse Osmosis
CEDI	continuous electrodeionization
CEM	cation exchange membrane
CERRO	Concentrate Enhanced-Recovery Reverse Osmosis
CFRO	Counter Flow Reverse Osmosis
CGE	carrier gas extraction
CIDS	Center for Inland Desalination
CIF	continuous ion exchange
CMCR	concentrate membrane cascade with recycle
CP	concentration polarization
CRO	cascade reverse osmosis
CTG	combustion turbine generators
DBOO	Design-Build-Own-Operate
DCMD	direct contact membrane distillation
DOE	Department of Energy
DVR	dynamic vapor recompression
DWPR	Desalination and Water Purification Research
ED	electrodialysis
EDI	electrodeionization
EDM	electrodialysis metathesis
EDR	electrodialysis reversal
EERO	energy-efficient reverse osmosis
EFC	eutectic freeze crystallization
END	electrochemical nano diffusion
EPOC	emerging pollutants of concern
ESD	electro-static deionization
EWM	Enviro Water Minerals
FC	freeze concentration
FTSH20	Fluid Technologies Solutions
FGD	flue gas desulfurization
FO	forward osmosis
FR	flow reversal
FRD	free radical disinfection
GE	General Electric
GWI	Global Water Intelligence
HDH	humidification-dehumidification
HDPE	high density polyethylene
HEEPM	High Efficiency Electro-Pressure Membrane
HERO	High Efficiency Reverse Osmosis
HIROX	high recovery RO
HR	high recovery
HTF	heat transfer fluid
ICCS	intermediate concentrate chemical stabilization
ICD	intermediate chemical demineralization
IX	ion exchange
LGMD	liquid gap membrane distillation
LTDis	Low Temperature Distillation
LTDry	Low Temperature Drying
LTEC	low temperature evaporation crystallization
MC	membrane crystallizer
MCDI	membrane capacitive deionization
MD	membrane distillation
MED	multi-effect distillation
MED-AD	Multiple-Effect Distillation Adsorption Desalination
MF	microfiltration
MI	Magna Imperio Systems Corporation
MLD	minimal liquid discharge
MSF	multistage flash
MVC	mechanical vapor compression
MVR	mechanical vapor recompression
NF	nanofiltration
NORM	naturally occurring radioactive materials
NTU	Nanyang Technological University
OACW	open air, closed water
OAOW	open air, open water
OARO	osmotic assisted reverse osmosis
OEM	original equipment manufacturer
OPS	optimized pretreatment and unique separation
OPEX	operational expenses
OSW	Office of Saline Water
PES	polyether sulfone
PFAS	per- and polyfluoroalkyl substances
PFRO	pulse flow reverse osmosis
PP	polypropylene
PTFE	polytetrafluoroethylene
PVDF	polyvinyldenefluoride
PVC	polyvinyl chloride
R&D	research and development
RDI	radial deionization
Reclamation	Bureau of Reclamation
RO	reverse osmosis
S&T	Science and Technology
SAGD	steam-assisted gravity drainage
SAR	sodium adsorption ratio
SAWACO	Saudi Arabia Water Company
SBIR	Small Business Innovation Research
SCE	selective chemical extraction
SE	solvent extraction
SGMD	sweeping gas membrane distillation
SPARRO	Slurry Precipitation and Recycle Reverse Osmosis
SWCC	Saline Water Conversion Corporation
SWRO	seawater reverse osmosis
T	temperature
TDS	total dissolved solids
TMDL	total maximum daily load
TNO	Toegepast- natuurwetenschappelijk onderzoek
TOC	total organic carbon
TPTEC	Thermal Purification Technologies
TSS	total suspended solids
TVC	thermally compressed
UF	ultrafiltration
UHP-RO	ultra high power-reverse osmosis
ULTAC	ultra low temperature adsorption crystallization
UTEP	University of Texas at El Paso
UV	ultraviolet
VADER	Vapor Adsorption Distillation with Energy Recycling (
VC	vapor compression
VMD	vacuum membrane distillation
VSEP	Vibratory Shear Enhanced Processing
WAIV	Wind Aided Intensified eVaporation
WET	whole effluent toxicity
WRF	Water Research Foundation
WWTP	wastewater treatment plant
ZDD	zero discharge desalination
ZLD	zero liquid discharge

Measurements

°C	degrees Celsius
$/yr/kgal	dollars per year per thousand gallons
$/yr/volume	dollars per year per volume
BTU/lb	British Thermal Units per pound
g/L	grams per liter
gpd	gallons per day
gpm	gallons per minute
kg	kilogram
kWh/kgal	kilowatts per thousand gallons
kWh/m3	kilowatt hours per cubic meter
lb	pound
lpd	liters per day
m3/d	cubic meters per day
m3/h	cubic meters per hour
mgd	million gallons per day
mg/L	milligrams per liter
MM$/yr	million dollars per year
ppm	parts per million
ppt	parts per thousand
psi	pounds per square inch
tph	tons per hour
µg/L	micrograms per liter
µS/cm	microSiemens per centimeter

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Executive Summary

Project Purpose

This report is a reference document to help utilities and industries better understand the current picture of high recovery processes being researched, emerging, and available commercially.

There was a two-fold purpose for the project. First was to support the Bureau of Reclamation's (Reclamation) in-house Concentrate Management Toolbox (Reclamation 2019) project by providing an assessment of the applicability of high recovery (HR) processing to municipal concentrate management. Second was to develop a stand-alone study of the status of HR processing.

High recovery processing is expensive and usually cost-prohibitive for municipal applications. There is, however, growing interest in achieving higher recovery levels in the municipal sector, where higher recovery processing can:

- make more efficient use of water resources;
- be an alternative to expanding an existing municipal desalination facility to produce more product water;
- reduce the volume of final residuals to be disposed; and
- in some cases, result in a disposal option where no other disposal option is available

HR processing here is defined as pushing the limits on water recovery regardless of the starting salinity of the feed water. For practical reasons, attainable recoveries generally decrease with increasing feed water salinity. For desalination of low salinity feed water typical of municipal applications by conventional reverse osmosis (RO) processing, HR may be considered as greater than 90-92%. HR processing of higher salinity feed water may involve a series of desalination steps, such as in minimal and zero liquid discharge (MLD and ZLD). Actual recovery levels may be considerably less than 90%. For example, ZLD treatment may have a recovery of 75% for a feed water of salinity with 100,000 mg/L processed to produce solids that may be land-filled. Thus, high recovery is not defined as a numerical value—but depends on the context.

For convenience, the report uses the term "brine" in a relaxed way to mean any feed water that may require desalination processing to be "managed" to enable its use or disposal. It includes processing of a full range of feed water salinities. As a result, "brine management" is used as a broad term that includes "concentrate management."

Report Approach

The project involved gathering and analyzing information about HR technologies and the companies developing and selling them. One of the project concerns was that a review of research and development (R&D) efforts at a single point in time does not indicate the rate of progress of the efforts toward providing less costly processing solutions. As a result, the assessment of technologies was done at two different times, approximately two years apart.

Report Content

The subject matter is broad with many different technologies, many different companies, and many different applications covering a wide range of brine salinities, compositions, and complexities. The technologies reviewed include modifications of conventional high recovery technologies, as well as newer technologies being developed for high recovery processing.

Early report chapters describe the context in which the R&D work is taking place. This includes discussion of historical brine management options and practices, conventional high recovery treatment systems, markets and applications, and brine characteristics. Several report chapters involve reviews of the technologies by technology area and the companies involved in the R&D effort. The technologies are described in terms of operating principles, attributes, limitations, applications, and the companies developing them.

Results

Common approaches taken to reduce unit energy requirements and operational expenses (OPEX) and capital expenses (CAPEX) are more generally discussed, and the potential impact of technology types on brine management markets is evaluated.

To date, HR processing systems have had a limited impact on the marketplace. It takes time to develop a commercial technology, particularly so when there are many possible applications and a wide range of feed water salinities, compositions, and complexities. This can increase the time it takes to bring clarity to performance capabilities, cost pictures, and definition of market niches. From this perspective, it is not surprising that the technologies have made little impact to date. However, for most technologies it is clear that companies have made progress in these areas and in the number of references (pilots, demonstrations, and commercial). The most promising technology area for short term impact in reducing HR costs is that of high recovery RO. Reasons for this include:

- HR RO technologies cover a wide range of feed water salinity levels and thus cover a wide range of possible applications.

- RO technologies are readily accepted in most, if not all, of the industries having brine management issues.

Municipal inland applications are low salinity applications and thus are more suitable for treatment by the HR RO technologies than others. Such technologies have begun receiving attention in various pilot tests at municipal sites. Some pilots have involved higher recovery at existing desalination facilities, and other pilots have involved treating wastewater effluent for indirect potable reuse.

1. Introduction

Commercially available technologies for high recovery processes and other brine management options are increasing. However, there are no standard reporting processes or measures to evaluate which technology would be most suitable for a particular use. This general reference guide and the Concentrate Management Toolbox help water planners understand these emerging technologies.

1.1. Project Purpose and Need

Across the country, new municipal desalination plants help diversify water supply portfolios, improve overall supply reliability, and provide enhanced reuse water and water for aquifer protection. Desalination plants are also increasingly built to treat waters from various industries, such as produced water from oil and gas operations, mine drainage water, cooling tower blowdown, and many others.

Managing concentrate from RO facilities and managing low salinity wastewater and higher salinity brine from various industries face increasing challenges for disposing wastewater in a cost-effective and environmentally sustainable manner. While disposing wastewater continues to be the most widely used management option, additional treatment and recovery of water from wastewaters is increasingly considered and implemented—particularly in industrial situations. In general, this processing is cost-intensive and cost-prohibitive in many situations. Several technologies are being researched and developed to reduce costs.

This Desalination and Water Purification Research (DWPR) project reviewed and analyzed the myriad of research and development (R&D) efforts to reduce costs associated with high recovery brine processing. While the market for high recovery processing is almost exclusively industrial, there is growing interest in achieving higher recovery levels in the municipal sector, where higher recovery processing can:

- make more efficient use of water resources;
- be an alternative to expanding an existing municipal desalination facility to produce more product water;
- reduce the volume of final residuals to be disposed; and
- in some cases, result in a disposal option where no other disposal option is available

The high processing costs of high recovery systems, however, have limited their use in municipal applications.

1.2. About This Report

The subject matter is broad with many different technologies, companies, and applications covering a wide range of brine salinities, compositions, and complexities. The technologies reviewed include modifications of conventional high recovery technologies as well as newer technologies that are being developed for the purpose of high recovery processing.

Some report chapters describe the context for the R&D work, including historical brine management options and practices, conventional high recovery treatment systems, markets and applications, and brine characteristics.

Several report chapters review the technologies by technology area and the companies involved in the R&D effort. As a review of R&D efforts at a single point in time does not indicate the rate of progress toward less costly processing solutions, the assessment of technologies was done twice, about two years apart.

Finally, the report is the author's interpretation of the subject matter duly noting the possibility of relevant omissions and misinterpretations.

1.3. Relationship to Reclamation Toolbox Project

Concentrate management has become a critical factor in determining the feasibility of implementing a municipal desalination facility. A Reclamation Science and Technology (S&T) Program research project, Concentrate Management Toolbox and Industry Analysis was undertaken to develop a practical toolbox for water treatment planners to plan the best approach to manage municipal desalination concentrate (Reclamation 2019).

Evaluating the performance and cost of these various technologies and their possible feasibility for increased recovery in municipal potable water and water reuse applications is critical to developing the S&T Concentrate Management Toolbox. This separate project supports the Toolbox project by identifying and characterizing emerging technologies that might be used in future municipal desalination settings for managing concentrate. It provides a critical assessment of technology suitability and the commercial readiness of these technologies. As such, it represents a stand-alone reference and overview for these technologies.

To support the Toolbox project, this DWPR project provides a unique and broad perspective for R&D activities, emerging and commercial technologies, markets, companies, and trends. We inventoried and analyzed cost reduction approaches and specific technologies for treatment and recovery of water, including company-related information and technical description, performance, and cost information. This inventory of existing technologies identifies practical and economic issues associated with implementing treatment processes for municipal concentrate management. With this inventory, water planners can more rapidly assess municipal concentrate management options—thus lowering implementation costs.

1.4. Use of Terms

Brine. For convenience, unless a specific reference is to municipal desalination concentrate, the report uses the term "brine" to refer to the entire range of waters that may be treated by desalination technologies.

High Recovery (HR). The terms: "high recovery technologies," "high recovery processing," "high recovery processes," and "high recovery systems" are used to refer to any processing sequence or systems involving HR and enhanced recovery technologies aimed at increasing recovery within practical and feasible limits. These terms have mostly been used with regard to lower salinity feed water processing where it has taken on the meaning of recoveries above that typically achieved by conventional RO. In this situation, high recovery has generally been used in the literature to mean recoveries above 90 or 92%.

Recovery in minimal liquid discharge (MLD) and zero liquid discharge (ZLD) processes varies with feed water salinity and final brine salinities. For example, where maximum final concentrations might be 250,000 milligrams per liter (mg/L), the recovery for a 50,000 mg/L feed water would be 80%. For a 125,000 mg/L feed water, it would be 50%. Feedwater salinities can range to above 200,000 mg/L (such as in some produced waters) and final brine levels (such as from crystallizer processing), can reach concentrations well above 300,000 mg/L. As a result, the use of the 'high recovery' term loses meaning when applied to these technologies. While a better term for some of these technologies might be "enhanced recovery technologies," this report uses the broad term "high recovery" (HR).

1.5. Project Background

This report covers a broader application area than treating desalination concentrate from municipal systems, which is the focus of the Toolbox project (Reclamation 2019). It includes treating industrial waters that may be more complex, can be of higher salinity, and contain more constituents than most municipal desalination concentrates.

There are instances where recovery levels above 90% can be achieved in a one-step membrane process. Over the wide range of feed water salinities, however, high recovery processing requires additional treatment steps beyond the initial membrane step. The added treatment steps may be membrane or thermal. Additional treatment steps increase the cost of the desalination process and most high recovery processing still produces a final residual to be managed.

The added cost of HR processing must be weighed against the benefits of HR processing.

HR processing benefits can include:

- reducing the volume of brine and possibly reducing disposal costs,
- increasing the amount of product water and thus, making better use of the water resource,
- supporting recovery of constituents of value,
- (sometimes) providing a feasible management solution where otherwise none might be possible, and
- (sometimes) simplifying the disposal permitting process.

The high capital and operating costs associated with commercial HR systems has constrained their use almost entirely to industrial situations where their implementation is driven by regulatory pressures. To date, the use of conventional higher recovery systems in utility water systems has been very limited. This, however, could change as HR technology costs decrease.

1.6. Project Timing

As mentioned, the existing HR processing market is almost entirely industrial. The market has been one of slow growth due to the high costs involved. However, there has been a perception that the HR processing market could significantly grow based on increases in unconventional oil and gas production and industrial water reuse, and more stringent disposal regulations. As a result, over the past 10 years many companies have been researching and developing new technologies and modifying older technologies to reduce the costs of HR processes. The conventional technical approach to HR processing of water and wastewater involves an RO system followed, where necessary, by thermal evaporative systems such as a brine concentrator (BC) and possibly a crystallizer. Newer technologies either replace the brine concentrator, modify the evaporative systems, or modify the initial RO system itself for higher recoveries, which in turn reduces the size, cost, and possibly the need for follow-on thermal evaporative systems.

There is now evidence of significant cost reductions from pilot studies and from limited commercial applications. However, the vast number of options for HR processing can overwhelm water treatment planners, making it difficult to determine which technology is the best for their situation. All new and expanding desalination facilities must spend time and resources evaluating these technologies and companies, which drives up even further the already high cost of desalination. The present project and the Toolbox project were undertaken to simplify consideration of concentrate management options.

1.7. Study Tasks and Methodology

The project gathered, analyzed, and synthesized information in two areas: the relatively slow changing area of municipal concentrate management and practices and the more rapidly changing area of HR processing. The first area provides the context for considering where and how emerging HR technologies might benefit municipal concentrate management practices. The first area was to support Reclamation's Concentrate Management Toolbox project effort through:

- **Identification and discussion of shared issues that form the bases for comparison of technologies and assist in development of a common set of evaluation criteria.** In partnership with Reclamation's S&T Project 5239-Concentrate Management Industry Analysis and Toolbox (Reclamation 2019), a common set of criteria was developed to review, assess, and evaluate each concentrate management practice was developed. These criteria as well as other considerations such as fouling, scaling, and flux were used to assess HR processes and other brine management technologies.
- **Identifying and categorizing potential concentrate management technologies** for further investigation, characterization, and evaluation. Technologies were identified by gathering and analyzing information from literature and the Internet. To simplify consideration and comparison, these technologies were categorized into groups based on mechanism of solid/water separation.
- **Providing background material on concentrate management methods and cost factors** to support Toolbox assessments. This included material on historical HR processing technologies.

Background material was based largely on previous reports (see references). Some results of these tasks are incorporated in the Concentrate Management Toolbox report. Other results are provided in this report as they provide context for understanding HR technologies used in brine management.

The second general area of tasks focused on HR brine management technologies. Information in this report is mostly from these tasks.

- **Characterizing emerging and commercial brine management high recovery technologies.** To assess the R&D interest and effort level for various technologies, BlueTech Research conducted patent and literature searches, and Mickley and Associates inventoried companies using an internet-based search of literature and websites. An initial list of over 80 companies was developed, each with a brief "snapshot-in-time" description of the technology, the development stage of the company and the intended application suite. Several companies were contacted and interviewed to provide more detailed information. The characterization of technologies included descriptions of technology performance, cost, and markets. Due to the time-related information regarding emerging technologies and associated companies, a second review of companies was conducted approximately 2 years later. This provided an indication of how the technologies were evolving.

1.8. Report Outline

This initial report section introduces the report purpose, tasks, methodology, challenges, and outline. The next three report chapters provide background contextual material from which to consider the project results:

- Chapter 2 provides background information on brine disposal options and general costs from the perspective of municipal concentrate management.

- Chapter 3 provides background information on conventional HR processing that sets the stage for discussion of the widespread R&D efforts to reduce the costs of HR processing.

- Chapter 4 reviews performance, cost, and energy issues associated with the HR technologies.

The next several chapters present project results:

- Chapter 5 introduces the technology areas reviewed and discusses the general approaches found to address scaling of membrane and heat transfer surfaces and to reduce capital, operating, and energy costs. The results of patent and literature searches are discussed.

- Chapters 6 through 12 review individual HR technology areas.

- Chapter 13 reviews HR markets.

- Chapter 14 summarizes project results and conclusions.

Appendix A reviews data from a 2008 ZLD report (Mickley 2008) that demonstrates the significant dependence of performance and cost of conventional ZLD systems on feed water salinity and composition.

2. Background: Disposal Methods

2.1. Introduction

The increasing challenge of finding a sustainable and cost-effective brine disposal option is a prime driver for consideration of high recovery processing. This chapter discusses disposal options to provide context for understanding the increased interest in high recovery technologies.

Only a limited number of disposal options are available for both municipal and industrial brines. The feasibility of an option depends on many variables, including the salinity and complexity of the brine, the brine flow rate, and the facility location.

2.2. Study Challenges

Not all data are equal. There are several challenges involved in evaluating emerging HR technologies. Not all technologies have been developed to the same extent—and thus vary in the degree of determination of their performance, cost, and marketing envelopes. As a result, companies with technologies at a pilot stage tend to sell the potential of the technology and have limited test information to support that potential. Companies with demonstration and commercial facilities can sell results. Thus, available website and literature information is a mix of projections and data, where the data can be from bench scale tests to commercial operations.

Not all applications and markets are equal. There is a wide range of potential applications for HR technologies. These can vary in the:

- Salinity and complexity of the feed water
- Nominal size of an individual site application
- Total potential number of sites of a given application

Determination of the market fit of a technology requires extensive study of both the performance capabilities of a technology and linkage of this capability with suitable applications. In addition, each company determines its marketing strategy based on consideration of market parameters and competitive technologies.

Not all technologies are equal. Technologies vary in their performance capabilities. Recovery limitations based on salinity and water composition parameters can be substantially different. Most installed RO systems have feed water salinities of less than 45,000 mg/L. Predicting the potential for scaling that can limit process recovery in RO is aided by the several software packages specific for RO and available from membrane and antiscalant manufacturers selling to the municipal market. One reason for the availability of software for this situation is the low complexity of feed water associated with municipal desalination applications. As a result, prediction of recovery based on scaling considerations in RO is relatively simple for most municipal desalination situations.

Predicting scaling potential at higher salinities for treatment processes other than RO, and for more complex feed water than in most municipal desalination situations is much more difficult. As the degree of concentration of feed water constituents increases, more constituents can reach solubility limits and result in scale formation. A classic example is the formation of the double salt, glauberite ($Na_2Ca(SO_4)_2$), which can limit recovery in evaporative brine concentrators. In addition, non-municipal brines frequently have constituents not typically found in municipal source waters.

For thermal evaporative systems, predicting performance and estimation of costs require interaction with thermal equipment manufacturers. This is due to the complex water chemistry, and also due to the small number of original equipment manufacturers (OEM) and the proprietary positions taken which limit shared understanding and knowledge.

To better understand the complex chemistry and physical effects that can take place, most OEMs use highly sophisticated, expensive geochemistry software, such as the OLI Stream Analyzer that contains several hundred different salts and other constituents and predicts their interactions as a function of concentration, temperature, and pressure (OLI 2019).

Challenges with evaluating energy use. Evaporative technologies have substantial energy requirements. While some applications may be able to use available waste heat to meet these high energy requirements and to possibly lower the cost of the energy, they do not lessen the energy requirement. Many companies with emerging evaporative technologies assume the use of waste heat but do not include any cost for thermal heat in their operating expense estimates. Waste heat is rarely "free," as there are costs associated with obtaining/recovering and delivering the heat. Key restrictions preventing heat recovery in a particular application can include cost, temperature limitations, and chemical composition of heat streams (Department of Energy [DOE] 2008).

Estimates by companies without commercial products and an established technology track history can be highly speculative.

Company estimates of performance are based on differing parameters and assumptions. Performance data from different companies are based on different treatment situations and comparing performance information from different companies can be comparing apples and kumquats.

Time-dependent information. The state of HR technologies and their applicability to municipal desalination changes with time. As a result, the project reviewed technologies a second time, approximately two years after the initial review. Still, however, the report is a picture in time as changes continue to occur with time. In addition to providing a comprehensive assessment of HR technologies, a report goal is to provide a framework for viewing this changing landscape and a method of assessment that can be used in future updates.

Summary. Due to the above challenges and in particular due to the lack of standardized test conditions, the wide range of possible applications and test conditions, and the limited testing of many of the technologies discussed, generalizations of performance and cost can be speculative. This applies to assessments made in this report and applies to assessments made by companies developing technologies.

2.3. General Management Options

Brine management options are broadly represented by three categories: disposal, beneficial use, and desalination treatment.

- **Disposal.** Most brines are disposed, particularly if they are of brackish salinity and have relatively low chemical complexity, such as municipal desalination concentrates. In the U.S. municipal water industry desalination concentrate is disposed in over 98% of the cases (Mickley 2018). Major disposal options include: surface water discharge, discharge to a sanitary sewer, deep well injection, evaporation ponds, and land application. Brine disposal options are increasingly environmentally unsustainable and do not make efficient use of the water resource. Lack of beneficial use opportunities and high cost of additional desalination processing (volume reduction) limit these options. Thus, most municipal and industrial brines are managed by disposal.
- **Beneficial Use.** While brine management includes a few isolated beneficial uses for brine, in the overwhelming majority of cases beneficial uses are rarely available, are unproven, and generally do not provide a final fate for the wastewater (Jordahl 2006 and Mickley and Jordahl 2011). However, given the growing challenges of finding an environmentally suitable and cost-effective disposal option, it is important to explore any beneficial use options for brine at an early planning stage of consideration of brine management.
- **Desalination Treatment (volume reduction).** Another way to manage brine is to reduce the amount of brine by additional desalination treatment. The treatment may be done to allow discharge or use of the recovered water, and/or to allow disposal of the final wastes (more concentrated brine or solids), or to recover products of value. This desalination treatment is the focus of the report. Various technologies have been used in non-municipal applications for this high recovery (HR) processing and are frequently referred to as minimal liquid discharge (MLD) and zero liquid discharge (ZLD) systems. As stated previously, in the past decade many new technologies or modifications of existing technologies have been developed or are undergoing development to reduce costs and to compete in what is perceived to be a growing market of HR processing applications.

2.4. Brine Disposal Options

Disposal options may be classified as (Mickley and Jordahl 2011):

- **Surface Water Discharge**
  - Direct ocean outfall (includes brine line when direct to ocean)
  - Shore outfall
  - Co-located outfall
  - Discharge to river, canal, lake

- **Disposal to Sewer**
  - Sewer line
  - Direct line to a wastewater treatment plant (WWTP)
  - Brine line (where brine line goes to a WWTP)

- **Subsurface Injection**
  - Deep well injection
  - Shallow well (beach well)

- **Evaporation Pond**
  - Conventional pond
  - Enhanced evaporation ponds/schemes

- **Land Application**
  - Percolation pond / rapid infiltration basin
  - Irrigation

Other options include landfill (for solids), either in a dedicated mono-fill or an industrial landfill. Table 1 shows the frequency of disposal option use by the roughly 400 U. S. municipal desalination facilities built through 2017.

Table 1. Disposal Option Frequency of Use by U.S. Municipal Desalination Facilities (Mickley 2018)

Disposal Option	Percentage use
Surface water discharge	45
Sanitary sewer	25
Deep well injection	17
Land application	6
Evaporation pond	5
Recycle	1

The recycle option, representing about 1% of the plants, has been used for a few microfiltration/RO (MF/RO) and RO plants processing low salinity WWTP effluent. Recycle is to the front of the WWTP facility.

This table, however, can be misleading in as much as these percentages may be taken to suggest that all five conventional concentrate disposal options are:

- Available at any location
- Applicable for every type of concentrate
- Feasible for every volume of concentrate

The location-specific nature of disposal options is illustrated in Table 2 and Table 3. (Mickley 2018). Discharge to surface water or sewer account for 70 percent of the plants nationwide and all plants in 27 of the 35 states with municipal desalination plants. Only 5 states use deep well injection, and 62 of 69 of these sites are in Florida. Only 4 states use land application, and 23 of the 27 sites are in Florida. Evaporation ponds are used in only four states, and 13 of the 21 sites are in Texas. Florida is the only state using all five disposal options.

Table 2. Number of States Using the Disposal Options

Disposal Option	Percent use	Number of states
Surface discharge	45	27
Discharge to sewer	25	24
Deep well injection	17	5
Land application	7	4
Evaporation ponds	4	4
Recycle	1	3

Table 3. States and Number of Facilities in Each State Using Various Disposal Options

	TOTAL	FL	CA	TX	KS	AZ	PA	CO
Deep well injection	70	64	1	2	1	0	0	2
Land application	27	20	1	5	0	1	0	0
Evaporation ponds	21	3	2	13	0	3	0	0
Recycle	6	0	4	0	0	1	1	0

The location dependence factor is also illustrated in Figure 1, where the percentage use of different disposal options is represented for California, Florida, Texas, and all other states combined.

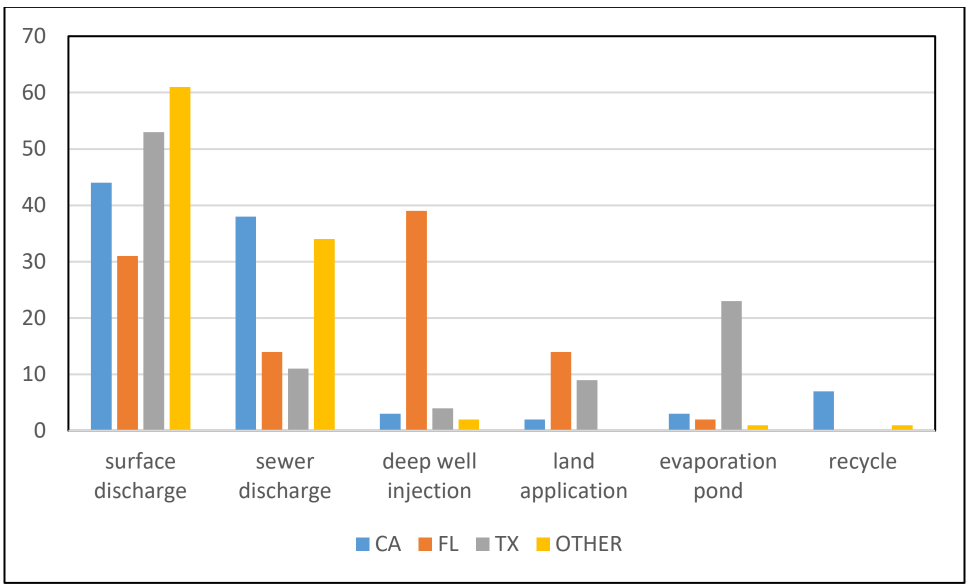

Figure 1. Percentage use of disposal options by state for U.S. municipal desalination facilities (Reclamation, 2018)

The size-related limitation to disposal options is reflected in Figure 2, which shows the frequency of use of conventional disposal options as a function of desalination plant size (Mickley 2018). Figure 2, illustrates that discharge to surface water has a high level of application regardless of plant size. Sewer discharge, however, is used less frequently as plant size increases because of the impact of concentrate salinity and volume on WWTP operation. Deep well injection has the opposite pattern because of high costs associated with feasibility determination, regardless of plant size. These costs are less of a burden to larger facilities. Disposal by land application (mainly irrigation) and to evaporation ponds are land intensive and climate dependent. They have little economy of scale and are used only for small plants.

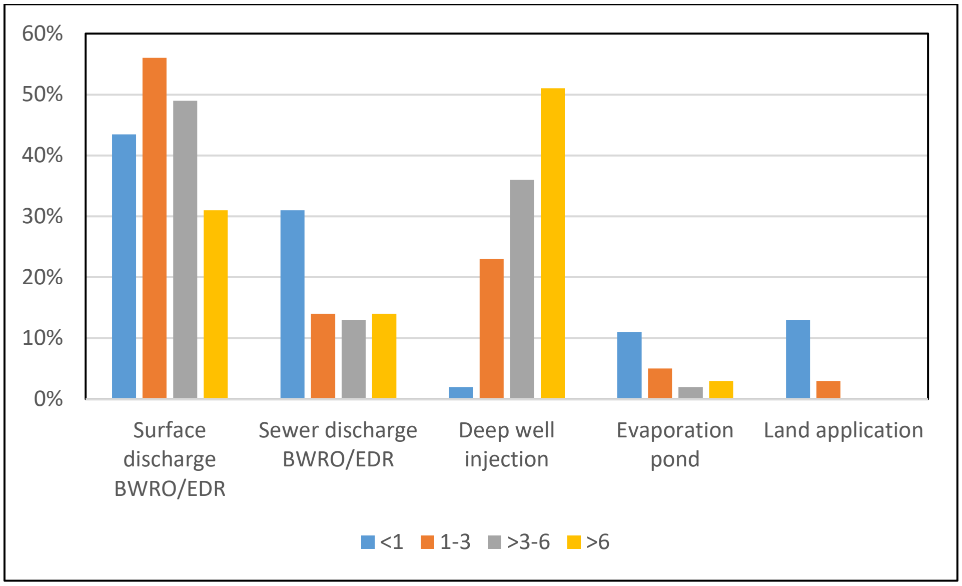

Figure 2. U.S. municipal desalination concentrate disposal option use by plant size in million gallons per day (mgd).

2.5. Disposal Option Costs—General Overview

The costs of each of these disposal options can also vary greatly, depending on site-specific circumstances—much more so than costs of desalination treatment. The cost of conveying concentrate from the desalination site to the disposal site can be a significant cost factor.

Figure 3 represents the general trend of capital costs for the five conventional concentrate management options and for ZLD processing. The trends in Figure 3 may be helpful in understanding some of the issues related to cost for different concentrate management options.

There are many exceptions to these trends; for one reason, the capital cost indicated does not take into consideration the site-specific conveyance cost. A long conveyance distance discharge to a surface water or discharge to a sewer can result in higher costs relative to the generally more expensive options. As previously mentioned, not all concentrate management options are suitable and available for the site in consideration. As a result, the more expensive options as indicated by Figure 3 may be the least expensive of available options at a given site.

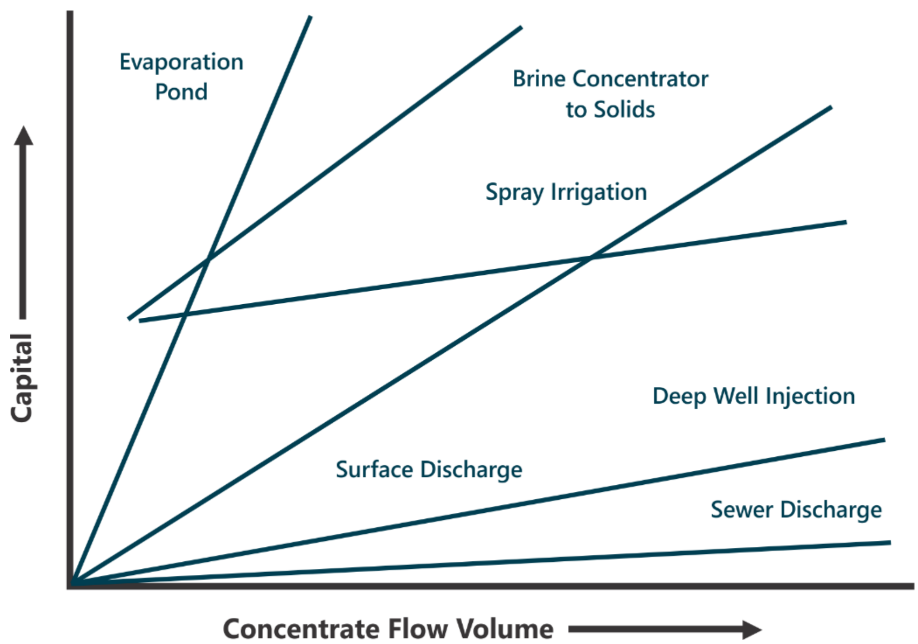

Figure 3. Relative capital costs of concentrate management options (not considering conveyance to the disposal site).

From Figure 3, it may be seen that:

- Discharge to surface water and to sewer are typically lower cost concentrate management options.
- Spray irrigation and evaporation ponds are typically cost-effective only for small volumes of concentrate as there is a lack of economy of scale.
- Deep well injection has an economy of scale but is expensive for small concentrate volumes and, like brine concentration to solids, is not used for small volumes.

NOTE: A detailed discussion of disposal costs is given in Mickley et. al., 2011.

2.6. Disposal to Surface Water

2.6.1. Description

Most inland waters receiving the concentrate have relatively lower salinity than the concentrate. Inland terminal lakes, such as the Great Salt Lake, may be an exception. The range of total dissolved solids (TDS) in concentrate from inland sites treating sources of water for municipal use is typically from 1,500 to 20,000 mg/L. While brackish groundwater for RO treatment can have salinity as high as 10,000 mg/L, raw water for municipal RO desalination plants is frequently less than 3,000 mg/L. Recoveries are typically in the range of 65% to 85%. At 85% recovery, the concentrate from such raw water would be at most 20,000 mg/L.

In high recovery processing of low salinity feed water, concentrate salinity can be much higher. For instance, if a feed water of 3,000 mg/L is processed with a recovery of 95%, the concentrate salinity would be roughly 60,000 mg/L. Higher salinity concentrate will increasingly occur as high recovery processing is more frequently used. Salinity increases but volume decreases.

Discharge permits usually dictate end-of-pipe limitations based on receiving water-specific water quality standards. Standards can be for individual constituents, discharge parameters (such as pH), whole effluent toxicity (WET) levels, and others.

Depending on the state regulatory policy, mixing zones may be a possible form of relief for the salinity and constituent(s) in question, in which case the end-of-pipe parameter limitations take this into consideration and allow for the water quality standards to be met at the edge of the mixing zones. Granting a mixing zone permit depends on receiving water conditions affording sufficient dilution under the state-specific regulations. A mixing zone permit is not possible if the receiving water already has a total maximum daily load (TMDL) limit for a constituent that is also in the concentrate.

When the volume of concentrate is reduced, some discharge concentrations and conditions may be increased to levels greater than the water quality standard levels. The effect of increasing concentrations on discharge feasibility, however, is not a simple function of salinity. As salinity increases upon volume reduction, with the exception of pre-treatment effects and possible precipitation of some salts, the salt load remains the same. Consequently, it may be possible to still obtain a mixing zone for constituents. Also, the effect of increasing concentration on toxicity depends on how the toxicity of a given constituent changes with salinity. For instance, reducing the volume of concentrate may increase the concentration of a potential toxicant by a factor of two, but the toxicity of that constituent at the higher salinity may be less than one half that at the lower salinity.

Most, but not all, heavy metal toxicity decreases with increasing salinity. Exceptions in some studies include lead and mercury. For some heavy metals, some pesticides, and fluoride, toxicity appears to increase with salinity. Major ion toxicity considers toxicity of common ions. Mickley (2000) looked at the toxicity of major ions and fluoride at salinities of 10, 20, and 30 parts per thousand (ppt). The major ions studied included Ca, K, Mg, HCO_3, B_4O_7, SO_4, and F. Toxicity of these ions decreased with salinity. For most contaminants/species where toxicity decreases with salinity, we do not know whether the decrease in toxicity with increasing salinity occurs at a rate greater than the volume-reduced concentration increases. As a result, the volume reduction of concentrate could increase the likelihood of WET test failure. Yet, not all states require WET tests for municipal desalination concentrate, and few states use the very sensitive mysid shrimp levels used in Florida. Thus, it is difficult to generalize on the likelihood of WET test failure with volume-reduced concentrate.

As surface water discharge requirements continue to become more stringent, surface water discharge, in general, will be more difficult to permit. The feasibility of surface discharge of a higher salinity concentrate must be determined on site-specific information. It is safe to say, however, obtaining a permit to discharge a high-salinity concentrate will be more difficult than to discharge a low-salinity concentrate.

2.6.2. Costs

2.6.2.1. Capital Costs

Capital expenses (CAPEX) may be associated with:

- Treatment equipment required for treatment of groundwater-based or surface water-based concentrates to remove naturally occurring constituents to meet water quality standards and eliminate toxicity based on WET tests. Concern for corrosion may prompt use of more expensive corrosion resistant materials. Treatment may include:

- Aeration to increase dissolved oxygen (for groundwater-based concentrate)
- Degasification for H_2S, CO_2, and NH_3 (for groundwater-based concentrate)
- pH adjustment
- De-chlorination (if cellulose acetate membranes are used)
- Particulate removal
- Removal of As, Se, and other naturally occurring contaminants
- Dilution to remove major ion toxicity
- Removal of naturally occurring radioactive materials (NORM).

- Treatment equipment that may be required to reduce levels of non-naturally occurring constituents in groundwater-based and surface-water-based concentrate that do not meet receiving water standards. Currently, only a few concentrates require such major treatment; however, this is an area of increasing concern due to increased occurrence of human-activity based contamination. Examples of contaminants where removal may be required include:
    - Nitrate
    - Perchlorate
    - Arsenic
    - Selenium
    - Various emerging pollutants of concern (EPOC). The present concern of per- and polyfluoroalkyl substances (PFAS) and small non-polar organics is rapidly becoming a major concern.

- Conveyance of concentrate to the receiving water. These costs depend on the distance from the desalination plant to the discharge site. Cost factors include:
    - Pumps
    - Pipeline (and possible pipeline protection)
    - Fabrication
    - Trenching of pipeline
    - Costs associated with obtaining right-of-way for piping.

- Conveyance from the shoreline to the outfall structure. Cost factors include:
    - Pipeline
    - Possible underwater fabrication
    - Possible dredging/trenching.

- Outfall structure
    - Pipe (diffuser)
    - Risers
    - Ports
    - Fabrication
    - Possible trenching and armoring.

Groundwater-based concentrates routinely require some minor treatment to increase pH and dissolved oxygen prior to discharge to meet receiving water standards. Treatment to remove contaminants prior to discharge is less frequently needed but is sometimes required for removal of dissolved gases naturally found in many groundwaters. A small but increasing number of systems require removal of other contaminants.

Many inland discharge systems have relatively simple outfall designs. The most significant and variable cost factor associated with inland surface water discharge is the piping and pumping requirement. This variable is site-specific and depends on the distance and terrain between the desalination plant and the discharge site.

2.6.2.2. Operating Costs

Operating costs associated with inland surface water discharge are usually on the low end of concentrate management options.

- Operating costs may be associated with:
  - Monitoring and reporting to the regulatory agencies
  - Routine operation and maintenance
  - Pumping

2.7. Disposal to Sanitary Sewers

2.7.1. Description

Concentrate from municipal desalination facilities typically has salinities greater, and sometimes much greater, than the WWTP influent flow. The potential impact of salinity on the WWTP's effluent salinity and thus on its discharge permit, depends on the volume of concentrate relative to that of the other inflows to the WWTP. An equal concern is the impact of salinity and constituents on the biological processes of the WWTP.

Discharge to a sanitary sewer requires permission of the receiving WWTP through a permit. Discharge to sewers has been used mostly for low volume discharge of concentrates.

As mentioned in the previous section, typically the mass (volume times concentration) of most constituents, cumulatively the salt load, is changed little by volume reduction. The blended volume (concentrate with other WWTP influent) will be somewhat less due to the smaller volume concentrate. Thus, the resulting blended concentration (amount of constituent divided by blended volume) will be of higher concentration, but likely not significantly higher. Where such discharge has been used in the past, volume reduction may still be acceptable to the WWTP.

With the exception of relatively low salinity concentrates and low volume higher salinity brines, discharge of high salinity brines to the sewer is not feasible due to the impact on the wastewater treatment plant's operation and on its effluent salinity level.

2.7.2. Costs

2.7.2.1. Capital Costs

Capital costs may include:

- Piping and pumping costs to the sewer or brine line; a function of the distance of the sewer line (or WWTP) or brine line from the desalination plant
- Possible one-time fee for purchasing capacity at the WWTP or brine line
- Possible costs associated with treatment of concentrate to meet discharge requirements

2.7.2.2. Operating Costs

Operating costs may include:

- A monthly charge based on characteristics of the concentrate (such as volume, salinity, organic load, level of suspended solids, etc.)
- Energy costs associated conveyance of the concentrate to the sewer, WWTP, or brine line
- Operation and maintenance costs associated with treatment of the concentrate prior to discharge.

Discussion of design factors and preliminary level cost models for discharge to the sewer are available in Mickley (2006).

2.8. Deep Well Injection

2.8.1. Description

Of the five conventional disposal options, deep well injection is the least likely to be affected by increased brine salinity. Use of deep well injection, however, is limited to availability of suitable receiving aquifers and by regulatory constraints. For example, presently, produced water from oil and gas is trucked from Pennsylvania to Ohio for deep well injection. Future use of deep well injection will increasingly be limited in some locations due to the potential for seismic activity.

Higher salinity concentrate raises some issues for deep well injection feasibility. The difference between injection salinity and composition and receiving water aquifer salinity and composition may be greater for high salinity brine. Blending high salinity brine with aquifer water may result in the formation of precipitates within the well bore or close to the injection point. Precipitates may form due to the blending interaction and/or from declining effectiveness of antiscalants and dispersants in the concentrate. Using more antiscalants and dispersants means that the high salinity concentrate will have some—and perhaps more—constituents (salt, metals, silica) at or above supersaturation. The effectiveness of these additives declines over time, and eventually precipitates will form. Thus, there is a higher probability of precipitates forming with higher salinity brine unless the potential precipitants have been removed prior to injection.

Frequently, high salinity goes hand in hand with high chloride levels and thus increased material corrosion concerns. Injecting higher salinity concentrate may more frequently result give rise to corrosion problems and require polyvinyl chloride (PVC) or other liners in the injection wells.

2.8.2. Costs

2.8.2.1. Capital Costs

Capital costs can occur during the preliminary level evaluation associated with drilling and testing of test wells. Other capital costs are associated with implementing deep water injection as the concentrate management option. Capital cost factors include:

- Possible concentrate pretreatment (pH change, adding anticorrosion inhibitors, etc.)
- Land purchase and easements
- Piping and pumping from the desalination plant to the injection field
- Land preparation
- Mobilization
- Logging, testing, and survey
- Drilling and reaming
- Well construction (casing, grouting, injection tubing, packer)
- Demobilization
- Backup disposal system for during system integrity tests (periodic)
- Monitoring wells

A cost-saving alternative to drilling new wells may be reworking abandoned wells, such as those associated with oil and gas drilling. These issues were reviewed in Water Research Foundation (WRF) (2015).

A preliminary level capital cost model for deep well injection is available from Mickley 2006.

2.8.2.2. Operating Costs

Class I wells undergo integrity tests every five years, and during this time a backup means of managing concentrate is required.

2.9. Evaporation Ponds

2.9.1. Description

Evaporation ponds are climate-dependent, land-intensive, lack economy of scale, and require flat land and thus are only feasible under the right conditions. Evaporation ponds have been used in only a few southern states in the United States for disposing municipal desalination concentrate.

Higher salinity and reduced volume concentrate affect evaporation pond feasibility by:

- Reducing the amount of land required, but not in exact proportion to the volume reduction (as the decreased evaporation rate of higher salinity water results in more land required per unit volume of concentrate/brine)

- More quickly filling up ponds with salts, such that the life of the pond may be decreased; this may mean that the pond would either need to be more frequently cleaned out during the life of the desalination plant (with salts being sent to a landfill) or covered over and retired (in which case new pond area would need to be provided).

Both of these factors increase the cost per unit volume of disposal to evaporation ponds.

Dissolved salt in the water results in a lower saturation vapor pressure due to the decreased chemical potential of the water. This results in a lower evaporation rate. Up to a 30% reduction in evaporation rates have been cited over the life of a pond due to salinity buildup (Mickley et al. 1993). For a water saturated with sodium chloride (26.4%), the evaporation rate is generally about 70% the rate for fresh water (Office of Saline Water [OSW] 1971). The initial evaporation rate of a higher salinity brine, such as 60,000 mg/L, might be 10% less than that of a 4,000 mg/L concentrate.

Theoretically, composition of concentrate should have some effect on evaporation rates through the effect of composition on water vapor pressure. However, while the effects may be significant in comparing vapor pressures of a solution of one salt with a solution of another salt, the variation in composition of concentrates does not generally have a significant impact on evaporation rates.

Despite the increased challenges with higher salinity brine, evaporation ponds may be feasible for small volumes.

There are enhanced evaporation technologies that can increase the net evaporation rate and decrease the size of the ponds. Most of these technologies increase the net evaporation rate by increasing the surface area for evaporation by spraying/misting the water or having water run down fabric or intricate solid surfaces. Another more recent approach is to use proprietary enzymes to increase the evaporation rate. These technologies increase the rate of solids accumulation, which may lead to increased frequency of pond cleanout.

2.9.2. Costs

2.9.2.1. Capital Costs

Capital cost factors include:

- Land
- Land clearing and preparation
- Pond liner(s)—synthetic or clay liner
- Fencing
- Roadway
- Piping and pumping system—depends on the distance from desalination plant
- Distribution system with associated valving and control for larger pond areas (possible)
- Seepage monitoring system

The cost of land can range from very low to very high. Liner costs can be significant, particularly when double liners with an inner liner leak detection system is required. Recent per acre pond costs have ranged from $60,000 to $600,000. Any savings related to larger size is offset by the need for a more complex distribution and pumping system, resulting in limited economy of scale.

Detailed design factors and a preliminary level cost model for evaporation ponds may be found in Mickley, 2006.

2.9.2.2. Operating Costs

Operating cost factors include:

- Routine pond maintenance (minimal cost)
- Pumping
- pond clean-out and disposal of sludge (possible periodic cost)
- cleanup of contaminated soil if pond leakage occurs(possible)
- Pond closure at end of useful pond life

Operating costs for evaporating ponds are generally low.

2.10. Land Application

2.10.1. Description

Land application includes irrigation and percolation ponds. Both are seldom used for concentrate. Concentrate typically has higher salinity levels than groundwater and requires dilution water to make irrigation feasible. The dilution water increases the volume to be disposed and may increase the amount of land required.

Factors limiting irrigation most frequently include concentrate salinity and volume, concentration of specific constituents like Na, Cl, B, and the need for sufficient and relatively level land. Treatment may be required to adjust the sodium adsorption ratio (SAR), depending on the vegetation being irrigated.

High recovery processing results in a reduced volume and higher salinity concentrate. The salt load (concentration times volume) is roughly the same (some salts may be removed, e.g., by chemical precipitation), but a slightly greater amount of dilution water would be required for the volume-reduced concentrate. This may be shown by the following example. Consider two concentrates: a 1 million gallon per day (mgd) concentrate of 2,000 mg/L and a volume-reduced concentrate of 0.2 mgd of 10,000 mg/L. Assume both concentrates are required to be diluted to 1,000 mg/L and that available dilution water is 500 mg/L. The 1 mgd conventional recovery concentrate will require 3 mgd of dilution water while the volume-reduced concentrate will require 3.8 mgd of dilution water. Both situations are not generally feasible due to the large amount of dilution water needed.

Increasing concentrate salinity may further decrease the feasibility of land application of concentrate due to the large volume of dilution water required for crop tolerance and groundwater protection and the resulting large land area required. Land application of nanofiltration (NF) concentrate is more frequently possible as this concentrate has less salinity.

Percolation ponds are possible only in situations where underlying groundwater is of a compatible salinity. The higher salinity concentrate from high recovery processing makes the possibility of this occurrence less likely.

See Mickley 2013 for a detailed consideration of these land application issues, in general.

2.10.2. Costs

2.10.2.1. Capital Costs

Possible capital costs include:

- Land
- Land clearing and preparation
- Pumping and conveyance of dilution water
- Equipment associated with blending, modifying, or treating concentrate prior to use
- Pipeline to the site of irrigation or percolation
- Pump
- Distribution systems (header, submain header, laterals, sprinklers, valves)
- Storage tank for rain days
- Underdrain (possible)
- Monitoring wells
- Surface runoff control system.

There is little economy of scale associated with land application systems, as larger operations require more extensive distribution and control systems.

2.10.2.2. Operating Costs

The primary operating cost is the energy associated with conveying concentrate to the land application site and then distributing the concentrate to the land. Other operation costs are associated with monitoring and standard operating and maintenance associated with treatment, conveyance, distribution, and application. The possibility of selling the concentrate to agricultural interests can be investigated.

2.11. Disposal of Solids to Landfill

When thermal crystallizers (or spray dryers for smaller volumes) are used to produce solids from brine in a zero liquid discharge (ZLD) situation, the resulting solids are usually of a mixed nature. Given that there are few uses of mixed solids, the solids are typically sent to a landfill. As with evaporation ponds, the mass of solids can be high and may be high enough to require a dedicated monofill to be built for disposal of the solids. Landfill costs can be significant, whether in terms of hauling costs to an existing landfill or through construction of a dedicated monofill.

By calculating the solids composition of feed water taken all the way to solids (without consideration of treatment effects), a worst-case chemical composition of the final solids can be estimated (Mickley 2008). If the solids composition resulting from this calculation is not classified as hazardous (due to metals, NORMs, arsenic, etc. content), then the feed water is likely a candidate for processing all the way to solids and for disposal in lower cost landfills.

If the solids contain constituents that would cause them to be classified as hazardous, then landfill disposal costs would be greatly elevated and likely prohibitively high for municipal situations. The mass of solids associated with a given volume of feed water to a high recovery process increases with its salinity. Taking 1 mgd of low salinity 2,000 mg/L TDS feed water to solids results in $^{1}/_{10}{}^{th}$ the mass of solids as taking 1 mgd 20,000 mg/L TDS feed water to solids.

2.12. Summary

The availability of a given disposal option is very location dependent. Costs are also heavily dependent on location: the site-specific brine water quality, local regulations, and local geography, hydrological, and climate. As a result, it is difficult and somewhat misleading to assign cost figures to the disposal options or to generalize costs based of limited number of examples.

While the same disposal options are possible for brine of all salinities, in general, the feasibility of disposal options decreases as brine salinity increases.

3. Background: Historical High Recovery Processing

3.1. Introduction

The previous discussion of disposal options included consideration of the effect of salinity on the feasibility of the option. This chapter focuses on the HR processing—which may produce brine over a wide range of salinity depending on the initial salinity of the wastewater being treated.

Characterization of historical HR processing provides the background with which to consider emerging HR technologies. This chapter reviews:

- Conventional ZLD systems
- Historical HR markets
- Disposal options for HR processes
- Energy requirements for traditional RO, BC, and crystallizers
- Relative costs of traditional RO, BC, and crystallizers
- Salinity operating ranges for traditional RO, BC, and crystallizers
- Powering of desalination systems
- Evolution of brine management

3.2. Definition of Zero Liquid Discharge

The term ZLD is not used in a consistent manner in the literature. The original definition means that there is no liquid discharge across the plant boundary. The first ZLD plants were mandated for the power industry in the U.S. so that plants near the Colorado River would not discharge into the Colorado River and further increase its salinity. The early mechanical vapor recompression evaporators (wastewater brine concentrators), were developed for this purpose. ZLD systems originally consisted of brine concentrators treating cooling tower blowdown with the resulting brine going to either thermal crystallizers (evaporators) or spray dryers (for lower flow rates), or to evaporation ponds within the plant boundary.

In an effort to reduce the volume of water going to the energy- and cost-intensive evaporators, where possible, the next generation ZLD systems used a RO step to reduce the wastewater volume prior to being processed by the thermal system. Later yet, some ZLD systems treating lower salinity feed water eliminated the thermal evaporators altogether and used membrane-only treatment systems. Thus, the term “ZLD” does not mean processing by thermal evaporators, nor does it mean taking feed water all the way to solids. Further, the term ZLD has been used in situations where the final disposal of brine is not within the plant boundary. The term “minimum liquid discharge” (MLD) has been used to represent HR processes that have higher recovery than conventional RO systems but less than that typically associated with ZLD processes. In this report, we refer to both ZLD and MLD systems as HR systems.

3.3. Historical ZLD Systems and Markets

Historically, the most widely used ZLD processing system is depicted in Figure 4.

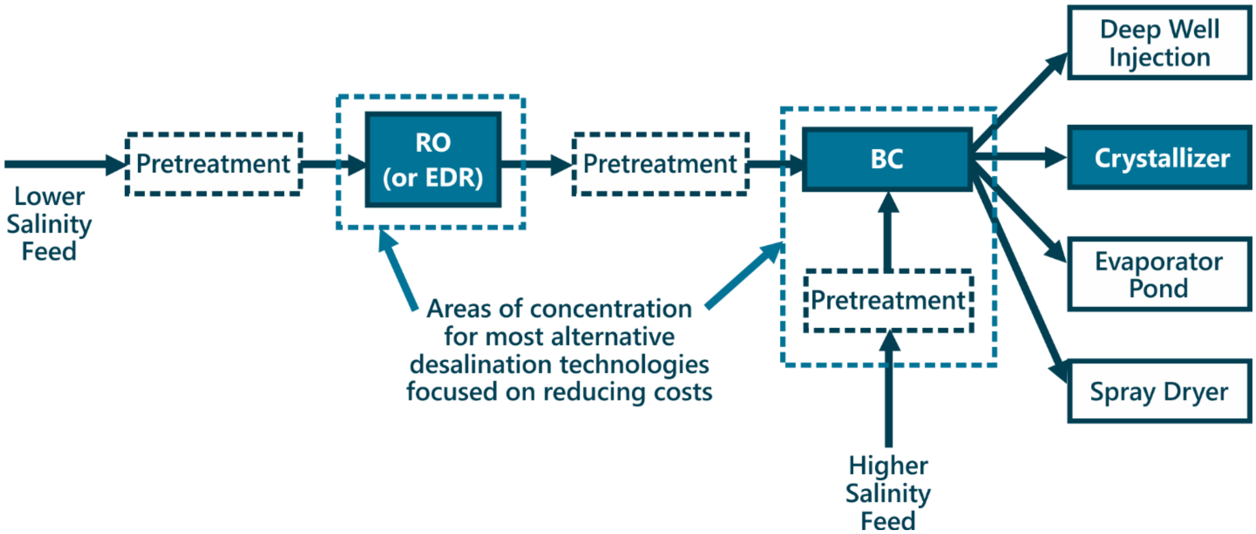

Figure 4. The most widely installed ZLD processing system. EDR = electrodialysis reversal.

Until recent years, the majority of applications have been in the power industry. After that, the major application has been treating produced water from the conventional oil and gas industry. More recently, applications have spread out over several other industries. Most applications of medium and large systems in the U.S. have been served by three U.S. OEMs: Aquatech, Suez (formerly General Electric [GE]), and Veolia. This market has been relatively small, with 8 to 20 medium and large systems installed each year. Markets for HR processing are discussed in detail in Chapter 13.

3.4. Disposal Options for HR Processes

Mainly due to high processing costs, HR systems have overwhelmingly been restricted to industrial applications. HR processing, however, has been increasingly considered for both municipal and industrial brine management.

As recovery increases and volume is reduced, the salinity and concentrations of constituents increase. Since HR processing can occur beginning with any feed water salinity, the final ‘brine’ can range from a brackish level to a very high salinity brine. Examples of the range of salinity for final brine residuals from HR processing include:

- Very low salinity residual:
    - From NF processing from municipal membrane softening or color removal operations
    - From water reuse operations associated with municipal wastewater treatment plants

- Low salinity residual:
    - Most municipal brackish RO concentrates

- Medium salinity residual:
    - From various industrial wastewaters
    - From some oil and gas produced waters

- High salinity residual:
    - From various industrial wastewaters
    - From some oil and gas produced waters

In some situations, disposal of the higher salinity brine may not represent any significantly greater disposal challenge than that of municipal brackish water lower salinity brine, including in:

- California, where inland brine may be discharged into a brine line leading to an ocean outfall

- Florida (and other locations), where deep well injection is possible

- Texas, where some facilities discharge into drainage ditches that ultimately discharge into the ocean

- Locations where evaporation ponds are possible

In other situations, disposing of HR brine of high salinity may be more challenging.

In situations where residuals are of higher salinity than normally encountered in conventional RO systems, these higher levels of concentration can bring salts that are not usually a concern in brackish water municipal desalination facilities closer to saturation limits. Depending on the technology used, these salts may limit recovery in the volume reduction process. As a result, brine from HR processing may have a wide range of salts near or at saturation limits. The higher concentration of some constituents may result in the need for pre-treatment of wastewater before volume reduction.

3.5. Relative Energy Requirements, OPEX, and CAPEX for High Recovery Technologies

Table 4 compares the relative unit energy requirements for various processes that involve evaporating water. For reference, energy requirements for conventional RO processes are also included. The initial entry is for the theoretical energy requirement of evaporating water—the latent heat of vaporization. This is the energy required at ambient conditions to vaporize water once the water is at boiling temperature, such as from an open pan. In the table, the sensible heat required to bring water up to the temperature at which vaporization is occurring is neglected as well as differences in the actual boiling temperature of the processes, which is dependent on pressure. Values in the table are representative of the various technologies.

Table 4. Hierarchy of Energy Requirements for Desalination Processes

Approximate unit energy Requirement in kWh/kgal (kWh/m^3)	**Process**
2,433 (643)	evaporation based on ~ 1,000 BTU/lb
1,410 (373)	spray dryer
235 (62)	conventional forced convection crystallizer
85 (22.5)	conventional MVR brine concentrator
8 (2.1)	seawater RO with energy recovery
3 (0,8)	brackish water RO

kWh/kgal = kilowatts per thousand gallons
kWh/m^3 = kilowatt hours per cubic meter
TU/lb = British Thermal Units per pound
MVC = mechanical vapor compression

Energy requirements in thermal HR processes are decreased from the initial value of 2,433 kilowatts per thousand gallons (kWh/kgal) by heat recovery and more efficient heat transfer such as:

- Recovering heat by preheating feed using exiting hot vapor or brine
- Recovering some or all of the vaporization heat by using multiple effects or vapor recompression.
- Avoiding heat transfer media by direct contact of heating fluid with feed water

As depicted in Figure 4, for feed water amenable to a first step of RO processing, conventional HR processes are used in a sequential order such as:

RO → BC → crystallizer
RO → BC → spray dryer (for small volumes such as <10 gallons per minute (gpm) (2.3 cubic meters per hour [m^3/h])
RO → BC → deep well injection
RO → BC → evaporation pond

After the initial RO step, each consequent desalination step treats a smaller volume of higher salinity water. The unit energy requirements for conventional thermal desalination processes increase with salinity due to the increasingly higher boiling point, pumping more viscous solutions, and using higher velocities to allow precipitation to take place without scaling of heat transfer surfaces (in the case of crystallizers).

As evident in Table 4, the unit energy requirements increase in the order:

Unit Energy requirements: RO < BC < crystallizer

As energy costs frequently represent over 80-90% of the operating expenses for the thermal desalination step OPEX, the unit OPEX (dollars per year per thousand gallons [$/yr/kgal]) increases in this same order:

Unit OPEX (dollars per year per volume [$/yr/volume]) RO < BC < crystallizer

More specifically, using the nominal unit energy requirements in Table 4 (and ignoring the difference in cost of thermal vs. electrical energy), and assuming RO energy (for seawater reverse osmosis [SWRO]) makes up 40% of the RO OPEX and evaporative energy makes up 85% of the BC and crystallizer OPEX, the resulting nominal unit OPEX ratios of the technologies are shown in Table 3

A similar work-up of installed unit CAPEX costs yields the nominal unit CAPEX ratios for installed equipment also shown in Table 5. Due to high installation costs associated with conventional thermal evaporative equipment, it is important to compare the CAPEX for installed equipment rather than just for the equipment alone. The heavy and bulky metal equipment typically requires a concrete installation pad and a crane to lift equipment into place. As a result, installation costs for BCs and crystallizers can be equal to the equipment costs. In Table 5, numbers are based on installed unit CAPEX ($/volume).

Table 5. Nominal Unit OPEX and CAPEX for ZLD Components of RO, BC, and Crystallizer

Cost Factor	**Relative Level**	**Approx. Ratio**
Nominal UNIT OPEX	RO < BC < Crystallizer	1:5:15
Nominal UNIT CAPEX	RO < BC < Crystallizer	1:5:20

Treating a unit volume of feed water by BC will cost roughly 5 times that of a RO system for both OPEX and CAPEX. While a more detailed analysis may yield different ratios, the hierarchy of costs will not change, and it is the effect of the hierarchy of costs that is the basis for the following conclusions.

3.6. Salinity Ranges for RO, BC, and Crystallization Technologies

Each of the processing steps has limits on how much concentration can take place. The limits for each step include:

- RO: solubility limits and osmotic pressure limits
- BC: solubility limits and practical limits based on boiling point rise
- Crystallizer: limits on foaming and boiling point rise

In nominal terms, conventional RO systems are typically limited to concentrates of 70 to 100 grams per liter (g/L). BC systems may concentrate feed up to and past 360 g/L, but may frequently be limited by formation of double salts to 150 g/L. (Note that it may not be practical to operate a system at 360 g/L.) Crystallizers may process up to 300 to 500 and higher g/L levels. As the solution becomes more viscous, higher temperatures are needed to process the concentrate. Other issues also contribute to the practicality of using crystallizers beyond 500 g/L. The relative size of the processing steps depends on site-specific feed water quality.

In the processing sequence of RO→ BC → Crystallizer, the volume treated by the later steps is smaller than the volume treated by the preceding step. The contribution of each processing step to the total OPEX and total CAPEX depends on the feed volume to that step.

From these general limits, however, if the feed water salinity is low then volumes may be considerably reduced with the RO step—resulting in much smaller volumes that need to be treated by the following more expensive evaporative steps. In this case, total CAPEX and total

OPEX can be dominated by the RO contribution to total costs. As the feed water salinity increases, less volume reduction occurs at the RO step and the relative contributions of the evaporative steps to CAPEX and OPEX begin to dominate total costs.

Volume reduction by RO may not be possible for feed water with high salinity levels. If so, then costs can be dominated by the crystallizer cost.

The result is that, for a given feed water volume, total CAPEX and total OPEX of HR processing heavily depend on feed water salinity. Similarly, the total costs are heavily dependent on the make-up of the feed water in terms of potential scalants, which can limit recovery at the RO and BC steps.

3.7. Disposal of Final Residuals

Disposal of final residuals from HR processing—whether brine or solids—is usually costly. In industries where HR processing is widely used, it is used for reasons other than to reduce disposal costs. It is usually done to provide an acceptable solution—from an environmental and thus regulatory standpoint, to reduce the time to achieve a permit, and to reduce outside water requirements for the industrial facility by providing recycled water. Thus, disposal of these waste streams of HR processes can be a major cost impediment to be addressed during feasibility evaluations.

Dependent on the presence of highly soluble salts (e.g., $MgCl_2$, $CaCl_2$), conventional thermal crystallizers may have a final brine that cannot be solidified, in which case there is a blowdown or purge stream from the crystallizer. The purge stream typically goes to a small evaporation pond or a small spray dryer.

3.8. Powering of Desalination Systems

Nearly all desalination systems are driven by steam and/or electricity. Conventional RO systems and most mechanical vapor recompression (MVR) systems are powered by electricity. Other conventional thermal systems are powered by steam (with some use of electricity for pumping, etc.).

Sources of electricity include grid electricity and site generation of electricity (such as by diesel or natural gas combustion turbine generators (CTG), diesel or gas reciprocating engines, or photovoltaic solar systems).

Sources of steam include boilers heated by combustion of fossil fuels. Waste heat in the form of hot exhaust gases, such as from a CTG, may be captured and used to generate steam. Waste heat in the form of steam may be used directly in desalination processes, depending on steam properties.

Whereas electricity is supplied to meet standard specifications, steam is not, and it may be available or produced in a wide range of temperatures and pressures.

3.9. Steam Versus Electricity for Evaporators

There are several issues that determine whether to power an evaporator by electricity or steam. The only practical evaporative systems that run on electricity are MVR systems which are typically of size 1 mgd (3,785 cubic meters per day [m^3/d]) or less. While this size limits the volume of water that can be treated by a single unit, it should be noted that typically the original water to be treated in a brine management situation is first treated by a RO step that reduces the volume to be treated by conventional thermal evaporative technologies.

This operative range of MVR technologies maps the general range of brine management desalination applications. It is in this range where the option of running the evaporative technologies on steam or electricity may exist. More specifically, the decision is between running an MVR electrically-driven system or a non-MVR steam-driven system.

A fundamental difference between MVR and non-MVR systems is in the recovery of the latent heat of vaporization. MVR systems fully recover this heat while non-MVR systems can recover only some of this heat, depending on how many effects are used. The energy requirement of MVR systems is usually equivalent to that for 10 to 25 effects in a non-MVR steam-driven system. Most steam-driven systems are less than 6 effects, as each effect in a conventional brine concentrator involves another piece of equipment. The number of effects used may depend on how much steam is available. Thus, the energy requirement for steam-driven systems is usually much higher than that of MVR systems. The lower cost of steam, however, typically results in the two systems being of similar cost. In the non-MVR systems, the final vapor is condensed, using either cooling water or an air-cooled condenser. The cooling system increases the footprint of the process.

Advantages of steam-driven systems include:

- Equipment is simpler
- While performance is much the same for the two types, a steam-driven evaporator can achieve higher concentrations, since it is not boiling-point-rise limited like an MVR evaporator
- Generally, requires more energy but not higher energy costs
- Does not have a compressor, making for a more robust and easier to maintain operation
- Gives more flexibility in handling feed water chemistry changes that might occur in the future
- A steam-driven crystallizer avoids the rotary blower of the MVR crystallizer seizing up due to foam (MVR crystallizers are notorious for having problems requiring frequent maintenance).

Disadvantages of the steam-driven evaporators include:

- Requires either cooling water or an air-cooled condenser
- Has a larger footprint
- Has a much higher energy requirement

If steam has a cost, it is typically more cost effective to use an MVR crystallizer. If steam is readily available at no cost, it is usually less expensive than an MVR system.

3.10. Waste Heat and Low-Grade Heat

Low-grade heat is often used to describe heat energy that is available at relatively low temperatures that is of minimal value to industrial and commercial processes. Waste heat, on the other hand, may or may not be low-grade heat and contains energy that is released to the environment without being used.

Most waste heat is in the form of exhaust gases where the heat recovery unit is normally a heat exchanger. For desalination processes, the heat needs to be converted to steam for use.

One major trend in characterizing newer thermal desalination technologies has been to highlight energy cost reduction by use of low-grade waste heat and solar heat. These statements can be misleading if they are interpreted to mean reduced energy requirements. They simply mean that less costly energy sources may be used.

Many company websites assume the major energy source is low-grade waste heat and do not include any cost for thermal heat in their OPEX estimates. Low-grade waste heat, however, is rarely 'free,' as there are costs associated with obtaining/recovering and delivering the heat. Key restrictions preventing heat recovery in a particular application can include cost, temperature restrictions, and chemical composition of heat streams (DOE 2008).

Conventional brine concentrators and crystallizers operating on electricity have high energy costs that can make up over 90% of the OPEX when using electricity and even high-quality steam as the energy source. If low-grade waste heat can be obtained and used at low cost, then energy-related OPEX can be reduced significantly from that of conventional electrically or steam-driven evaporators.

3.11. Evolution of Brine Management

The subject and issues of concentrate management and, more broadly, brine management have changed over the years. This is depicted graphically in Figure 5. In the early 1990s, there was a somewhat adversarial relationship between municipal utilities and regulatory groups concerning regulations dealing with disposal of concentrate. This has changed with time as environmental concerns and issues have become an accepted reality. In the late 1990s, the term "concentrate management" came into use—recognizing that other concentrate management options besides disposal exist and should be considered. While most brine is still disposed of, there has been a greater consideration of researching and evaluating other alternatives.

The term and issues of "sustainability" have become more and more widely used and considered since the early 2000s in concentrate management. Since then, the subject of sustainability has itself broadened to where sustainability considerations now include social, cultural, and economic as well as the natural environment. Terms such as "resiliency" and "circular economy" are newer aspects of sustainability. Also, the early 2000s saw a significant increase in the number of studies addressing the recovery of values from concentrate and brine. Finally, the interest in HR processing in municipal applications resulted in many research studies that showed that HR was achievable by several different processing approaches and that the issue was one of cost.

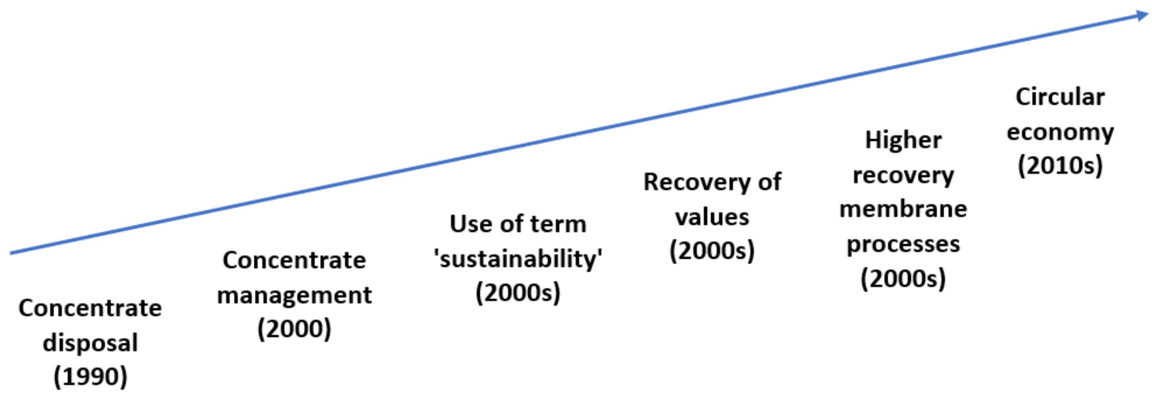

Figure 5. Evolution of Brine Management Terms and Issues

3.12. Value Recovery

This chapter focused on disposal of brine from high recovery processing. Final residuals are typically disposed. However, there has been increased interest in the recovering valuable materials from brine to offset the high costs of treatment. There are several challenges associated with this undertaking that include:

- The desalination entity taking on marketing of a commodity
- Finding a market for recovered products
- Producing salt products of higher value that require specific grain size and purity for market use
- Producing enough product during piloting to test the marketplace

While there have been isolated instances of success, this area of venture is still at an early stage of development.

Few references discuss selective salt recovery in general terms. For more detailed information, the reader is referred to Mickley (2008, 2009, and 2013). More recently, the full scale recovery of value project of Enviro Water Minerals at the Kay Bailey Hutchinson Desalination Plant in El Paso marks an important milestone in pursuing the goal of recovering of values.

Marketable products include:

- Potable-Quality Water (TDS<700 mg/L)
- Caustic Soda (50% concentration)
- Hydrochloric Acid (35% concentration)
- Gypsum (high purity, 100% soluble)
- Magnesium Hydroxide (98% purity, 56% solid)

3.13. Chapter Summary

This chapter describes conventional HR systems highlighting the energy- and cost-intensive nature of the process. The modern history of HR processing began with the development of the brine concentrator (BC) for ZLD treatment of cooling tower blowdown to prevent discharge of high salinity blowdown to the Colorado River. When the BC was invented in the 1970s, early processes fed feed water directly to the BC. Over time, systems evolved to include RO treatment before using the BC as part of the typical ZLD processing scheme. The vast majority of major ZLD systems have used this general processing sequence with BC brine going to either an evaporative crystallizer, a spray dryer, or an evaporation pond. This is the context in which new technology development takes place with the goal of significantly decreasing costs to participate in the increasing market for HR processing.

4. Challenges of Predicting Performance, Energy, and Costs of HR Processes

4.1. Introduction

Chemical and physical properties of dilute solutions are relatively simple to predict. As salinities increase, prediction of properties becomes increasingly difficult. Instead of using readily available computer programs to predict performance, complex, proprietary, and expensive software programs are needed. The prediction challenge increases when treatment systems include temperature and pressure variables—such as in evaporative systems.

The size of a following treatment step in a multi-step high recovery system depends on the performance (and thus size) of the preceding treatment step. As a result, estimating system costs for a multi-step high recovery system requires good estimates of performance for each treatment step.

These issues are discussed and illustrated in this chapter.

4.2. Prediction of Performance and Costs in Treatment at Higher Salinity Levels

4.2.1. Software for Conventional RO Performance Simulation

Computer programs are readily available for estimating recovery of conventional RO systems that concentrate feed water to salinity levels of generally less than 100 g/L. Input information includes feed water concentrations for major ions, silica, and for other components that can form sparingly soluble salts upon concentration of the feed water. Other input information includes feed water parameters such as pH and temperature. Many programs also allow specification of the particular membrane used to take the rejection properties of the membrane into account when computing permeate and concentrate concentrations as a function of recovery. Comparing salt and silica concentrations with programmed solubility limits allows estimates of the degree to which solubility limits are reached or exceeded. This identifies components that can limit recovery in a system without pH adjustment and/or use of antiscalants. The effects of pH changes and adding antiscalants are also estimated to predict the maximum possible recovery.

4.2.2. Recovery Prediction at Higher Salinities

As concentrations of major ions increase beyond that typically achieved in conventional RO systems, in addition to sparingly soluble salts and silica, now moderately soluble salts are also of concern (such as Na_2SO_4, Na_2CO_3) as are double salts (such as glauberite, $Na_2Ca(SO_4)_2$).

When higher salinity processing is involved, it is speculative to make estimates and generalizations of treatment performance without a well-defined water quality and adequate software. A striking example of this is illustrated in the cost study (Mickley 2008) discussed below with additional details in Appendix A.

4.2.3. Past Studies of High Recovery Processing Costs

The examples provided here are for the historical (conventional) and most widely used MLD/ZLD processing systems that involve the sequence of desalination technologies of

RO → BC → Crystallizer as discussed in Section 3.3.

4.2.3.1. Pipeline or Evaporation Pond vs. HR Processing

Mickley and Associates (Mickley 2003) looked at ZLD disposal options based on a hypothetical situation in the Phoenix area. Various regional brackish RO sites were considered to produce a total of 20 mgd of concentrate of a specific water quality. This basis was used in a Reclamation study (Reclamation 2000) that considered two disposal options: transporting the concentrate via a long-distance pipeline to the Sea of Cortez, and a multi-square mile area system of evaporation ponds. Mickley & Associates looked at two additional scenarios:

- Treating the concentrate with a thermal brine concentrator followed by evaporation ponds
- Sending the concentrate to a second stage RO system whose concentrate then went to a brine concentrator followed by evaporation ponds.

The results reflect the general challenge of implementing conventional HR systems. While CAPEX decreased by a factor of 2 to 5 due to the HR processing, OPEX increased by a factor of 18 to 41. Details of the cost analysis are provided in Appendix A.

4.2.3.2. Effects of Salinity and Composition on ZLD Performance and Costs

A 2008 WateReuse Foundation study (Mickley 2008) investigated the effects of salinity and composition on several ZLD processing systems. Eight concentrates, some actual and some projected from raw water qualities, were used to compare performance and costs of five different commercially used ZLD approaches. To uncouple effects of salinity and composition, both of which varied among the concentrates, concentrate salinities (which varied from about 4,000 to 11,000 mg/L) were normalized to 8,000 mg/L. Each constituent was ratioed in the same manner to provide the 8,000 mg/L composition. This approach eliminated salinity as a variable, focusing on the effect of composition alone. The five most widely used HR commercial approaches considered are shown in Table 6. In addition, the effects of concentrate volume and salinity were explored using a single relative composition to provide an additional four concentrates, to give a total of 12 concentrates and 5 processing approaches.

Table 6. Commercial ZLD Process Schemes Chosen for Evaluation

Scheme	Processing Step Sequence
1A	Conc. --> BC --> EP
1B	Conc. --> BC --> Cryst. --> EP & LF
2A	Conc. --> LS --> RO2 --> BC --> EP & LF
2B	Conc. --> LS --> RO2 --> BC --> Cryst. --> EP & LF
3	Conc. --> LS --> RO2 --> EP & LF

Conc. = Concentrate; BC = brine concentrator; EP = evaporation pond;
Cryst. = crystallizer; LF = landfill; LS = lime softener; RO2 = 2nd stage RO

Individual process step performance, system performance, and costs were evaluated as a function of processing scheme, salinity, composition, and plant size. The choice of variable conditions allowed independent study of these effects. Although high costs of HR processing are evident in all the situations studied, the results illustrate a wide range of costs.

The highest unit annualized cost (million dollars per year [MM$/yr]) processing scheme in nearly every case was 1B Concentrate → Brine Concentrator → Evaporation Pond. Using a second stage RO prior to brine concentrators is nearly always beneficial in terms of cost. The lowest cost ZLD approach is usually 2A Concentrate → Lime Softener→ Second stage RO → brine concentrator→ Evaporation Pond and Landfill, but not always. This illustrates an important point that the lowest cost (in terms of unit annualized cost) processing scheme is a function of salinity and chemical components of the TDS.

ZLD systems are made up of several processing steps. Performance and cost of each step are dependent in different ways on salinity and composition. Due to this complex interaction between processing steps, simple rule of thumb predictions of performance and cost for ZLD systems can be misleading and inaccurate. The study results predicted significant effects of salinity and composition on performance and cost of ZLD systems.

Perhaps the most important point from the study is that it is risky to generalize performance and cost from a single study case, whether a desktop study, a pilot test, or a full-scale installation, as results, particularly for the BC, depend greatly on salinity, composition, and concentrate volume. Details of this study are provided in Appendix A.

4.2.4. Alspach and Juby Article

Alspach and Juby (2016) analyzed the costs of the conventional RO → BC → Crystallizer process. One of their conclusions was that "overall costs (including primary RO + ZLD) [are] roughly comparable to seawater desalination." The paper was written from the perspective of low salinity feed water typical of municipal applications. Such feed water is much less complex in composition than that of many industrial brines. They conclude that increasing the RO recovery, such as from 80% to 90% and thus reducing the volume going to expensive evaporation steps significantly decreases ZLD costs.

For lower salinity feed water and with reduced costs possible with alternative and modified technologies that are being researched and developed, the overall ZLD costs will decrease. In some cases, for low salinity and less complex feed water, costs to treat concentrate may approach that of seawater desalination.

The complexity of the situation raises caution about the validity of performance and cost claims made for relatively new and not-yet commercialized desalination technologies.

4.2.5. Chapter Summary

This chapter discussed the challenges of estimating performance and costs of high recovery in multi-step treatment systems. Because of the strong dependence of system performance and cost on the salinity and composition of feed water, it is misleading to make generalizations of performance and cost based a site-specific test or installation. The increased degree of concentration, higher salinities, and more complex composition found in many HR processing applications require sophisticated software for prediction of solubilities that determine recovery and performance of HR process steps.

5. Results: Desalination Technologies Covered and Approaches Taken to Address Common Issues

5.1. Introduction

Companies use various means to reduce or limit the impact of scale on membrane and thermal process performance and to reduce energy usage in thermal processes and several common approaches are taken to reduce OPEX and CAPEX. This chapter introduces these topics and the results of a patent search and a literature search of various technologies.

5.2. Desalination Technologies Identified and Reviewed

In following chapters, these technologies are discussed:

- Reverse osmosis processes
- Electrolytic processes: electrodialysis (ED), electrodeionization (EDI), electrodialysis metathesis (EDM), electrodialysis reversal (EDR), and capacitive deionization (CapDi)
- Forward osmosis (FO)
- Membrane distillation (MD)
- Humidification-dehumidification (HDH)
- Other evaporative processes
- Other technologies

Figure 6 illustrates one approach to categorize the broad range of technologies being researched and developed to lower the costs of high recovery processing systems. Many categories have subcategories, and the figure distinguishes between conventional and newer technologies. R&D efforts include both the ‘newer’ technologies and modifications of the ‘conventional’ technologies.

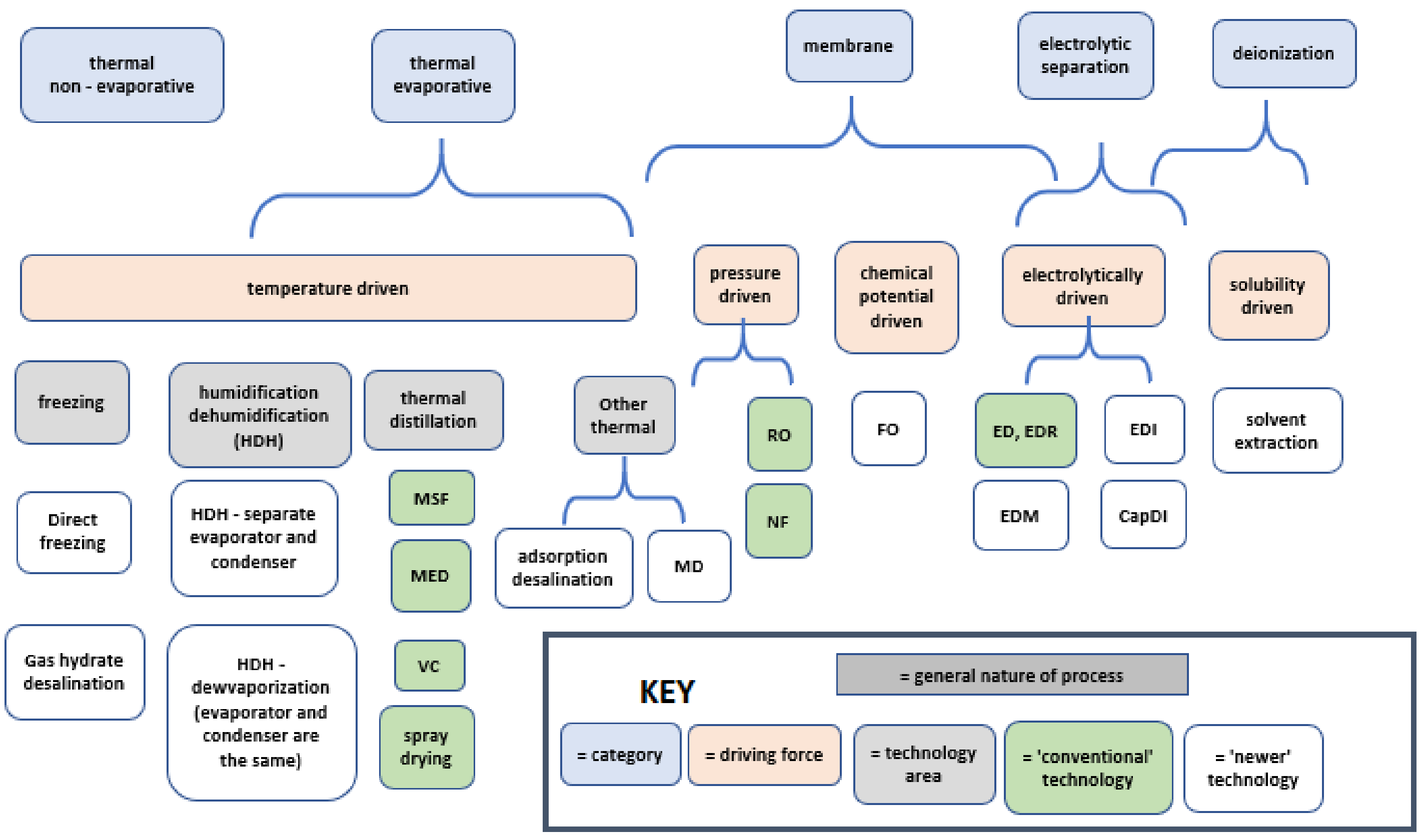

Figure 6. Representation of desalination technologies used in concentrate management.

5.3. Performance—Means Used to Reduce Scale Impact

There are ways to limit or eliminate the effect of scaling on membrane and heat transfer surfaces (Figure 7), including:

- Pretreatment of the feed water to lower the driving force for precipitation.
  - Adding:
    - Acid changes the distribution of carbonate species, minimizing carbonate-related scale formation potential, such as $CaCO_3$ scaling.
    - A base can change the distribution of silica species to more soluble forms.
    - Antiscalants and dispersants can slow or inhibit the chemical reaction steps, leading to formation of precipitants. The effect is temporary, but this can prevent scale formation during the residence time of water in equipment.
  - Pretreatment of feed water to reduce concentrations of scale-forming ions and silica. Concentrations of scale-forming ions (and silica) in feed water can be reduced by pretreatment steps such as forced precipitation (coagulation and flocculation) and ion exchange.

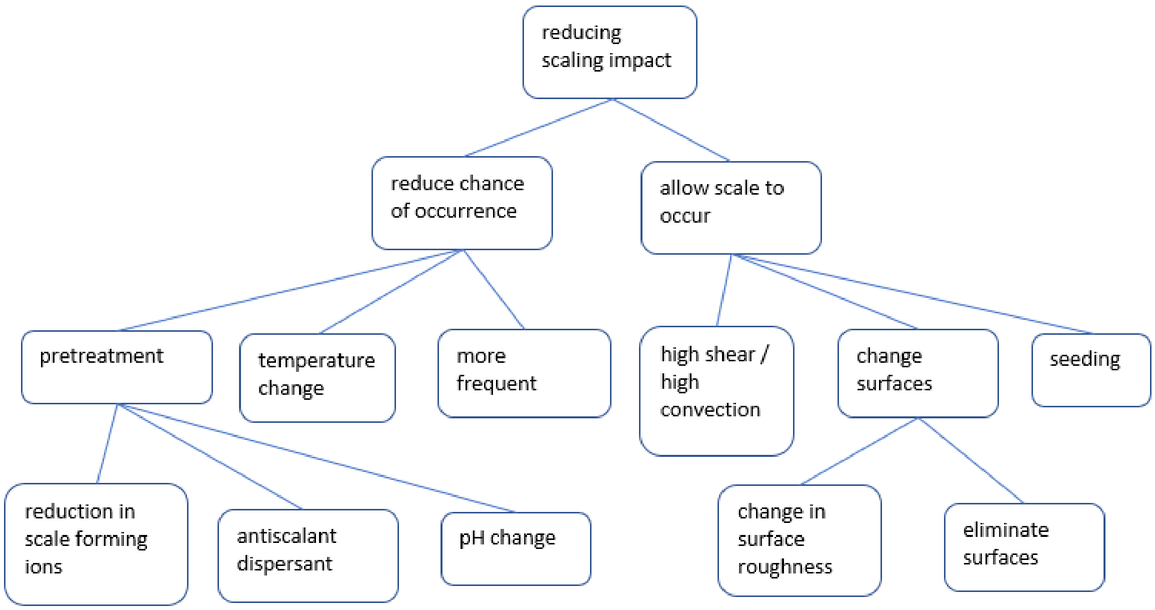

Figure 7. Means of reducing scaling impacts.

Pretreatment of feed water is standard practice in desalination processes. The importance and need for pretreatment in conventional desalination technologies increases as the feed water chemistry becomes more complex—whether from the nature of the source water or to the increased salinity of the feed water due to previous processing. There is a trade-off between the cost of the pretreatment scheme, which may consist of several steps, and the benefit in terms of performance of the desalination process. In a sequence of desalination steps, such as in many high recovery processing schemes, increased pretreatment to improve performance (recovery) of a preceding desalination step, can reduce equipment size and thus CAPEX of processing steps that follow.

Other means of reducing the impact of scale include:

- **High shear and high convection systems.** High shear at membrane and heat transfer surfaces can reduce contact of and provide a force to reduce adhesion of precipitants at the surfaces. The high shear and high convection systems have higher energy costs due to increased pumping or mechanically moving the surfaces. An example of high shear is the Vibratory Shear Enhanced Processing (VSEP) membrane system of New Logic Research. The typical design of thermal crystallizers is an example of high convection is where precipitation is occurring—but solids are kept from settling on equipment surfaces by high internal flow velocities.

- **Seeding.** Seeding includes solids in the circulating water to provide alternative surfaces for newly formed precipitants to adsorb onto. An example of this is the conventional seeded slurry brine concentrator, which typically adds $CaSO_4$ solids to the feed water to adsorb precipitating silica and $CaSO_4$. There have also been attempts to develop seeded RO systems, but scouring of membrane surfaces may be a problem.

- **Lower Temperatures.** Temperature affects the solubility of salts; however, it is not typically used to reduce the impact of scale but to induce precipitation. An example is the lowering of temperature to induce Na_2CO_3 precipitation and recovery. Another example is the Veolia CoLD crystallizer where pressure is reduced to a vacuum which lowers the temperatures and decreases the solubility of highly soluble constituents ($CaCl_2$, $MgCl_2$, nitrates, and organic acids), thereby avoiding the need for up-front pretreatment.

Some systems operate to allow more than conventional levels of scaling and fouling, reduce the impact by more frequent cleaning. The trade-off is between less pretreatment and more frequent cleaning.

Several newer thermal desalination technologies avoid scaling on heat transfer surfaces by eliminating the surfaces upon which evaporation and scaling can occur. This is known as direct contact where evaporation (or condensation) occurs only at the air-water interface away from surfaces.

5.4. Performance—Means of Reducing Impact of Fouling

Fouling is reduced by feed water pretreatment to remove foulants. Technologies typically used for removal of organic foulants include activated charcoal, dissolved air flotation, chemical coagulation, advanced oxidation, and electrocoagulation. Surface roughness of membranes as well as surface functionality (chemical groups) have been changed to produce less-fouling membranes.

5.5. Reducing Energy Costs

Reducing energy costs is a major thrust of new thermal technologies aimed at replacing the brine concentrator. Figure 8 lists paths to reduce energy costs.

Several of the thermal technologies tout use of waste heat as a major benefit in reducing operating costs. As discussed in Chapter 3, however, the linkage with waste heat is not always available and not without cost. Where feasible, the linkage can reduce the cost of providing energy.

An approach taken by several thermal technologies is direct contact heating where the heating fluid directly contacts the water to be evaporated. This eliminates materials that separate the two fluids, such as metal tubing, that offer resistance to the transfer of heat. Systems that still use heat transfer media have used higher conductivity and thinner materials to reduce the heat transfer resistance.

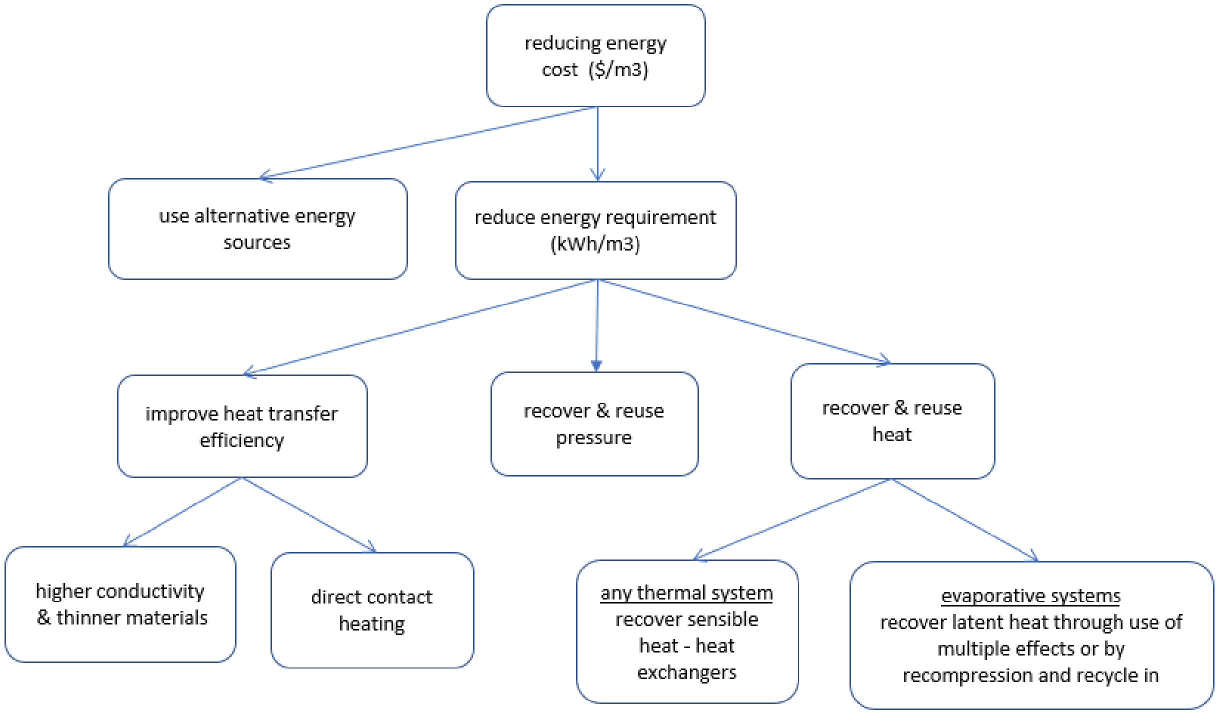

Figure 8. Paths to reduce energy costs.

Thermal systems routinely recovery some of the sensible heat from the exiting product streams by heating up influent streams. Latent heat is recovered by either using the exiting non-product high temperature streams in subsequent processing stages or in a vapor compression unit where pressure and temperature are increased back up to original feed conditions and recycled to the same vapor body.

5.6. Approaches to Reduce Capital Expenses

General ways to reduce costs of the conventional high recovery process sequence include:

- Reduce the unit cost of any of the three component steps. Most of the efforts in this direction have been with the RO and brine concentrator steps.
- Improve the recovery performance in the lower cost early steps to decrease the size of the more cost-intensive follow-on step(s) as unit costs increase with each succeeding step.

5.6.1.1. Reducing Unit Costs

Ways to reduce unit costs include:

- Using lighter weight materials can significantly reduce installation costs— particularly costs associated with the conventional brine concentrators and crystallizers, which typically include the need for a concrete pad and cranes to install. For these systems, installation costs can be as much as the equipment costs.

- Using plastic and resin-based materials will also reduce costs relative to more expensive metal costs. This also lowers corrosion concerns, which can increase the range of applications and reduce pretreatment requirements. In thermal systems, using less expensive materials usually allows lower temperature evaporation, which also lowers energy requirements.

- Using modular construction can reduce costs of custom design and facilitate scale-up.

5.6.1.2. Improving Recovery

Ways to improve recovery include:

- Allowing precipitation to take place. Scaling potential limits performance and determines recovery limits for the brine concentrator as well as for RO. Pretreatment steps typically use chemicals and/or other steps to specifically remove scaling agents to address scaling. An alternative system where precipitation can take place can push recovery performance past solubility limits. This also reduces the pretreatment and chemical requirements.

- Limiting residence time to less than induction and nucleation times for scalants. This allows feed water to concentrate past solubility limits. Such systems produce concentrate that will precipitate solids after exiting the desalination equipment.

5.7. Approaches to Reduce Operating Expenses

General approaches to lower operating expenses include reducing for energy costs, chemical use, and system complexity and associated labor requirements. As with capital expenses, operating expenses can be reduced by improving the recovery of the less cost-intensive step so that its size will increase, and the size of the more cost-intensive step(s) will decrease.

5.7.1.1. Reducing Unit Operating Expenses

Ways to reduce unit cost expenses include:

- Improving heat transfer efficiency. Using direct contact heat transfer between the heat source and feed water eliminates the need for heat transfer surfaces, which in turn reduces heat transfer resistance and eliminates a site for fouling and scaling. Where heat transfer surfaces are used, heat transfer efficiency can be improved by using higher conductivity and thinner heat transfer surfaces.

- Using waste heat where practical and feasible. Note that using waste heat will not reduce the energy requirement but can reduce the energy cost.

- Combining the BC and crystallizer operation into a single heat transfer system can reduced heat requirements.

- Using vacuum in thermal systems lowers energy requirements as lower pressure results in a lower driving force needed for evaporation. This can also lower solubility of certain salts and eliminate some pretreatment needs, reducing the need for pretreatment chemicals.

- Reducing system complexity to reduce labor requirements and system down time. This is particularly an important issue with thermal systems. Conventional thermal systems are complex and not very robust.

- Reducing and /or eliminating pretreatment chemicals.

5.7.1.2. Improving Recovery to Lower Operating Expenses

Improving recovery can lower operating expenses. Ways to improve recovery include:

- Allowing precipitation in the desalination step: higher recovery is achieved since performance is not limited by scaling issues.

- Using vacuum in crystallizers can reduce or eliminate blowdown of highly soluble salts as a result of the lower solubility at lower temperatures. The water associated with the blowdown is saved and increases the amount of water product.

- Improving recovery in RO-based systems (RO and ED) by using smart control and/or strategically placed precipitation steps that avoid scaling.

5.8. Benefits Claimed by Technologies/Companies

The common issues discussed above and faced by companies developing new desalination alternatives, whether they are new technologies or modifications to conventional technologies, result in a common set of benefits claimed by such companies. General benefits and claims include:

- Improved performance
  - recovery
  - membrane properties (flux, rejection)

- Reduced equipment and operational complexity

- Use of alternative and/or lower cost energy cost via use of waste heat and solar heat

- Increased energy efficiency
  - Direct contact heating—no phase change on heat exchange surfaces (leads to greater energy efficiency)

  - Multiple stages

- Inexpensive construction materials
- Limited pretreatment required
- Advanced control system
- Treatment robustness
- Small footprint
- Modular nature
- Environmental stewardship (for energy use, waste production, carbon footprint, etc.)
- Adaptability for future

5.9. Patent and Literature Searches

Both patent and literature searches were conducted to provide reflections of the interest in and effort given to various technologies within the context of R&D efforts to reduce the costs of conventional HR processing.

One major difficulty in conducting the searches was that conventional technologies (e.g., RO, EDR, MVR) have many patents and literature references that do not directly apply to efforts in reducing costs of HR processing. As an example, many RO-related patents deal with membrane or element design—areas that may reduce costs somewhat but were not done to address the HR processing barrier of very high processing costs.

5.9.1. Patent Analysis: (2010 to present)

Among the major new technology alternatives for brine treatment, a large percentage of applications for membrane distillation (MD), forward osmosis (FO) and humidification-dehumidification (HDH) are for MLD and ZLD brine management applications. Figure 9 shows that these three technologies account for 72% of the total patents identified. Only a small percentage of electrodeionization (EDI) and capacitive deionization (CapDi [also referred to as CDI]) apply to concentrate management situations but these two technologies make up 26 and 3% of the patents.

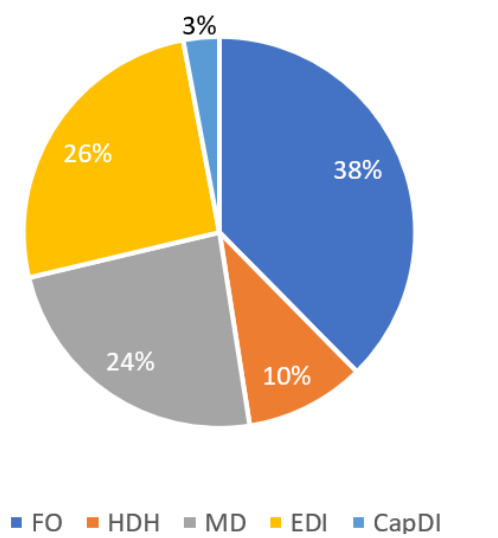

Figure 9. Potential technology alternatives for brine treatment application.

Entities with the greatest number of patents for MD, FO and HDH technologies, as per our analysis, are:

- FO: Oasys Water Inc. Samsung Electronics Co. Ltd., and Yale University USA

- HDH: Gradiant Corporation, Saltworks Technologies Inc., and Massachusetts Institute of Technology

- MD: Toegepast- natuurwetenschappelijk onderzoek (TNO) (Netherlands)

Other brine treatment technologies exist in the market; however, for the following reasons, they have not been included in the patent analysis:

1) The focus in this study was mainly on the major new/potential technology alternatives to conventional HR brine management technologies.

2) A large number of RO, conventional thermal technology, ED/EDR patents are associated with low recovery treatment of brackish water and seawater and not with HR brine management applications. It is difficult to determine the number of RO and thermal technology patents that do apply to higher salinity brine management. Thus, the focus is on new technology alternatives.

3) The new technology alternatives of solvent extraction, absorption desalination and freezing are not included due to their very low number of patents.

5.9.2. Research Literature Analysis

An analysis of research literature was undertaken to determine the relative attention given to different areas of technology relevant to high recovery processing. Analysis is challenged by the fact that a technology may be written about for reasons other than HR processing. This is particularly true for conventional RO and evaporative technologies, and others that have applications beyond HR processing. The case is somewhat clearer for newer technologies such as membrane distillation, forward osmosis, and humidification-dehumidification that are primarily targeted for HR applications. Survey results are dependent on search terms and results of several searches are provided in Figure 10.

Of most interest is the sharp increase in the number of ‘hits’ occurring after 2010. These results are consistent with previously published results (Fane 2015) for MD, FO, and ED. Reasons for this increase may include the economic rebound and the aforementioned anticipation of applications in unconventional oil and gas operations.

Our reading of the patent and literature searches, along with observations from dedicated conference sessions given to technologies is that the attention given to various technology areas for MLD and ZLD brine management applications is in this frequency order:

FO $\geq$ MD > HDH > EDI and CDI.

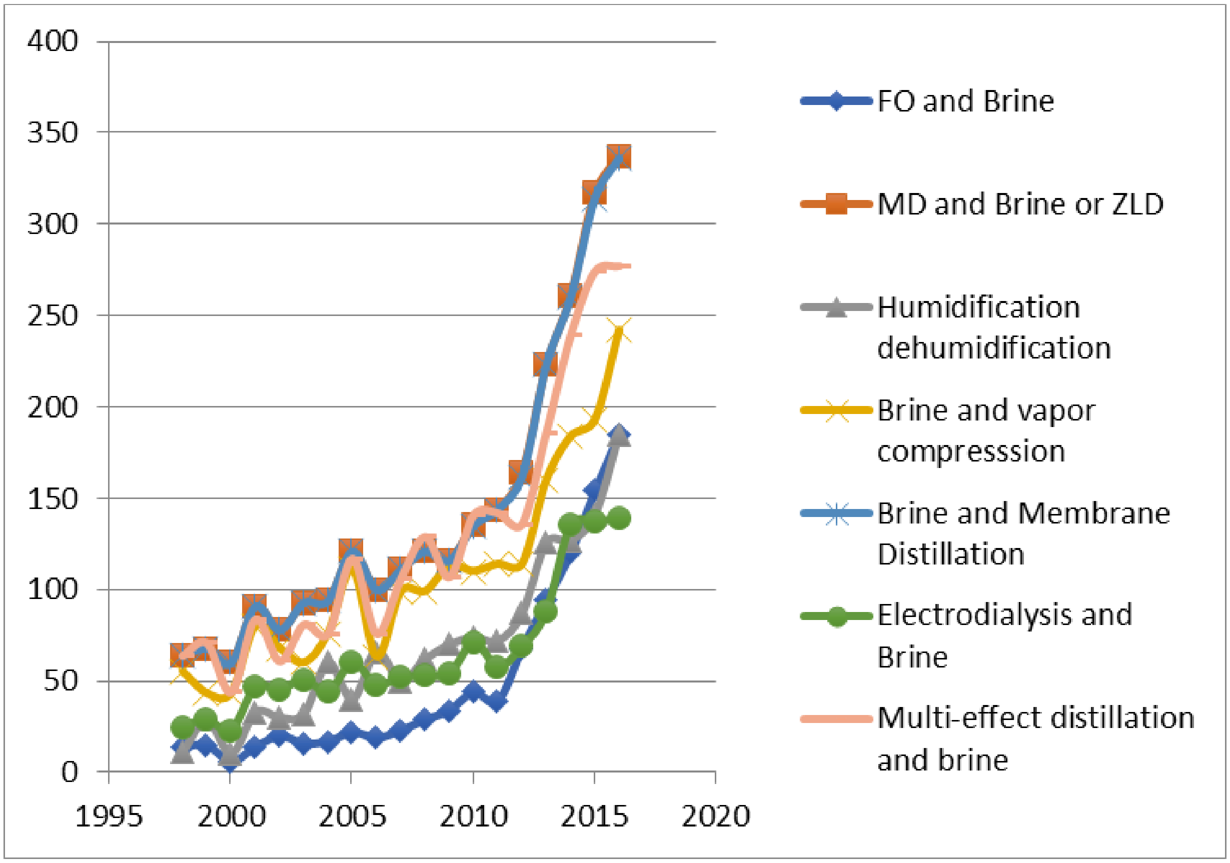

Figure 10. Research literature trends.

6. Reverse Osmosis (Non-Standard Systems) RO Technology

Over 400 municipal desalination facilities have been built in the 50 U.S. states. These are nearly all membrane facilities with the specific technologies as shown in Table 7 (Reclamation, 2018).

Table 7. Types of Municipal Desalination Technologies Built in the U.S.

Membrane Technology	Percent of Total
RO	81
NF	14
EDR	5

Membrane desalination technologies have an established successful track record in the U.S. municipal sector, and modifications of pressure-driven RO-based technologies, in particular, are more likely to be accepted for high recovery applications over other technologies. Because of this, the current chapter takes a more detailed look at these technologies as opposed to the level of coverage of technologies discussed in other chapters. In addition to technologies and companies that have made it to the commercial stage, the following discussion takes a broader perspective to include other non-standard high recovery RO systems that have been considered historically.

6.1. Conventional RO Systems

Figures in this chapter show simplified diagrams of these RO processes where most pumps, valves, recycle streams, possible bypass streams and pressure recovery units are not indicated in the schematics. Figure 11 shows a single stage, single pass conventional RO unit schematic:

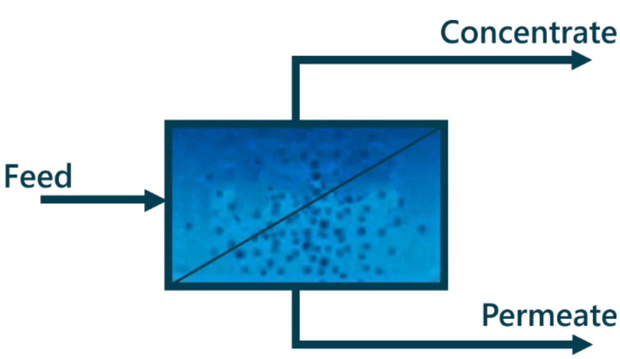

Figure 11. Conventional RO step.

To increase system capacity, increase the number of parallel units. To increase recovery, increase the number of concentrate stages (Figure 12). The size of the added stage is lower than that of the initial stage as there is a lower volume of feed.

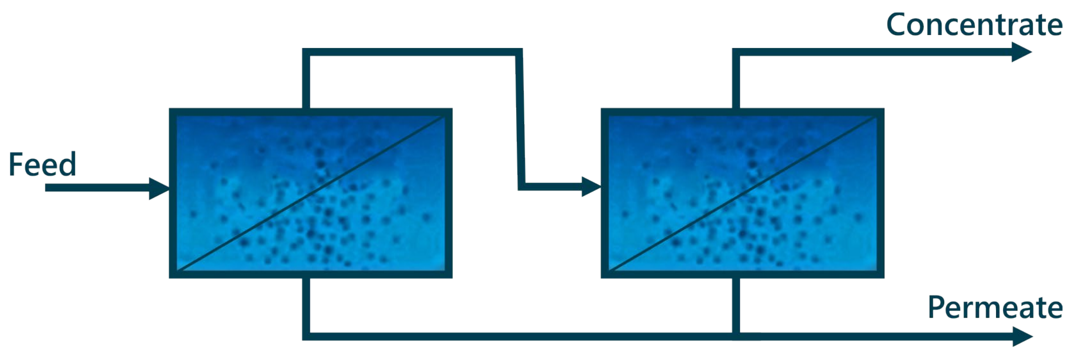

Figure 12. Two-stage RO system.

To decrease permeate TDS, increase the number of permeate stages (referred to as passes) (Figure 13). Again, the size of the added stage is smaller than that of the initial stage as there is a lower feed volume.

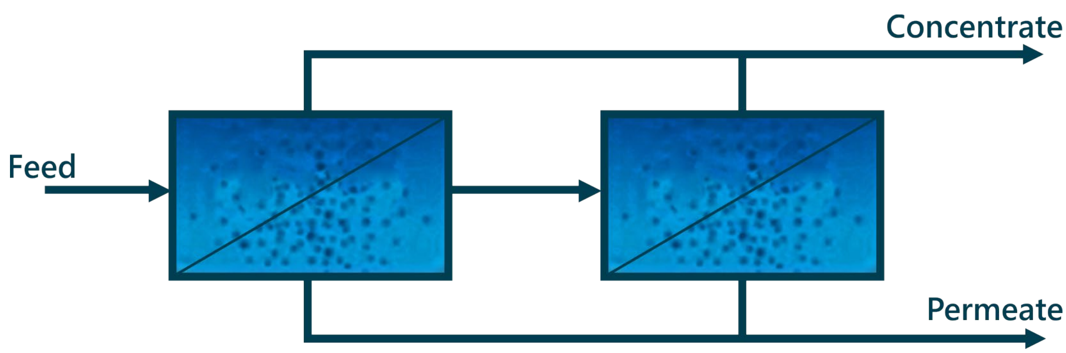

Figure 13. Two-pass RO system.

Some of the high recovery RO systems achieve high recovery in a single stage. Others may use additional RO stages and passes, as is common with conventional RO systems. Other HR RO systems would be used after a conventional RO stage.

6.2. Introduction to Non-Standard RO Systems

The term "non-standard RO" is used here to mean a RO system that differs from the conventional processing sequence of pretreatment followed by RO that has typified RO systems during most of their history. The main driving force for non-standard RO systems has been to increase water recovery. Higher recovery RO systems can play an important role in MLD/ZLD processes. When RO can be used as the initial processing step for a multistep MLD/ZLD system, higher recovery at the RO step can reduce the size of follow-on cost-intensive evaporative steps. In some cases, for lower salinity feed waters they can comprise the entire processing sequence.

The technologies described in this chapter fall into four general categories:

Higher pressure RO systems: Conventional RO systems have been limited to operating pressures of about 1,000 -1,200 pounds per square inch (psi) due to the design limits of membrane elements and modules. The high-pressure RO systems discussed here can operate up to 1,700-2,600 psi. Most of these systems use flat sheet membranes.

These systems include:

- Aquatech: AquaR2RO
- Aveng: HIPRO
- CH2M Hill: MAX RO
- Pall: Disk Tube
- Saltworks: UHP RO

Smart control RO systems: These systems are characterized by sophisticated monitoring and control systems that change operating parameters such as flow, direction of flow, and pressure based on both monitored conditions. Some of these systems operate in a batch mode. These systems include:

- AdEdge: Flow Reversal
- Aquatech: Advanced Recovery Reverse Osmosis (AARO)
- Concentrate Enhanced-Recovery Reverse Osmosis (CERRO)
- Desalitech: Closed Circuit Reverse Osmosis (CCRO)
- IDE: MAXH2O
- IDE: MAX H2O Pulse Flow RO
- ROTEC: Flow Reversal Reverse Osmosis (FR-RO)
- Saltworks: Ultra High Pressure Reverse Osmosis (UHP RO)

Cascade osmotic assisted RO (OARO) systems: Flow in these multi-unit systems is typically countercurrent with the composition of flow on the permeate side providing some osmotic force to lessen the feed side pressure needed for permeation. RO systems covered include:

- Battelle: Cascade Reverse Osmosis (CRO)
- Gradiant: Counter Flow Reverse Osmosis (CFRO)
- Hyrec: Osmotic Assisted Reverse Osmosis (OARO)
- Nanyang Technological University (NTU), Singapore: Energy-Efficient Reverse Osmosis (EERO)

Other non-conventional RO systems: This category is a catch-all for RO-based systems that do not fit conveniently into the other categories.

- Aquatech: High Efficiency Reverse Osmosis (HERO)
- EET: High Efficiency Electro-Pressure Membrane (HEEPM)
- King Lee: Tandem RO
- New Logic Research: Vibratory Shear Enhanced Processing (VSEP)
- O'Brien & Gere: Advanced Reject Recovery of Water (ARROW)
- Osmoflow: Brine Squeezer
- Slurry Precipitation and Recycle Reverse Osmosis (SPARRO)

Many research studies involved chemical precipitation before or between stages of conventional RO units. The processes are not commercial systems but are simply the result of smart engineering considerations and were named to be more unique-sounding, including:

- accelerated chemical demineralization (ACD),
- accelerated chemical precipitation (ACP),
- accelerated precipitation softening (APS),

- intermediate concentrate chemical stabilization (ICCS),
- intermediate chemical demineralization (ICD), and
- optimized pretreatment and unique separation (OPS)

One of the more recent studies of this type involved comparing conventional and pelletized lime softening to enhance RO recovery (He et al., 2011). These processes are not considered further in this chapter, but this general approach may offer solutions to treatment challenges.

6.3. Operating Principles of Non-Standard RO Systems

6.3.1. High Pressure RO systems

Feed-side concentration and thus osmotic pressure increase as the feed solution becomes more concentrated. Feed-side pressure must be greater than the osmotic pressure for permeation to occur, and high enough for a reasonable flux to occur. Feed-side pressure is limited by the pressure limits of the membrane equipment, which has been 1,000 -1,200 psi in conventional RO systems. This places an operating limit on how high the concentrate salinity can get—and thus a limit on recovery.

High pressure RO systems are designed to operate at higher pressures. This allows higher feed side salinity levels to be reached, and thus higher recovery. Most of the high-pressure RO systems use flat sheet membranes, which are more easily incorporated into high pressure containers.

These systems have higher unit CAPEX and OPEX than conventional RO systems, and there is an increased potential for scaling to occur. As a result, an initial conventional RO stage may precede the high-pressure RO stage, and usually more substantial pretreatment is used.

6.3.2. Smart Control—Time Dependent RO Systems

Conventional RO systems are conservatively designed to enable operation over a range of feed conditions. In that sense, the systems rarely operate in an optimal manner. Within the membrane modules and across the multiple modules, concentrations, pressures, and velocities change with location. Aside from scaling and fouling, the systems operate in a continuous steady-state manner. The variables are not independently controlled and thus are not optimal by location. Many smart systems operate in a batch or semi-batch mode where all or a portion of concentrate is recycled and feed solution concentration increase with time. While conventional RO systems operate continuously at set conditions while producing permeate, nearly all of the smart systems change operating conditions with time and are sometimes referred to as "time-dependent RO systems." Some of the smart systems use periodic reversal of flow direction. Some or all of these operating variables are independently controlled, which allows more optimal use of the variables over time. As a result, the systems require less energy, concentrate to higher levels while avoiding precipitation of salts and silica, and in general, result in more efficient operations.

In some cases, conventional RO systems can be converted into smart systems simply by installing smart control systems and changes in piping and valves. In other cases, the smart systems include more extensive hardware differences from conventional RO systems.

Figures for a few selected smart HR RO systems are provided under the company discussions of Section 6.4.2.

6.3.3. Cascade Osmotic Assisted RO (OARO) Systems

In FO systems, the permeate side osmotic pressure exceeds the feedside pressure through the use of high osmotic pressure draw solutions on the permeate side. Water is drawn into the permeate side by the osmotic pressure difference. In OARO systems, the permeate side osmotic pressure is increased by recycling some feedside concentrate to the permeate side; however, the permeate side osmotic pressure does not exceed the feedside osmotic pressure. As with conventional RO, flow to the permeate side is driven by the pressure difference, which is now achieved at a much lower feed side pressure.

Figure 14 is a schematic of a single OARO membrane unit.

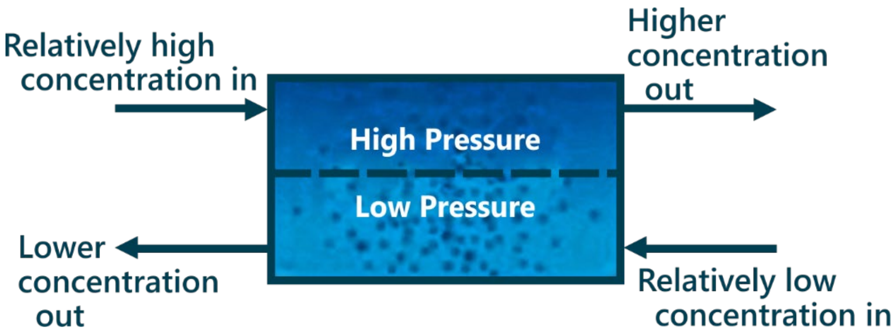

Figure 14. Single OARO membrane unit.

OARO units are typically arranged in series with mostly counter current flow between them. The simplest case has multiple units (shown in Figure 14) arranged in series. The sequence of units, each operating at a lower feed side pressure than in a conventional RO unit, allows high recovery operation to be attained at much lower pressures. Variations on this general arrangement include crossover flow from the permeate side of one unit to the feed side of another unit and flow from the feed side concentrate of one unit to the permeate side of another. This may occur at some or all of the stages. Another variant is to place the feed into the system other than at an end unit. An example of such a more complex OARO system is shown in Figure 15.

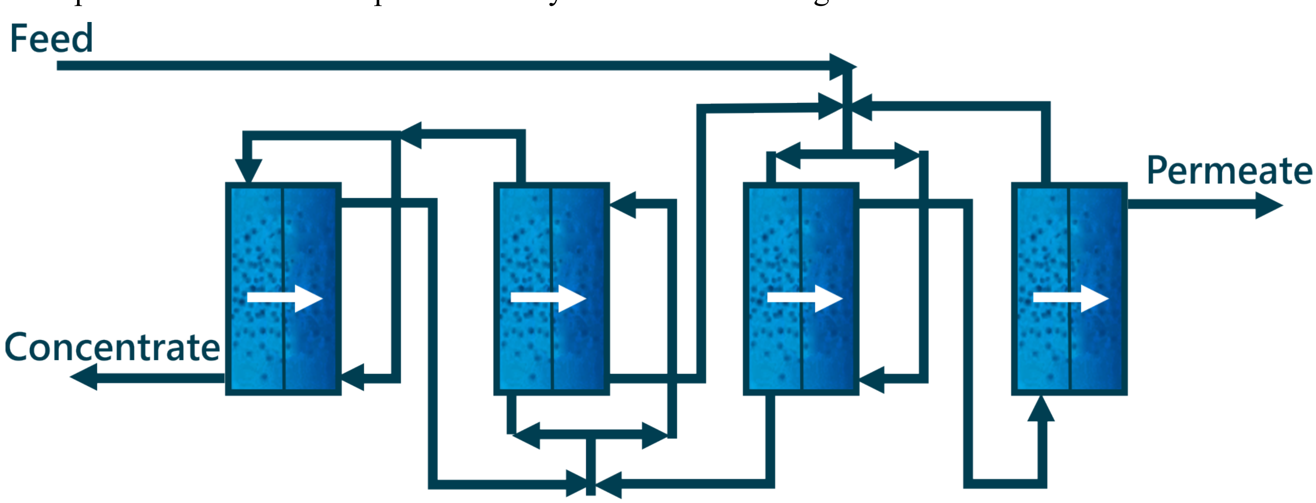

Figure 15. Example of a more complex OARO cascade system design (without pumps, interstage pressure control valves shown).

The OARO system may include using lower rejection membranes in some steps. Due to the number of units, more sophisticated control of interstage pressure, and multiple flow connections, the system unit CAPEX is higher than that of conventional RO systems. The unit OPEX can be less.

6.3.4. Other Non-Conventional RO Systems

There is a variety of high recovery RO systems that differ from designs of the above three categories. Most, if not all, of these systems were used as commercial systems earlier than the systems in above categories. A brief description is given here with more detailed descriptions of each provided in the company reviews below.

- Aquatech: HERO operates at higher pH levels to avoid silica scaling and minimize organic fouling. It frequently includes use of ion exchange or lime softening to reduce calcium and other scaling potential.

- EET: HEEPM is a unique arrangement of a source tank supplying feed to an RO unit that produces product water and recycles concentrate to the source tank and supplies feed to an EDR system that produces concentrate and recycles product water to the source tank.

- King Lee: Tandem RO is a batch system that pushes recovery past silica solubility limits but stops operation before slow forming silica solids result.

- New Logic Research: VSEP uses vibrations that produce high shear at the membrane surface, resulting in minimal scale adherence; system can push past solubility limits.

- O'Brien & Gere: Arrow is a two-stage conventional RO system with treatment step placed after the second stage to remove potential scalants. The treated water is recycled back to between the membrane stages.

- Osmoflow: Brine Squeezer is a brute force operation at higher temperatures, higher pressures, and frequent cleaning. Membrane life is sacrificed for high recovery.

- SPARRO recirculates seeded gypsum slurry to provide a surface for scale formation, thus minimizing formation on the membranes.

- Interstage Precipitation uses a chemical precipitation between stages to allow high recovery in the second stage.

6.3.5. Attributes for High Recovery RO Systems

- Reduces volume of concentrate.

- Expands the performance envelope of RO systems by (depending on the particular technology) overcoming limitations of conventional RO due to osmotic pressure, applied pressure, scaling, and need for pretreatment.

- Can be an alternative to expanding an existing installation.
- Can reduce MLD/ZLD costs through reducing the size of follow-on, more cost-intensive thermal evaporative systems.

6.3.6. Energy Considerations

- RO-based technologies have significantly lower energy requirements than evaporative processes.
- Some of the HR RO technologies (higher pressure operation, use of high velocity, and high shear conditions) result in increased unit energy requirements relative to conventional RO—but still require considerably less energy than evaporative systems.
- Other HR RO technologies (e.g., several smart control systems that monitor conditions and change operating conditions) have lower unit energy requirements than conventional RO.
- The OARO cascade arrangement reduces opposing osmotic forces and thus reduces pressure (and thus unit energy) requirements. Increased pumping needs offset this somewhat.

6.3.7. Limitations

- Some of the systems have limited testing and consequently limited definition of performance envelopes, costs, and most promising market applications. This is particularly true of the cascade designs.
- Track records for many of the technologies are limited.
  Unknowns for time-dependent RO systems include the effect of stoppage and changing conditions on membrane life and system integrity.

6.3.8. Applications

- Most of these RO-based systems can provide the initial desalination step in MLD/ZLD processes—for a wide range of applications.
- For lower salinity applications, the technologies may be used without follow-on additional desalination steps.
- It is likely that each type of technology will find a marketing niche.
- Smart RO systems have been increasingly considered for municipal applications including water reuse.

6.3.9. Operating Cost Considerations

- The energy proportion of the OPEX varies with the type of HR RO system.

- The membrane life of time-dependent RO systems is not well defined but may be lower than that for conventional RO systems.

- OPEX is likely less than that of FO systems and definitely less than that of MD systems (and other evaporative systems).

6.3.10. Capital Cost Considerations

- Unit CAPEX varies with the type of HR RO system.

- The unit cost of smart RO systems is less than that of high-pressure RO systems. Unit cost of smart systems is usually higher than that of conventional RO due to the more complicated hydraulics, valving, and additional control; However. in some cases, the cost may be comparable to that of conventional RO
.

- The unit costs of OARO systems are less defined than those of high-pressure and smart RO systems.

- The higher recovery of these systems brings their application into the space held by more cost- and energy-intensive thermal brine concentrators. In these applications, non-standard RO systems can reduce the overall MLD/ZLD costs – both CAPEX and OPEX.

6.4. RO Companies

6.4.1. High Pressure RO Systems

6.4.1.1. Aquatech International Corporation: AquaR2RO (USA)

URL: https://www.aquatech.com

Status: *This information was provided in 2017 website. In the 2020 website review, the AquaR2RO system was mentioned only in two 2015 news releases. It is assumed the system is no longer being marketed.*

Company Information: The AquaR2RO process features a plate and frame configuration of membranes operating at very high pressure (up to 2,000 psi) with short flow channels. The feed distribution pattern and turbulent flow prevent foulants/scalants from depositing on the membrane surface. Due to its distinctive design, AquaR2RO can tolerate feed characteristics that are high in organics, dissolved oil, and turbidity. The process can provide high recovery while handling high TDS water due to its ability to withstand higher than normal operating pressures. The AquaR2RO process maximizes recovery across the membrane system and minimizes the volume of concentrate to be treated in the thermal-based ZLD steps with a brine concentrator and/or crystallizer. In most cases, it can replace the brine concentrator, thus optimizing the solution. The system is for smaller flow, high concentration reject streams of > 12%.

6.4.1.2. Aveng Company: HIPRO (South Africa)

URL: https://www.aveng.co.za/

Status: *Information on the 2017 website showed that Aveng is a large engineering construction company with Aveng Water as a subsidiary. There is very little information available on HIPRO. Latest website news is dated 2016.*

The 2020 website revealed that the company had been sold and the new focus is international infrastructure, mining, and resources group. There is only historical mention of the HIPRO technology.

Company Information: HQ is in South Africa. HIPRO is a high recovery precipitating reverse osmosis mine water treatment process which provides new supplies of potable water, while also restoring balance in the natural environment by limiting the impact of polluted water through effective treatment. The HIPRO process achieves its high recovery through the use of multiple stages of ultrafiltration (UF) and reverse osmosis (RO) membrane systems, operating in series, and with inter-stage precipitation of low solubility salts. The final RO stage is high pressure. HIPRO's unique feature has the ability to process water at high recovery rates, with minimal brine.

6.4.1.3. CH2M Hill: MAX-RO (USA)

URL: none that covers the technology

Status: *The technology was mentioned in a 2015 presentation and in a few papers. Statement made that there is significant chemical consumption and solids production; viability hinges on salt use. No additional information has been found since 2016. There is no website. Jacobs Engineering Group Inc. <www.jacobs.com> purchased CH2M Hill.*

Company Information: MAX RO is a non-proprietary innovative RO technology developed by CH2M to achieve high recovery. It combines a series of established treatment technologies in a unique manner. The process chemically removes silica via a lime/magnesium precipitated softening, followed by a ceramic ultrafiltration step and then a weak cation ion exchange step. Water is then treated by a series of three RO steps of increasing pressure; the final step being a disc-tube/flat plate RO system. The process operates at high pressures up to 1,800 psi allowing RO concentrate to be further concentrated to 160 g/L TDS. The process has been tested at bench-scale and was set to be piloted in Australia.

6.4.1.4. Pall Corporation: Disc Tube (USA)

URL: www.pallwater.com

Status: *2020 website states over 220 installation for leachate treatment. Modules are from 4 to 25 gpm (0.9 to 5.7 m^3/h).*

Company Information: The technology is called the Pall Disc Tube TM Module system, a stacked flat disk membrane system which is designed and constructed to provide an open channel, unrestricted and fully turbulent feed water system. This means that suspended solids carried in the feed water cannot be trapped or easily settle out inside the membrane module, thereby minimizing membrane scaling and fouling. The system can be operated at pressures of up to 2,300 psi —much higher than conventional RO systems. Originally, these were designed to produce drinking water from sea water; however, now they are successfully applied to other markets such as leachate, petroleum contaminated water, and industrial wastewater streams.

6.4.1.5. Saltworks Technologies, Inc.: UHP RO (Canada)

URL: https://www.saltworkstech.com/

Status: *In 2017, Saltworks' focus was more on an Electrochem ED system (Saltworks licensed the EDM technology after Veolia had given up their license) and the SaltMaker HDH evaporation system. There was anticipation of a commercial EDR-RO later in 2017. Commercial sales of Saltworks were mostly due to SaltMaker product. Mention of the UHP RO technology began in 2020. BrineRefine is mentioned in a September 2020 company news article for a US mining site with a specific ion-of-concern problem.*

Company Information: Saltworks' ultra high-pressure RO system was commercialized in May 2020 at a U.S. manufacturer of advanced materials. Previously, pilot testing had been conducted on various customer applications including mining waters, factory wastewater, ion exchange regeneration waste, and cooling tower blowdown. One key was membrane development by Nitto to achieve high performance at high pressure. The UHP RO is teamed with a softening technology, BrineRefine, to extract scaling compounds from concentrate of a conventional RO step prior to use of the UHP RO technology. Combination is called Xtreme RO.

The UHP RO system also has some aspects of smart control systems (next set of systems discussed). This can include flow reversal, partial brine recirculation, batch or semi-batch operation, and—for batch operation—brine discharge in periodic small and larger volumes that cause disruption that inhibits scale formation and biological growth.

Saltworks makes several other technologies that can be use with the Xtreme RO technology including: XtremeUF, for concentrating slurries; IonSelect, selective ion removal; SaltMaker evaporative crystallizer; and FlexEDR, for selective removal of monovalent ions.

6.4.2. Smart Control RO Systems

6.4.2.1. AdEdge Water Technologies, LLC.: Flow Reversal (USA)

URL: www.adedgetechnologies.com

Status: *ROTEC was founded in 2009 and went commercial in 2014. In 2017 they had about 20 plants from 88 to 2,200 gpm (20 to 500 m^3/h).*

AdEdge sells several different treatment technologies and the main product is an adsorption process that has been installed at over 600 locations—mainly for arsenic removal, iron and manganese reduction, and uranium removal. Their blog is current through October 2020.

Company Information: *AdEdge* is the licensee for North, Central, and South America for the Flow Reversal (FR) technology from the Israeli company, ROTEC. The system is based on the principles of FR technology, enabling improved recovery/performance for RO systems. FR is a smart, innovative, and proprietary process for scale prevention on membranes surfaces, which works by periodically switching the flow direction in RO pressure vessel arrays. A main product is a scale-sensing system which is used to control the flow reversal. The frequency of switching is dictated by the time it takes for a supersaturated solution in the concentrate to reach induction time leading to precipitation. By using the under-saturated feed to sweep away the beginning scale particles in the concentrate before they exceed a critical size, extensive precipitation is prevented. The system can be incorporated into an already existing RO facility with no additional stages added and no change in footprint. This approach affords operating at much higher recoveries than what can be achieved with antiscalants alone. *AdEdge* claims the system can decrease or eliminate anti-scalant consumption and minimize biofouling and membrane replacement frequency. The technology is applicable to retrofitting RO plants or for grassroots design of new plants. The RO system can be operated in its conventional mode without turning on the RORO system.

6.4.2.2. Aquatech International Corporation: AARO (USA)

URL: www.aquatech.com

Status: *There is no mention of the AARO system in the 2017 website. The 2020 website mentioned the Advanced Recovery RO (AARO) system. Very little additional information is available on the website.*

Company Information: The AARO system, unlike most smart RO systems, is not a time-dependent system. AARO is a high recovery, smart system with pre-programed flush frequencies based on feed water quality. Initial stages are operated at lower concentrations, reducing maintenance needs. The flushing is done with permeate that is later recycled. An automatic osmotic cleaning option is available. Modules are available from 50 to 250 gpm (11.4 to 57 m^3/h).

6.4.2.3. University of Texas at El Paso (UTEP) Center for Inland Desalination: CERRO (USA)

URL: www.utep.edu/engineering/cids

Status: *A 2020 information search revealed that there is no specific website for this technology. It is mentioned on the UTEP website and two professors and a graduate student are listed at developers of a 2018 patent. Conference presentations were given. The initial installation was in 2014. It appears that the technology, in part, was follow-up to studies conducted with UTEP participation and discussed below as Tandem RO technology*.

Company Information: CERRO is a batch system with recirculating concentrate. Solutions are allowed to become supersaturated but batch processing stops before precipitation occurs. There are installations at three El Paso Water Utility well sites up to 140 gpm (32 m^3/h).

6.4.2.4. Desalitech, Inc.: CCRO (USA)

URL: www.desalitech.com

Status: *The 2020 website review shows the RO systems referred to as ReFlex and ReFlex Max. Installation sizes range from 50 to 900 gpm (11.4-205 m^3/h). There have been hundreds of installations in several different industries. There is a concentrated effort to enter the U.S. municipal market – particularly the California reuse applications. The technology uses off the shelf standard components. The 2017 website had similar information but with fewer case studies. The product was already well launched in 2017.*

Company Information: This was one of the first innovative low energy smart, high recovery RO technologies. It independently controls pressure, velocity, and flux resulting in higher recoveries with lower average pressure. It is a semi-batch system (Figure 16) in which the pressure is gradually increased as the salinity of the recirculating concentrate increases and permeate is replaced with feedwater. The pressure is increased just enough to keep permeate flowing constantly. The production mode ends when peak recovery is reached. Brine flush occurs and the next production cycle is initiated with fresh feed filling the entire system. Feed continuously replaces permeate and permeate production is maintained at a lower rate during the system flush. The system uses shorter membrane arrays to provide better flux distribution and membrane performance. Average pressures are lower than in conventional RO resulting in lower energy requirements. The system can be retrofitted onto existing conventional RO systems as an added stage.

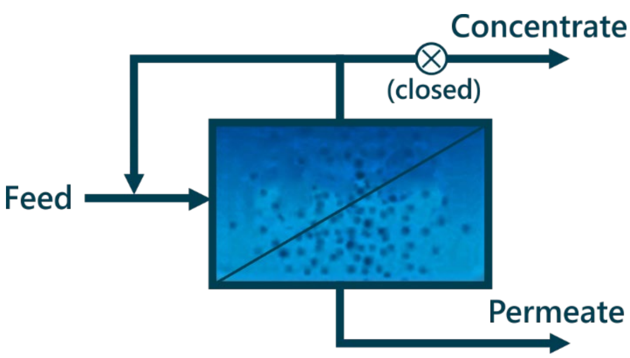

Figure 16. Desalitech CCRO system.

6.4.2.5. IDE Technologies: MAXH2O Desalter (Israel)
URL: www.ide-tech.com

Status: *From a 2017 IDE webinar, the precipitation cycle was described as a fluidized bed pellet reactor manufactured by a Dutch company. There is no chemical addition to the RO process. It was stated that in January 2018 tests will begin to treat acid mine drainage water and cooling tower blowdown. The following information is based on a March 2020 webinar presentation and the 2020 IDE website.*

Company Information: MAXH2O Desalter, is a high recovery single stage system applicable to treatment of RO brine or industrial effluents of high scaling tendency. A simplified process schematic is shown in Figure 17. The Desalter is a semi-batch system with an integrated salt precipitation cycle for continuous de-saturation of RO brine. The process is not limited by supersaturation of sparingly soluble salts, but by osmotic pressure. Osmotic pressure, however, decreases as salts are removed. Due to the precipitation step, the process has high flexibility—operating with variable feed water qualities, concentrations, flows, and recoveries. The process can achieve different total recovery levels in the same systems—the brine recirculation to the feed tank can be stopped at any recovery, at any RO brine level. The process has low chemical consumption and unlike other high recovery RO-based systems the final brine has low scaling tendencies. The system operates in cycles of increasing pressures as salts are precipitated and brine from the precipitation reactor is returned to the feed side. Treatment ends when pressure reaches a final set pressure. At the end of the processing cycle the feed tank is drained and operation begins on a second feed tank. Low CAPEX and OPEX are projected along with an energy consumption similar to that of SWRO. The vendor claims variable operating conditions reduce biofouling potential. The system can operate at high pressure up to 140 bar and uses an energy recovery device.

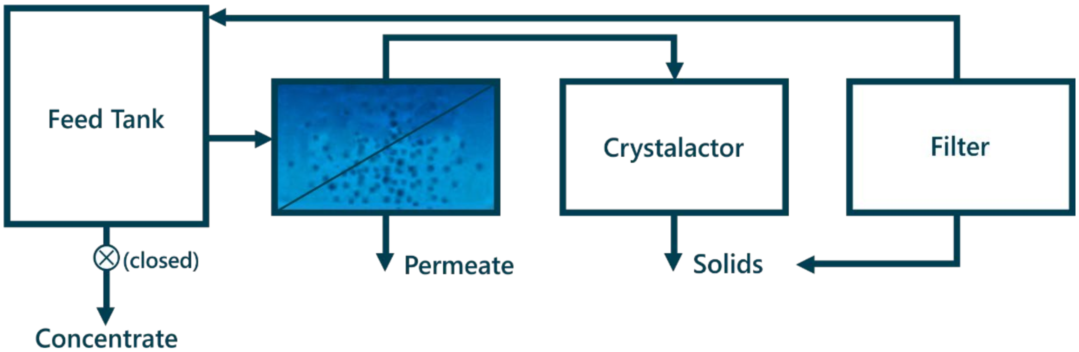

Figure 17. IDE MAXH2O desalter.

6.4.2.6. IDE Technologies: MAXH2O Pulse Flow RO (Israel)

URL: www.ide-tech.com

Status: *The following information is from the 2020 IDE website and from various IDE webinars given in 2015, 2018, and 2020. A 2020 webinar discusses 2016 pilots and a 10-month demonstration at a California municipal facility that began in late 2018. In 2020 forthcoming installation was announced for at a wastewater site in Colorado.*

Company Information: The Pulse Flow RO is a single stage batch flow RO system with all pressure vessels operating in parallel. Figure 18 is a schematic of the pulse flow reverse osmosis (PFRO) system in the production cycle. The pressure vessels continuously receive feed flow and continuously produce permeate. The dead-end batch flow processing takes place at increasing pressure as the feed side concentration builds up. There are two operating cycles: production and flush. Concentration builds up during the production cycle. Brine is discharged during the flush cycle brine in pulse flow by short, forceful surges. During the flush cycle, increasing permeate-side pressure results in converting the system into a forward osmosis mode where permeate water flows into the feed side. This provides membrane backwash and bacteria dehydration. The pulse strokes result in detachment of fouling and prevent formation of biofilm and attachment of particles to the membrane. The residence time is short, and concentration takes place before induction time of scalants occurs.

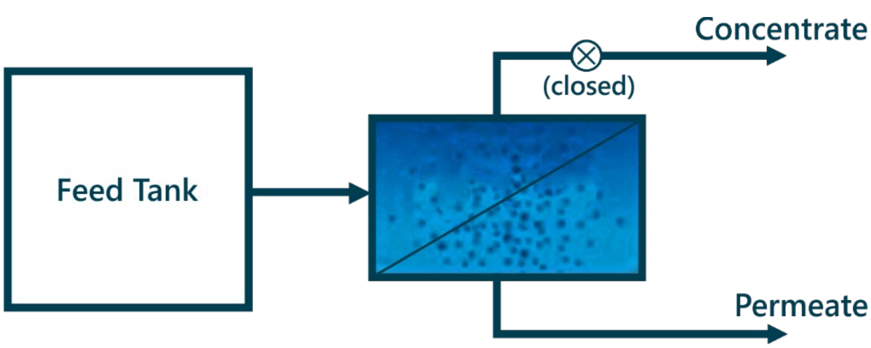

Figure 18. IDE MAXH2O PFRO.

6.4.2.7. Pall Corporation: IMPRO CCRO (USA)

URL: **www.pallwater.com**
Pall CCRO technology, IMPRO CCRO, is the Desalitech system.

6.4.2.8. ROTEC WFI Group: FR-RORO (Israel)

URL: **www.rotec-water.com**

Same as ADEDGE, who is the US distributor

6.4.2.9. Saltworks Technologies Inc.: UHP RO (USA)

See discussion above under high pressure RO systems.

6.4.3. Osmotically Assisted RO (OARO) / Cascade RO Systems

6.4.3.1. Battelle Memorial Institute: CRO (USA)

URL: www.battelle.org

Status: *Battelle licensed the technology to Gradiant, and there are no search results for the technology on the Battelle 2020 website.*

Company Information: Battelle is a large research and product manufacturing organization crossing many disciplines. The cascade RO (CRO) system is fed by concentrate from a conventional RO step. Feed is to an intermediate RO unit in the cascade sequence. There may be some additional recycle/mixing of streams to enhance the general system to influence the osmotic pressure difference across the membrane (e.g., mixing some concentrate with permeate). Lower rejection membranes could be used at some steps.

6.4.3.2. Gradiant Corporation: CFRO (USA)

URL: www.gradiant.com

Status: *The 2020 website review mentioned that a demo project has been in operation since November 2019 in Saudi Arabia and that Saudi Arabia Water Company (SAWACO) and GRADIANT are in the process of forming a joint venture to deploy counter flow reverse osmosis (CFRO) and other seawater desalination technologies across the Kingdom of Saudi Arabia. It was mentioned that the technology is now being scaled up to 917 gpm (5,000 m^3/h). A September 2020 press release mentioned that Gradiant consolidated its membrane innovations into an integrated technology suite, RO Infinity (ROi), that included CFRO, advanced RO, and FO technologies. An August 2020 news article mentioned that Gradiant won 12 projects across the Asia Pacific region which included ZLD and industrial wastewater reuse projects (Smart Water Magazine, 2020).*

The 2017 website made no mention of work in the RO area. Since that time, Gradiant licensed the cascade technology developed by Battelle.

Company Information: In the CFRO process, a dilute saline solution is introduced to the product side of the membrane. This reduces the osmotic pressure differential across the membrane and thereby reduces the required feed pressure. Brine is cascaded through multiple CFRO stages without exceeding the maximum pressure limitations of standard RO equipment, producing a saturated brine stream and purified product water stream.

Overall, a somewhat high salinity feed (such as concentrate from a standard RO unit) enters one end of the cascade and flows counter-current to the concentrate exiting the same end.

6.4.3.3. Hyrec Su ve Enerji Teknolojileri A.S.: OARO (Turkey)

URL: www.hyrec.co

Status: *Hyrec was established in 2015 to develop commercial applications of the founders' patented osmotically assisted reverse osmosis (OARO) Technology. In 2017, the website stated that Hyrec's prototype was operational and an 18 gpm (4.1 m^3/h) pilot system was under construction in Turkey. The 2020 website mentioned that since February 2018, Hyrec has been operating a near commercial-sized plant with a feed capacity of 32 gpm (7.3 m^3/h). Industrial scale projects are expected to take place in conjunction with commercial partners from the U.S., Indonesia, Kuwait, Japan, India, and Germany in mid-2019. In 2019, Saudi Arabia's Saline Water Conversion Corporation (SWCC) and Hyrec Technologies Ltd. signed a Memorandum of Understanding to deploy Hyrec's OARO technology for Zero Liquid Discharge desalination in the Kingdom of Saudi Arabia.*

Company Information: The Hyrec Membrane Concentrator is a cascade RO system with feed to an intermediate stage. The intent of the system was to replace the energy- and cost-intensive thermal brine concentrator. There may be some changes in end unit. The cascade may involve an FO step feeding the cascade system.

The website mentioned that that the design is especially feasibly for textile manufacturers because it allows them to use higher salinity brine in their process. Recovery of Na_2SO_4 and NaCl for use in textile dyeing process was also mentioned.

6.4.3.4. Nanyang Technological University: EERO (Singapore)

URL: www.ntu.edu.sg

Status: *There is no specific website for the technology. There are a few published papers and conference presentations (e.g., Chong et al. 2015 and Chong, and Krantz 2018).*

Company Information: The energy-efficient reverse osmosis (EERO) process involves a countercurrent membrane cascade with recycle (CMCR) system where the feed to the system is typically concentrate from a single stage RO unit. Nanyang Technical University (Singapore) has applied for patents, and some testing has been done. Extensive modeling and simulation studies have provided insights into best configurations, and resulting performance, cost, and energy projections.

6.4.4. Other RO Systems

6.4.4.1. Aquatech International Corporation: High Efficiency Reverse Osmosis (HERO)

URL: www.aquatech.com

Status*: The HERO system has had many commercial sales over the years and is referenced in the Aquatech website.*

Company Information: The HERO process has a long history. It is a specialized reverse osmosis system that operates at high pH to minimize silica scaling potential and to minimize organic fouling. It may include an ion exchange step, and/or a lime softening step - dependent on the feed water quality.

6.4.4.2. Clean TeQ Holdings Limited Water (Australia)

URL: www.cleanteq.com

Status: *The 2020 mentions offices in both Australia and China and technologies, including evaporation, ion exchange, and others in addition to reverse osmosis. An initial study of HIROX RO technology took place in 2010, and there were two sales in China in 2017 and 2018 for 55 and 65 gpm-sized equipment.*

Company Information: The high RO recovery HIROX technology can treat a wide range of feed waters by removing both suspended particles (TSS), di- and tri-valent cations, hardness, sulfate, and other dissolved contaminants via the integrated ion exchange and RO. The ion exchange step, DESALX, is a chemical free pretreatment that uses RO brine to continuously regenerate the ion exchange resins. The result is a robust high recovery process. The website claims low operational costs.

6.4.4.3. EET Corporation: HEEPM (USA)

URL: http://www.eetcorp.com

Status: *The HEEPM system was one of the early high recovery membrane-based technologies (Mickley, 2009). The RO portion was conventional. The ED portion appeared to be a unique design. Most of the information was dated in the 2000-2010 time period. EET Corporation is no longer operating.*

Company Information: High efficiency membrane electrodialysis technology is used to concentrate brines in desalination applications, and to treat high salinity water streams. A unique processing arrangement was used where the ED and RO (or NF) technologies both take feed from the same working tank. ED product water has several thousand ppm TDS and is returned to the tank and the RO (or NF) concentrate is returned to the tank. Thus, the system waste is the ED waste and the system product is the RO (or NF) product. This processing arrangement has smaller ED membrane areas than ED-only systems and less salinity in the RO feedwater.

6.4.4.4. Tandem RO (USA)

URL: none

Status: *There appear to be two versions of Tandem RO mentioned in the literature (Ning and Tarquin 2010). Both technologies were discussed in the 2006-2009-time frame and are associated with studies done in conjunction with UTEP. Evidently, the processes were not patented and/or never pursued further.*

Company Information: One version involves a brackish water RO followed immediately with a higher-pressure RO to attain high recoveries of over 95% for treatment of brackish water. The process is based on using effective antiscalants and cleaners and the finding that the rapid attainment of maximum TDS favors stabilization of RO concentrates with respect to scaling. The system is run in batch mode with a treatment time of about 2 hours. The process has been demonstrated at two locations one being at Kay Bailey Hutchinson Desalination Plant in El Paso. Studies were conducted with the participation of the University of Texas at El Paso (UTEP). The other version has a precipitation step between the two RO stages and is run on a continuous basis.

6.4.4.5. New Logic Research: VSEP (USA)

URL: www.vsep.com

Status: *The 2020 website shows that spiral wound RO units have been added to the product list. They may be used for treating lower salinity feed water before using the VSEP system.*

Company Information: New Logic Research's VSEP membrane system was one of the earliest high recovery systems on the market. The membrane system uses a vibratory shear mechanism to reduce fouling and increase membrane flux. The high sheer at the membrane-solution interface minimizes the effect of sparingly soluble salts, silica, and foulants on the membrane and thus on membrane performance. Sparingly soluble salts and silica are allowed to precipitate, and thus high recoveries are attained without pre-treatment. No chemicals are required in the process. Due to mechanical considerations, the individual module size is limited to flows of up to 60 gpm (14 m^3/h); however, many individual modules are easily incorporated into a multiple mgd processing scheme. Due to unique behavior of silica under shear, the system can process high salinity silica feed water. There are well over 200 installations in a wide range of industries.

6.4.4.6. O'Brien & Gere: ARROW (USA)

URL: www.obg.com

Status: *In 2017, there was no mention of the ARROW technology on the O'Brien & Gere website. In January 2019, O'Brien & Gere merged with Ramboll USA, Inc, and the 2020 website did not mention desalination in any form. The ARROW technology was highlighted in Mickley 2007 and Mickley 2011 reports and appeared in O'Brien & Gere websites during that period.*

Company Information: The unique aspect of the ARROW technology is where the treatment step to allow high recovery processing is located in the process steps. Instead of the typical front-end or inter-stage treatment, the ARROW technology places the treatment step at the back-end after the second membrane unit. The back-end treated water is then recycled, most typically, to the inter-stage site. Although the feasibility of this processing scheme is not obvious, modeling of the process reveals that this design can allow very high recovery operation. The primary benefits of this processing configuration are that the size of the stream to be treated is smaller in volume and the process has a smaller footprint. The result is a savings in capital cost.

6.4.4.7. Osmoflo Pty Ltd: Brine Squeezer (Australia)

URL: www.osmoflo.com

Status: *The 2017 website information revealed that Brine Squeezer technology had been deployed at a few sites and was now "available for viewing." Osmoflo is the largest Australia based desalination and water recycling company. An undated brochure describes the Brine Squeezer and the 2020 website lists a handful of case studies using the brine squeezer technology. It is not obvious what proportion of the Osmoflo RO desalination installations use the brine squeezer technology.*

Company Information: Brine Squeezer is a patented brute force process use of RO to achieve high recovery of up to 150,000 mg/L TDS. It is over 20 years old and uses high temperature, higher pressure, frequent cleaning, and a sacrificial coating for membrane protection. A portion of the concentrate is recycled. The result is lower flux, a 3-4 months membrane life but a high recovery process. Trade-offs between increased RO costs and smaller follow-on thermal processing costs were favorable for studies conducted. High RO recoveries may eliminate the need for thermal processing to achieve high recoveries. The system can be installed after a conventional RO system.

6.4.4.8. Slurry Precipitation and Recycle Reverse Osmosis (SPARRO) (USA)

URL: http://www.carollo.com/

Status*: SPARRO was invented by Graham Juby. There is no website. A Reclamation report and other literature discuss the technology (Juby et al., 2013).*

Company Information: The SPARRO process is a hybrid of conventional RO technology incorporating recirculation of seeded slurry through the RO system and promoting homogeneous nucleation and precipitation from the solution. Seed crystals (gypsum) are introduced to the feed stream, which is then pumped into tubular RO membranes. As the water is concentrated along the membranes, the solubility products of calcium sulfate, silicates, and other scaling salts are exceeded, and they preferentially precipitate on the seed material rather than on the membranes (Juby et al., 2013).

6.5. Summary

Performance and cost envelopes depend greatly on the salinity, volume, and composition of the feed water. For many of the technologies, performance and costs are not well defined due to limited number of implementations and the lack of published information. As a result, it is challenging and a bit speculative to generalize on the performance and costs of the technologies. However, there are some general statements that can be made.

HR RO systems extend the operating range of RO technologies to treat higher salinity feed waters and to concentrate feed waters to higher levels of salinity. In many situations, the HR RO technologies may follow the use of conventional RO steps due to the relative costs. An exception may be the application of smart systems in low salinity applications where the HR RO system may be the only RO system used.

One promising application area is in providing higher recovery treatment of lower salinity feed water, such as in municipal applications. Such treatment can be an alternative to expanding existing treatment facilities when greater water production is sought. Non-standard RO technologies are more likely to be accepted by the municipal sector than other high recovery technologies due to previous acceptance of RO technologies and due to their suitability to treating lower salinity feed water. It is clear that smart systems are the most likely of these technologies to make inroads into municipal applications due to their relative simplicity and indications of lower costs than the other types of non-standard RO systems.

Another promising area of impact is on MLD/ZLD processing where the non-standard RO technologies can take over some of role played by more energy- and cost-intensive BC and thus reduce the overall costs of MDL/ZLD processing.

Of the types of non-standard RO technologies addressed in this chapter, the status and role of OARO systems is the least well defined.

As with all desalination technologies, final residuals need to be managed and the residuals from higher recovery processing are not necessarily easier to manage than those from lower recovery processes. Yet, a frequent stated advantage of high recovery systems is that they reduce the volume of waste. As the final brine becomes more concentrated it generally makes disposal more difficult and costly and may eliminate alternatives. Some of the technologies, smart systems in particular, push past solubility limits in increasing the system recovery. The resulting brine must be quickly diluted or sent to settling tanks for handling. Final management of residuals is frequently not mentioned, although increasingly, the possibility of recovery of salts is mentioned without much detail.

As one exception and an example of addressing these issues, the Israeli MAX H2O Desalter system is of interest. It is still at a development stage with a limited track record but may be an indication of companies addressing the larger picture and taking steps to address final residual issues. It is a smart system that recovers solids as the final residual.

7. Electrolytic Technologies

7.1. Introduction

Electrolytic technologies use electrical current from powered electrodes to drive and separate ions of different charge. The two general types of technologies are deionization and electrodialysis. The technologies may involve ion exchange membranes and may also involve resins and adsorbing electrodes.

The types of technologies include:

- Electrodeionization: EDI, continuous electrodeionization (CEDI)
- Capacitive deionization: CapDi, membrane capacitive deionization (MCDI)
- Electrodialysis: ED, electrodialysis reversal (EDR), and electrodialysis metathesis (EDM)

These electrodeionization technologies are suited for polishing very low salinity feed water to produce very high purity water. Applications typically require feed to be first treated by RO to obtain the low salinity feed. These technologies do not play a part in high recovery processing. However, they are included here as they represent part of the continuum of electrolytic technologies and provided the basis for development of modifications to treat higher salinity feed water.

Capacitive deionization technologies were developed to treat higher salinity levels. They are most suited for brackish waters of less than perhaps 4,000 mg/L TDS. Some companies are conducting R&D to extend treatment for higher salinity feed waters.

The ED-related technologies are used for treating brackish waters of higher salinity levels. EDR systems have generally not competed well with RO systems when salinity levels are above perhaps 15,000 mg/L TDS. Changes in EDR design and use of EDR systems in conjunction with RO can take advantage of some of the relative benefits of EDR over RO. Some companies are looking to extend the feasible operating range to high salinity levels.

Because of the distinct differences between the types of technologies the discussions in this chapter are separated by technology type.

7.2. EDI and CEDI Technologies

7.2.1. Operating Principles

Figure 19 shows the general cell design of EDI devices. EDI combines ED and ion exchange technologies. Cation and anion resins in the feed channel are initially in their H+ and OH- forms. During operation, the ion exchange resins remove and temporarily retain the ions from the feed solution—allowing these to be transported across the ion exchange membranes toward the powered electrodes.

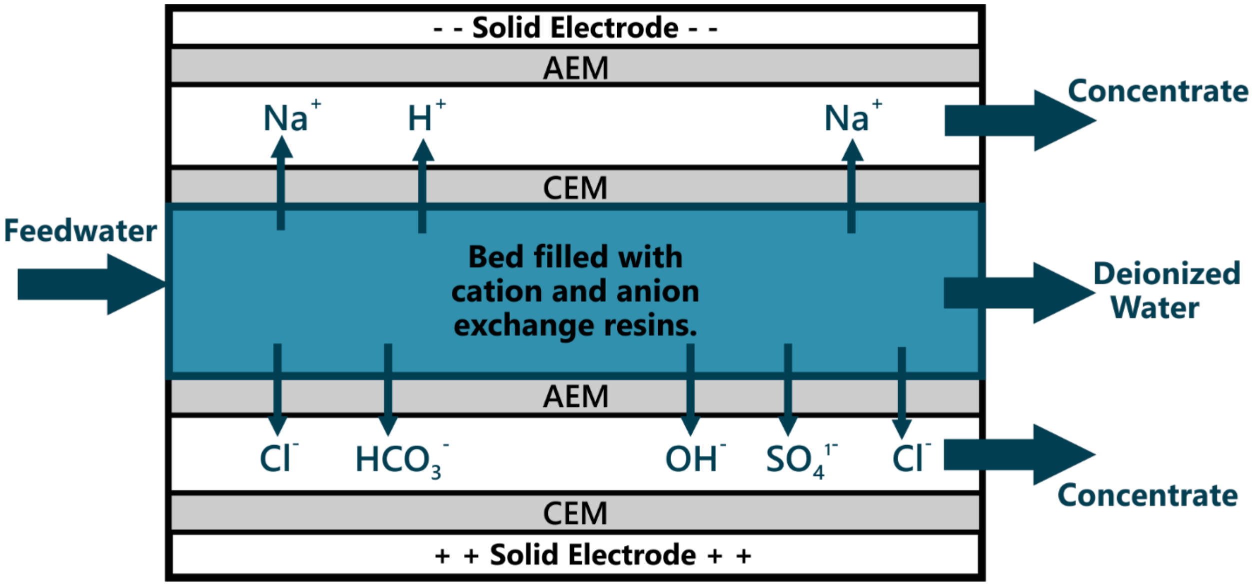

Figure 19. EDI schematic. AEM = anion exchange membrane; CEM = cation exchange membrane.

EDI devices may comprise media of permanent or temporary charge, and may be operated batchwise, intermittently, or continuously. The process can be continuous without chemical regeneration of the ion exchange (IX) resin. In continuous electrodeionization (CEDI), the resins remain in their salt form and the electric current regenerates the resin mass continuously as a result of water splitting producing H^+ and OH^-. CEDI technique can achieve very high purity, with conductivity below 0.1 microSiemens per centimeter (µS/cm). Other variants of the technology allow removal of weakly ionized compounds and sequential removal of ions and silica in stages.

CEDI requires extensive pretreatment of the feed water to achieve TDS levels below 30 mg/L and to remove dissolved gases and foulants. The low conductivity of the water at these salt levels is very low and below that where ED will work effectively. CEDI is a polishing step and is often used in combination with a RO system; this method can provide very pure water.

Applications include:

- High purity water: for semiconductor industry, power industry, laboratories, pharmaceutical, biotechnology and hospitals. EDI and CEDI can produce water with very low salt concentrations from 0.01 to 0.1 mg/L.

- Boiler and steam generation feed water

- High quality rinsing water: for electronics, surface finishing, and optical glass applications.

7.2.2. EDI and CDI Companies

7.2.2.1. Current Water Technologies, Inc. (Canada)

URL: currentwatertechnologies.com

Status*: Current Water technologies last press release on its website was in early 2019. A video mentions multiple systems installed worldwide.*

Company Information: Current Water has patented electro-static deionization (ESD) (deionization) and patented AmmEL (ammonia removal) technologies for producing very high-quality water for boilers and cooling systems. This is the same technology previously developed under a subsidiary, ENPAR, and presented in ENPAR's 2017 website, which no longer exists.

7.2.2.2. Evoqua Water Technologies, LLC. (Pennsylvania)

URL: www.evoqua.com

Status: *The 2017 website described the NEXED EDR system. The 2020 website mentioned that thousands of CEDI systems have been set up and are in commercial operation to create ultrapure water at capacities that range from less than 0.5 to more than 1,100 gpm (0.11 to 250 m^3/h). There was no mention of the NEXED EDR system in the 2020 website – an inquiry confirmed that production had been suspended.*

Company Information: The combined NEXED EDR and Ionpure CEDI system is designed to desalinate seawater at about 35,000 mg/L TDS to less than 500 mg/L TDS by using ED followed by polishing with EDI. More typically the NEXED EDR process would be used as:

1) treatment to feed water up to 15000 mg/L—as replacement to RO
2) pretreatment to RO for higher salinity applications.

The CEDI process is for polishing only (low salinity feeds) to provide high quality product water.

7.2.2.3. Mega a.s. (Czech Republic)

URL: www.mega.cz

Status: *Both the 2017 and 2020 websites discussed a wide range of industrial applications and case studies.*

Company Information: Mega is an established company that makes both EDR systems for treating high salinity water and EDI systems for low salinity polishing applications. The EDR systems were developed for high salinity water treatment in industrial applications such as RO brine concentration, pre-concentration before evaporation, ZLD applications and treatment of different types of industrial waste waters. Systems can concentrate up to 200,000 mg/L. Claims are made for greater performance and smaller footprint designs than other versions of the technology. The EDI systems are designed for up to 600 gpm (136 m^3/h) processing to provide high purity water. Mega also provides electrodialysis equipment with bipolar membranes which can use the contained salts to produce acid and caustic that can be locally used in further production.

7.2.2.4. Snowpure (California)

URL: https://www.snowpure.com/

Status: *The 2020 website shows products made for conducting hemodialysis as well as for power, pharmaceutical, and laboratory applications. The website mentions that products are installed in over 50 power plants in China.*

Company Information: Snowpure was founded in 1979 after purchasing the EDI part of Electropure. The company also provides gas removal membrane products and ultraviolet (UV) equipment.

7.2.2.5. Suez Water Technologies (France)

URL: www.suezwatertechnologies.com

Status: *The global company Suez makes multiple water treatment products and offers a wide variety of related services. The 2020 website references several electrolytic products including ED, EDR, EDI, and bipolar ED.*

Company Information: Suez makes industrial EDI stack with a module with nominal flow of 15 gpm (3.4 m^3/h) for feed levels of less than 25 mg/L.

7.3. CapDi, CDI, RDI, and MCDI Technologies

7.3.1. Operating Principles

As depicted in Figure 20, CapDI/CDI uses porous electrodes to adsorb and later desorb ions from the water. For CDI with porous carbon electrodes, the ions are transported through the interparticle pores of the porous carbon electrode to the intraparticle pores, where the ions are adsorbed. Co-ions as well as adsorbed counter-ions enter the porous electrode. After the electrodes are saturated with counter-ions, the adsorbed ions are released for regeneration of the electrodes by reversing or reducing the electrical potential between electrodes. Both types of ions leave the electrode pores and are flushed out of the cell resulting in a high salt concentration brine stream.

The MCDI version, depicted in the right side of Figure 20 includes ion selective membranes. The membranes restrict the movement of co-ions in a way that enhances the movement of counter-ions through the membranes and into the porous electrode. This results in MCDI using less energy than CDI.

7.3.1.1. Attributes

- Operation requires no high pressure or temperatures.
- Modular systems are scalable and simple to operate.
- Simple, chemical free operation.
- Tunable: can change input and output easily; unlike RO.

- Low energy cost for treatment of low salinity water.

- The energy cost per volume of treated water scales approximately with the amount of removed salt, while in other technologies such as RO, desalination energy scales roughly with volume of treated water. This makes CDI a viable solution for desalination of low salt content streams, or more specifically, brackish water.

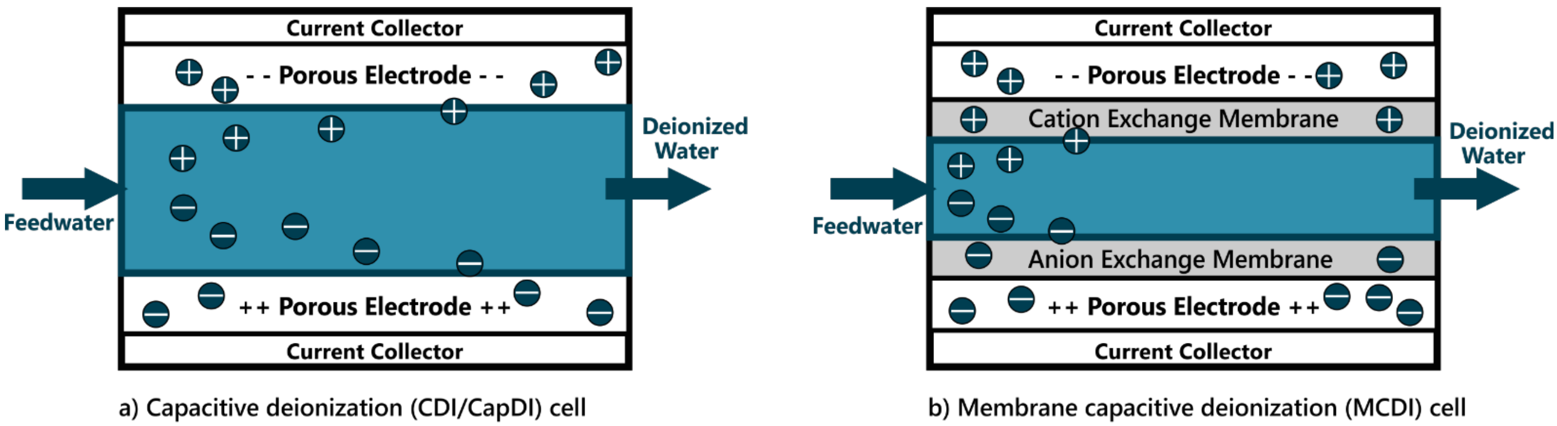

Figure 20. CDI/CapDI and MCDI cell configurations shown during adsorption cycle.
Where + = cations and - = anions.

7.3.1.2. Limitations

- Use is restricted to low salinity applications.
- Units cannot remove uncharged particles
- Units cannot remove silica & clay

7.3.1.3. Applications:

- The market for CDI, CapDI, and MCDI is small relative to that of EDI.

- These systems can soften feed water to boilers and cooling towers, polish tertiary wastewater effluent for reuse and desalinate low salinity brackish surface or ground water to make it suitable for industrial reuse.

- The applications generally are for salinity levels above what EDI technologies can treat, and below that which EDR and RO systems can treat.

7.3.2. CapDi, CDI, RDI, and MCDI Companies

7.3.2.1. Atlantis Technologies (California)

URL: www.atlantis-water.com

Status: *The 2020 website shows 6 pilot case studies covering mining, oil and gas, power, and groundwater applications. Four have treated feed water of less than 8,000 mg/L TDS. Product water ranges from 400 to 1,200 mg/L TDS. Two others treated feed water of 43,000 and 83,000 mg/L TDS where product water TDS were 12,000 and 28,000 mg/L respectively.*

The 2017 website review had similar information as the 2020 review other than the case study listings.

Company information: Radial deionization (RDI) is a proprietary form of CDI where each device in a series removes a portion of ions from the stream until the target dissolved solids level is reached. This design aspect is stated to be critical to its superior performance and a key difference between and other versions of CDI. The 2020 website review showed a module size of 5 gpm (1.1 m^3/h). A 4 foot by 14 foot skid contains 20 cylinders and is designed to fit in a semi or flatbed. This system can process up to 100 gpm (23 m^3/h) depending on the incoming salinity level. The design allows for water to flow across 1 to 10 meters of continuous electrode. The current state-of-the-art CDI only allows for flow across 10 cm of material, or $^1/_{100}{}^{th}$ of the distance. The long distance allows for greater TDS reduction and for processing of very high TDS streams and flow rates. Recovery is said to be regularly above 80% and can reach as high as 95%.

Precipitation of low-solubility salts such as sulfates and hardness do not cause fouling within the device. The TDS capability range is said to span from 500 mg/L to over 100,000 mg/L and thus outperforming competitive CDI technologies. The RDI system removes any salt without fouling including carbonates, sulfates, nitrates, and heavy metals.

7.3.2.2. AQUA Ewp LLC. (Texas)

URL: www.aquaewp.com (no longer active)

Status: In 2020 t*here was no website or company. A discussion with the owner suggested that AQUA Ewp worked mainly with CDI and that CDI, MCDI and CapDI were essentially the same and were never financially viable. This 2020 picture was somewhat in contrast to the 2017 website review showed an article claiming over 1,000 installations of small systems.*

Company Information: The technology was used to desalinate low salinity feed waters and thus on a smaller market than that of EDI which is mainly for polishing.

7.3.2.3. Idropan Plimmer dell'Orto Depuratori S.r.l. (Italy)

URL: www.idropan.it (no longer active)

Status: *There was no website in 2020. A 2016 website review showed small units being used for treating very low TDS waters. The website said there were over 400 installations of the Plimmer CDI unit.*

Company Information: Most of the units listed in the 2016 website had capacities of less than 1 gpm (0.23 m^3/h). The largest unit was close to 2.5 gpm (0.57 m^3/h). Applications included providing drinking water for rural and urban areas, health centers, schools, hotels, and kitchens, as well as process water for food and beverage and pharmaceutical manufacturing sites.

7.3.2.4. PowerTech Water, LLC. (Tennessee)

URL: www.electramet.com

Status: *The 2020 website review showed PowerTech, founded in 2014, having received several innovative technology awards.*

Company Information: In early 2020 the ElectraMet CDI technology was introduced as the most advanced solution for removal of heavy metals from industrial wastewater. A 7 gpm (1.6 m^3/h) system was installed at as light bulb manufacturing plant to address lead removal. Company literature refers to 100 gpm (23 m^3/h) systems.

7.3.2.5. Voltea, LTD. (The Netherlands)

URL: www.voltea.com

Status: *Voltea has an office in the Netherlands and one in Texas. The 2020 website lists case studies from 2020, mostly from breweries and coffee shops.*

The 2017 website mentioned applications for treating water up to about 2,000 mg/L TDS and that the energy use is 40-70% that of RO. A 2018 memo from the Texas office stated that as of late 2018 orders had increased over 300% in a 12-month period.

Company information: The tunable water deionization technology is designed to remove dissolved salts from a variety of water sources ranging from tap water and brackish groundwater to industrial process water. Module size was 2 gpm (0.45 m^3/h) but had been used in multiple unit arrangements to treat 100 gpm (23 m^3/h) inflow. The 100 gpm system was housed in a 40-foot container.

7.4. ED and EDR Technologies

Electrodialysis (ED) is an electrochemical technique to remove ions from water (Figure 21). In ED, water flows through a flow channel between a pair of ion exchange membranes; one side of the flow channel is formed by a cation exchange membrane (CEM) selective for positive ions, and the other side by an anion exchange membrane (AEM) selective for negative ions. Under the influence of an electric field, positive ions will travel towards the negative electrode, and negative ions towards the positive electrode. Half of the flow channels in an ED stack are therefore used to transport water with an increased ion concentration and the other half to transport water with a decreased ion concentration. In this process, ions are transported through membranes and water molecules stay behind. The process requires pretreatment to limit feed water turbidity, hardness, organics, and scalants other than silica. Electrodialysis reversal (EDR) is based on a similar principle as ED, with the difference that the polarity of the electrodes is reversed at regular intervals. This leads to a certain degree of self-cleaning of the membranes, as forces bringing scalants and foulants to the membrane are reversed. Frequent polarity shifts lead to lower the water recovery.

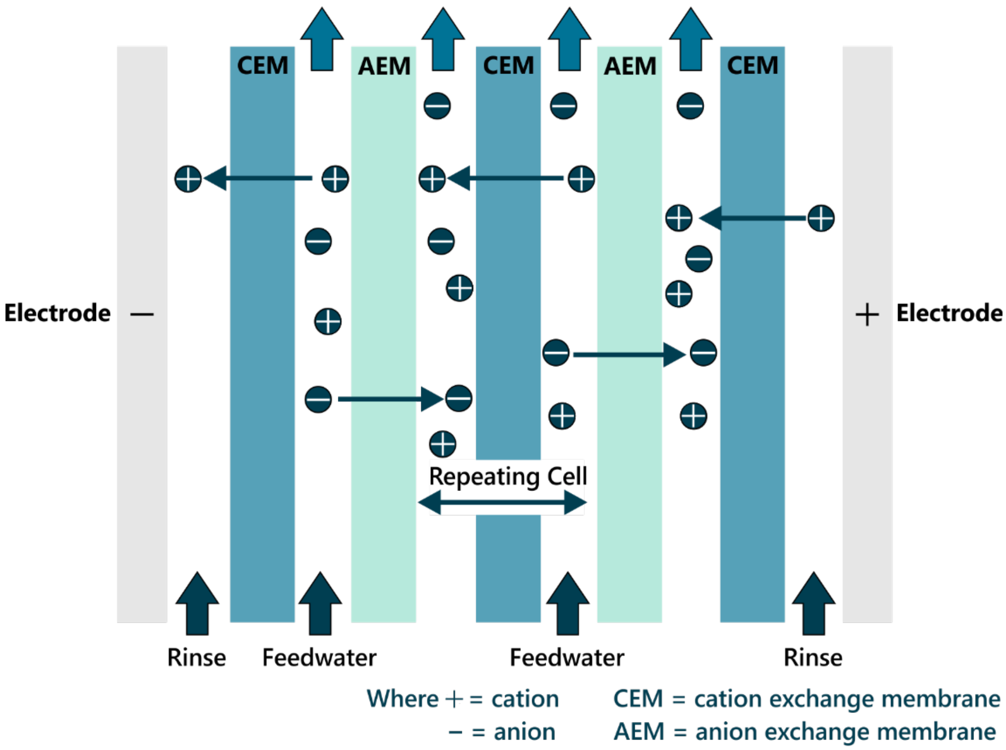

Figure 21. Electrodialysis cell configuration.

7.4.1.1. Attributes

- Historically, EDR has been used as an alternative to RO for the treatment of lower salinity brackish water.
- Cost competitive with RO for feed TDS < 15,000 mg/L
- Cleaning is less disruptive than with RO; can maintain production by turning up energy on units still producing
- Longer life than RO due to low pressure operation
- Tunable: can change input and output easily; unlike RO
- No specialized valves, piping, and pumps
- Quieter than RO

7.4.1.2. Limitations

- **Pretreatment:** Silica passes through the ED membranes and does not pose a scaling or fouling issue. However, as other scalants (e.g., calcium sulfate and calcium carbonate) have a charge, they can concentrate and cause fouling and scaling and usually require pretreatment to remove those species that coat, precipitate onto, or otherwise "foul" the surface of the ion exchange membranes. Like RO, frequently antiscalants are needed to manage scale formation. ED and EDR use chemicals and require monitoring and control to prevent biofouling and scaling.

- **Removal capabilities:** Won't reduce total organic carbon (TOC) or total suspended solids (TSS)

- **Product water quality:** ED and EDR become less economical and less efficient when very low salt concentrations are required in the product water.

- **Operations:**
    - Requires sophisticated controls
    - Energy requirement increases with feed water salinity
    - Cannot handle particles that are not charged; including silica and clay
    - Low energy efficiency at low salinity levels as greater voltage is required to provide current necessary for removal of charged species.

- **High costs:** EDR becomes costly as the amount of salt removed increases; thus, when recovery increases and when feed water salinity increases. The historical operating region is between that of deionization devices and RO.

7.4.1.3. Applications

- **Brackish water desalination:** The major application of ED/EDR has historically been the desalination of brackish water as an alternative to RO.

- **Large scale water production:** ED/EDR is a suitable method to produce desalinated water at large scale, supplying towns and large factories.

- **Industrial wastewater treatment:** ED/EDR is applied in wastewater treatment systems in processing rinse waters where it is a suitable method to reduce not only TDS, but particularly inorganic elements like nitrates, sulfates, radon, and bromides.

7.4.2. ED and EDR Companies

7.4.2.1. BDL Environmental Technologies

URL: www.bldcleanwater.com

Status: *The 2020 website information is identical to that of the 2017 website, thus the status and activity of BDL is not known.*

Company information: BDL Environmental Technologies, LLC, has developed a ZLD system that incorporates extensive proprietary components, including pretreatment, and a unique combination of pressure and electrically driven membrane technology. A laboratory system has successfully treated various produced waters including treatment of extremely high TDS waters of over 300,000 mg/L. In early 2017, a 100 gpm (23 m^3/h) treatment facility will be built in Texas. Treatment can provide a range of product water including potable water, 12-pound (lb) brine, and various reuse liquids. The technology includes recovery of salts and metals resulting in near-zero and zero waste. Over $3 million has been invested in technology development and complete modular equipment systems have been produced. In 2015, the company (including a diagnostic/test laboratory) relocated to Colorado to take advantage of the sizeable oil & gas headquarter presence in the Denver area. The company is taking a Design-Build-Own-Operate (DBOO) marketing strategy.

7.4.2.2. Magna Imperio Systems Corporation (MI)

URL: www.magnaimperiosystems.com

Status: *The 2020 website content describes the innovative approaches taken to address limitations of conventional ED/EDR systems.*

From 2018: The higher recovery and lower energy was explained to result from a combination of items including the smart control system, the configuration of the system but mostly from the spacers in between the membranes. MI stated that they expect to have several more installations and will expand their operations considerably in 2019. The units being planned for 2018 go up to 50 gpm (11.4 m^3/h).

Company information: MI has a patented an electrochemical nano diffusion (END) process that they claim revolutionizes the EDR process and establishes new benchmarks in terms of energy efficiency and recovery for desalination technology. The END system can provide multiple product streams while treating water containing up to 100,00 mg/L of TDS. An example is given that one stream can contain less than 500 mg/L TDS, another stream could be less than 150 mg/L TDS, and a third stream containing as low as 1 mg/L of TDS and zero hardness. The system has low scaling and fouling potential and minimum anti-scalant use. Early impressive test results suggest that the END system may challenge RO. The early stage company has received over $200M investment capital (Global Water Intelligence [GWI], 2020).

7.4.2.3. Suez Water Technologies (FRANCE)

URL: www.suezwatertechnologies.com

Status. See Section 7.3.5.

Company information: The global company Suez makes EDR system with module sizes up to 150 gpm (34 m^3/h). Typical feed concentrations are listed as up to 4,000 mg/L.

7.5. EDM Technologies

7.5.1. Operating Principle

While ED/EDR systems use the conventional two-compartment cell, the EDM system uses a four-compartment electrodialysis metathesis stack (Figure 22). The input cells include one for the feed water and one for an NaCl stream. The system uses ion exchange membranes to separate multivalent cations from multivalent anions in one step. One exiting concentrating stream has mixed sodium salts and the other has mixed chloride salts. This prevents the formation of $CaSO_4$ solids and allows higher than otherwise recovery. The elimination of treatment limitations due to high feed levels of $CaSO_4$ is at the expense of adding NaCl.

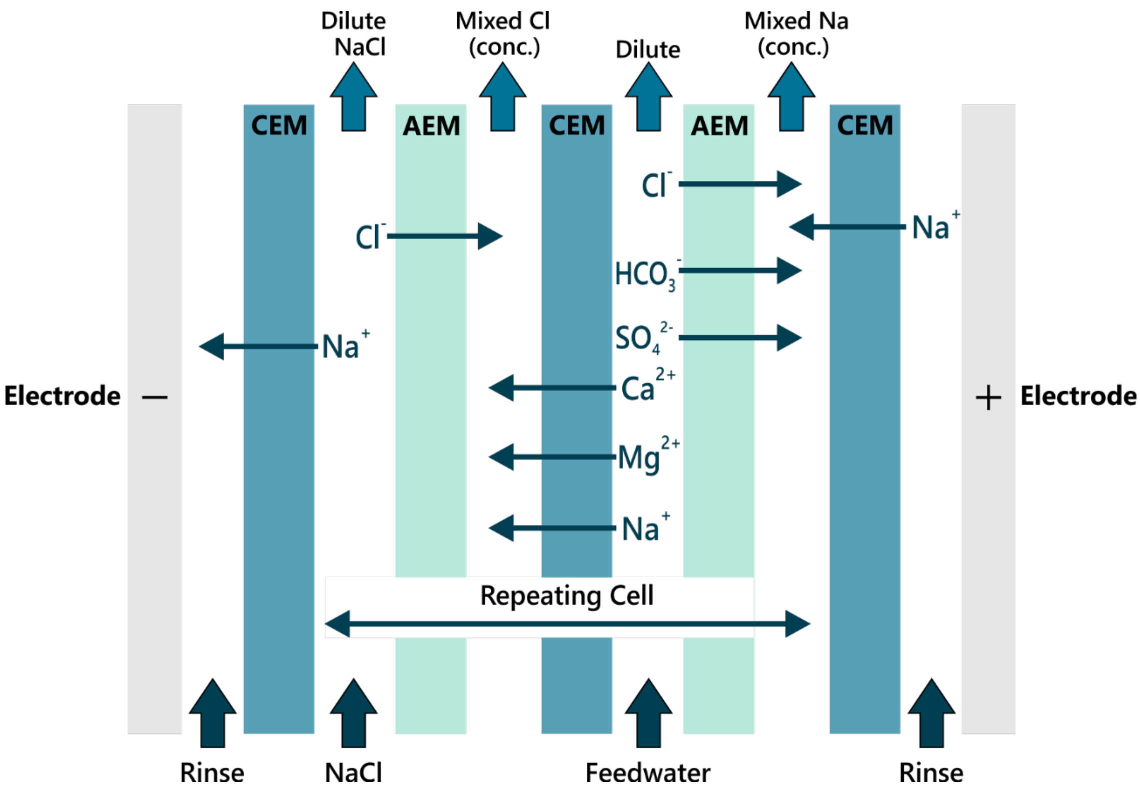

Figure 22. Electrodialysis metatheses cell configuration.

7.5.1.1. Attributes

- EDM technology is ideal for waters with a high risk for scaling hardness and for waters with high levels of sulfates.

- EDM is a high concentration process producing separate concentrate streams for SO_4 and Mg/Ca ions.

- Because EDM avoids some scaling issues with silica and $CaSO_4$, it requires less pretreatment and can get to higher degrees of concentration of these constituents.

- EDM is suitable as hybrid (bolt-on) brine concentration technology for brackish water RO
- RO-EDM hybrid concept may can achieve water recoveries of 98-99%, resulting in higher water income and lower disposal cost
- Low waste volume

7.5.1.2. Limitations

- The original system requires a surplus of monovalent anions and cations in feed stream. Otherwise NaCl addition into feed stream is needed to keep mass balance.
- EDM which is restricted to waters that have high levels of Ca and SO_4.
- As with all ED-based processes, EDM costs increase more rapidly with feed water salinity than do RO-based systems.

7.5.1.3. Applications

- Treatment of groundwater and industrial waters having high levels of hardness and sulfate

7.5.2. EDM Companies

7.5.2.1. Fujifilm Manufacturing Europe B.V. (The Netherlands)

URL: www.fujifilm.com

Status: *Tests conducted in 2016-2017 at two desalination plants in Spain showed higher recovery levels and lower energy consumption than published results from earlier EDM systems.*

In April 2020, it was announced that researchers from the Center for Inland Desalination Systems (CIDS) at the University of Texas at El Paso, have partnered with Fujifilm to study the electrical and hydraulic efficiency obtained from brackish water through the use of new methods of electrodialysis.

Company information: Fujifilm, a maker of ion exchange membranes, has developed a variation of the EDM system that overcomes the limitation of having to supply NaCl for operation. This is brought about by using a combination of monovalent and divalent ion exchange membranes. The entering feed stream, the only input stream, flows between two monovalent ion exchange (IX) membranes. The resulting product stream having lower levels of monovalent ions, is recycled to flow between two divalent IX membranes where divalent ions are removed before exiting the system. The other two exiting streams, like that of the original EDM design, consist of one concentrate stream containing mixed sodium salts and another concentrate stream containing mixed chloride salts.

7.5.2.2. Veolia

URL: https://www.veoliawatertechnologies.com/en

Status: *Zero Discharge Desalination (ZDD) EDM technology was invented by Tom Davis, the founder of ZDD and later the CIDS Director. CIDS and Veolia Water Technologies (Veolia) demonstrated the technology in a Reclamation DWPR project. Reclamation (2014) summarized the results obtained from the multi-year research effort. In 2017, Veolia licensed the original EDM technology from ZDD to broaden their extensive water treatment portfolio. The license was later abandoned and there was no mention of ED, EDR or EDM in the 2020 Veolia website.*

Company Information: The ZDD EDM technology was demonstrated at the Brackish Groundwater National Desalination Research Facility (BGNDRF) in Alamogordo, New Mexico, and piloted in Colorado and California. High recovery (96-98% overall recovery) was demonstrated at each site and data for evaluating capital and operational and maintenance costs were gathered for use in cost models.

7.5.2.3. Saltworks

URL: www.saltworkstech.com

Status: *Saltworks licensed the original ZDD EDM technology after Veolia gave up the license. The 2020 website does not mention the term EDM.*

Company information: The Saltworks EDR system was described as using next generation IonFlux IX membranes and their patented electrode protection approach that blocks hardness out of EDR electrode. As a result, there is no need to remove hardness before treatment. The system can use monovalent selective membranes for (as examples) removal of lithium, separate chlorides from sulfates. The EDR system is still in the piloting stage.

Saltworks makes several other technologies that can be use with the Xtreme RO technology including: XtremeUF, for concentrating slurries; IonSelect, selective ion removal; SaltMaker evaporative crystallizer; and FlexEDR, for selective removal of monovalent ions.

7.6. Other Technologies

7.6.1. New Sky Energy (Colorado)

URL: www.newskyenergy.com

Status: *The 2020 website has a copyright date of 2016 and no mentioned of activity beyond 2016.*

Company information: The company won several technology awards from 2009 through 2014 for a SaltCycle Process that converts industrial waste and agricultural brines into useful acid, base, and carbonates. A first stage concentrates and sequentially precipitates salts (e.g., sodium chloride or sodium sulfate). In the second stage, these salts are converted in patented New Sky chemical or electrochemical reactors to produce acid, base, and sulfates. The base (sodium or potassium hydroxide), can be converted via New Sky's CarbonCycle Process into useful carbonates such as soda ash or bicarbonate.

7.7. Summary

To date, of the electrolytic technologies, only electrodialysis has made an impact on high recovery processing as an alternative to RO. Deionization technologies are currently suitable only for treatment of low salinity feed water. EDI/CEDI units typically polish feed water of only 30 mg/L TDS or less and CapDI-type technologies are used to treat feed water of about 4,000 mg/L TDS and lower. There has been interest, however, in extending the treatment salinity range of CapDI devices and that is the reason including these in the chapter.

Due to energy requirements ED and EDR technologies historically have been focused on treating lower salinity feed waters.

Some companies, however, have been developing designs for EDR systems to allow higher salinity applications. Potential impact of EDR systems on high recovery processing would likely be in:

- Increasing the performance of EDR systems through innovative design (such as may be the case with Magna-Imperio and Saltworks).
- Use of specialized EDM systems providing costs can be reduced (such as may be the case with Fujifilm).
- Using integrated EDR/RO processing sequences that would take advantage of the advantages and disadvantages of each technology.

One such historical integrated effort was the High Efficiency Electro-Pressure Membrane (HEEPM) system developed by EET Corporation (see Chapter 6). A common feed tank provides source water for both a high efficiency EDR device and an RO device. The EDR product is returned to the tank and the RO concentrate is returned to the tank. Thus, the system waste is the EDR waste and the system product is the RO product. This arrangement minimizes EDR membrane area relative to EDR only systems while maximizing recovery relative to RO only systems. There is no mention of the HEEPM device in recent literature.

8. Forward Osmosis (FO) Technology

8.1. Operating Principles

In FO, water is spontaneously drawn through a semipermeable membrane due to osmotic pressure differences. Water flow is from the more dilute feed solution to a more concentrated draw solution with the result that the feed side solution becomes more concentrated. This process (referred to as osmotic dilution) is not a desalination process as the permeate side solution consists of the draw solution diluted by the transported water. This situation is illustrated in Figure 23.

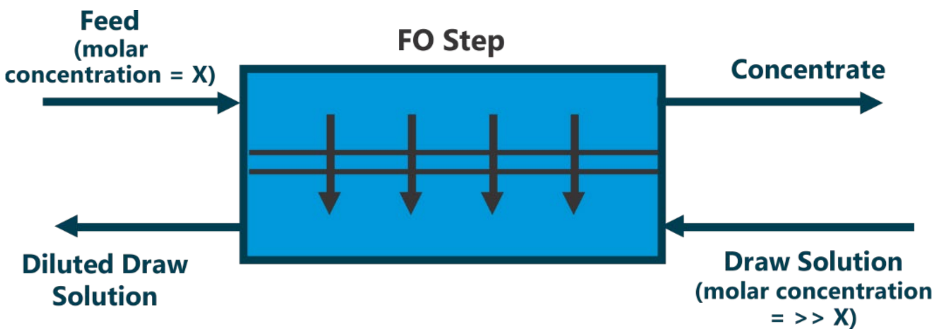

Figure 23. Stand-alone FO without recovering the draw solution.

FO without separation of transported water from the draw solution is a low energy process step compared to RO, but FO must be paired with a draw solution regeneration process for desalination applications. As depicted in Figure 24, the separated draw solution is reused (recovered). An RO, NF, thermal, or other separation step may be used to recover the draw solution and provide the desalinated water.

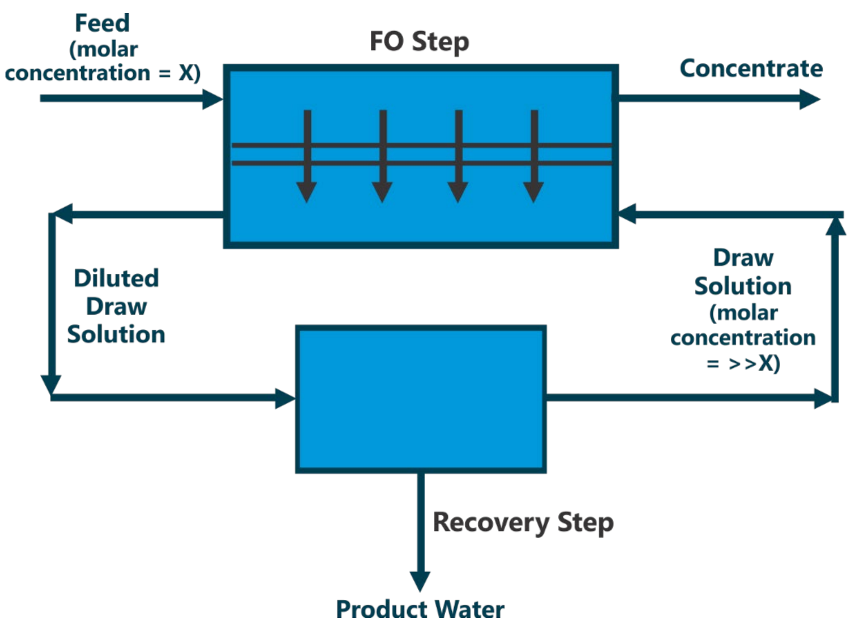

Figure 24. Hybrid FO system.

The osmotic pressure difference is not a hydraulic pressure difference, but this pressure difference can force an equivalent flow. The osmotic pressure driving force in FO can exceed that possible in pressure-limited RO systems, and as a result, FO can treat feed waters of higher salinity and concentrate feed waters to higher salinity levels than possible with RO.

8.1.1. Attributes

- **Low Fouling Propensity.** Because FO operates at low pressure, the propensity for fouling can be less, and fouling layers are less compact and more reversible than in higher pressure RO systems. In most cases FO membrane fouling can be reversed by water flushing, and chemical cleaning may not be necessary. This can result in reduced operating cost for fouling control and in extending the use of FO to treat feed waters with high fouling potential. Low pressure operation and fouling reversibility can lead to less frequent membrane replacement.

- **High Rejection.** High rejection of feed water contaminants supports higher quality water demands due to changing water quality standards

- **High Salinity Operation.**

    - Feedwater can be concentrated to higher salinity levels than RO, resulting in higher salinity feed water applications and competing with conventional thermal evaporative systems for concentrating feed water.

    - Low temperature high-level concentration maintains the quality of components susceptible to heat. This is important to food and pharmaceutical industries.

- **Low Cost Materials.** There is no need for high pressure tubing or high temperature operation. This reduces system material costs.

8.1.2. Energy Considerations

While the FO step is low energy, the FO-hybrid process includes a high energy draw solution recovery step. This system is not more energy efficient than other membrane processes. A thermodynamic energy analysis (Shaffer et al., 2015) reveals that an FO system with draw solution recovery by RO (hybrid FO-RO) consumes more energy than RO alone to achieve a certain recovery. An FO-hybrid system with thermal evaporative recovery of draw solution is even more energy intensive.

Relative to the FO-RO hybrid, other FO hybrid systems may provide energy cost savings. For example, low-cost thermal energy (such as waste heat) can be used to power the draw solution recovery step (a hybrid FO-thermal process). Waste heat, however, is often not available without cost.

In the non-desalination process of osmotic dilution, both the diluted and concentrated solutions are the products, and no draw solution recovery is necessary. Elimination of the energy intensive draw solution recovery results in a very low energy FO process). An example of this non-desalination application is the extraction of water from raw sewage by liquid fertilizers with subsequent use of the diluted fertilizer (Bilad, 2019).

8.1.3. Membranes

A major limitation of the FO technique is the lack of enhanced and reliable, specifically designed membranes. Water transport through the FO membrane is limited by a number of phenomena—internal concentration polarization, external concentration polarization, fouling, and reverse salt diffusion (Blandin et al., 2014). Membrane considerations include structural parameters, reverse solute flux selectivity, surface properties for fouling control, and permeability-selectivity tradeoff. Present FO membranes are of low flux that result in large membrane areas for treatment, leading to high capital costs.

8.1.4. Draw Solution

A wide variety of draw solutions have been studied, and along with membrane development this area continues to be a research focus. Desired properties for draw solutions include high osmotic pressures, low viscosity, and low energy requirements for recovery. A major drawback has been the unavailability of effective draw solutions for the use of FO for high salinity reject brine treatment.

8.1.5. Recovery of Draw Solution

Feed water foulants and scalants are excluded from the draw solution, enabling the conventional desalination processes to operate at high recovery for draw solution re-concentration. Recovery of the draw solution requires separation of the draw solution from the dilution water. Various membrane- and thermal-based processes have been used, including RO, NF, and evaporation/distillation. RO recovery is limited by the osmotic pressure of the diluted draw solution relative to the pressure limits of the RO process. Brackish water RO may be used for lower draw solution osmotic pressures; seawater RO for intermediate levels; and high recovery RO for higher levels. However, at some higher osmotic pressure level, only thermal-based processes, including membrane distillation and evaporation, can be used.

In other words, when FO is used to concentrate feed water beyond the salinity limit of RO, the osmotic pressure of diluted draw solution will surpass the bearable pressure limit of RO, and thus RO cannot be used to recover the draw solution. The development of draw solutes recoverable by thermal processing, such as ammonia−carbon dioxide (NH_3/CO_2), may allow FO to be incorporated into ZLD brine treatment systems (Tong and Elimelech, 2016).

Hybrid FO systems that use draw solutions recoverable by heat may be energetically favorable to distillation technologies for treating high salinity feed solutions. Only relatively small volumes of the draw solute must be vaporized and recovered from the draw solution, as opposed to vaporizing and recovering the solvent (water) in conventional distillation.

8.1.6. Limitations

Membrane-related and draw solution-related limitations of FO include:

- **Membranes:**
  - Lack of enhanced and reliable, specifically designed membranes
  - Low membrane flux
  - Limitation on mechanical resistance for some applications

- **Water and solute transport:**
  - Concentration polarization (CP)—both the internal CP that forms on the porous support side and the external CP that forms on the membrane's active layer —can decrease the overall water recovery
    Reverse salt diffusion lowers the efficiency of the separation process

- **Draw solution:**
  - Lack of effective draw solutions limits the use of FO for higher salinity brine treatment.

The high energy requirement of the draw regeneration step is a limitation. The use of waste heat will not reduce energy requirements, but may reduce energy costs.

Another limitation of FO, as with all emerging technologies, is that it is not well established compared with RO and for higher salinity brine treatment, compared with MVC brine concentrators. More pilot and field studies are necessary to validate their large-scale performance, energy consumption, and costs.

8.1.7. Applications

FO can excel with challenging feed waters. While FO is not more energetically favorable than RO for separation, in applications with feed waters that are challenging to treat because of high salinity, high fouling potential, or the presence of specific contaminants, FO can outperform or enhance RO and other desalination technologies (Shaffer et al., 2015). With suitable draw solutions FO can be used to desalinate high-salinity feed waters, while consuming less total energy than applicable thermal desalination technologies.

Operating at high concentrations and low temperatures makes FO more attractive than RO or thermal evaporation for concentration of heat-sensitive pharmaceutical and food and beverage compounds.

8.1.8. Operating Cost Considerations

While the stand-alone FO system (without draw solution recovery) is of low energy, the draw solution recovery requires energy. When the recovery step uses RO, the overall system has a greater energy requirement (Shaffer et al., 2015) than if a conventional RO system were used to accomplish the same separation. If recovery requires evaporation, then any the energy requirement for the system increases significantly. If available, the use of waste heat may lower the energy cost. Reducing the energy consumption of the recovery process is key issue determining applicability of FO systems in lowering the costs of high salinity processing and is a major research area for FO.

8.1.9. Capital Cost Considerations

The means of recovering the draw solution is an integral part of the FO equipment system and as a result, high CAPEX is a major issue with FO systems. Low membrane flux increases FO CAPEX by requiring greater membrane area per product produced.

8.2. FO Companies

A literature and Internet search found over 15 companies involved in making FO membranes, membrane modules, and treatment systems. Several other companies distribute membrane modules and systems. Some companies are new since 2017, and some companies operating in 2017 are no longer in the FO business. OASYS halted commercial operation in November 2018, after being a darling of the industry with a strong history of funding and with major installations in China. In 2017, Aquafortus had a unique and powerful osmotic draw solution suitable for driving an FO system. Since then, they have focused on a solvent extraction system where a patented absorbent uptakes water and, as a result, crystallizes the salts from the wastewater. The absorbent is regenerated to be recycled and, as a result, releases product water.

Major FO system makers include Forward Water (Canada), FTSH2O (Washington), Modern Water (UK), and Trevi (California). Major companies making and suppling membranes and membrane modules include Aquaporin (Denmark), FTSH2O (Washington), Porifera (California), and Koch (Massachusetts).

8.2.1. Forward Water Technologies, Inc. (Canada) – System Provider

URL: www.forwardwater.com

Status: *In 2017 Forward Water stated that they plan to be working with their first pre-commercial unit in the field by the end of 2017 and, by the summer of 2018 (or earlier), be ready to move onto the next step — "Design, Build and Transfer." In August 2019, Forward Water reported that they had moved into industrial scale piloting of a thermolytic forward osmosis draw solution with the launch of a 2.75 gpm (15 cubic meters per day [m^3/day]) wastewater treatment demonstration site in Canada.*

Company information: Forward Water Technologies uses a hollow fiber forward osmosis membrane technology developed by the Danish water technology company Aquaporin. According to a recent article published by Filtsep (Filtsep, 2020), an industrial scale pilot plant is demonstrating low cost, low energy consumption Zero Liquid Discharge (ZLD) of oil and gas flow back water and produced water.

8.2.2. Fluid Technologies Solutions, Inc. (*FTS H20*) (Oregon) – System Provider and Membrane Manufacturer

URL: www.ftsh2o.com

Status: *In 2017, FTSH20 was already commercially successful. They were making their own membranes, had a commercial FO site, and produced personal hydration products. Since then, various partnerships have been formed, and many application studies have been conducted.*

Company information: FTS H2O sells a wide range of desalination system equipment including RO, FO, and evaporation systems. Another FTS H2O product, the Low Temperature Evaporation Crystallization system, is discussed in the evaporative systems chapter.

8.2.3. Modern Water, plc. (UK) – System Provider

URL: www.modernwater.com

Status: *Modern Water's 2017 website revealed a focus on FO-based desalination and forward osmosis as a pre-treatment to reverse osmosis. The company had successfully developed, tested and commercialised the process, with plants in Gibraltar and Oman. Their process solution was fully operational & commercially available (Al Khaluf, Oman - the world's first commercial FO plant began operation in 2010).*

In 2020, Modern Water's website mentioned that their pioneering work on forward osmosis and osmotically-driven membrane processes had resulted in its first full-scale prototype being successfully built and operated in India. Partnerships had been formed in India, China, and Africa. Featured was the AMBC ('All Membrane Brine Concentrator'), an FO-RO system for brine concentration.

Company information: The AMBC was referred to as significantly reducing wastewater treatment requirements and maximizing clean water reuse by concentrating brine streams up to, and beyond, 160,000 mg/L. The RO recovery portion of the system could use either BWRO or SWRO units. The maximum size of each module is 92 gpm (21 m^3/h).

8.2.4. Trevi Systems (California) – System Provider

URL: **www.trevisystems.com**

Status: *In 2017 Trevi had 25 full-time employees. In 2014 plants had been sold to Kuwait and UAE. In 2017 Trevi was piloting many sites in the Middle East. Also, in late 2017 Trevi, along with Abengoa, Suez, and Veolia, was chosen to be part of the MASDAR desalination pilot program to research and develop energy-efficient, cost-competitive desalination technologies powered by renewable energy (Cleantechnica, 2015).*

In 2020, the Trevi website mentioned their negotiation with three suppliers of hollow fiber membrane elements for producing the membranes. As a back-up, in case these vendors do not meet the timeframes needed, Trevi is currently spinning its own membrane.

Company information:

The Trevi FO system uses an organic draw solution that is recovered by heating and separation by a coalescer. Trevi states that in addition to their proprietary draw solution their contribution to FO is in an energy recovery process associated with the system.

8.2.5. Aquaporin A/S (Denmark) – Membranes and Modules

URL: www.aquaporin.com

Status: *Aquaporin is the global leader in developing, producing, and marketing biomimetic membranes. Membranes for RO and FO were available in 2017 and Aquaporin was active with projects and business arrangements in Singapore and China. A 1 gpm (0.23 m^3/h) pilot to treat semiconductor wastewater was noted.*

In 2020, the Aquaporin website listed three different size FO membrane modules, the largest of which was for less than 1 gpm (0.23 m^3/h). Both RO and FO present focus is on small household, restaurant, hotel water, and medical hemodialysis systems.

Company information:

The Aquaporin membrane is a composite membrane which has an active layer consisting of aquaporin proteins, stabilized in a polymeric structure that is embedded on the surface during the polymerization process. The polymer structure provides physical support to the protein and protects the protein from proteases. The membranes can tolerate similar pH and temperatures and cleaning conditions as conventional membranes. The higher flux compensates the higher cost (BlueTech, 2016).

8.2.6. Koch Membrane Systems (Massachusetts) – Membranes

URL: www.kochmembrane.com

Status: *The 2020 website states that Koch has developed FO systems to process food and beverage streams from 3 to 50 gpm (0.68 to 11.4 m^3/h) and that the units are easily scalable to larger flow rates.*

Company information: Koch offers many types of membranes, including TIDAL Forward Osmosis Spiral Elements, which are available as sanitary and hard overwrap spiral wound elements. Individual module capabilities were not listed.

8.2.7. Porifera (California) – Membranes and Systems

URL: www.porifera.com

Status: *2017 website information discusses an FO concentrator technology that uses RO for draw solution recovery. The 2020 website lists RO recovery of draw solution as an option. Main focus appears to be on food and beverage applications.*

Company information: A membrane module specification sheet lists feed and draw solution rates of up to 10 gpm (2.3 m^3/h). An industrial FO-based ZLD system is listed for a minimum flow of 2 gpm (0.45 m^3/h) with upward scaling possibilities.

8.3. Summary

FO has been researched for many years and has received much attention in the literature and at conferences. In the past, it might well have been considered as a technology in search of a market. Within the past few years, the performance range of capabilities, applications, and costs has become better defined. Before going out of business in 2018, OASYS appeared to make great strides with multiple installations in China. There are still only limited numbers of FO other installations. Now, however, a handful of companies have more pilot, demonstration, commercial installations, have increased partnerships, and have more clearly defined their marketing niches. FO will continue to define and acquire a role in desalination processing—one substantially less than that of RO-based membrane systems.

In general, for lower salinity desalination applications, FO is more costly because it requires a draw solution recovery step. FO requires more energy than RO, has higher rejection and less fouling tendencies than RO, and due to low pressure operation, can be made of less expensive materials than RO. FO can treat higher salinity feed water and concentrate the feed water to higher salinity levels than can RO. RO will continue to be a process of choice for lower salinity feed water. However, the higher rejection and less fouling attributes of FO enable it to treat more challenging feed waters than RO, and FO may be used for these lower salinity feed waters.

With appropriate draw solutions, FO is well suited for higher salinity applications, extending the recovery by membrane processes into the realm mostly covered by more expensive thermal evaporator processes, i.e., high recovery MLD and ZLD processing.

Another general application is for treating heat-sensitive pharmaceutical and food and beverage compounds, replacing thermal evaporative systems where high levels of solids concentration are needed (e.g., orange juice concentrate).

Major research areas include developing improved membranes and draw solutions. Improvements in these areas will lead to cost reduction in FO systems.

9. Membrane Distillation (MD) Technology

9.1. Operating Principles

MD is a thermally driven membrane-based desalination process where a partial vapor pressure difference drives water vapor across a hydrophobic, microporous membrane. The vapor pressure gradient is produced by a temperature difference across the membrane. The vapor passes from the side with the higher temperature and condenses on the other side. The temperature difference may be as low as 10 to 20 degrees Celsius (°C). The concentrated phase containing more dissolved salts and other chemicals is retained on the feed side by the hydrophobic membrane. Feed side temperatures are typically 60 to 90 °C.

9.1.1. Configurations

The aqueous permeate can be in direct contact with the membrane (direct contact membrane distillation). Alternatively, the water vapor can be collected on a condensation surface separated from the membrane. More specifically, the four general configurations used (shown in Figure 25 where T = temperature) for the MD technology are:

- In a typical direct contact MD (DCMD) system, the condensate side has a cooled solution into which the vapor condenses. Permeate comes in direct contact with the membrane. In the variant Liquid Gap MD (LGMD), there is no additional cooled solution.

- In an air gap MD (AGMD) system, the hot permeating vapor condenses across a stagnant air layer on a condensing surface side of the membrane. This design offers reduced conductive heat loss, and the air gap increases the resistance to mass transfer, thus lowering the production rate of distillate.

- In sweeping gas MD (SGMD), a sweep gas collects permeated vapor toward a condensing surface. Since the gas is not stagnant (as in AGMD), the resistance to mass transfer is less. However, because the subsequent concentration is low, a large condensing surface is required.

In a vacuum MD (VMD), condensation occurs outside the membrane module, resulting in little heat loss via conduction.

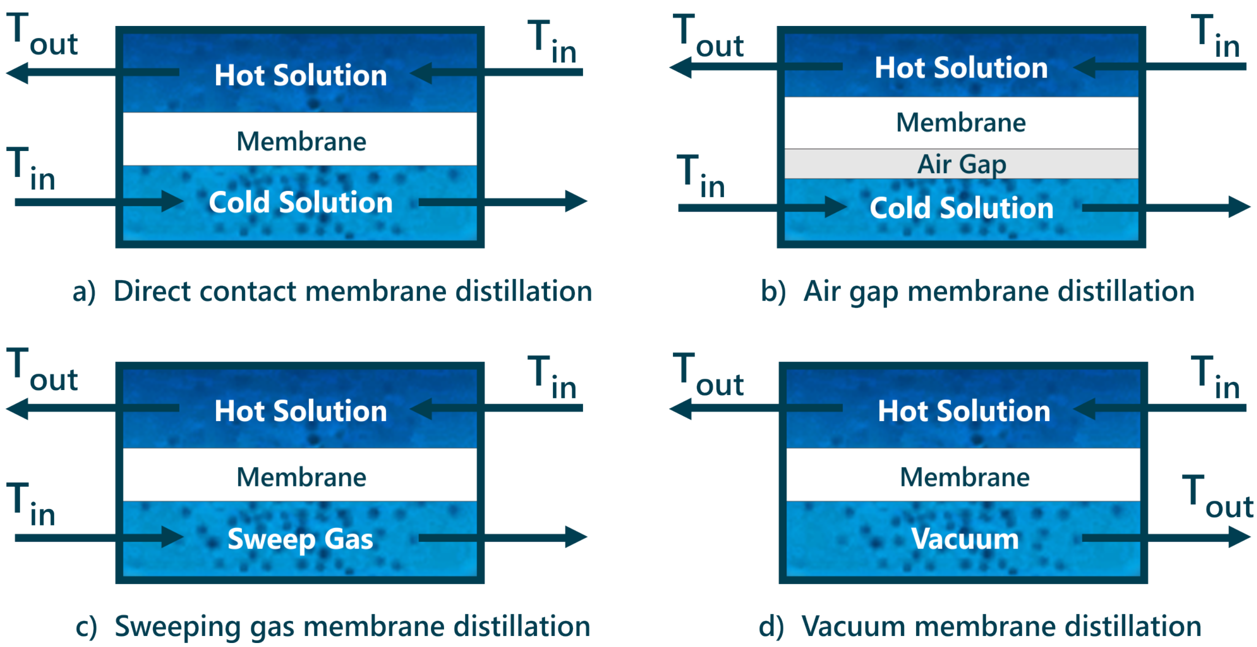

Figure 25. Membrane distillation techniques. T = temperature.

9.1.2. Attributes

- **Low fouling propensity.** MD operates at low pressure and has a low propensity for inorganic fouling as fouling layers are less compact and more reversible than in higher pressure RO and NF systems. Low pressure operation and fouling reversibility can lead to less frequent membrane replacement.

- **High rejection – high quality distillate**. MD has 100% rejection of non-volatiles.

- **Lower operating temperatures**. Operating temperatures are lower than used in conventional evaporation/distillation systems. Lower supply temperatures permit re-use of residual waste heat and the use of alternative energy sources such as sun, wind, and geothermics.

- **High salinity operation**. Similar to FO, feed water can be concentrated to higher salinity levels than in conventional RO systems resulting in higher salinity feed water applications and competing with conventional thermal evaporative systems for achieving high concentrations of feed water constituents.

- **High recovery applications**. MD has potential for high water recovery applications where concentrate is pushed to near saturation levels.

- **Lower cost materials**. Due to the use of considerably lower working pressures and temperatures, MD is less complex and cheaper in terms of construction and installation than higher pressure RO systems and higher temperature evaporator systems.

- **Modularity.** Modularity results in a wide range of possible applications as it can treat both small as well as large feed volumes.
- **Robustness.** Vapor pressure driving force is not considerably affected by high salt concentrations (Giwa et al., 2017). Also, there is less need for pretreatment than RO.
- **Simpler treatment system.** Less need for pretreatment than RO, production of high quality permeate leads to reduced number of steps to produce high quality water
- **Lower carbon footprint.** When low-grade energy is available, MD achieves both cost-saving and a reduced carbon footprint relative to electricity-driven desalination technologies.

9.1.3. Energy Considerations

MD is significantly more energy intensive than RO, ED/EDR, and FO because, like other evaporative processes, water separation requires a liquid-vapor phase transition.

Single stage MD energy use is comparable to that of a single stage evaporator. Energy requirements of multiple effect MD systems are still substantially greater than those of MVC thermal brine concentrators. As a result, application of MD is generally limited to situations where waste heat can be used, a situation not widely available and not necessarily without cost. Electrical energy is used mostly for pumping.

9.1.4. Membranes

Membranes for MD processing are hydrophobic in nature to prevent liquid molecules from passing through the pores. Only vapor molecules pass through the MD membranes; thus, the permeate side can reach high purity and the rejection rate can be over 99%.

The most commonly used membranes in membrane distillation are polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinyldenefluoride (PVDF). PVDF has high hydrophobicity, thermal resistance, and oxidation resistance, while PVDF has high mechanical strength with good hydrophobicity and thermal resistance. PP also has good thermal and chemical resistance. Membranes of novel materials have been introduced recently, including carbon nanotubes, fluorinated copolymer materials and surface modified polyether sulfone (PES) to increase the mechanical strength, porosity, and hydrophobicity (Gude, 2016).

9.1.5. Limitations

The high thermal energy requirement limits MD to applications where lower cost thermal energy is available.

Other major limitations include the low flux rate compared with pressure-driven membrane processes and the low recovery of MD modules. Low permeate flux leads to larger surface areas and associated costs. Low recovery leads to the need for more stages and thus higher costs. The low flux rates and low recovery have led to higher CAPEX than for RO.

The presence of volatile pollutants or surfactants in feed water can result in membrane wetting and the passage of volatile compounds into the permeate. This deteriorates product water quality and can lead to process downtime. If water enters the pores due to wetting or pressure, porosity decreases, membrane vapor flux decreases, and the pores can become blocked.

Other limitations include a large process footprint which can limit scalability, and there are mature and well-established competitive technologies in the niche use for MD.

Membrane development is an area of research as well as energy efficiency associated with heat conduction losses, and membrane wetting and polarization.

9.1.6. Applications

MD can achieve higher levels of concentration than RO and do this with higher levels of rejection. Feed water can be concentrated to near saturation of feed water salts and silica. As a result, MD is suitable for coupling with RO to achieve MLD.

Applications are generally restricted to where waste heat can be used. Because conventional thermal desalination produces hot concentrated brines and waste heat of low grade, MD can be considered as an ideal solution for heat recovery and increasing system water recovery of these conventional systems.

In general, large-scale applications of MD are hindered by the high energy requirement, low flux, and recoveries that lead to a large footprint per production level.

The most promising applications are small systems where waste heat can be used at low cost and the attributes of high-quality product water are important. MD will not replace RO—but may find applications in extending water recovery into the concentration levels achievable by more expensive evaporative processes. Very small MD systems may find increased application in providing drinking water powered by solar energy.

9.1.7. Membrane Crystallizers

In conventional crystallizers, solvent evaporation and crystallization occur in the same location. In membrane crystallizers (MC), these two processes occur in different locations offering better control over temperature gradients. Membrane crystallizers may provide well-controlled nucleation and growth kinetics, faster crystallization rates and shorter induction times. Based on these benefits, MC may offer an attractive alternative method for water recovery as well as for crystal production, especially for a certain high-value by-product (e.g. lithium) (Tsai et al., 2017). MC incorporates the benefits of MD, such as lower operating temperatures and energy requirements, as well as the limitations of MD, such as high energy requirements and low flux rates. The Aquatech Advanced Vacuum MD (AVMD) system appears capable of serving this purpose.

9.1.8. Operating Cost Considerations

- MD units have higher energy requirements than conventional brine concentrators.

- High energy requirements are best met with use of waste heat to lower the energy cost.

9.1.9. Capital Cost Considerations

- Low flux rates and low recovery require more membrane area and result in higher unit CAPEX than RO systems.

- Use of less expensive materials of construction lowers equipment costs.

- Costs can be less than those of conventional brine concentrators.

9.2. MD Companies

Several research organizations conducted early studies of membrane distillation that eventually led to spin-off companies. These companies, however, have had limited success— and several are no longer in business. In general, MD has had relatively little impact as measured by commercial installations. This is mostly due to the limitations of the technology, primarily the high energy requirement and low flux rates. Most of the installations are small systems of 10 gpm (2.3 m^3/h) or less. The companies that can provide systems of size greater than 1 gpm (0.23 m^3/h) include Memsys (China and Germany), KMX (Canada), Pacific States (California), Xzero (Sweden), and Aquatech (Pennsylvania). There are a few companies (e.g., Hvr [Sweden]) are focused on providing very small units of less than 1 gallon per day (gpd) to produce drinking water.

9.2.1. Memsys Group (originally Germany)

- **Memsys (New Concepts Holding Limited) (Germany and China)**
- **Abengoa (Spain)**
- **Aquaver (Netherlands)**
- **Evcon GmbH (Germany)**

URLs:
www.primeworld-china.com/
www.abengoa.com
www.aquaver.eu (no longer active)

Status: *Memsys was one of the early companies to get involved with MD. It had offices in Germany and Singapore. In 2016, the Chinese investment holding company New Concepts Holdings Limited (NCHL) purchased Memsys.*

When NCHL purchased Memsys in 2016, the intellectual property remained with the founder, Wolfgang Heinzl. EvCon, founded in 2016, uses Memsys technology and has developed a system that combines vacuum MD with multi effect distillation (MED) having multiple effects to reduce the energy requirement to that of several single-effect evaporators. EvCon Water is a part of the Cevital group, an Algerian multi-industry conglomerate with expertise in heat exchange.

In 2017, Memsys still maintained a website. In 2017, other groups such as Abengoa (Spain) and Aquaver (Netherlands) were involved in Memsys-related pilots.

In 2018, Evcon revealed a 26 gpm (5.9 m^3/h) installation and plans for a 250 gpm (57 m^3/h) seawater desalination plant in Algeria for a sugar manufacturer (BlueTech Research, 2018 and Bailey 2018).

The 2020 website made no reference to this effort and website literature is dated 2018. In 2020, the Memsys website still had a 2017 date and there was very little information available on the NCHL website. In 2020, neither Abengoa nor Aquaver websites mentioned MD.

9.2.2. Memstill Group (Originally Netherlands)

- **Memstill (Netherlands)**
- **Keepel Seghers (Netherlands)**
- **Aquastill (Netherlands)**

URLs:
www.keppelseghers.com
www.aquastill.nl

Status: *The Keepel Seghers website is still dated 2011 and the Aquastill website, 2015. Aquastill had discontinued their license after 5 years. There is no evidence for continued MD-related work for the Memstill product.*

Company Information: The MD product Memstill was a patented product of TNO (Netherlands Organization for Applied Scientific Research), first patented in the late 1990s. To investigate the technology, the Dutch government formed a consortium along with nine partners and six industrial companies to further test the technology. The group, along with TNO and others, included Keppel Seghers and Aquastill who hold licenses for the TNO technology. Various pilot and other investigations were conducted.

9.2.3. Petro Sep Group (Originally Canada)

- **Petro Sep Corporation (Canada)**
- **KMX Technologies, LLC. (Canada)**
- **Pacific States Water, Inc. (California)**

URLs:
www.petrosep.com
www.kmxtechnologies.com/
www.pacificstateswater.com

Status: *Petro Sep is a Canadian research organization that developed the Aqua Sep MD system. KMX (Canada) obtained an exclusive license around 2016 and Pacific States Water (California) was engaged by KMX to explore applications in the U.S. A 2016 Pacific States Water PowerPoint file listed 3 installations—the largest being an 18 gpm (4.1 m^3/h) system at a metal finishing plant. In 2017 the KMX website was focused on pervaporation with only a brief mention of the MD technology. On March 12, 2020 Antelope Water Management announced that it had acquired membrane distillation company KMX Membrane Technologies.*

Company information: Antelope is the latest oilfield water services firm to acquire in-house treatment expertise for produced water recycling in US oilfields. Since 2017, Pacific States has conducted tests in California (2018) and at Reclamation's Brackish Groundwater National Desalination Research Facility (BGNDRF) testing site at Alamogordo, New Mexico (2019) with a 4 gpm (0.9 m^3/h) pilot. Pacific States is continuing their work, now with Antelope rather than KMX. KMX has some continuing business ventures but is no longer involved with MD.

9.2.4. Fraunhofer Ise Group (Originally Germany)

- **Fraunhofer-Gesellschaft (Germany)**
- **SolarSpring GmbH (Germany)**

URLs:
www.fraunhofer.de/en.html
www.solarspring.de

Status: *The 2020 Solar Spring website states that there are well over 250 MD modules built and installed in over 20 countries. These are small systems (< 10 gpm or 2.3 m^3/h) with most using solar energy.*

Company Information: Fraunhofer Institute continues to be a leading European applied research organization. Solar Spring is a 2009 spin off of Fraunhofer Institute for Solar Energy in Germany.

9.2.5. Scarab Development Group (Originally Sweden)

- **Scarab Development AB (Sweden)**
- **Xzero (Sweden)**
- **Hvr Water Purification AB (Sweden)**

URLs:

www.scarab.se
www.xzero.se/en
www.hvr.se

Company information and status: Scarab Development is a Swedish organization formed in 1972 to establish commercial solutions to environmental issues. Today it is a cluster of companies working on several applications of water purification. In 2017, the focus was on small MD units with tests conducted on pharmaceutical waters. Xzero (Sweden) is a 1997 spin-off of Scarab Development. In 2018, the MD technology was still at a pilot stage. The 2020 website lists major inflow of investments and a focus on two applications: production of ultrapure water and recovery of water after use. A few installations are shown, the largest being 280 gpm (64 m^3/h).

Hvr Water Purification AB (Sweden) was a 1990 spinoff of Scarab Development to develop equipment for purification of drinking water. The 2020 website states the aim is to produce small systems to provide a daily supply of 2-4 liters of drinking water to everyone. The first demos will be installed in India, Bangladesh, Indonesia, and Gambia in 2021. Full-scale commercial operations will start in 2022.

9.2.6. Aquatech International Corporation (Pennsylvania)

URL: www.aquatech.com

Status: *The 2017 website did not mention MD technology. In 2018 a new technology, AVMD had been successfully piloted at about 0.5 gpm (0.11 m^3/h). In 2020, the website included a 4-page flyer showing skid-mounted AVMD systems available in sizes from 2 to 9 gpm (0.45 to 2.0 m^3/h).*

Company information: Aquatech is a major international company providing large membrane and thermal evaporation systems. The AVMD system recirculates brine without allowing salt crystals to reach the membrane, and thus concentrates brine to 32-35% solids. Pictures show large systems of up to 8 gpm (1.8 m^3/h). The system is designed to provide a lower CAPEX solution than conventional thermal evaporation in low capacity applications.

9.2.7. Markel Corporation (Pennsylvania)

URL: www.markelcorporation.com

Status: *As of October 2020, the website account was suspended.*

Company information: Markel has been making fluoropolymer products since the 1950s. They make hollow fiber PTFE membranes for various liquid and gas separation processes. More recently they have been making PTFE membranes and modules for MD systems. Markel states that the PTFE membranes are more durable and chemically resistant than PVDF membrane that have been used in some MD systems.

9.2.8. Solardew International B.V. (Netherlands)

URL: www.solardew.com

Status: *The 2020 website lists household solar energy applications and links to thermodew.com for industrial applications.*

Company information: Solardew originally focused on small pervaporation systems and then switched to making hydrophobic membranes and incorporating them into the pervaporation systems—making them MD devices. The solar-powered units are aimed at providing up to 2 gpd for use in underdeveloped countries.

9.3. Summary

MD has been under development for over 50 years and has been one of the most researched non-conventional desalination areas. In this regard, there are similarities to FO technology. Since about 2010, both technologies have far greater numbers of publications and conference session time given to them than other less conventional desalination technologies. Along with FO, MD has been considered as a technology in search of a market, and several companies focusing on MD have come and gone.

Despite the large number of attributes of MD, the major limitations of high thermal energy requirement and low flux rate lead to high costs and suitability mainly for small applications.

Like FO, definition of performance capabilities, applications, and costs of MD are becoming better defined. There are still only limited numbers of installations. The future market for MD technologies is more restricted than that for FO due to the high energy requirements, large footprint, and resultant high costs.

The niche markets for MD technology will be for small and medium-sized applications where waste heat is feasible to use and small solar-driven remote applications.

10. Humidification-Dehumidification (HDH)

10.1. HDH Technology

10.1.1. Operating Principles

The HDH process mimics nature's rain cycle by producing fresh water at sub-boiling temperatures, yet atmospheric pressures. Air can carry large quantities of water vapor with the vapor-carrying capability increasing with temperature. At 80°C, 1 kilogram (kg) of air can carry 0.5 kg of water vapor. When a heated feed water solution is exposed to flowing air, a certain quantity of water vapor is extracted by air. By bringing the humid air in contact with a cooling surface, part of the water vapor in the air condenses. The condensation typically occurs in a heat exchanger where the cooler feed water is preheated by transfer of the latent heart of condensation from the condensing vapor. The HDH system thus includes a humidification section and a dehumidification (condensing) section.

In HDH systems, evaporation occurs away from heat transfer surfaces. Heat transfer occurs in pre-heating water and/or air and in condensing water vapor.

Even though distillation or evaporation in the mode of traditional thermal desalination processes is not occurring, the heat of evaporation is still associated with air becoming humidified, and thus the process is one of evaporation. As with all evaporation processes, the thermal energy requirement is higher than other systems such as RO.

10.1.2. Configurations

Several configurations are possible for HDH systems. Each involves a humidification (H) section and a dehumidification (DH) section with water and air flowing between them. Figure 26 represents a typical HDH system. The ambient temperature feed water cools and condenses the hot humidified air in the DH section before exiting the section. In the humidifier chamber, the feed water is sprayed into the air creating the humidified air. The loss of water due to evaporation results in a brine that is collected at the bottom of the humidifier.

The various configurations have different air and water stream flows that are heated in a closed loop (Kabeel et al., 2013). These possible configurations are represented by the dotted lines in Figure 26, and specific configurations are shown in Figure 27.

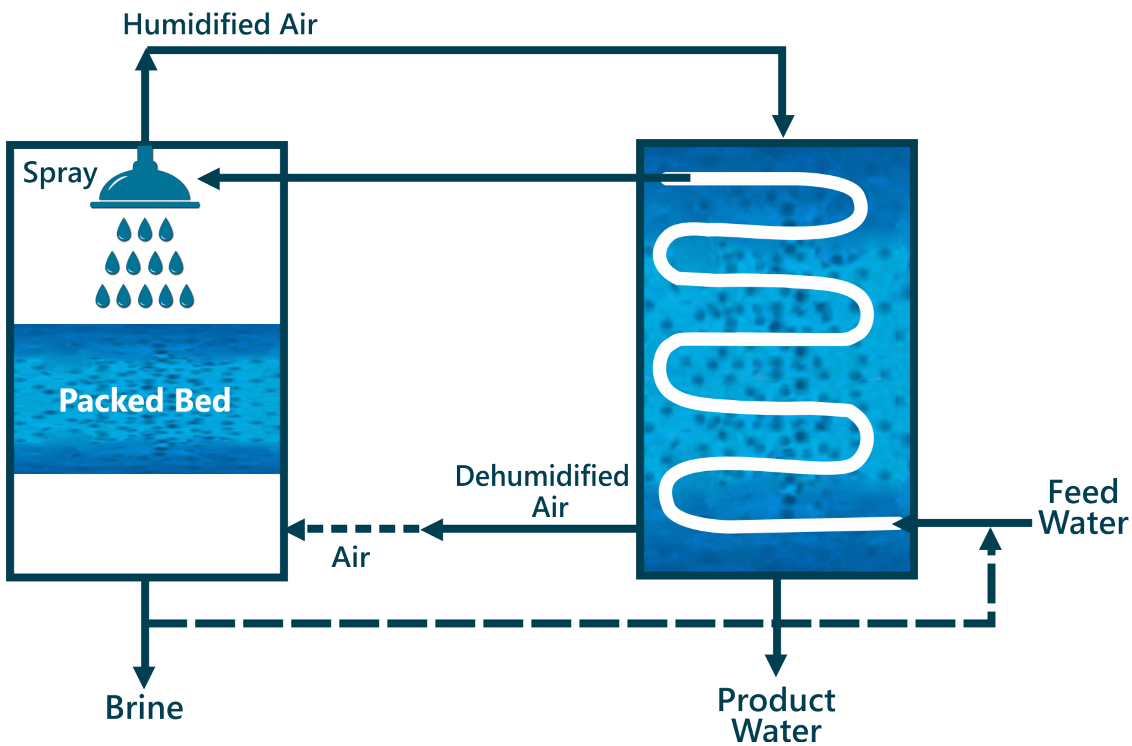

Figure 26. General representation of an HDH system.

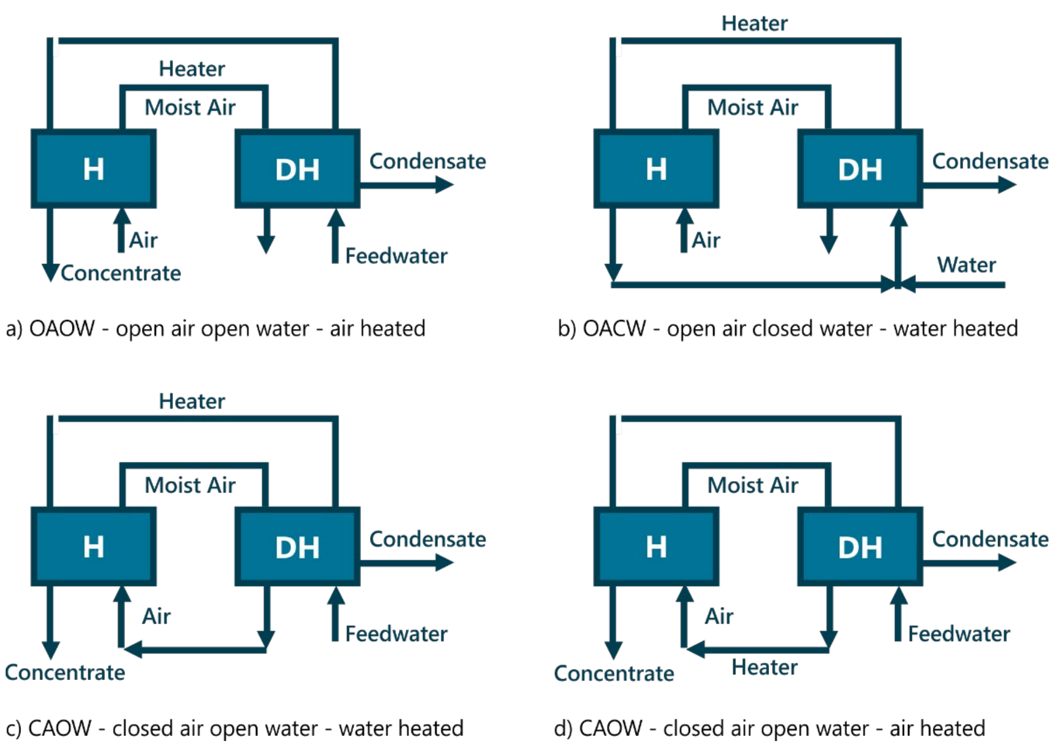

Figure 27. Selected HDH configurations.

The HDH configurations can also differ in the H and DH chambers' internal designs.

Operating temperatures in HDH systems are usually between 50 and 90 °C. Closing the air or water loop can increase the internal energy recovery and decrease the total energy consumption. As with other evaporation systems, stages can be added to increase product water per input energy.

Dewvaporation is an HDH process where the humidification and dehumidification processes are in one chamber: evaporation and condensation occur on opposite sides of a flat surface that separates the single chamber into two parts.

10.1.3. Attributes

Operation

- No high-tech membranes
- No high-pressure pumps
- Operate at relatively low temperatures and ambient pressure

Construction Materials

- Less expensive plastic and resin-based materials of construction reduce CAPEX
- Non-corroding, non-sticky surfaces
- Lighter weight systems reduce installation costs

Design Features

- Simple in concept and in construction
- Simplicity of design supports small solar-based applications in remote arid locations.
- Can be designed to avoid large partially evacuated chambers of conventional evaporation systems
- Easily cleanable
- Low simple maintenance
- Can be designed to serve as a one-step evaporator system replacing conventional brine concentrators and crystallizers

High Quality Product Water

- Produces high quality water

Robustness

- Minimal if any chemical use
- Can run on any feed water concentration

Modularity

- Modular expandable
- Modularity can result in system with no single point of failure

Energy

- Can use solar or waste heat

10.1.4. Limitations

- High energy requirement as with any evaporative technology
- Linkage with waste heat—a limitation in terms of applications
- Large footprint
- Lack of definition of optimal configurations
- Lack of definition of performance and costs

10.1.5. Applications

A simple HDH desalination process is suitable for decentralized small- and medium-scale fresh water production. HDH systems are simple in design and easy to manufacture. It requires low maintenance and can be operated by renewable or low-grade energy.

The HDH technique is especially suited for sea water desalination in arid regions when the demand for water is decentralized. Solar desalination based on the HDH cycle may be the best method of solar desalination because of overall high energy efficiency (Kabeel et al., 2013).

While HDH is not restricted to small-sized solar powered systems, much of the early research and current work is directed toward such applications in arid regions.

10.1.6. Operating Cost Considerations

- OPEX is lowered from limited pretreatment, low maintenance, and use of inexpensive waste heat.
- OPEX is increased if waste heat not available.

10.1.7. Capital Cost Considerations

- CAPEX is lowered from polymer materials and scalability (for relatively small size systems)
- CAPEX is increased for larger systems by adding more modules and creating a larger footprint

10.2. HDH Companies

10.2.1. Ail Research (New Jersey)

URL: www.ailr.com

Status: *Ail Research is an old company that in 2017 listed a patent for air-gap desalination as well as air-gap distillation. In 2020, the AIL website showed solar powered units being developed for small size applications.*

Company information: The company states that the air-gap desalination is an improvement over both MD and other HDH devices. It does not use a membrane. The prototypes were very small at less than 0.1 gpm (0.023 m^3/h). The target market was for units less than 2 gpm (0.45 m^3/h). The 2020 website mentioned several Small Business Innovation Research (SBIR) awards, including a $650,000 award in 2019. Systems are at an early prototype stage.

10.2.2. Altela, Inc. (Colorado and Arizona)

URL: www.altelainc.com

Status: *The 2020 information search showed Altela entering bankruptcy in early 2019. The 2017 website was dated 2015 but had some descriptions of equipment, including a DOE study in the Marcellus shale region, dated 2009-2011.*

Company information: Altela had licensed the Dewvaporation technology. The 2017 website mentioned that the company had raised over $19 million.

10.2.3. AguaRaider LLC (Texas)

URL: www.aguaraider.com/

Status: *The 2020 website information was relatively unchanged from the 2017 website content.*

Company information: AguaRaider makes a direct contact evaporator called the AguaRaider Unit for disposal of wastewater, using natural gas or other gas source. Source water is sprayed into the heated air flow, not to the sides of the stack vessel, producing small droplets of water. The spray assemblies are designed to significantly reduce the potential for entrainment or carry-over of dissolved solids. This was stated to significantly reduce the heat energy (gas) required for evaporation and produce a more effective and efficient evaporation process. The brine concentrate is recirculated to improve the evaporation efficiency of the entire process and maintains movement of the brine fluid to minimize deposition in the bottom of the stack. The stack is designed to efficiently push the steam plume and residual heated air out of the stack. Condensation does not occur in the stack. The evaporated water is vented to the atmosphere and not recovered. The main focus is on oil and gas exploration and production applications. A full-scale unit has been operating in Texas for about two years to develop the technology. The final reduced volume brine is disposed by deep well injection.

10.2.4. Creative Water Technology, LTD (Australia)

URL: www.creativewater.com.au (no longer available)

Status: *An information search in 2020 found that an application for closing the company was filed in November of 2018.*

Company information: The company was founded in 2006. The 2017 website discussed recovery of up to 97% from wastewater streams with scalable equipment arrays to process a minimum of 2 gpm (0.45 m^3/h) to any capacity requirements. The system was stated to produce dissolved solids concentration up to 300,000 mg/L. The system was called a heat pump with no use of the term “humidification-dehumidification.” The distinguishing feature of the technology was stated as the ability to perform fractional crystallization of minerals, enabling the recovery of salts such as sodium chloride from seawater or produced water.

10.2.5. Gradiant Corporation (Massachusetts)

URL: www.gradiant.com

Status: *The 2017 website offered more information and featured both the CGE and SCE systems and mentioned the introduction of the CFRO and FRD systems. Gradiant's 2020 website has updated information on systems. An August 2020 news article mentioned that Gradiant won 1 2 projects across the Asia Pacific region which included ZLD and industrial wastewater reuse projects (Smart Water Magazine, 2020).*

Company information: The website discusses processes:

- carrier gas extraction (CGE); brine minimization
- HDH system along with counterflow RO (CFRO); brine minimization
- free radical disinfection (FRD)
- selective chemical extraction (SCE)

The CGE system is said to concentrate brines up to 25% salinity. Relatively little detailed information is available.

Gradiant is focused on the produced water market and offers a build-own-operate service of mobile, re-deployable systems powered by steam generated by a gas-fired boiler. Pilots were installed at various produced water sites. The CGE HDH system sprays water on a packed bed for evaporation, and the water-saturated air is pumped through small holes, which results in high surface areas for heat transfer required for condensation. A system was said to be in design phase for China for treating flue gas desulfurization (FGD) wastewater with several units in planning for China. To make the HDH technology work over a wide range of feed water qualities, Gradiant developed various pretreatment technologies.

10.2.6. MAGE Water Management GmbH (Germany)

Status: *The 2020 information search did not find a website but found information which showed connecting a simple solar still using an HDH-type system with solar energy.*

Company information: MAGE is primarily a solar company making arrays. A 2 gpm (0.45 m^3/h) unit requires a 40' trailer. There was limited information available in 2017: only mention of small-scale solar seawater systems and a watercone product that can capture 1.5 liters per day (lpd). One internet source described the technology as a Dewvaporation system for drinking water applications up to 18.3 gpm (4.3 m^3/h) with a solar heat source.

10.2.7. Saltworks Technologies, Inc. (British Columbia)

URL: www.saltworkstech.com

Status: *The 2020 website has news articles from September 2020.*

Company information: The SaltMaker is a single step evaporator system, a crystallizer system that requires no pretreatment. A circulating slurry continuously forms and grows crystals. Solids are produced without the need for centrifuges or filter presses. The HDH system operates on an air cycle with temperatures < 90 °C. The multi-effect system is built from process sets to avoid a single point of failure that MVR evaporators can have. The system is built of low cost engineered plastics for lower weight. High circulation rates and non-corroding, non-stick wetted surfaces resist corrosion, plugging and scaling. It is a smart system that detects and initiates cleaning cycles. A less expensive air breather version vents water to the atmosphere instead of recovering it.

The 2017 website mentions three steam-assisted gravity drainage (SAGD) blowdown system pilots. Systems are available in 18.3 and 74 gpm (100 and 400 m^3/d) sizes enclosed in 20- and 40-foot containers. An interview revealed 6 crystallizer sales in the range of 18.3-36.6 gpm (100-200 m^3/d). Saltworks states that the SaltMaker can treat any brine of greater than 200,000 mg/L TDS, and that others ignore this market niche.

Saltworks makes other equipment, including ultra high-pressure Xtreme RO technology, XtremeUF (for concentrating slurries), IonSelect (selective ion removal), and FlexEDR (for selective removal of monovalent ions).

Recent news about SaltWork's RO technology may suggest an enhanced focus on high recovery RO technology.

10.2.8. Terrawater GmbH (Germany)

URL: www.terrawater.de

Status*: Although the 2017 website discusses the HDH technologies, the 2020 website has much more information available. The systems were stated to be suited for feed salinities of < 70,000 mg/L TDS.*

Company information: TerraSaline is a closed air evaporation system that uses waste heat from other processes and is stated to work without chemicals. The distillate from the Terrawater evaporation process has a very high purity (conductivity lower than 10 µS). The TerraCrystalizer extracts solids and may be used to separate specific salts from wastewaters. The website illustrates small containerized systems of up to 10 gpm (2.3 m^3/h).

10.2.9. TMW Technologies (France)

URL: www.tmw-technologies.com

Status: *The 2020 website showed Ecostill units for treating up to 10 gpm of industrial wastewater and Aquastill units for treating seawater of <0.2 gpm.*

Company information: Recoveries were stated to be from 83-95% for the system evaporating at atmospheric pressure and temperature of 85C. The system is entirely made of plastics.

The 2017 website mentioned the Ecostill system for treating small capacities of up to 0.5 gpm (0.11 m^3/h). Funding of Euro 3.5 million was mentioned. TMW also sells heat exchangers with very low pressure drops. There was no information on installations.

10.2.10. Cirtec B.V. (The Netherlands)

URL: www.cirtec.nl

Status: *The 2017 website provided few data on performance and cost. The 2020 website revealed several products, one of which is a direct contact evaporator that can be combined with a condenser to recover water.*

Company information: No size information is given although a Middle East textile installation of 22 gpm (5 m^3/h) is mentioned. Market focus is listed as municipal wastewater, food, and slaughterhouses. The company states that the process can concentrate to above saturation limits. The GaLiCos HDH system is patented. Liquid flows down along an inclined plat and so generates by cavitation a slightly negative pressure in the downward directed, protruding openings that are present on the upper surface of this plate. The negative pressure causes the gas to pass from underneath the plate into the flow of liquid as long stretched bubbles. These bubbles stay long enough in contact with the liquid to become saturated. A low-pressure ventilator transports the gas and enhances the gas/liquid contact. This patented method provides a very intensive gas/liquid contact, offering an optimal exchange of components at minimal energy input. Waste energy from heating, cooling, and ventilating may be used to power the system.

10.2.11. Clean TeQ Water (Australia)

URL: www.cleanteqwater.com

Status: *The 2020 website information describes an evaporation/crystallization HDH system producing semi-dry salts.*

Company information: Limited information is available. Mention is made of two China installations at 12.5 and 15 m^3/h (55 and 66 gpm), dated 2017 and 2018. The company also has a continuous ion exchange (IX) system (CIF) and a high recovery RO (HIROX) system that combines CIF with HIROX. HIROX and uses ion exchange to remove di- and tri-valent cations such as calcium, magnesium, and heavy metals from waste waters. Brine concentrate is used to regenerate the IX system—resulting in chemical-free pretreatment.

10.2.12. Seachange Technologies, Inc. (North Carolina)

URL: www.seachangetechnologies.com

Status: *The 2017 website mentioned that full-scale pilot systems would be available for on-site deployment in the first quarter of 2017. The 2020 website revealed a strong focus on the textile industry, which was stated to be responsible for over 20% of wastewater globally.*

Company information: The system was described as operating by aerosolizing contaminated water, separating contaminants from the water vapor in a cyclonic separator; and finally releasing the clean water vapor into the atmosphere. Processing leaves a solid mineral residual. No mention is made as to whether air or water is heated.

Focus was on produced water, as it was mentioned that the system is easy to scale up capacity for larger wells and move the vaporization units to other wells, as production dictates. Such a technology could be particularly beneficial for wells in remote locations where trucking costs for wastewater disposal are too expensive for production to continue.

10.2.13. QWAIR GROUP (Germany)

URL: www.qwair-group.com

Status: *The 2020 website review showed the evaporator labeled as an MED system for seawater desalination and ZLD applications.*

Company information: The system is an HDH device where either air and/or water may be heated. Very high surface area for evaporation is produced using a vertical axis rotating cylinder with many long fibers attached to the center column. Feed is from a bottom sump using high velocity air flow from bottom up. The claim is for high efficiency humidification. Little other information is available.

10.3. Summary

Saltworks and Gradiant have been development leaders in the HDH technology, both with commercial units of 40 gpm and larger. Several companies focus on providing smaller units, and many focus on small solar-driven units.

HDH technology has appeared in three general applications to:

1. replace the conventional brine concentrator,
2. replace a combined brine concentrator and crystallizer system which produces solids, and
3. use for small applications with solar energy.

11. Evaporation Technologies

11.1. Introduction

The evaporation technologies discussed in this this chapter are those involved with high recovery processing. The categories discussed for evaporation technologies are:

- mechanical vapor recompression (MVR)
  - brine concentrators
  - one step brine concentrator/crystallizer systems
- direct contact—one step non-MVR brine concentrator/crystallizer systems

See Chapter 10 for humidification-dehumidification evaporation technologies which are direct contact devices—although not necessarily one-step brine concentrator/crystallizer processes.

11.2. Operating Principles

In general, conventional evaporative technologies fall into three categories:

11.2.1. Mechanical Vapor Recompression (MVR) Systems

Vapor Compression (VC) systems are where vapor from the evaporator is mechanically (MVR) or mechanical vapor compression [MVC]) or thermally compressed (TVC), raising its temperature and pressure, such that it is used in subsequent evaporation of feed water in the same chamber.

Steam is needed only at start-up. In vapor compression (VC) processes, evaporation and condensation occur in the same vessel and there is no need for cooling water, unlike multi-stage flash (MSF) and multi-effect distillation (MED)systems. As with the MED process, in conventional VC systems feed water is sprayed onto tube bundles of flowing steam; evaporation takes place outside the tube and condensation inside it. Although VC can be accomplished thermally, MVR systems are the most common. They require electrical energy for pumping and for compression making CAPEX higher. For this reason, MVR systems are used in small and medium sized applications, typically less than 1 mgd.

MVR systems recover latent heat by compression, whereas many other evaporation systems may recover latent heat by adding stages. Each added stage reduces the overall energy requirement by a factor roughly equal to the number of stages. An MVR system can be equivalent to 10 to 20 stages.

A conventional MVR brine concentrator requires from 65-90 kWh/kgal of electrical energy. Figure 28 depicts a typical MVR system.

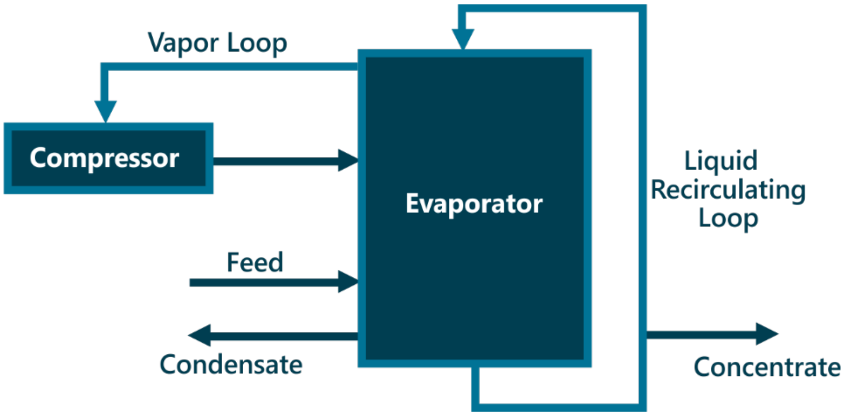

Figure 28. Typical MVR (MVC) system.

11.2.2. Multi-Stage Distillation

In conventional multi-effect distillation, feed water is sprayed as a thin film onto hot tubes containing flowing steam from a boiler. Heat exchange takes place: the feed water boils off the outside of the tube, while inside the tube the steam condenses to form pure product water. The vapor rising from the outside is collected and passes through a subsequent set of tubes in the next chamber, where feed water is sprayed on it, repeating the process. Although this "secondary" vapor is cooler than the original steam, each successive chamber is kept at a lower pressure, so that the boiling point is lowered, enabling multiple stages to be used. Electrical energy is required for pumping.

In Thermal Purification Technologies' modified MED system, evaporation takes place at a water droplet-air interface rather than on a heat exchange surface.

11.2.3. Single Stage Evaporation

The evaporators developed by Fluid Technology Solutions and Heartland are single stage non-MVR evaporators. For conventional single stage units, this would be similar to the MVR system without compression.

In summary, the latent heat exiting an evaporator may be recovered through compression (MVR system), recovered by using additional stages (multi-stage evaporators), or not recovered (single stage evaporation). The unit energy requirement increases in the order:

MVR < multi-stage < single stage.

11.3. MVR Companies

11.3.1. Encon Evaporators (New Hampshire)

URL: www.evaporator.com

Status: *2020 website information was relatively unchanged from 2017 information.*

Company information: Encon is an established company founded in 1993 that provides small volume (up to about 60 gpm or 13.6 m^3/h) MVR and wastewater evaporators for several industrial applications. In ZLD applications, the MVR evaporator brine is sent to a holding tank where the supernatant is further concentrated by a wastewater evaporator and the residuals sent back to the holding tank. Water vapor is typically vented to the atmosphere. Slurry from the holding tank is treated by a centrifuge with the liquid from the centrifuge going back to the holding tank.

11.3.2. Evatherm, Ltd. (Switzerland)

URL: www.evatherm.com

Status: *2020 website has detailed information covering a wide range of evaporation and crystallization applications.*

Company information: Evatherm is a well-established Swiss company founded in the early 1980s with offices in Germany and Hungary that makes evaporation and crystallization systems. A multi-stage vacuum evaporation system is used for treating brine when low pressure steam for heating is available. The MVR evaporation system is used when electrical power is available. The company states that it was the first to use titanium tubes and that the technology has become an industry standard.

Evatherm also makes a cooling crystallization system for when the solubility gradient of the solution increases steeply with falling temperature or when a vaporization of the solvent has to be avoided. They also feature a recrystallization salt process which renders very high purity salt using comparably little thermal energy.

The company's website information indicates that it has major large salt recovery systems.

11.3.3. Vacom Systems, LLC. (Utah)

URL: www.vacomsystems.com

Status: *The 2017 website appeared more focused on oil and gas applications than the 2020 website. The 2020 website, however, mentioned a July 2020* Global Water Intelligence (GWI) Global Water award "2020 Industrial Project of the Year" for a major produced water project involving Aramco, Vacom Systems, and Tahilyan. Aramco plans to use this new MVC technology to kick off a wide-ranging reuse program in its oil operations, with potential total groundwater savings of 2.2 billion gallons annually after full implementation.

Company information: Vacom has a one-step MVR evaporator/crystallizer which uses submerged boiling and turbulent flow to concentrate salts above the precipitation point. The website states that the system accepts high suspended solids, requires no pretreatment, is self-cleaning, and is non-scaling. The original focus was on oil and gas applications. Now applications include mining, treatment of digester effluent, and others. The company has pilots and installations in the U.S., China, and Saudi Arabia. Vacom systems are mostly smaller systems than systems provided by Suez, Veolia, and Aquatech.

212 Resources was a subsidiary of Vacom, originally formed when Vacom was getting into crystallization. Vacom now oversees the 212 Resources work.

11.3.4. Salttech (Netherlands)

URL: www.salttech.com

Status: *The 2020 website information was similar to that of the 2017 website. The 2017 website revealed 10 plants in total in the Middle East, U.S., and Europe. The size ranged from 1.5 to 25 m^3/h (6.6 to 110 gpm). Work was underway to increase capacity to 100 m^3/h (440 gpm).*

Company information: Salttech's DyVaR process is a modular, patented desalination technology that achieves thermal distillation through an MVR variation called dynamic vapor recompression (DVR). This is a one-step evaporator/crystallizer system. The "dynamic" variation in a DVR system uses a cyclone as the evaporation chamber, which allows for crystallized salts to be separated from the brine by centrifugal force. The DyVaR system operates without pretreatment and can be fully automated and remotely operated. This is a one-step evaporator that is stated to operate without scaling and fouling, with no down time required for CIP and no need for redundancy. Modular 44 gpm (10 m^3/h) units can be combined in parallel to treat larger flows. The 2020 website reflected expansion and growth with 11 global offices and a list of job openings. The unit operates under a slight vacuum. Presently, there is one installed unit in the U.S.

11.3.5. Purestream Services (Utah)

URL: www.purestream.com

Status: *The 2020 website information was similar to 2017's. The 2017 website information mentioned three pilots at the Electric Power Research Institute sites and a focus on distilling produced waters at the well head.*

Company information: The Purestream AVARA evaporator is a fully automated modular VC technology targeted mainly for oil and gas applications. The modules are 35 gpm (8 m^3/h) and can be combined for applications up to 300 gpm (68 m^3/h). The system includes submerged boiling, high flow rates, and other means to minimize scaling. The system uses a hydrocyclone to reduce solids in the recirculated brine flow.

11.4. Direct Contact Companies

11.4.1. Fluid Technology Solutions Inc.: FTS H2O (Oregon)

URL: www.ftsh2o.com

Status: *In 2020, FTS joined the Imagine H2O Asia 2020 Startup Accelerator Cohort, a Singapore-based, regional accelerator to jumpstart their solutions in the wider region.*

Company information: The FTS offers advanced treatment technologies (including FO) to realize the most economical zero liquid discharge (ZLD) solutions for the most challenging wastewater. The direct contact, one-step low temperature evaporation crystallization (LTEC) system has been used for over 20 years to concentrate wastewater from oil and gas and electric power applications to achieve ZLD. This system uses heat from waste and ambient pressure to crystallize and/or concentrate high-salinity wastewaters. The process uses an intermediary heat transfer fluid (HTF) that is both a different density from and immiscible with wastewater. The warm HTF transfers heat into the brine through direct, immiscible liquid-to-liquid contact; the brine heats and the HTF cools, and the immiscible and differing densities of the brine and the

HTF promote rapid separation. The HTF has no solubility for scaling minerals, so the cool HTF can be returned to conventional heat exchangers for reheating and reuse. The system is constructed of durable plastic components and the LTEC system is modular and portable. The humid air is discharged without recovery of water. No information is provided on equipment size.

11.4.2. Heartland Water Technology, Inc. (Massachusetts)

URL: www.heartlandtech.com

Status: *The 2017 review mentioned new hires, a $12 million equity round of financing, a company move to Waltham, Massachusetts, and a pursuit of long-term treatment service contracts in addition to selling equipment. The 2020 website showed the addition of a biosolids dryer product, more references, and installations up to 100 gpm (23* m^3*/h).*

Company information: Heartland offers advanced thermal evaporator technology for achieving ZLD in a single unit. The LM-HT (low momentum – high turbulence) concentrator is a direct contact evaporator system bringing thermal energy and the targeted wastewater into direct contact. The system can directly use flare gas or other waste heat. A process schematic is shown in Figure 29. Fouling and scaling issues are eliminated as well as operating and maintenance issues. System focus has been on robustness rather than energy reduction. Heartland claims reduced capital costs, reduced footprint, and increased operating reliability and uptime. Several installations treat leachate. The system vents water vapor to the atmosphere and produces a solids slurry for solids/liquid separation.

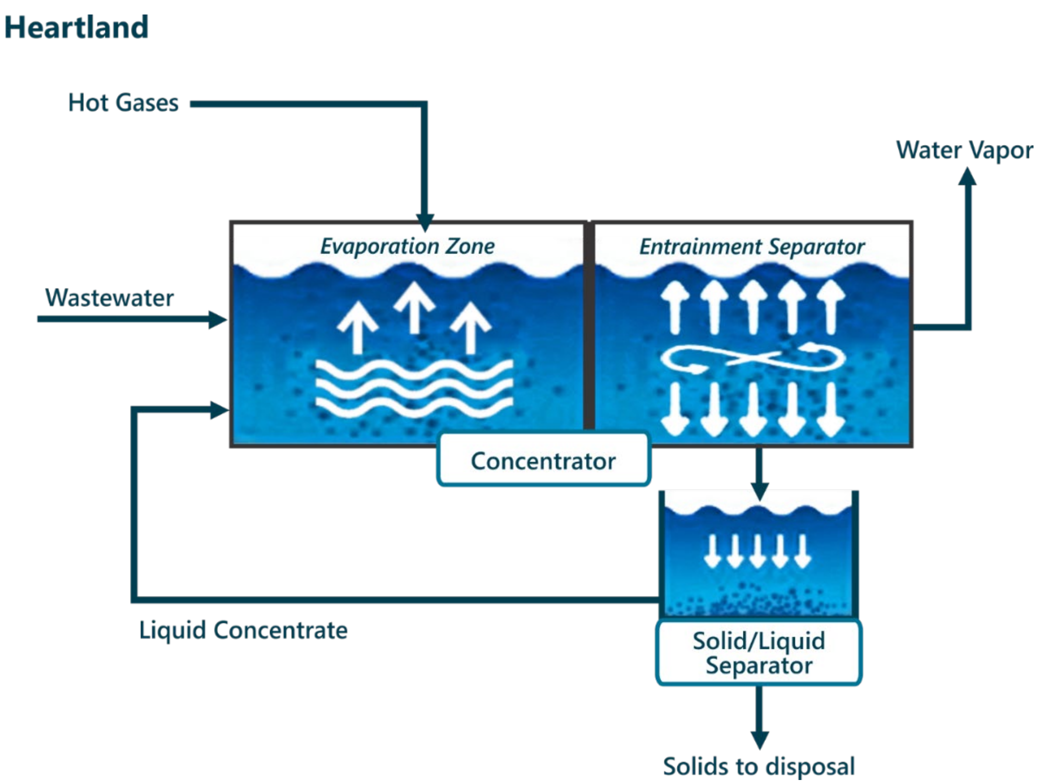

Figure 29. Heartland direct contact evaporator.

11.4.3. Thermal Purification Technologies (TPTEC), GmbH (Switzerland)

URL: www.t-p-tec.ch

Status: *Established in 2013, TPTEC obtained patents from WaterSolutions focusing on applications other than producing drinking water. In September 2014, Dubai-based Metito made a significant investment in TPTEC as part of a strategic partnership to exclusively introduce, and help develop Low Temperature Distillation (LTDis), among other technologies, in markets across Asia and Africa, where the feasibility of desalination and the resources required for water and wastewater purification continues to be a challenge. The 2017 website mentioned several new installations in the works—a mix of pilot and full-scale installations in Hungary, Germany, and California. The 2020 website includes a partnership with Crystal Clearwater Resources (Texas).*

Company information: LTDis is a modified MED system, a cascade distillation process that uses low pressure operation through the use of vacuum pumps. The system typically uses waste heat from various sources including industrial processes, power generation, and solar thermal. As indicated in Figure 30, evaporation takes place at a water droplet-air interface rather than on a heat exchange surface. This avoids scaling on the heat transfer surfaces and tolerates high salinity and hydrocarbons, as well as provides high recovery. It also leads to small temperature differentials between the heat source and the re-cooling source. Lower temperature differentials can lead to more efficient application of heat sources, resulting in lower energy requirements. Condensation takes place in an adjacent chamber.

Low Temperature Drying technology (LTDry) is a wet solid drying process that uses integrated system of screw conveyers, heat exchangers, and vapor condensers.

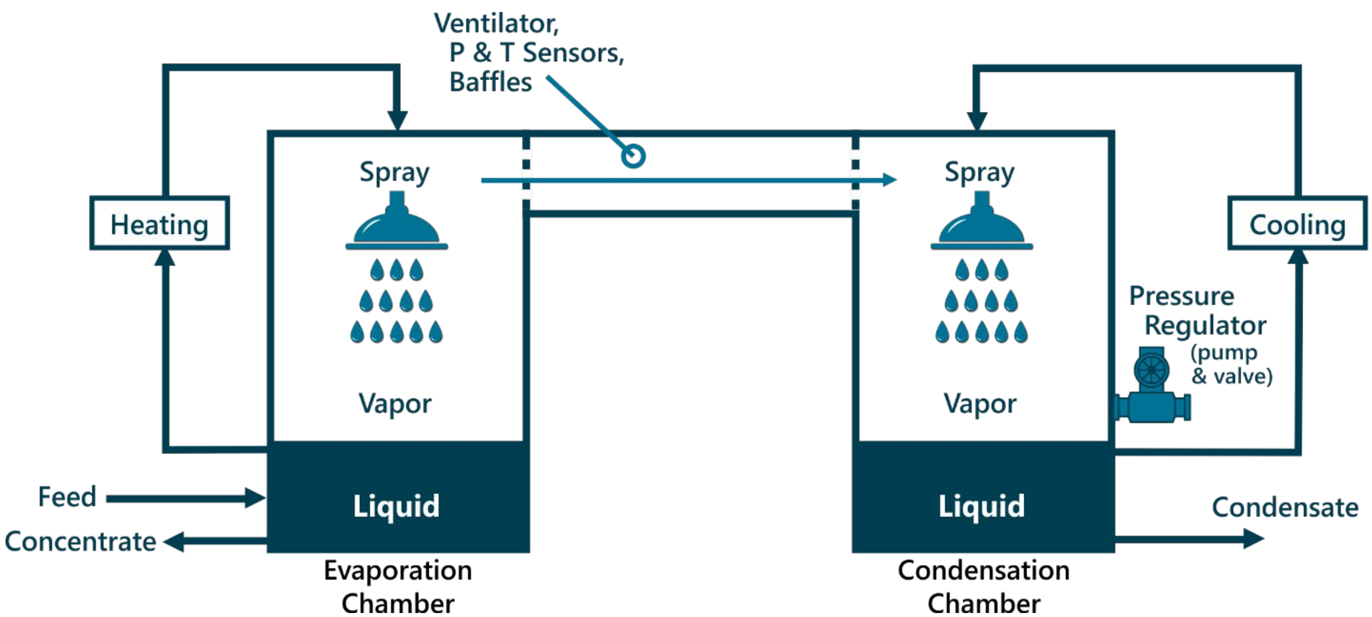

Figure 30. TPTEC direct contact evaporator

11.5. Other Companies

It is noted that several companies included in 2015-2017 reviews no longer maintained websites, including:

- Aqua-Pure Ventures (Canada)
- AquaExplorer (The Netherlands)
- HipVap Technologies (Canada)
- ZanAqua Technologies (New Hampshire)
- WaterVap (U.S.)

11.6. Summary

These evaporation technologies focus on reducing the costs of conventional brine concentrator and crystallizer systems and are best suited for treating higher salinity feed water. Approaches include:

- Reducing energy requirements (through direct contact heating)

- Reducing material requirements (using lower cost resin materials)

- Increasing robustness (and thus decreasing downtime)

- Increasing performance (one-step combined concentrator and crystallizer systems have lower energy requirements, require less pretreatment, and are in general, more robust)

12. Other Technologies

12.1. Introduction

Some technologies do not fit conveniently under the previous technology categories and are included here for discussion. Four technologies are desalination technologies. Two other areas are addressed: enhanced evaporation technologies and value recovery from brine. Enhanced evaporation technologies are used in conjunction with evaporation ponds and the entry for recovery of values from brine represents a milestone effort in brine management. Although these areas do not fit under the high recovery desalination focus of the report, they represent technology advances associated with brine management.

Desalination technologies:

- Absorbent desalination
- Adsorption desalination (AD)
- Freezing
- Solvent extraction

Enhanced evaporation technologies:

- Enhanced evaporation systems

Value recovery from brine

Because of the distinct differences in the technologies highlighted in this chapter, they are discussed separately.

12.2. Absorbent Desalination

12.2.1. Aquafortus (New Zealand)

URL: www.aquafortus.com

Status: *The 2020 website states that the technology is up to 60% less expensive in OPEX than existing thermal ZLD technologies—with all operational costs factored in, including consumables. Two recent licensing agreements were mentioned to support the company's commercial activities in the U.S. and Europe. In the U.S., Aquafortus has formed Hyperion Water Technologies in a joint venture with Berkshire Hathaway backed Pilot Corporation. Hyperion has committed $25 million to deploy Aquafortus's ZLD technology within the oil and gas market. In Europe, Aquafortus has signed a non-exclusive licensing agreement with Lenntech for industrial wastewater applications in Europe. The technology is in the pilot stage having been tested at small scale on brine ranging from 12,000 to over 400,000 mg/L.*

Company information: The Aquafortus ABX system is a novel liquid-to-liquid crystallizer that promotes the formation of salt crystals via a proprietary direct contact crystallization process using Aquafortus's patented solutions.

As shown in Figure 31, the Aquafortus ABX system works by a two-stage solvent exchange process with the patented absorbent acting as a transfer medium for water. When wastewater brine contacts the absorbent, salts from the wastewater brine instantly crystallize due to removal of water by the absorbent. Solids are separated from the absorbent solution. After this, a regenerant is added to the wet absorbent. The regenerant switches off the absorbent's ability to absorb water and releases the water to the regenerant. This recovers the absorbent to its concentrated state for reuse in the process. The diluted regenerant is passed across a reverse osmosis module producing clean water and recovering concentrated regenerant for reuse in the process. The continuous treatment system is envisioned as replacing both the thermal evaporator and crystallizer in ZLD processes with a considerable energy savings.

Aquafortus

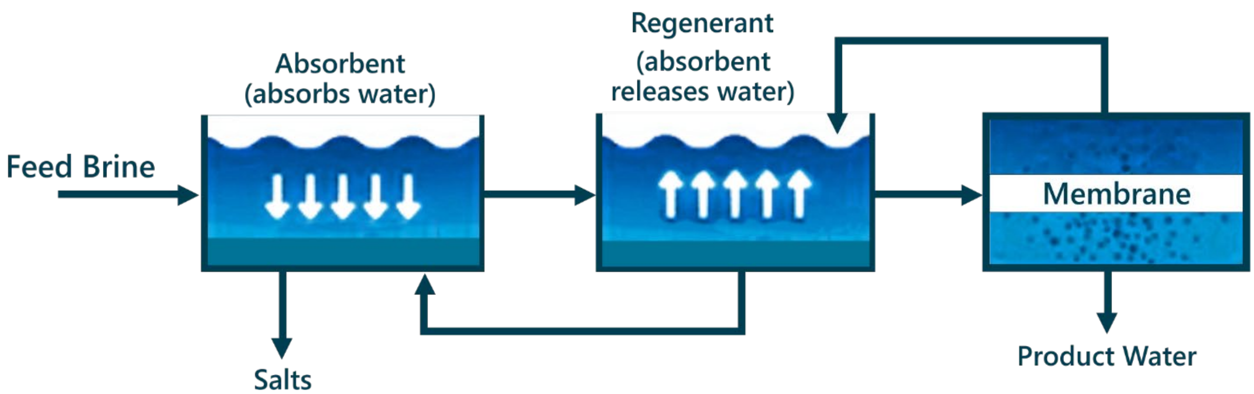

Figure 31. Aquafortus's absorbent technology, ABX.

12.3. Adsorption Desalination (AD)

12.3.1. Greenblu (NEW JERSEY)

URL: www.greenblu.co

Status: *The technology is at an early stage of development, and little information is available about performance, cost, and projected equipment size. The 2020 website states that the patented distillation method recycles the heat of adsorption, the latent heat of vaporization, and the sensible heat multiple times.*

Company information: Greenblu was founded in 2016 and has received government funding (DOE and Small Business Innovation Research [SBIR]) to develop the technology called Vapor Adsorption Distillation with Energy Recycling (VADER). This new distillation method is enabled by a patented high thermal conductivity nanocomposite adsorbent.

The adsorbent acts as a water vapor pump, adsorbing and desorbing pure vapor without contacting the input water. High purity product is produced. The process is claimed to require less pretreatment than RO. A desiccation process can dry input liquids, regardless of concentration, into solids. The vapor adsorption distillation cycle is powered by waste or solar heat to achieve low operating costs by not using membranes and minimizing electricity use.

12.3.2. Medad Technologies Pte Ltd (Singapore)

URL: www.medad-tech.com

Status: *The 2020 website was similar to that reviewed in 2017. The last news item was dated in 2017. At least one ULT-MED and one ULTAC system are operating in Saudi Arabia.*

Company information: Medad's Multiple-Effect Distillation Adsorption Desalination (MED-AD), technology uses multiple beds of powerful adsorbents to achieve a continuous evaporative desalination process. The website states that AD is able to operate robustly at feed inputs with solids levels up to crystallization. There are no moving parts in the AD beds. Very low-grade heat drives the adsorption process.

As represented in Figure 32, silica gel beads adsorb water vapor from an evaporation step at temperatures as low as 7 °C and release the vapor at temperatures 55-85 °C. The valved process has no moving parts and cycles through the adsorption and desorption modes. Since the system can operate over a wide temperature range, the AD beds can be arranged in stages to operate at decreasing temperature levels, similar to stages of a conventional MED process. Since the stages operate at lower temperatures than MED stages, they can be added to the MED process resulting in additional water recovery. The is referred to as the ULT-MED system. Other applications involve the ultra low temperature adsorption crystallization (ULTAC) system where the MED-AD is hybridized with a crystallizer to replace MVR crystallizers and to operate at lower (< 50°C).

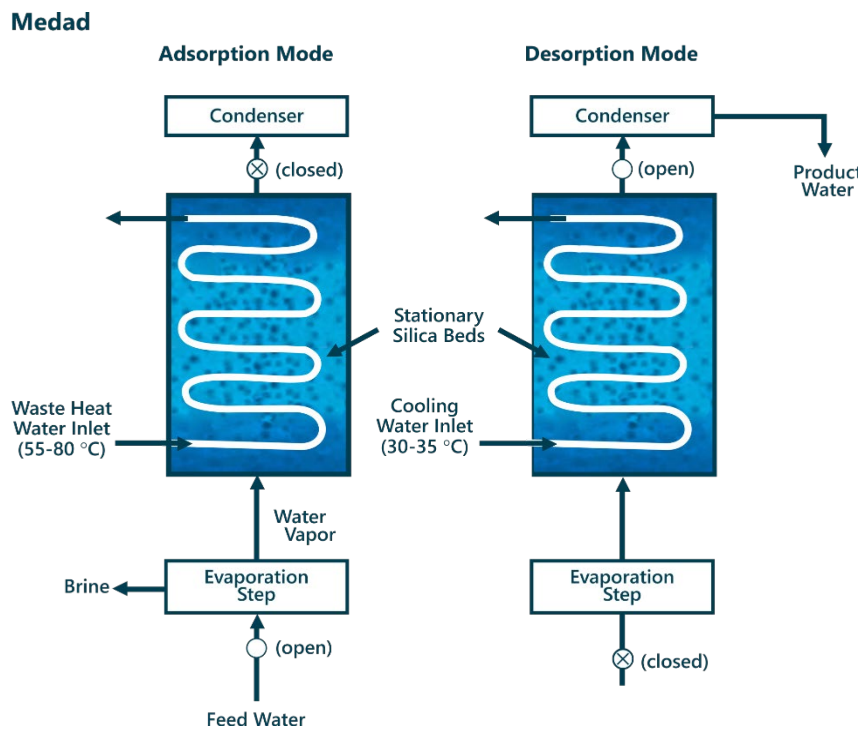

Figure 32. MEDAD adsorption technology.

Medad was founded in 2012 and initially acquired patents from the National University of Singapore, and later added patents from King Abdullah University of Science and Technology, after Professor Ng Kim Choon, the technology's inventor, moved to Singapore to continue his research in the field. In September 2016, the company began a commercial 100 m^3/d (18 gpm) pilot in Saudi Arabia, for recovering RO brine.

12.4. Freezing

12.4.1. Cool Separations (Netherlands)

URL: www.coolseparations.nl

Status: *The 2020 website describes these as low temperature, energy efficient methods to concentrate aqueous process streams and to produce clean water (ice) and pure salt.*

Company information: The technology came out of Delph University of Technology with the company formed in 2009. Cool Separations was previously known as EFC Separations. Cool Separations provides eutectic freeze crystallization (EFC), freeze concentration (FC) and cooling crystallization (CC) technologies. The EFC process is represented in Figure 33. The FC technology solely removes water in the form of ice at a higher temperature than needed for crystallization of both water and salts. CC technology is where the first crystallizing component is a salt; the products are the salt and a dilute remaining stream. EFC systems simultaneously crystallize water and salt at the eutectic temperature. In ZLD situations, a CC may be followed by an EFC where the remaining dissolved salts are recovered while recovering clean water in the form of ice.

The processes are continuous. The intake volume is between 1-50 m^3/h (4 to 220 gpm) of high salinity brine. Several commercial installations are shown in the website. The largest EFC installation is 7.5 tons per hour (tph. The company states that CAPEX and OPEX savings of up to 50% can be realized over conventional evaporative crystallizers.

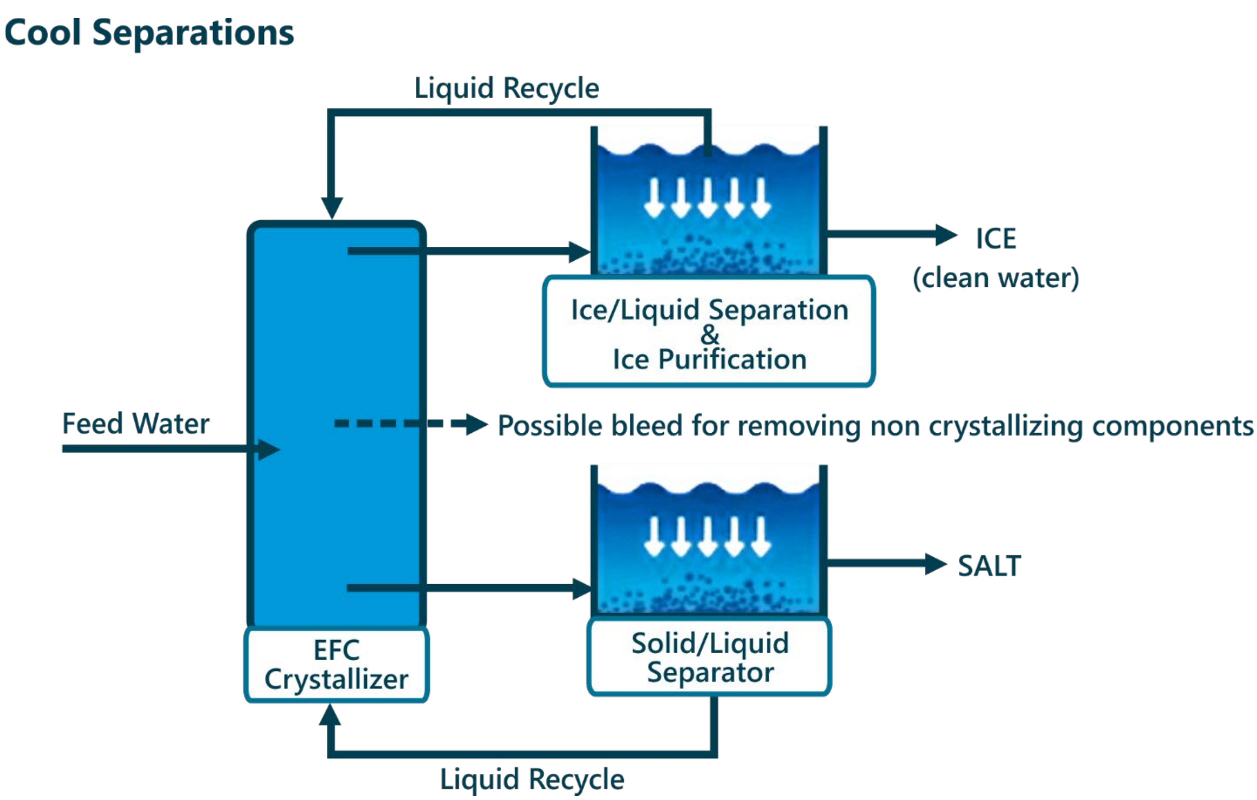

Figure 33. Cool Separations' freezing processes.

12.4.2. Saltworks Technologies Inc. (Canada)

URL: www.saltworkstech.com

Status: *In September 2020 Saltworks announced a pilot project involving their chilled crystallizer, SaltMaker ChilledCrys.*

Company information: The system works in tandem with the ultra-high pressure RO (UHP-RO) system which is stated as concentrating certain salts (e.g., sodium sulfate) to over 20% by mass. The concentrated brine solution then enters the chilled crystallizer, which takes advantage of steep solubility changes with temperature. As the solution cools, salt crystals are formed, which can be separated and removed. The process is stated to be a viable option for ZLD or MLD—if the feed water solution consists predominantly (>90%) of the following ion pairs:

- Sodium or potassium sulfate
- Sodium or ammonium carbonate/bicarbonate

Saltworks makes several other technologies that can be used with the Xtreme RO technology including: XtremeUF, for concentrating slurries; IonSelect, selective ion removal; SaltMaker evaporative crystallizer; and FlexEDR, for selective removal of monovalent ions.

12.5. Solvent Extraction

12.5.1. Adionics (France)

URL: www.adionics.com

Status: *The 2020 website mentioned 4 million Euros in 2018 funding to expand the scope of the technology to recovering lithium. The 2017 website listed other pilots and applications being planned. There was no reference to these in the 2020 website, and focus appears to be on recovery of high-value constituents.*

Company information: Adionics was formed in 2012 to take advantage of the lower energy requirement associated with removing small volumes of salts from feed water rather than removing large volumes of water from feed water. Key to the technology was development of an extraction solvent system that could extract a wide range of both cations and anions. The proprietary organic system of solvents, Flionex, can be tailored to selectively remove individual or groups of salts, as well as removing bulk salt—by adding ion-specific resin materials. Cations and anions are separately complexed and thus cannot interact to form scale during salt removal.

As shown in Figure 34, adsorption takes place in an extraction (adsorption) column. The salt laden stream then moves to a regeneration column where the solvent is regenerated by moderate temperature changes. Scaling upon regeneration can be avoided by various means, including putting two regeneration columns operating at different temperatures in series—taking advantage of ion-dependent temperature desorption rates. The process is continuous. A countercurrent multistage system can achieve high recovery rates. The technology is built with inexpensive glass reinforced resin materials. Adionics was a participant in the 2016-2017 Masdar desalination challenge (Cleantechnica, 2015).

Adionics

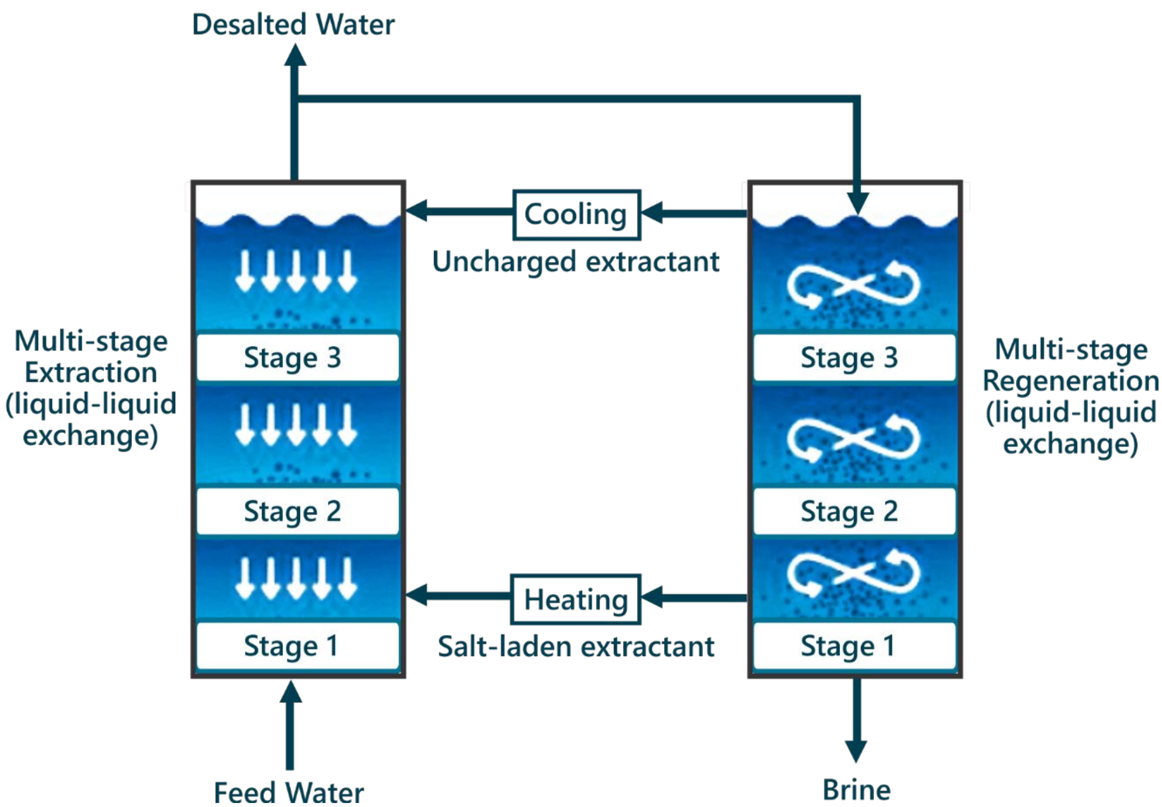

Figure 34. Adionics solvent extraction process.

12.6. Enhanced Evaporation

12.6.1. ECOVAP (Utah)

URL: https://www.ecovap.com/

Status: *The 2020 website states that ECOVAP was "recently recognized as one of the "Top 10 Wastewater Technologies-2019." In 2020 Tallgrass Energy obtained exclusive rights within the oil and gas industry to use the ECOVAP technology.*

Company information: ECOVAP has produced an enhanced evaporation system that employs high density polyethylene (HDPE) panels with a patented airfoil design that creates hundreds of saturated vertical water columns that hold water in suspension. This provides a very high available surface area to enhance solar- and wind-driven evaporation via convection—without using a fan or other power source. Tower saturation is reached in minutes using a low-pressure recirculating pump. The cubical structures are claimed to increase evaporation rate over 50 times. The typical effluent from the system can reach 250,000 to 300,000 mg/L TDS.

The units can reduce the pond area or allow a given pond area to service a much greater inflow.

12.6.2. Clear Creek Environmental Solutions (Colorado)

URL: www.ccenv.us

Status: *Clear Creek, founded in 2013, is focused on providing more sustainable and natural means to dispose liquid wastes. In addition to the enhanced evaporation products, they have processes that use plants and wetlands to manage wastewater.*

Company information: Clear Creek offers green sustainable natural solutions that include two brine management technologies associated with evaporation ponds. Clear Creek is the sole U.S. distributor of the Israeli Wind Aided Intensified eVaporation (WAIV) enhanced evaporation system.

The WAIV system has evolved over time to achieve enhanced net evaporation rates of up to 15 times. The unit is a stand-alone structure which uses wind to evaporate water by creating a high density of wetted surface area within a small footprint. This can result in reducing pond areas or increasing the evaporation efficiency of a given pond area.

A second technology uses a mixture of different microbes to enhance the evaporation rate. When added to the pond water, the non-toxic chemical solution can increase net evaporation rates by a factor of up to 2 to 4. This approach uses no energy and has no mechanical equipment. The higher the salt content, the more effective it is. Its use is recommended for salinities above 80,000 mg/L TDS. It can be used in addition to other enhanced evaporation approaches.

12.7. Value Recovery

12.7.1. Enviro Water Minerals - EWM (Texas)

URL: https://envirowaterminerals.com/

Status: *EWM has encountered many equipment and operational challenges in this highly complex processing facility. The entire focus of the company has been on startup and operation of the full-scale El Paso facility.*

Company information: EWM offers a Full Recovery Desalination process that achieves ZLD and chemically separates the wastewater into high-purity, industrial-grade mineral products that are highly valued in commercial markets. While recovery of values has been a subject of interest and research, EWM installed and commissioned a full-scale demonstration facility at the Kay Bailey Hutchinson Desalination Plant in El Paso in April 2107. The facility treats influent of 2.25 mgd (355 m^3/h) to produce 2 mgd (315 m^3/h) of drinking water with the remaining water tied up in products (caustic soda, hydrochloric acid, gypsum, and magnesium hydroxide). The company has over 10 patents on the integrated use of modern brine treatment processes: stripping, electrodialysis, nanofiltration, biological selenium removal, and modern mineral recovery processes: mechanical vapor recompression crystallizers, vacuum crystallizers, and hydrometallurgical leaching. Energy efficiency is achieved via combined heat and power natural gas engines. The operation has had and continues to have many challenges. The facility represents an important milestone in serving to demonstrate how recovery of values may be done.

12.8. Summary

Each of the technologies discussed has a potential marketing niche and may find more widespread commercial success. Cool Separations and Aquafortus both provide a one-step process to take feed water to solids. While Cool Separations may have finally commercialized a freezing desalination technology, Aquafortus represents a new approach to desalination.

Saltworks continues to expand their technology portfolio with a freeze crystallizer for a class of salts having reduced solubility at lower temperatures.

Greenblu and Medad are both vapor adsorption technologies with high energy requirements that limit their potential range of application. Medad appears to have found a niche application in extending the performance of MED desalination facilities.

Adionics also offers a new approach to desalination. It has been searching for a market and perhaps has found one in recovering high value products such as lithium. Like Aquafortus, the performance and costs are still being defined and definition will provide clarity on appropriate applications.

Ecovap and Clear Creek may become important in removing some of the cost- and land-intensive limitations of evaporation ponds.

Enviro Water Minerals may provide increased clarity on the general feasibility and pathway to recovery of values from brine.

13. High Recovery Markets

13.1. Introduction

This chapter reviews the historical and current markets for HR technologies and the perception that existing markets will increase due to unconventional oil and gas operations deepen and that new markets will emerge due to the increased performance and decreased costs of emerging HR technologies. In review:

- Disposal of wastewater is the most widely used brine management option (Chapter 2).
- Conventional technologies used in HR processing are both capital and energy intensive (Chapter 3 and 4).
- However, increased regulation of disposal options, increased volumes of wastewater, and droughts have resulted in greater consideration for HR processing for wastewater (Chapter 1).
- Many companies have been developing new technologies or modifications of conventional technologies to reduce HR processing costs (Chapters 5 through 12).

Nearly all installations have been industrial.

13.2. Historical Markets for Medium and Large Brine Concentrators and Crystallizers

Three major suppliers of historical HR systems (described as ZLD and MLD systems by these companies) in the U.S. have dominated the U.S. market and are major players in the global market: RCC (division of Suez), HPD (division of Veolia), and Aquatech. They have supplied most of the medium- and large-scale systems in the U.S.

Based on analyses of installation lists, the average size of the installations from Aquatech and Suez since 2000 is roughly 550 gpm (125 m^3/h) for brine concentrators (BC) and 55 gpm (12.5 m^3/h) for crystallizers. These averages include some large units that bias the averages. Without the top 10% of the BCs and the top single crystallizer, the average sizes drop to 364 gpm (83 m^3/h) for BCs and 11 gpm (2.5 m^3/h) for crystallizers.

Table 8 lists the combined global number of sales by decade from these three companies as interpreted from installation lists. Also indicated is the percentage of these sales that were in the U.S. Observations include:

- Over the last two decades, the number of yearly sales has not grown.
- Over the entire period covered, the percentage of sales that are in the U.S. has steadily decreased.

Table 8. Number of High Recovery (ZLD/MLD) Installations by Aquatech, Suez, and Veolia by Decade and Percent in the U.S.

Decade	Number	Percent in U.S.
1970s	7	100
1980s	20	95
1990s	71	68
2000s	119	50
2010s	117	27
Total	**334**	**49**

In a recent personal communication with a systems engineer for one of these companies, the continuing market trend for these HR systems was stated to be "5 to 15 yearly sales ranging from $2 to $100 million each." The data in Table 8 for the last two decades support this number showing an average of about 12 installations per year. As shown in Table 9, four industries (power, chemical, oil and gas, and pulp and paper) have accounted for about 81% of all the ZLD/MLD systems installed by Suez, Veolia, and Aquatech.

Table 9. Percent of Installations by Decade and by Industry.

Decade	Power	Chemical	Oil and gas	Pulp and Paper	Total %
1970s	100	0	0	0	100
1980s	70	5	0	5	80
1990s	28	27	10	11	76
2000s	39	17	13	18	87
2010s	16	19	26	15	76
TOTAL	32	19	16	14	81

In the 1970s, the power industry accounted for all 7 of the installations. Through the first 30 years, the power industry was the major market served by these high recovery systems. Since the late 1990s, the chemical and oil and gas industries have accounted for larger market segments than the power industry. The market segment of the oil and gas industry has increased in each decade and in the most recent decade was the largest segment.

In addition to these four markets, other markets served make up the other 19% of the installations. They are listed by decreasing percentages of installations:

- Mining and metals
- Coal to chemical
- Biofuels
- Electronics
- Municipal
- Manufacturing
- Pharmaceutical

The largest of these industry segments (metals and mining) has less than 5% of the installations.

13.3. Market Focus of Selected New Concentrate Management Technologies/Companies

Another indication of market focus or perceived markets may be found in the listings of target markets identified by companies conducting R&D on new or modified HR technologies.

In 2018, target markets were identified from websites, literature, and interviews for companies listed with their primary HR technology in Table 10.

Table 10. Companies and HR Technology

Company	HR technology
Oasys	forward osmosis (FO)
Trevi	forward osmosis (FO)
Forward Water	forward osmosis (FO)
Modern Water	forward osmosis (FO)
Aquastill	membrane distillation (MD)
KMX	membrane distillation (MD)
Memsys	membrane distillation (MD)
Altela	humidification-dehumidification (HDH)
Gradiant	humidification-dehumidification (HDH)
Saltworks	humidification-dehumidification (HDH)
Heartland	evaporation
TPTEC	multi-effect distillation (MED)
Salttech	mechanical vapor recompression (MVR)
Adionics	solvent extraction (SE)
BDL	electrodialysis reversal (EDR)

Table 11 lists the percent of companies highlighting each of the markets listed. All companies except Modern Water mention the oil and gas market reflecting the significant activity and perceived potential for high recovery processing.

Table 11. Percentage of Companies Targeting Various Markets

Market	Percent listing market as a target
Oil and gas	93
RO brine	53
Power	40
Chemical	40
Food and beverage	27
Industrial wastewater	27
Pharmaceuticals	27
Metals and mining	20
Leachate	20
Agricultural	20
Municipal	13
Textile	13
Electroplating	7
Sugar	7
Bioproducts	7

Observations include:

- At the time of the website reviews (2018 and 2020), a few companies were specifically focused on the oil and gas market (e.g., Gradiant and BDL). Gradiant does have some flue gas desulfurization installations in the power market. Gradiant has since had commercial sales in several other markets.

- Only two companies specifically mention the municipal market; the RO brine market is interpreted to be primarily non-municipal RO concentrate.

- Many companies mentioning the oil and gas market did not mention the power market. This may reflect the entrenched position that the major MLD/ZLD equipment suppliers have in this oldest of MLD/ZLD applications, and the perception that this conservative industry will not easily consider alternative solution providers—at least for medium and larger scale systems.

- There is likely overlap in some areas; the general area of industrial wastewater can be considered to include some of the specifically mentioned industrial markets.

13.4. Range of Salinities for Various Applications

As mentioned in Chapter 1, from 2008-2010, there was a significant interest in and upscale in unconventional oil and gas activities. The perception that applications in these areas could significantly increase the market for high recovery processing resulted in the widespread increase in R&D activities discussed in this report. As frequently mentioned in the report, the applications cover a wide range of feed water salinities. Table 12 lists representative ranges of several of these applications.

Table 12. General Salinity Ranges of Various High Recovery Applications

Application	Wastewater Salinity range (mg/L)
Power plant cooling tower blowdown	1,500 – 8,000
Power plant flue gas desulfurization (FGD wastewater)	20,000 – 50,000
Marcellus, Barnett, Haynesville shale flowback/produced water	45,000 – 200,000
Several other U.S. produced waters	< 45,000
Coal seam gas produced waters (Australia)	2,000 – 13,000
Coal to liquid wastewaters (China)	6,000 – 16,000
SAGD blowdown from steam generators (Canada)	1,200 – 3,000
Acid mine drainage (West Virginia)	1,500 – 9,000
Inland municipal applications (RO concentrate)	4,000 – 15,000
Municipal WWTP effluent	750 – 1,500
Food & Beverage	500 – 10,000
Pharmaceuticals	1,000 – 30,000
Agricultural	700-1,500
Leachate	1,000 – 20,000
Textile	1,000 – 20,000
Microelectronics	500 – 5,000

13.5. Market Dr

Application	Wastewater Salinity Range (mg/L)
Power plant cooling tower blowdown	1,500 – 8,000
Power plant flue gas desulfurization (FGD wastewater)	20,000 – 50,000
Marcellus, Barnett, Haynesville shale flowback/produced water	45,000 – 200,000
Several other U.S. produced waters	< 45,000
Coal seam gas produced waters (Australia)	2,000 – 13,000
Coal to liquid wastewaters (China)	6,000 – 16,000
SAGD blowdown from steam generators (Canada)	1,200 – 3,000
Acid mine drainage (West Virginia)	1,500 – 9,000
Inland municipal applications (RO concentrate)	4,000 – 15,000
Municipal WWTP effluent	750 – 1,500
Food and Beverage	500 – 10,000
Pharmaceuticals	1,000 – 30,000
Agricultural	700-1,500
Leachate	1,000 – 20,000
Textile	1,000 – 20,000
Microelectronics	500 – 5,000

13.6. Drivers and Barriers

13.6.1. Historical Market Drivers

As the data in Section 13.2 show, the market for medium and large high recovery wastewater processing systems has been one of slow growth with little change over the past two decades. Favored applications and installation locations have changed, but the number of yearly installations has been relatively constant.

Due to high costs, regulatory requirements used to be the primary driver for high recovery processing. A few years ago, major equipment suppliers would say that no one goes ZLD unless they are forced to. While this is still largely true, there are other drivers that influence brine management decisions.

There are a few unusual drivers for high recovery. In Oman, where salt is mostly imported, recovery of salts via high recovery processing has received interest in providing a new, in-country salt source. Another example is in Australia, where some industries receive raw materials via shipment across the Great Barrier Reef. Environmental concerns associated with possible accidents has driven some companies to recover salts to be used as precursors in manufacturing products such as acids that otherwise might be shipped. The driver in this case is minimizing company risk.

13.6.2. New Market Drivers

Companies are increasingly concerned with environmental and sustainability issues. Public sentiment and increasing competition for water between the public and industrial sectors are resulting in companies setting water and energy use goals. Per product use is one facet of this. Another area is water recovery and reuse. Where desalination treatment is required for reuse treatment, high recovery processing is increasingly considered.

The broad path toward sustainability regarding water treatment includes the recovery of salts and other elements from brines. Companies making high recovery thermal evaporative equipment tend to focus on either wastewater treatment or producing products. Companies focused on product recovery mostly treat feed waters that have a dominating salt or constituent that makes recovery profitable. Product recovery is of growing interest with regard to wastewater treatment. While it is easy to produce a given salt or other product, it is much more difficult to produce a product of a given grain size and purity that is of greater value. Whether ultimately successful or not, the Enviro Water Minerals facility in El Paso at the Kay Bailey Hutchinson Desalination Plant represents a milestone in the path toward product recovery from municipal concentrate. Other historical efforts along these lines may be found in Mickley, 2011.

A general driver resulting in the significant number of R&D efforts discussed in this report is the potential market that could open up if high recovery costs are decreased.

13.6.3. Market Barriers

High cost of treatment has been the major market barrier for high recovery processing—and a driver for reducing costs.

There are barriers for individual high recovery technologies, including time-related challenges of defining performance and cost envelopes and establishing a track record to minimize client-perceived risks. Some of the technologies involving newer approaches to desalination may have an additional barrier of market inertia in accepting the technologies.

Another company-related barrier is that clients want solutions to problems, not just a technology that may provide part of a solution. Companies that have broader technology portfolios may have greater marketing success.

There are additional barriers for use of high recovery technologies in the municipal sector. The high cost is a larger barrier for municipal clients than for industrial clients simply due to the economic reality of municipalities. In addition, municipalities are less experienced in operating more highly technical systems.

Further, many companies developing high recovery processing technologies do not focus on municipal applications because of the time and effort associated with participation in the bidding process and the need for technologies to be certified with regards to health and safety issues.

13.6.4. Market Impact

Despite the significant R&D efforts to reduce high recovery processing, the market impact has been minor. Economic issues have affected high recovery markets, especially the oil and gas market—the largest historical market and the market perceived to be on the verge of significant growth due to unconventional oil and gas applications (see Section 13.4).

Another reason why the significant growth in the oil and gas market has not happened is that changes in the past decade have avoided the need for blowback frack water to be desalinated for reuse. The chemical makeup of frack water now enables frack water to be reused with only minor treatment, including reducing suspended solids levels.

Desalination has also proved difficult to compete with deep well injection. Despite growing concerns with location-specific seismic activities associated with deep well injection, it remains an easy disposal solution.

Long timeframes associated with bringing technologies to the marketplace are another major reason for the low level of market impact, as discussed in market barriers (O'Callaghan et al., 2018). Company-related factors that affect technology development times include the strength of company management, company strategy, protection of intellectual property, and ability to obtain funding during the critical early survival years.

13.7. Market Forecast

Clearly, the general market forecast is that membrane technologies will strongly influence the future of HR processing. Reduced costs will spur lower salinity applications, such as in municipal and industrial water reuse. High recovery RO technologies will be used, and will eliminate the need for follow-on non-membrane evaporative steps in some cases. In higher salinity applications, where RO processing is still feasible, non-RO membrane technologies, such as FO and MD, may be used after RO treatment and reduce concentrate volume before—and in some cases replace—follow-on evaporation steps. Reduced costs in these applications can expand existing market applications and create new markets.

Other high recovery technologies will find market niches and contribute to market growth.

13.8. Summary

High recovery markets have been almost entirely industrial and have been of slow growth and mostly driven by regulation because of the high processing costs of conventional high recovery technologies. Newer market drivers have resulted in widespread R&D efforts to reduce the processing costs. The marketplace includes many applications over many industries, covering a wide range of feed water conditions. Markets, however, remain limited. Some perceived market drivers (e.g., increase in unconventional oil and gas applications) have not been realized. More generally, there has been only minor impact of the R&D efforts on market growth due to a mix of economic-, technology-, and company-related factors. But, the potential for market growth is real; only the timing is in question. The largest market impact will likely be from high recovery RO technologies that have the broadest range of applications and can have the largest impact on cost reduction.

14. Summary of Results

14.1. State-of-the-Industry Changes

Project work focused on evaluating high recovery technologies and the companies involved in their development, in order to assess their current and potential impact in the marketplace.

Over the three-year time period of the project, there has been increased definition of performance, costs, and applications of the different technologies. There have also been changes in the economy, in markets, and in the companies involved.

Companies have taken various approaches to reduce the high costs of conventional HR processing. Costs have been reduced in three ways:

- Increasing robustness and decreasing the need for and thus cost of pretreatment steps.
- Increasing the recovery of the initial, less cost- and energy-intensive RO step
- Decreasing the unit costs of any of the desalination steps.

Some of the cost savings are simply based on the nature of different technologies. Others are based on innovative modifications of conventional technologies.

14.1.1. Increasing Recovery and Reducing Costs in Membrane Systems

High pressure systems: Conventional RO systems have hydraulic and osmotic pressure limitations of due to the strength of materials of construction. Changes in these materials in high pressure systems allow higher pressure operation and feed solutions to be concentrated to higher osmotic pressure levels, i.e., higher concentrations. The result is higher recovery.

The higher concentrations can lead to an increased potential for scaling to occur and as a result, more substantial pretreatment may be required. While CAPEX and OPEX for the RO step may increase, the higher recovery results in reducing system CAPEX and OPEX for multistep high recovery systems which have follow-on evaporative steps.

Smart control -time dependent RO: Conventional RO systems are conservatively designed to enable operation over a range of feed conditions. In that sense, the systems rarely operate in an optimal manner. Concentrations, pressures, and velocities change with location but are not independently controlled. Aside from scaling and fouling with time, the systems operate in a continuous steady-state manner. Many smart systems operate in a batch or semi-batch mode, where all or a portion of concentrate is recycled and feed solution concentration increases with time. Some of the smart systems utilize periodic reversal of flow direction. Some or all of these operating variables are independently controlled, which allows more optimal use of the variables with time. As a result, most smart systems require less energy, concentrate to higher levels while avoiding precipitation of salts and silica, and, in general, result in more efficient operation. In a few cases precipitation is allowed to occur. In some cases, conventional RO systems can be converted into smart systems simply be installing smart control systems. In other cases, the smart systems include hardware differences from conventional RO systems, with some consisting of a single membrane stage.

These systems can have lower unit costs relative to conventional RO. As with other HR RO systems, the higher recovery reduces costs for multistep systems that involve evaporative technologies following the RO step.

Osmotically assisted RO (OARO): In conventional RO systems, for permeation to occur, feedside pressure must be greater than the osmotic pressure difference between feedside and permeate side solutions. The difference in osmotic pressure can be lessened by allowing higher permeate side concentrations. As a result, permeate flux can be achieved at lower feedside pressure. The permeate, however, has a higher salinity than that occurring in conventional RO. OARO overcomes this by arranging units in series with counter current flow between them. This results in increasing the reject concentration on one end of the cascade and decreasing the permeate side concentration on the other end. By this means, separations can be attained similar to and beyond that of conventional RO. The series of membrane steps can include a mix of NF, RO, and FO units.

Since recovery is not limited by pressure issues, higher recovery is achieved. Due to the number of units, along with more sophisticated interstage pressure and flow connections, the system unit CAPEX for the OARO step is higher than that of conventional RO systems. The unit OPEX can be less due to the lower pressure levels required for permeation. As with other high recovery RO systems, the higher recovery of the RO step can reduce total system costs for high recovery multistep systems.

Robustness: Some of the HR RO systems incorporate high velocity flow and more open flow channels to reduce scaling and fouling. This can lead to lower needs for pretreatment and membrane cleaning. Increases in CAPEX are balanced by decreases in OPEX.

14.1.2. Reducing Costs in Thermal Systems

There have been innovative approaches taken to decrease costs.

Direct contact heating: Some thermal systems use direct contact heating where the water to be evaporated is directly contacted by the high temperature fluid. Humidification-dehumidification devices are based on this principle, and some other types of evaporation systems incorporate this mode of heating. This eliminates the heat transfer resistance of a transfer surface such as a tube wall, and eliminates a scaling/fouling surface. As a result, direct contact heating can reduce the unit energy requirement.

One-step evaporation systems: Some evaporative systems have combined the function of the brine concentrator and the crystallizer. Precipitation occurs in this single step system and thus reduces pretreatment otherwise needed to reduce scaling and fouling. The unit energy requirement in these systems appears to be between that of conventional brine concentrators and conventional crystallizers.

Use of waste heat: Some thermal systems are designed for use with waste heat. Where waste heat is available and feasible, its use can reduce energy costs.

Use of resin-based materials of construction: Conventional metal brine concentrators and crystallizers, due to their weight, require concrete pads and cranes for installation. Installation costs can equal equipment costs. The use of lower cost and lower weight resin-based materials can decrease both equipment and installation costs. Resin-based materials also eliminate corrosion concerns.

14.1.3. Increasing System Robustness

Conventional crystallizers frequently have maintenance issues that leads to down-time. As a result, some companies focus on increasing robustness. This can involve reducing moving parts and simplifying the internals by going to direct heating, which eliminates heat transfer surfaces and makes cleaning operations easier. Robustness is particularly important in the treatment of more complex feed water such as found in many oil and gas applications.

14.2. Likely Areas of Technology Impact

The project has witnessed changes occurring over a two-year period and the present analysis will shift due to changes in the future. However, the following statements are supported by the present reading of the status of the various technologies.

Figure 35 illustrates where the likely impact area of some of the technologies will be felt relative to the conventional HR processing sequence of RO → brine concentrator → crystallizer.

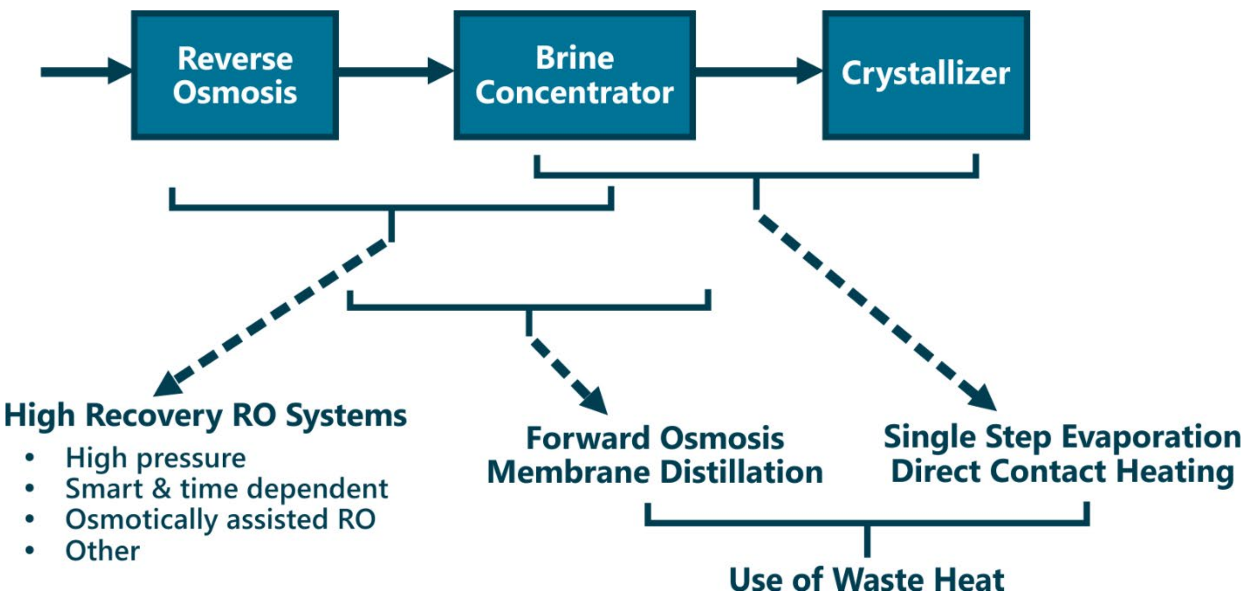

Figure 35. General Areas of Potential Impact

14.2.1. High recovery RO

HR reverse osmosis systems can process higher salinity feed water and can concentrate the feed water to higher salinity levels than conventional RO systems. As a result, they can take over some of the role held by the cost- and energy-intensive conventional brine concentrator. The high recovery RO technologies have fewer remaining development challenges than with other high recovery membrane-based technologies. The market for these systems is large and across most industries, including the municipal sector.

14.2.2. Forward osmosis and membrane distillation

Both FO and MD can concentrate feed water to even higher salinity levels than HR RO, and thus can cover a larger part of the role held by conventional brine concentrators. For lower salinity feed water, it is likely that the FO and MD steps will be preceded by a less expensive RO step. FO technology still has development issues (low membrane flux, several different draw solutions). MD technology has limited market application due to the high energy requirement and linkage with the use of waste heat. There may be a scalability issue associated with a large unit footprint (footprint/gpm).

14.2.3. One Step Evaporator Systems

Single step evaporator systems combine the roles of the conventional brine concentrator and crystallizer. Some single step evaporators are humidification-dehumidification systems; others are MVR systems or variants of other conventional designs.

14.2.4. Other Evaporation Systems

Other HDH systems and modifications of MVR and other conventional evaporation designs are competing just for the role of the conventional brine concentrator. HDH, like all evaporative systems, has high energy requirements and a linkage with the use of waste heat. These issues reduce its marketing applications relative to those for high recovery RO systems.

14.2.5. Electrolytic Systems

A few EDR systems are pushing into higher recovery areas of RO processing and others are incorporating different membranes to achieve specialized treatment objectives. The other technologies such as EDI, CDI, and CapDI are primarily used in polishing situations and in most cases compete with ion exchange systems. The high recovery market application for electrolytic systems is less than that of high recovery RO systems. The Magna Imperio EDR technology may, however, challenge RO in various applications.

14.2.6. Other Processes

Some interesting and innovative different approaches to desalination and concentrate management are discussed in Chapter 12. Many are in the development stage of defining their general feasibility and applicability. These technologies may have a greater market acceptance hurdle due to market inertia in warming to new technology approaches.

14.3. Most Promising HR Cost Reduction Technology

High recovery RO is the most promising technology area for short term impact in reducing HR costs. Reasons for this include:

- HR RO technologies cover a wide range of feed water salinity levels and thus cover a wide range of possible applications.

- RO technologies are readily accepted in most, if not all, of the industries having brine management issues.

Municipal inland applications are low salinity applications and are thus more suitable for treatment by the HR RO technologies than other technologies. Such technologies have begun receiving attention in various pilot tests at municipal sites. Some pilots have involved higher recovery at existing desalination facilities and other pilots have involved treating wastewater effluent for indirect potable reuse.

14.4. General Impact to Date

To date, HR processing systems have had a limited impact on the marketplace. However, for most technologies companies have clearly made progress in the definition of performance and cost, in definition of promising market niches, and in the number of references (pilots, demonstrations, and commercial). There are several factors that affect the time involved in commercializing high recovery technologies.

14.4.1. Limited Number of References

The number of references is a major factor that limits consideration of new technologies. There are both short-term and long-term risks for using a treatment process that has a limited track record. Once a technology has established itself through several successful installations, the short-term risk is significantly reduced. Long-terms risks are those associated with issues of long-term reliability and performance of the technologies. For example, the metal material systems in conventional thermal evaporators have operated for over 30 years, in some cases. The life-time of thermal evaporators constructed with resin-based materials is not known and may well be less than 30 years. Similarly, the life-time of membranes and system components used in high recovery RO systems that involve higher pressures and/or time-dependent changes in operating parameters is an unknown. These risks can only be determined after years of tracking.

14.4.2. Economy and Regulation

The economy affects most industries. Applications in the oil and gas industry are strongly dependent on the economy and applications in the power industry are driven by regulations. The downturn in the economy has affected applications in the oil and gas industry, and the more recent roll-back of regulation has affected application in the U.S. power industry. The economy also affects companies' stability and their rate of progress in developing technologies.

14.4.3. Technology

It takes time to develop a commercial technology, particularly so when there are many possible applications and a wide range of feed water salinities, compositions, and complexities. This can increase the time it takes to bring clarity to performance capabilities, cost pictures, and definition of market niches. From this perspective, it is not surprising that the technologies have made little impact so far.

14.4.4. Company limitations

Company progress is dependent on the strength of company management, market strategies, intellectual property protection, and success at obtaining funding to make it through the early years.

14.5. Recommendations

The report is a picture in time of the status of the high recovery processing sector of brine management. The picture needs to be periodically updated. As illustrated in this report, it is recommended that considerations beyond Technology Readiness Levels be used to indicate the status of a technology and potential a technology has in making an impact on the marketplace.

These considerations include interaction with companies involved in developing the technologies.

It is important to view the present study and the efforts to reduce HR processing costs from the perspective of the evolution of brine management considerations. The focus of the technologies reviewed has been on the reduction of the **volume** of wastes. This has various benefits that facilitate the handling of brines and allow less costly management of brines within the present regulatory framework. The efforts are but a stepping stone in the necessary evolution of brine management methods.

In the future it will be of increasing importance to reduce not only the volume of brine but the amount of problematic constituents in the final residuals. More generally, important future considerations include:

- converting some constituents to less problematic forms,
- recovery of products of value,
- implementing circular economy solutions where possible,
- and, in general, pushing toward greater sustainability.

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Appendix A: Historical MLD/ZLD Cost Studies of High Recovery Technologies

A.1. Introduction

Chapter 4 introduced the challenges of predicting performance, energy usage, and costs of HR processes for conventional ZLD systems represented by Figure A-1.

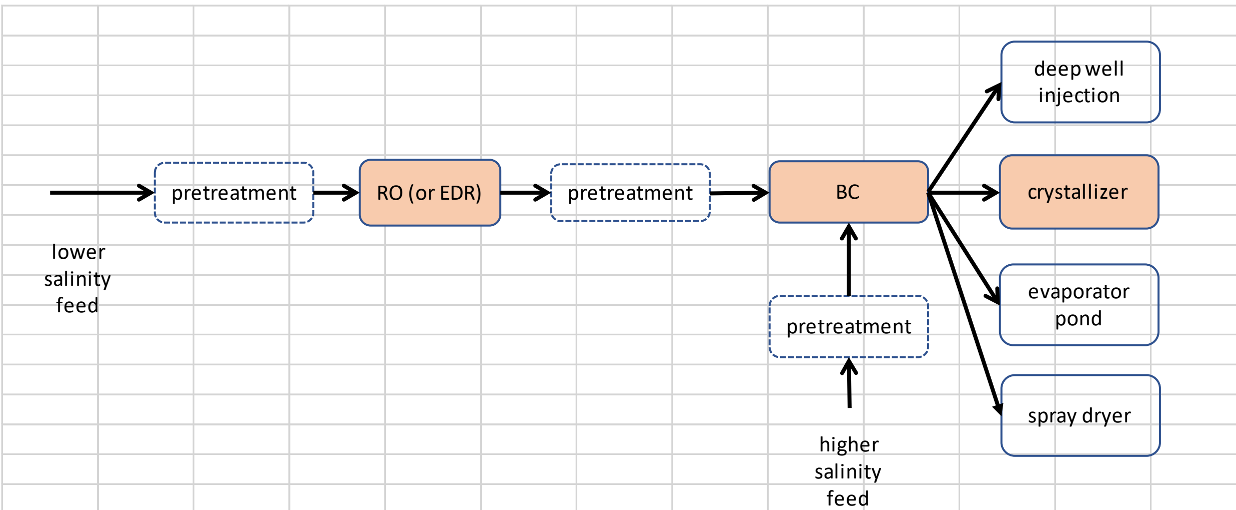

Figure A-1. The most widely installed ZLD processing system. EDR = electrodialysis reversal.

To further explain these challenges, the appendix reviews two previous studies that estimated performance and costs of ZLD systems. Although the studies are dated, the issues examined have not changed. These studies illustrate several points:

- The high OPEX/CAPEX ratio of thermal evaporative technologies relative to disposal options that do not involve evaporative processes
- The difficulty of predicting performance and cost of the thermal evaporative steps
- The dependence in different ways of individual process steps on salinity and composition of feed water
- The strong dependence of total system costs on salinity and composition of feed water

As a result, it is misleading to generalize performance and costs based on a single set of conditions.

A.2. Pipeline or Evaporation Pond vs. ZLD Options

Mickley and Associates (Mickley, 2003) looked at ZLD disposal options based on a hypothetical situation in the Phoenix, Arizona, area. At the time, many thought that ZLD could be the solution to the high costs of concentrate disposal in arid locations. In the hypothetical study, various regional brackish RO sites produced a total of 20 mgd (75,700 m^3/d) of concentrate of a specific water quality. This basis was used in a 2000 Reclamation report (Reclamation, 2000) that considered two disposal options—transport of the concentrate via a long- distance pipeline to the Sea of Cortez and a multi-square mile area system of evaporation ponds. Mickley & Associates looked at two additional scenarios:

- Treating the concentrate with a thermal brine concentrator followed by evaporation ponds
- Sending the concentrate to a second stage RO system (Aquatech's HERO system) whose concentrate then went to a brine concentrator followed by evaporation ponds.

Estimates of capital, operating, and annualized costs for these four scenarios are given in Table A-1 and Table A-2.

The costs in Table A-1were figured at $0.05/kWh; sludge disposal at $30/ton; annualized cost at 40 years and 7.125% interest (the basis for Reclamation 2000). The capital cost savings of the ZLD technology schemes (options 3 and 4) are evident in the capital cost row. The much higher operating costs are evident in the operating cost row. The annualized costs are higher in the two ZLD cases than in the original cases. Table A-2 shows details of the operating cost for options 3 and 4.

Table A-1. Capital, Operating, and Annualized Costs for the Four Scenarios

	Option 1 Pipeline	**Option 2 Evaporation ponds**	**Options 3 Thermal evaporation + evaporation ponds**	**Option 4 HERO + thermal evaporation + evaporation ponds**
CAPEX, (MM$)	310	410	136	76
OPEX (MM$/yr)	0.8	1.6	33	29
ANNUAL ($/yr)	24	33	43	35
Water Lost (mgd)	20	20	0.8	0.8

Table A-2. Operating Costs for the two ZLD Options

	Options 3 Thermal evaporation + evaporation ponds	**Option 4 HERO + thermal evaporation + evaporation ponds**
Labor (MM$/yr)	1.1	3.1
Energy (MM$/yr)	31.0	3.9
Chemicals (MM$/yr)	-----	6.2
Sludge disposal (MM$/yr)	-----	14.7
Evaporating Pond (MM$/yr)	0.8	0.8

In this analysis, thermal options were not credited with recovered water. Including high recovery RO dramatically reduces the size of the thermal brine concentrator that follows and thus reduces the energy costs significantly. The decreased energy costs, however, are made up for by the increased costs of chemicals and sludge disposal. Although the scope of the study was limited, the results indicated that, based on cost, the ZLD option is not necessarily an attractive one.

A.3. Performance Issue—Scaling

Scaling can occur when the concentration of a salt and other constituent (such as silica) reaches the solubility limit and precipitate forms and coats membrane or heat transfer surfaces. Fouling refers to the adherence of other constituents, usually organic in nature, onto membrane or heat transfer surfaces due to the affinity of the constituent to the surface. Both scaling and fouling can significantly decrease mass transfer and heat transfer rates and thus compromise performance.

Solubility limits are a function of temperature and are also dependent on the presence and amount of other salts and constituents in the water. However, general categories of solubility limits can be defined in Table A-3:

Table A-3. Solubility Categories

General solubility level	Salt examples
Sparingly soluble salts	calcium carbonate, calcium sulfate
Moderately soluble salts	sodium carbonate, sodium sulfate
Soluble salts	sodium chloride
Highly soluble salts	calcium chloride, magnesium chloride

In conventional brackish RO processing, recovery is typically limited by the occurrence of scaling by sparingly soluble salts and/or silica. In conventional seawater RO processing, scaling is not limiting as the feed water levels of sparingly soluble salts are low. Recovery instead is limited by the pressure limits of the pressure vessels as high pressure is needed to overcome the osmotic pressure of the concentrate which increases with recovery. Conventional seawater RO (SWRO) may be limited to a concentrate of 60,000 to 70,000 ppm TDS. When using conventional SWRO technology to process feed water other than seawater, recovery is typically limited by scaling of sparingly soluble salts. When scaling is not limiting, (e.g., from extensive pretreatment), recovery is limited by osmotic pressures, as seawater treatment using SWRO. However, as the makeup of feed water is different than seawater, much higher salinity concentrates, up to over 100,000 ppm TDS may be possible before osmotic limits are reached.

In high recovery processing of lower salinity feed water, RO and EDR are widely accepted as the initial desalination technology to be used in order to minimize the size of following thermal technologies.

Regardless of the water source, the complexity of water chemistry increases as salinity increases. Scaling of sparingly soluble salts are still a concern and the scaling of moderately soluble and soluble salts may become a concern. In general terms, the number of constituents that may form scale increases with increasing salinity depending on the water quality. In thermal technologies where pressure and temperature are variables, water physical-chemical effects become more complex.

In RO systems, readily available software can be used to simulate and predict system performance and costs. In thermal process, there is no such widely available software. Both prediction of performance and estimation of costs require interaction with thermal equipment manufacturers—mainly due to the complex water chemistry but also due to the limited number of OEMs tightly holding onto their knowledge. To understand the complex chemistry and physical effects that can take place, OEMs such as Suez, Veolia-HPD, and Aquatech use a highly sophisticated, expensive geochemistry software called OLI that contains several hundred different salts and other constituents and predicts their interactions as a function of concentration, temperature, and pressure.

A.4. Effects of Salinity and Composition on ZLD Performance and Costs

A 2008 WateReuse Foundation study (Mickley, 2008) investigated the effects of salinity and composition on several high recovery processing schemes operating as ZLD systems. Eight concentrates, some actual and some projected from raw water qualities, were used as the basis to compare performance and costs of five most widely used commercial ZLD approaches (Table A-4).

Table A-4. Commercial ZLD Process Schemes Chosen for Evaluation

Scheme	Processing Step Sequence
1A	Conc. --> BC --> EP
1B	Conc. --> BC --> Cryst. --> EP & LF
2A	Conc. --> LS --> RO2 --> BC --> EP & LF
2B	Conc. --> LS --> RO2 --> BC --> Cryst. --> EP & LF
3	Conc. --> LS --> RO2 --> EP & LF

Note: Conc. = Concentrate; BC = brine concentrator; EP = evaporation pond; Cryst. = crystallizer; LF = landfill; LS = lime softener; RO2 = 2nd stage RO

To uncouple effects of salinity and composition, both of which varied among the concentrates, concentrate salinities (which varied from about 4,000 to 11,000 mg/L) were normalized to 8,000 mg/L. Each constituent was ratioed in the same manner to provide the 8,000 mg/L composition. This approach eliminated salinity as a variable, allowing focus on the effect of composition alone. In addition, the effects of concentrate volume and salinity were explored using a single relative composition to provide an additional four concentrates to give a total of 12 concentrates and 5 processing approaches. Table A-5 and Table A-6 list the compositions and flows of the 12 cases. Concentrations units are mg/L.

Table A-5. Composition, Salinity, and Flow of Cases 1-5

CASE #	**1 low salinity low flow**	**2 low salinity high flow**	**3 BASE CASE**	**4 high salinity low flow**	**5 high salinity high flow**
Na	613	613	1,226	1,840	1,840
Ca	365	365	731	1,096	1,096
Mg	178	178	355	533	533
K	32	32	63	95	95
SO_4	1,782	1,782	3,564	5,346	5,346
Cl	555	555	1,111	1,666	1,666
HCO_3	464	464	928	1,393	1,393
Si (as SiO_2)	11	11	22	32	32
approx. TDS	4,000	4,000	8,000	12,000	12,000
flow (MGD)	1	20	10	1	20

These five cases are at a single base composition (case 3) and at higher and lower combinations of the flow and salinity as illustrated in Figure A-2.

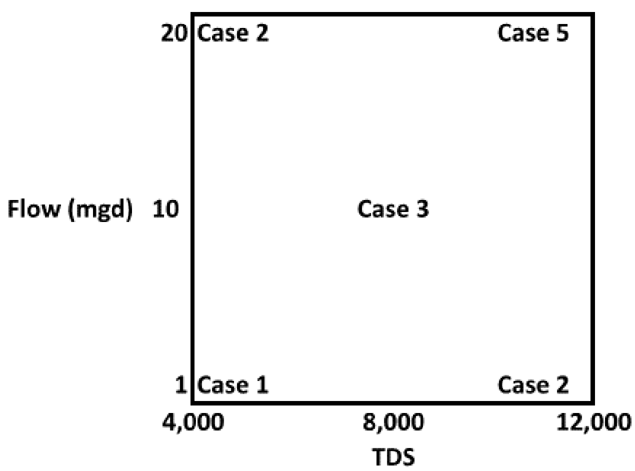

Figure A-2. Definition of Cases 1-5

Cases 6 through 12 (Table A-6) are at the salinity (8,000 mg/L) and flow (10 mgd or 37,850 m^3/d) as case 3, thus providing 8 total cases where composition is the only variable.

Table A-6. Composition of Cases 6-12

CASE #	6	7	8	9	10	11	12
Na	456	1,074	2,062	1,009	2,043	1,015	1,857
Ca	912	967	574	941	75	944	488
Mg	677	212	147	310	36	338	206
K	114	73	97	24	63	81	7
SO_4	4,577	2,206	638	1,669	6	3,313	3,852
Cl	798	1,158	4,141	1,640	95	1,323	1,376
HCO_3	336	2,176	161	2,212	5,682	920	184
Si (as SiO_2)	130	134	180	194	0	64	29
approximate TDS	8,000	8,000	8,000	8,000	8,000	8,000	8,000
flow (MGD)	10	10	10	10	10	10	10

Individual process step performance, system performance, and costs were evaluated as a function of processing scheme, salinity, composition, and flow rate. The choice of variable conditions allowed independent study of these effects.

Performance and cost of each step are dependent in different ways on salinity and composition. Due to this complex interaction between processing steps, simple rule of thumb predictions of performance and cost for ZLD systems can be misleading and inaccurate.

As previously mentioned, there are no readily available simulation programs to predict the performance and cost of brine concentrators and crystallizers. This type of information is held closely by the limited number of companies manufacturing these systems. As a result, the project paid one of the major manufacturers to estimate the performance of these evaporative technologies for the 12 cases listed in Table A-5 and Table A-6.

The estimated performance results of the brine concentrator and crystallizer are shown in Table A-7.

Table A-7. Performance Characteristics of BC and Crystallizer Treatment of Cases 1-12.

Situation 1: brine concentrator / crystallizer treatment - for schemes 1A and 1B

1	2	3	4	5	6	7	8	9	10	11	12	13	14
	brine concentrator									crystallizer			
Case	**Feed TDS mg/l**	**Feed flow mgd**	**effluent TDS mg/l**	**type evaporator**	**chemicals added**	**limiting parameter**	**energy kWh/kgal**	**material level**	**effluent flow gpm**	**crystallizer feed, gpm**	**crystallizer purge?**	**purge salinity mg/l**	**purge volume gpm**
1	8,000	10	257,000	seeded slurry	H_2SO_4	glauberite	75	low	210	210	Y	450,000	11
2	4,000	1	257,000	seeded slurry	H_2SO_4	glauberite	75	low	21	21	Y	450,000	0.6
3	4,000	20	257,000	seeded slurry	H_2SO_4	glauberite	75	low	421	421	Y	450,000	11
4	12,000	1	263,000	seeded slurry	H_2SO_4	glauberite	75	low	30	30	Y	384,000	3
5	12,000	20	263,000	seeded slurry	H_2SO_4	glauberite	75	low	604	604	Y	384,000	62
6	8,000	10	261,000	seeded slurry	H_2SO_4	glauberite	75	low	210	210	N	---	0
7	8,000	10	226,000	seeded slurry	H_2SO_4	glauberite	75	low	231	231	Y	411,000	7
8	8,000	10	358,000	seeded slurry	H_2SO_4	NaCl	95	high	154	154	Y	???	80*
9	8,000	10	226,000	seeded slurry	H_2SO_4	TSS	85	low	231	231	Y	374,000	29
10	8,000	10	167,000	seeded slurry	H_2SO_4	glauberite	75	low	302	302	N	---	0
11	8,000	10	258,000	seeded slurry	H_2SO_4	TSS	85	low	210	210	Y	410,000	14
12	8,000	10	199,000	seeded slurry	H_2SO_4	glauberite	75	low	278	278	N	---	0

* = assumed

Situation 2: brine concentrator / crystallizer treatment after lime softening and 2nd stage RO - for schemes 2A and 2B

	brine concentrator									crystallizer			
Case	**Feed TDS mg/l**	**Feed flow mgd**	**effluent TDS mg/l**	**type evaporator**	**chemicals added**	**limiting parameter**	**energy kWh/kgal**	**material level**	**effluent flow gpm**	**crystallizer feed, gpm**	**crystallizer purge?**	**purge salinity mg/l**	**purge volume gpm**
1	60,803	1.21	145,000	seeded slurry	$H_2SO_4/CaCl_2$	glauberite	75	low	352	352	N	---	---
2	61,010	0.06	145,000	seeded slurry	$H_2SO_4/CaCl_2$	glauberite	75	low	17.5	17.5	N	---	---
3	61,010	1.2	145,000	seeded slurry	$H_2SO_4/CaCl_2$	glauberite	75	low	350	350	N	---	---
4	58,506	0.19	145,000	seeded slurry	$H_2SO_4/CaCl_2$	glauberite	75	low	53.2	53.2	N	---	---
5	58,506	3.74	145,000	seeded slurry	$H_2SO_4/CaCl_2$	glauberite	75	low	1047	1047	N	---	---
6	57,623	1.45	145,000	seeded slurry	$H_2SO_4/CaCl_2$	glauberite	75	low	400	400	N	---	---
7	58,953	0.92	145,000	seeded slurry	$H_2SO_4/CaCl_2$	glauberite	75	low	282	282	N	---	---
8	61,156	1.3	263,000	seeded slurry	$H_2SO_4/CaCl_2$	NaCl	95	high	161	161	N	---	---
9	58,578	0.92	143,000	seeded slurry	$H_2SO_4/CaCl_2$	glauberite	75	low	284	284	N	---	---
10	61,851	1.26	247,000	falling film	H_2SO_4	NaCl	95	high	219	219	N	---	---
11	59,153	1.24	145,000	seeded slurry	$H_2SO_4/CaCl_2$	glauberite	75	low	283	283	N	---	---
12	60,766	1.25	145,000	seeded slurry	H2SO4/CaCl2	glauberite	75	low	291	291	N	---	---

Situation 1 described in the top half of the table is where the concentrate of columns 2 and 3 is the feed water to the brine concentrator (processing schemes 1A and 1B). Situation 2, described in the bottom half of the table, is where the concentrate is first treated by lime softening and reverse osmosis prior to treatment by the brine concentrator (processing schemes 2A and 2B). The other columns in the table are:

- column 4 is the TDS of the brine from the brine concentrator
- column 5 is the type of evaporator used;
- column 6 lists the chemicals added as pretreatment;
- column 7 lists the constituent that limits brine concentrator recovery;
- column 8 is an indication of the general energy requirement of the brine concentrator;
- column 9 is an indication of the relative cost of materials of construction – mainly due to corrosion concerns
- column 10 gives the effluent flow rate exiting the brine concentrator and going to the crystallizer.
- column 11 lists the feed rate to the crystallizer
- column 12 designates whether there is a purge stream from the crystallizer to purge highly soluble salts from the unit.
- column 13 lists the salinity of the purge stream.
- column 14 lists the purge volume.

Note the significant difference in brine concentrator performance (column 4) due to feed composition. These differences lead to significant CAPEX and OPEX differences for the evaporator steps due to 1) different evaporator sizes and 2) need for different materials of construction (in some cases as indicate in column 9). This information on the evaporation steps was then used in the determination of total treatment system costs for each of the 5 processing schemes and 12 cases. Of note:

- The range of final salinities after brine concentrator processing (column 4) is large:
    - 167,000 to 358,000 ppm TDS for Situation 1
    - 143,000 to 263,000 ppm TDS for Situation 2

- The limiting factor (column 7) most frequently occurring is precipitation and scaling of the double salt glauberite, $Na_2Ca(SO_4)_2$. Note that if calcium were to be removed with and ion exchange step following the RO step, the limiting factor would be precipitation of Na_2SO_4, which in most of the cases would occur at a much higher salinity.

- The levels of salinity achieved when feed water was first treated by lime softening and then RO (situation 2 of Table A-7) was lower than when feed water was directly treated by the brine concentrator (situation 1 of Table A-7). This is due to the increased formation of glauberite. Note the one exception to this in case 5 where the dominant salt is NaCl.

- The brine flow from the BCs (column 10) dictates the size (which reflects the cost) of the crystallizer (or evaporation pond) that would complete the treatment process. Note the wide range in flows from 133 to 400 gpm.

The total unit annualized cost results for the 12 cases and 5 processing schemes are represented in Figure A-3.

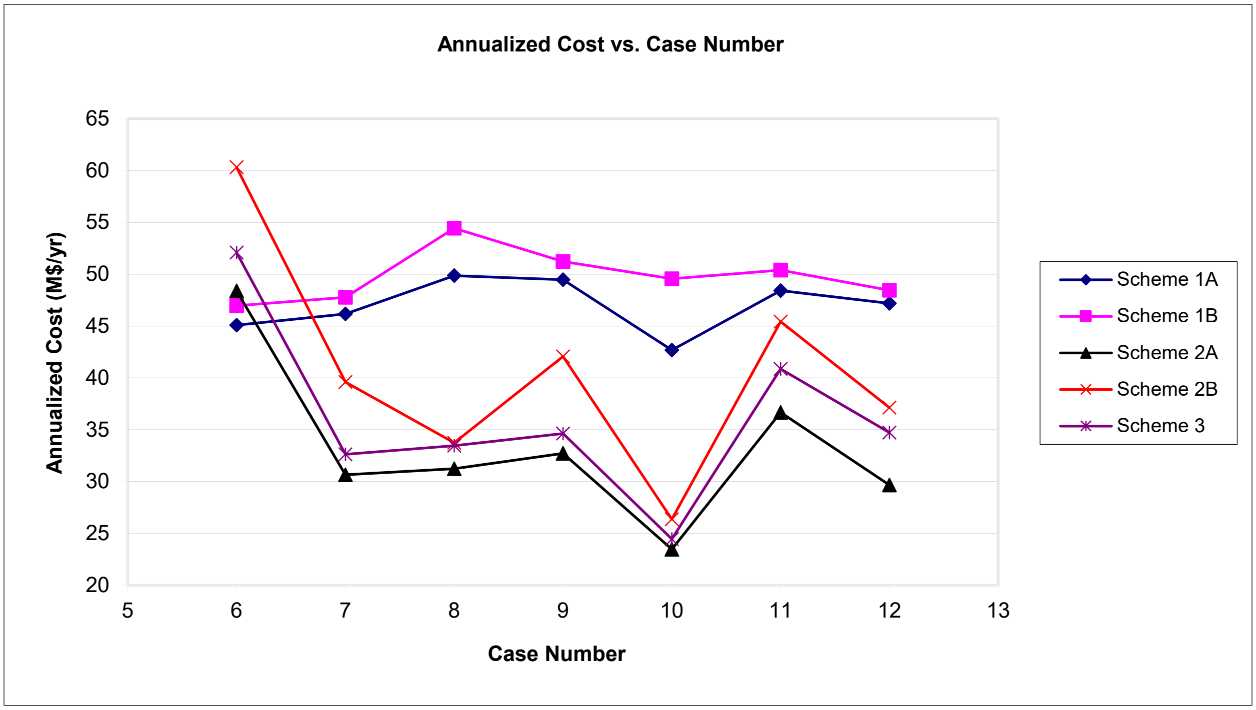

Figure A-3. Unit annualized cost by case number for the 5 processing schemes.

The cases from top to bottom at the far right are: 1B, 1A, 2B, 3, 2A where the processing sequence is:

- 1B = BC → crystallizer (CRYST) → Evaporation pond (EP) and landfill (LF)
- 1A = BC → EP
- 2B = Lime softening (LS) → RO → BC → CRYST → EP and LF
- 3 = LS → EP and LF
- 2A = LS → RO → BC → EP and LF

Although high costs of high recovery processing are evident in all the situations studied, the results illustrate a wide range of costs.

The highest annual cost in cases 7 -12 is with processing schemes 1B and 1A, which are the schemes without an RO step. The lowest annual cost in cases 7-12 are processing schemes 3 and 2A, where and RO step is used but without a crystallizer step. Note however, that using crystallizers may be necessary to achieve a solution in some situations—such as where evaporation ponds are not possible. As an example of how CAPEX and OPEX vary due to feed water composition, Figure A-4 and Figure A-5 show total costs as well as costs of each processing step for the processing scheme 2A.

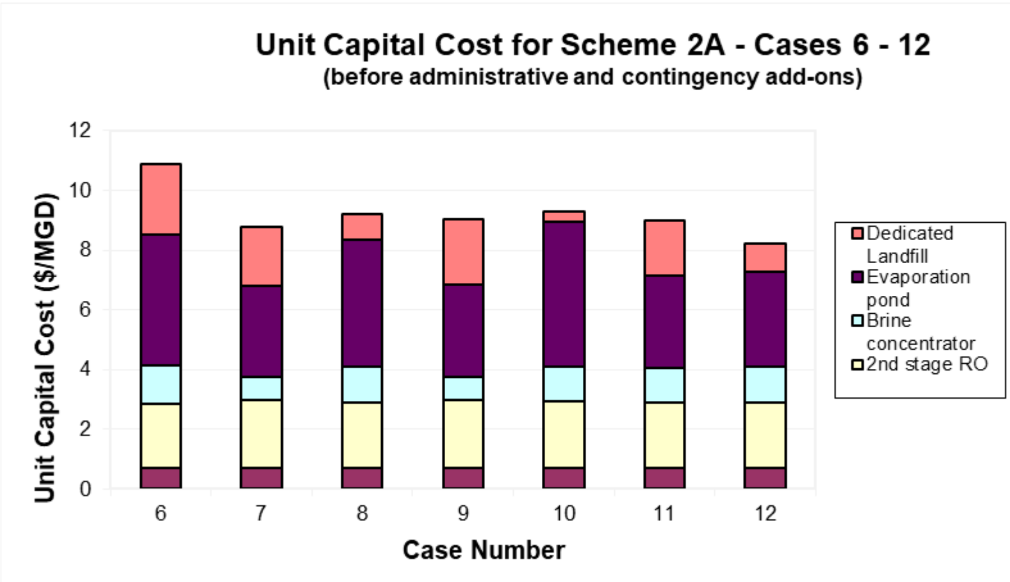

Figure A-4. CAPEX for processing scheme 2A and cases 6-12.

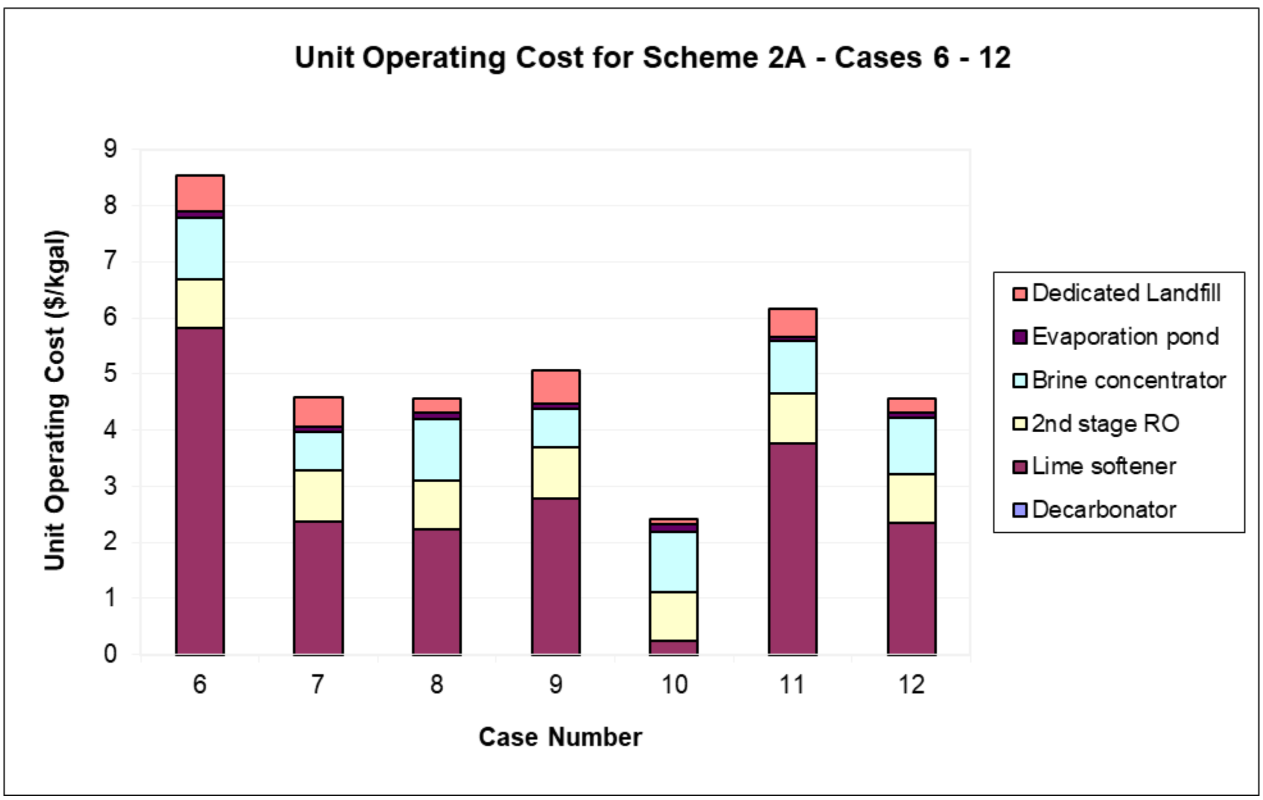

Figure A-5. OPEX for processing scheme 2A and cases 6-12.

As illustrated in this example and for nearly all processing schemes, OPEX varied more than CAPEX.

A.5. Summary

The primary results from the study:

- Illustrate that the performance of the brine concentrator and crystallizer vary significantly on the composition of the feed water to the system.

- Illustrate significant effects of salinity and composition on performance and cost of commercial ZLD systems

Perhaps the most important point from the study is that it is risky to generalize ZLD process performance and costs based on results from a single study case - whether a desktop study or a pilot test, as results are highly dependent on salinity, composition, and concentrate volume.