An Integrated Framework for Treatment and Management of Produced Water

TECHNICAL ASSESSMENT OF PRODUCED WATER TREATMENT TECHNOLOGIES

1st EDITION

RPSEA Project 07122-12

November 2009

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This report presents a comprehensive literature review and technical assessment to evaluate existing and emerging technologies that have been used for treatment of produced water or novel technologies that could be tested and considered in the future. This technical assessment includes stand-alone water treatment processes, hybrid configurations, and commercial packages developed for treatment of oil and gas produced water and zero liquid discharge (ZLD). This assessment considers pretreatment, desalination, post-treatment, and concentrated waste disposal to meet the required water quality standards for beneficial use scenarios. It should be noted that many commercially available products for produced water treatment are usually unique combinations of unit processes. This document focuses on primary unit processes, and attempts to include the major commercial packages/processes for produced water treatment. This document can be used to evaluate various treatment processes in a generic fashion even if their vendors are not listed in the report.

The report was developed as part of a collaborative research project (#07122-12) led by the Colorado School of Mines (CSM) and funded by the Research Partnership to Secure Energy for America (RPSEA).

TECHNOLOGIES ASSESSED

A total of 54 technologies were reviewed and assessed in the study. The technologies are classified into stand-alone technologies and combined treatment processes.

Stand-alone/primary	Multi-technology processes
Basic Separation o Biological aerated filters o Hydroclone o Flotation o Settling o Media filtration **Membrane Separation** o High pressure membranes ▪ Seawater RO ▪ Brackish water RO ▪ Nanofiltration (NF) ▪ VSEP o Electrochemical charge driven membranes ▪ Electrodialysis (ED), ED reversal (EDR) ▪ Electrodionization (EDI) o Microfiltration/ultrafiltration ▪ Ceramic ▪ Polymeric o Thermally driven membrane ▪ Membrane distillation (MD) o Osmotically driven membrane ▪ Forward osmosis (FO)	**Enhanced distillation/evaporation** o GE: MVC o Aquatech: MVC o Aqua-Pure: MVR o 212 Resources: MVR o Intevras: EVRAS evaporation units o AGV Technologies: Wiped Film Rotating Disk o Total Separation Solutions: SPR – Pyros **Enhanced recovery pressure driven** o Dual RO w/ chemical precipitation o Dual RO w/HEROTM: High Eff. RO o Dual RO w/ SPARRO o Dual pass NF o FO/RO Hybrid System **Commercial treatment RO-based processes** o CDM o Veolia: OPUS™ o Eco-Sphere: Ozonix™ o GeoPure Water Technologies

EVALUATION CRITERIA

This review broadly documents state-of-the-art research and development efforts in produced water treatment. The technologies and configurations identified in the review are technically assessed in terms of several important criteria, which are summarized in **Table 1**. The technologies are evaluated based on water quality bins: (i) feed water quality, and particularly salinity and constituents of concern for treatment processes (e.g., hydrocarbons, suspended solids, hardness, silica, barium, iron, manganese, boron); (ii) product water quality and its relation to water quality requirements for different produced water discharge regulations and beneficial use applications, including surface water discharge, agriculture irrigation, life stock irrigation, and USEPA drinking water standards. Another key criterion in the technical assessment is production efficiency in terms of product water recovery, which is directly related to waste (liquid or solids) generated on site that has to be disposed offsite. Other key criteria included power requirements, chemicals used, enclosure and footprint, reliability, robustness, costs, O&M considerations, pretreatment and post treatment requirements, and concentrate management options. The applicability of the technology in produced water treatment is qualitatively scored from poor to excellent. The ranking is based on:

- Poor - the technology can not be used to treat CBM produced water
- Moderate - there are significant hurdles, but under certain circumstances the technology may be appropriate for treatment of CBM produced water.
- Good – the technology has merit, but there may be some factors that limit its broad utilization for treatment of CBM produced water.
- Excellent – the technology can be used for treatment of CBM produced water and is commercially available. The technology can be deployed in the field (with appropriate pretreatment or design considerations) and will perform its desired function.

The goal of this report is to provide potential users with an objective and unbiased technical assessment. In addition to the description of the technology theory and key technical and economic considerations listed in Table 1, the report summarizes important findings from field trials, pilot studies, or bench scale studies. The report expands on benefits and limitations of each treatment technology based on previous studies.

This report is a synthesis of published material, including peer-reviewed journal articles, conference presentations and proceedings, technical reports, contract reports, reviews, feasibility analysis, annual reports, media reports, and information posted on vender's website and brochures. Although the report delimits between manufacturer claims and peer-reviewed scientific data through the case studies, the users should be aware that, for some technologies/processes, manufacturer brochures are the only available source for information.

Table 1. Description of assessment criteria

Criteria	**Description/Rationale**
Industrial status	Emerging or existing technology in which industry, whether being previously employed for produced water treatment and to what level (full-scale, pilot-scale, bench-scale), whether it is a competitive or non-competitive vendor market (including supplier names), minimum and maximum plant size
Feed water quality bins	Applicable TDS range, types of water chemistry makeup, constituents of concerns including: hydrocarbons, suspended solids, hardness, boron, silica, barium, iron, manganese, etc
Product water quality	Overall reported or estimated rejection in terms of TDS, sodium, organic constituents, heavy metals, ammonia, and others
Production efficiency (recovery)	Specific production efficiency in terms of reported and/or estimated product water recovery
Infrastructure considerations	Known infrastructure constraints or considerations such as modularity, mobility, energy type, relative footprint, electrical supply, housing, brine discharge, chemical storage, etc.
Energy consumption	Types of energy needed and power requirements
Chemicals	Types of chemicals required for process control (such as for regeneration, fouling, scaling, alkalinity, corrosion, and disinfection) and cleaning
Life cycle	Expected life of the process and replacement needs
O&M considerations	Levels of monitoring and control required, including quality control Level of skilled labor required Level of flexibility: easy to adapt to highly varying water quantity and quality Level of robustness: ability of the equipment to withstand harsh conditions, such as cold weather climates, shut-down and restart Level of reliability – little down time, need for maintenance Types of energy required
Overall costs	Reported treatment, capital, operation, and maintenance costs. Identification of major cost components including waste disposal. Identification of components offering most cost reduction opportunities
Pre-and post treatment	Types and levels of pre- and post-treatment required by the technology
Concentrate management or waste disposal	Waste to feed volume ratio. Concentrate treatment and/or available disposal options of concentrate or solid wastes. Special disposal considerations, if any
Applicability in produced water treatment	Qualitatively scoring the technology for the produced water application criterion (excellent to poor)

WASTE DISPOSAL COST

Because waste disposal is a common consideration for all water treatment technologies, the costs of waste disposal are discussed here prior to the review of water treatment technologies. Waste disposal costs strongly depend on the location of and distance of the disposal facility from the production site, disposal method, the type of waste (quality and quantity), and the extent of competition in the local or regional area [1]. In 1997, Argonne National Laboratory (ANL) compiled data on costs charged by offsite commercial disposal companies to accept produced water, rain water, and other "water type wastes" [2]. In 2005, ANL began collecting current information to update and expand the database [1]. This section provides information about the new 2005–2006 database and focuses on the availability of offsite commercial disposal companies, the prevailing disposal methods, and estimated disposal costs.

The categories of waste in the database include:

- Contaminated soils
- Naturally occurring radioactive material (NORM),
- Oil-based muds and cuttings,
- Produced water,
- Tank bottoms, and
- Water-based muds and cuttings.

The different waste management or disposal methods in the database include:

- Bioremediation,
- Burial,
- Salt cavern,
- Discharge,
- Evaporation,
- Injection,
- Land application,
- Recycling,
- Thermal treatment, and
- Treatment.

Produced water disposal costs reported in the ANL report [1] are briefly presented below. The reported costs are assumed to be lower than or comparable to the costs available for onsite management by the operators themselves. It should be noted that the types of waste are important to disposal costs. For example, a facility in Wyoming charges \$8/bbl, for particularly dirty wastes that need pretreatment before injection, while the same facility charges as low as \$0.75/bbl for cleaner wastes [3]. This implies that the disposal costs of more concentrated or solidified wastes after produced water treatment might be more costly than disposal of more diluted produced water. However, the volume of the wastes will be minimized and might result in reduced overall disposal costs.

Overall disposal costs range between \$0.30/bbl and \$105.00/bbl depending on the disposal method. The higher costs are charged by a thermal treatment facility in Texas, an evaporation facility in Colorado, and a landfill facility in Louisiana. The lowest costs are charged by one cavern operator in Texas as well as several injection facilities in Oklahoma. By far, the most common commercial disposal method for produced water is injection, followed by evaporation and burial.

Injection of produced water on a commercial basis occurs throughout the U.S. Texas, Louisiana, and Oklahoma hold the most significant shares in commercial disposal well operations. The disposal costs range between $0.30/bbl and $10/bbl. In most cases, costs do not reach $1/bbl. Newpark Environmental Services in Louisiana and Texas disposes of produced water through solids injection. Costs range between $5/bbl and $10.50/bbl.

Today, evaporation of produced water is most widely practiced in Wyoming (seven companies), followed by Colorado (four companies), Utah (four companies), and New Mexico (three companies). Except in one case, the disposal costs range between $0.40/bbl and $3.95/bbl. One company in Colorado charges $84/bbl.

Burial in landfills is available for produced water across the nation. However, solidification, which is generally required, drives up the costs. Volume-based costs range between $3/bbl and $22/bbl in Texas and North Dakota, and $18 cubic yard ($3.75/bbl) in New Mexico. Weight-based costs vary significantly by state, but generally range between $15/ton and $80/ton. Mississippi and Louisiana report higher ranges of up to $128/ton and $250/ton, respectively. Burial of produced water in commercial pits is not widely reported. Three companies, in Oklahoma, Utah, and Wyoming, report costs ranging between $0.35/bbl and $4/bbl.

Cavern disposal is a competitive option for produced water in Texas. Five companies at multiple facilities offer their services for a cost between $0.30/bbl and $10/bbl.

Discharge of produced water under an NPDES permit was reported by three companies in Pennsylvania and one company in Wyoming. The costs range between $0.045/gal and $0.055/gal ($2.25/bbl and $2.75/bbl) in Pennsylvania, and between $2.50/bbl and $3.50/bbl in Wyoming. All four companies apply treatment prior to discharge. Two facilities in Pennsylvania discharge produced water to a POTW for a disposal fee of between $0.015/gal and $0.050/gal ($0.75/bbl to $2.50/bbl).

Land application of produced water is offered in Arkansas (one company), New Mexico (two companies) and Utah (one company). Costs are between $0.30/bbl and $0.40/bbl in Arkansas, $5.18/bbl to $18/bbl in New Mexico, and $100/ton ($26.25/bbl) in Utah. Treatment of produced water is offered by CCS Energy Services LLC in Alabama and Eco Mud Disposal in Texas. Costs range between $5/bbl and $14/bbl. Recycling of produced water is not widely reported. One company identified in California charges $5/bbl. Another company in Oklahoma indicates a cost of $25/load. Thermal treatment of produced water is offered by Clean Harbors Environmental Services at its Deer Park facility. Costs range between $0.02/lb and $0.20/lb ($40/ton to $400/ton, or $10.5/bbl to $105/bbl).

REVIEW AND ASSESSMENT OF WATER TREATMENT TECHNOLOGIES

The following section presents a descriptive write-up corresponding to each technology, based on the list of criteria included in Table 1. A detailed tabular summary, or synopsis, of the assessment matrix is presented to facilitate an overall assessment with respect to the evaluation criteria.

Biological Aerated Filters

The term biological aerated filter (BAF) refers to a class of technologies, including fixed film and attached growth processes, roughing filters, intermittent filters, packed bed media filters, and conventional trickling filters. A BAF consists of permeable media, such as rocks, gravel, or plastic media. The water to be treated flows downward over the media and over time generates a microbial film on the surface of the media (

Figure **1**). The media facilitates biochemical oxidation/removal of organic constituents. This is an aerobic process and aerobic conditions are maintained by pumps and fans in the system. The thickness of the microbial layer continues to increase as the filter is used. Eventually, the microbial layer becomes thick enough that part of the slime layer becomes anaerobic and the microbial layer begins to slough off in the filter effluent [4]. Media should have high surface area per unit volume, be durable, and inexpensive. The type of media is often determined based on what materials are available at the site. Media can be field stone or gravel and each stone should be between one and four inches in diameter, to generate a pore space that does not prohibit flow through the filter and will not clog when sloughing occurs [5].

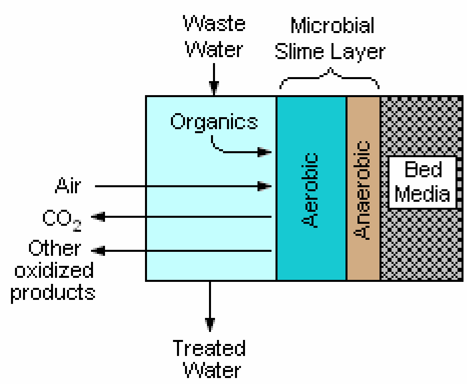

Figure 1. Schematic drawing of a biological aerated filter.

BAF can remove oil, suspended solids, ammonia, and nitrogen, chemical oxygen demand (COD), biological oxygen demand (BOD), iron, manganese, heavy metals, soluble organics, trace organics, and hydrogen sulfide. Iron and manganese removal in BAFs is mainly due to chemical oxidation rather, not a biological process. Since BAFs do not remove dissolved constituents, however, high concentrations of salts can decrease the effectiveness of this technology due to salt toxicity effects. At chloride levels below 6,600 mg/L, there is no diminished contaminant removal with BAFs and at 20,000 mg/L chloride levels there will be a reduction in slime growth and BOD removal [6]. This technology can be used to treat water with much greater organic contaminant concentrations than typically found in CBM produced water.

BAF is a well established technology and has been used for produced water treatment for many years [7, 8]. Because of this technology's ability to remove oil and grease, it has been primarily used for oil-field produced water treatment [7]. Informal versions of BAFs require minimal equipment, can be made by flowing water over rock beds. These types of BAFs have also been used in CBM produced water treatment for iron removal and suspended solids removal.

Removal capability of BAFs is dependent on the hydraulic loading rate on the filter and the raw water quality. The following are approximate removal capabilities of this technology: 60 to 90% nitrification, and 50 to 70% total nitrogen [4], 70 to 80% oil, 30 to 60% COD, 85 to 95% BOD, and 75 to 85% suspended solids [7].

There is nearly 100% water recovery from this process. The residuals generated are from the settling of the microbial layer that sloughs off of the media. The residuals generation, which is highly dependent on the water quality, is approximately 0.4 to 0.7 pounds of dry solids per 1000 gallons of water treated (for wastewater treatment) [9].

Primary sedimentation should be employed upstream from BAFs to allow the full bed of the filter to be used for removal of non-settling, colloidal, and dissolved particles if the water requires a large degree of contaminant removal. Sedimentation should also follow BAFs to remove the microbial layer that sloughs off of the filter. Other equipment that may be used includes pumps and fans for aeration, and distribution nozzles. The estimated energy demand for BAFs is 1 to 4 kWh/day. No chemicals are necessary [5]. A summary of the BAF assessment is provided in **Table 2**.

Table 2. Biological Aerated Filter Assessment

Criteria	**Description/Rationale**
Industrial status	Well established technology and has been used for treatment of produced water [8]. Numerous vendors.
Feed water quality bins	Most effective on waters with chloride levels below 6,600 mg/L [6]. Oil < 60 mg/L; COD < 400 mg/L; BOD < 50 mg/L. * Maximum feed water concentrations depend on % removal and target water quality
Product water quality	50 to 70% total nitrogen [9] 70 to 80% oil [7] 30 to 60% COD [7] 85 to 95% BOD [7] 75 to 85% suspended solids [7]
Production efficiency (recovery)	Waste from this process is removed as a solid, therefore, water recovery is nearly 100%
Energy use	The power requirement for BAFs is 1 to 4 kWh
Chemicals use	No chemicals are required for BAFs during normal operation, no cleaning is required
Expected lifetime of critical components	Long expected lifespan. Some types of BAFs consist only of rock beds hand holding ponds and do not require any equipment.
Infrastructure considerations	BAFs require upstream and downstream sedimentation, therefore, they have a large footprint and are not very mobile or modular

Table 2. Biological Aerated Filter Assessment

Criteria	**Description/Rationale**
O&M considerations	Very little monitoring required Occasional emptying of sedimentation ponds required Does not require skilled operators Easy to adapt to highly varying water quantity and quality Little down time or need for maintenance Electricity required for pumps and fans for aeration and circulating water
Overall costs	The majority of the overall cost of this technology is capital. O&M costs are very low.
Pretreatment of feed water	Sedimentation may be required upstream of BAFs and is required downstream of BAFs.
Post-treatment of product water	Typically none required.
Concentrate management or waste disposal	Solids disposal is required for the sludge that accumulates in the sedimentation basins. Can account for up to 40% of total cost of technology.
Note: 1 barrel = 42 US gallons	

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Hydrocyclone

Hydrocyclones are used to separate solids from liquids based on the density of the materials to be separated. Hydrocyclones normally have a cylindrical section at the top where the liquid is fed tangentially and a conical base (**Figure 2**). The angle of the conical section determines the performance and separating capability of the hydrocyclone. Hydrocyclones can be made from metal, plastic, or ceramic and have no moving parts. The hydrocyclone has two exits, one at the bottom, called the underflow or reject for the more dense fraction and one, called the overflow or product at the top for the less dense fraction of the original stream [10].

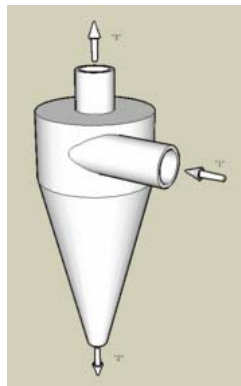

Figure 2. Schematic drawing of a hydrocyclone.

Hydrocyclones can be used to separate liquids and solids or liquids of different densities. Hydrocyclones can be used to remove particulates and oil from produced water. Depending on the model of hydrocyclone employed, they can remove particles in the range of 5 to 15 µm [11]. Hydrocyclones will not remove soluble oil and grease components [12].

Hydrocyclones have been used extensively to treat produced water and are marketed by numerous companies for produced water treatment [13, 14]. Hydrocyclones were used to treat fracturing brine in the Barnett Shale play [15]. In this research study, hydrocyclones were used in combination with organo-clays as a pretreatment to reverse osmosis.

Hydrocyclones do not require any pre- or post-treatment. They do not require any chemicals or energy. The hydrocyclone is the only piece of equipment necessary. There are no energy requirements unless the plant setup requires a forwarding pump to deliver water to the hydrocyclone. Depending on the size and configuration of the hydrocyclone, a large pressure drop can occur across the hydrocyclone.

The waste generated from a hydrocyclone is slurry of concentrated solids. This is the only residual that requires disposal. A summary of the hydrocyclone assessment is provided in **Table 3**.

Table 3. Hydrocyclone Assessment

Criteria	**Description/Rationale**
Industrial Status	Hydrocyclones have been widely used for produced water. They are mainly used for oil/water separation and can also be used for particulate removal.
Feed water quality bins	Applicable to all TDS bins, independent of salt type and concentration. High organic concentrations. High oil and grease or high particulate concentrations.
Product water quality	Can reduce oil and grease concentrations to 10 ppm.
Production efficiency (recovery)	High product water recovery.
Energy use	The hydrocyclone does not require energy unless a forwarding pump is necessary to deliver water to the hydrocyclone or to recover pressure lost through the hydrocyclone.
Chemicals use	None.
Expected lifetime of critical components	Long, no moving parts, may suffer from abrasion.
Infrastructure considerations	Minimal. Forwarding pump may be required to pressurize feed stream.
O&M considerations	Solids can block inlet and scale formation can occur requiring cleaning, however, typical cleaning is minimal.
Overall costs	Contact vendor.
Pretreatment of feed water	None required.
Post treatment of product water	This process is usually used as part of a treatment train. Post treatment may be required to remove other constituents from feed water.
Concentrate management or waste disposal	Disposal required for slurry.
Note: 1 barrel = 42 US gallons	

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Flotation

Flotation is a process in which fine gas bubbles are used to separate small, suspended particles that are difficult to separate by settling or sedimentation (**Figure 3**). Gas is injected into the water to be treated and particulates and oil droplets suspended in the water are attached to the air bubbles and they both rise to the surface. As a result, foam develops on the surface, which is commonly removed by skimming. The dissolved gas can be air, nitrogen, or another type of inert gas. Dissolved air/gas flotation can also be used to remove volatile organics and oil and grease. Dissolved air flotation units have been widely used for treatment of produced water [16-18].

Gas flotation technology is subdivided into dissolved gas flotation (DGF) and induced gas flotation (IGF). The two technologies differ by the method used to generate gas bubbles and the resultant bubble sizes. In DGF units, gas (usually air) is fed into the flotation chamber, which is filled with a fully saturated solution. Inside the chamber, the gas is released by applying a vacuum or by creating a rapid pressure drop. IGF technology uses mechanical shear or propellers to create bubbles that are introduced into the bottom of the flotation chamber [14]. Coagulation can be used as a pretreatment to flotation.

The efficiency of the flotation process depends on the density differences of liquid and contaminants to be removed. It also depends on the oil droplet size and temperature. Minimizing gas bubble size and achieving an even gas bubble distribution are critical to removal efficiency [16]. Flotation works well in cold temperatures and can be used for waters with both high and low TOC concentrations. It is excellent for removing natural organic matter (NOM). Dissolved air flotation (DAF) can remove particles as small as 25µm. If coagulation is added as pretreatment, DAF can remove contaminants 3 to 5 µm in size [11]. In one reported study, flotation achieved an oil removal of 93% [19]. Flotation cannot removal soluble oil constituents from water. Treatment costs are estimated to be $0.60/m^3$ [18].

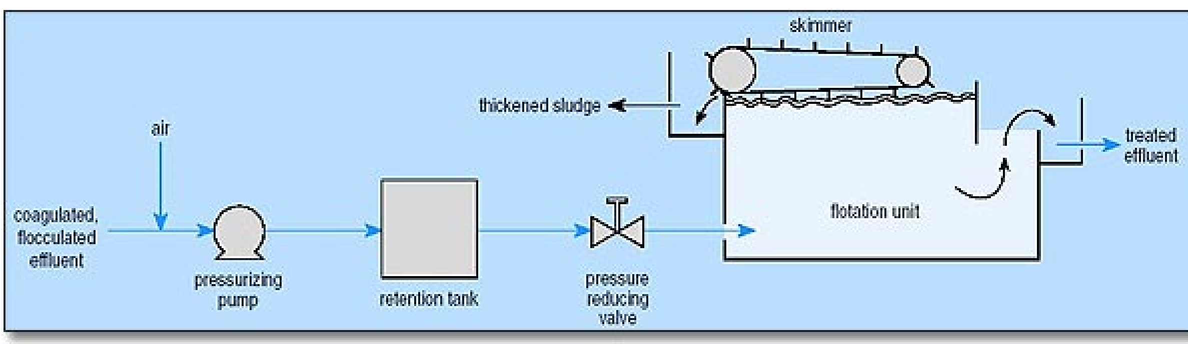

Figure 3. Flotation unit (Source: [20]).

Because flotation involves dissolving a gas into the water stream, flotation works best at low temperatures. If high temperatures are present, a higher pressure is required to dissolve the gas in the water. A summary of the flotation assessment is provided in **Table 4**.

Table 4. Flotation Assessment.

Criteria	Description/Rationale
Industrial Status	Widely used for produced water treatment, primarily for conventional oil and gas produced water [16-18]
Feed water quality bins	High TOC, oil and grease, particulates < 7% solids [21] Not ideal for high temperature feed streams
Product water quality	93% oil removal [19] 75% COD removal [21]; 90% removal of H_2S [21]
Production efficiency (recovery)	High recovery, nearly 100%
Infrastructure considerations	Dissolved air flotation requires an external pressurized tank
Energy consumption	Energy is required to pressurize the system to dissolve gas in the feed stream.
Chemicals use	Coagulant chemical may be added to enhance removal of target contaminants.
Expected lifetime of critical components	No information available.
O&M considerations	Chemical coagulant and pumping costs are the major components of O&M costs for flotation.
Capital and O&M costs	No information available. Contact vendor.
Pretreatment of feed water	Coagulation may be used as a pretreatment for flotation
Post treatment of product water	No post treatment required.
Concentrate management or waste disposal	Solids disposal will be required for the sludge generated from flotation.
Note: 1 barrel = 42 US gallons	

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Adsorption

Adsorption can be accomplished using a variety of materials, including zeolites, organoclays, activated alumina, and activated carbon. Chemicals are not required for normal operation of adsorptive processes. Chemicals may be used to regenerate media when all active sites are occupied. Periodically the media is backwashed to remove large particulates trapped between the voids in the media. Typically, these processes can be gravity fed and do not require an energy supply, except during backwash.

Adsorbents are capable of removing iron, manganese, total organic carbon, BTEX compounds, heavy metals, and oil from produced water. Adsorption is generally utilized as a unit process in a treatment train rather than as a stand-alone process. The adsorbent can be easily overloaded with large concentrations of organics, so this process is best used as a polishing step rather than as a primary treatment process [14].

Media usage rate is one of the main operational costs for adsorptive processes. When all active site of the adsorptive material have been consumed, the material must either be regenerated or disposed of. Regenerating the materials will result in a liquid waste for disposal. Solid waste disposal is necessary when the material needs to be replaced entirely. A summary of the adsorption assessment is provided in **Table 5**.

Table 5. Adsorption Assessment

Criteria	**Description/Rationale**
Industrial status	Adsorption is commonly used for treatment of produced water
Feed water quality bins	Applicable to all TDS bins, independent of salt type and concentration. Can remove iron, manganese, TOC, BTEX, and oil. Zeolites can also be used to exchange calcium for sodium to reduce SAR
Product water quality	> 80% removal of heavy metals [22]
Production efficiency (recovery)	Nearly 100% product water recovery.
Energy use	Minimal.
Chemicals use	Chemicals may be required for media regeneration.
Expected lifetime of critical components	Media may require frequent replacement or regeneration depending on media type and feed water quality.
Infrastructure considerations	Adsorption processes require a vessel to contain the media and pumps and plumbing to implement backwashes.
O&M considerations	There will be a pressure loss incurred across the filter, however, depending on the plant configuration; this may not require any additional pumps. Pumps will be necessary to backwash the filters.
Capital and O&M costs	None available.
Pre and post treatment	Adsorption is best used as a polishing step to avoid rapid usage of adsorbent material.
Concentrate management or waste disposal	Waste disposal is required for spent media or the waste produced during regeneration of the media.
Note: 1 barrel = 42 US gallons	

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Media filtration

Filtration can be accomplished using a variety of different types of media: walnut shell, sand, anthracite, and others. Filtration is a widely used technology for produced water, especially walnut shell filters for the removal of oil and grease. There are many vendors available that market filtration technologies specifically for produced water.

Filtration does not remove dissolved ions and performance of filters is not affected by high salt concentrations, therefore filtration can be used for all TDS bins regardless of salt type. Filtration can be used to remove oil and grease and TOC from produced water. Removal efficiencies can be improved by employing coagulation upstream from the filter. A summary of technical assessment on media filtration is provided in **Table 6**.

Table 6. Filtration Assessment

Criteria	**Description/Rationale**
Industrial status	Filtration has been used extensively for produced water treatment. Multiple vendors available that market filtration technologies specifically for produced water treatment.
Feed water quality bins	Applicable to all TDS bins, independent of salt type and concentration.
Product water quality	> 90% oil and grease removal
Production efficiency (recovery)	Nearly 100% water recovery is achieved with filtration; some filtrate may be used for backwashes.
Energy consumption	Minimal energy is required for these processes. Energy is required for backwashing the filter.
Chemicals use	Coagulant may be added to the feed water to increase particle size and enhance separation. Chemicals may be required for media regeneration.
Expected lifetime of critical components	Media may require frequent replacement or regeneration depending on media type and feed water quality.
Infrastructure considerations	Filtration processes require a vessel to contain the media and pumps and plumbing to implement backwashes.
O&M considerations	There will be a pressure loss incurred across the filter, however, depending on plant configuration; this may not require any additional pumps. Pumps will be necessary to backwash the filters.
Capital and O&M costs	Contact vendor.
Pre and post treatment	None.
Concentrate management or waste disposal	Solid waste disposal is required for spent media or the waste produced during regeneration of the media.
Note: 1 barrel = 42 US gallons	

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Oxidation

Chemical oxidation treatment can be used to remove iron, manganese, sulfur, color, tastes, odor, and synthetic organic chemicals. Chemical oxidation relies on oxidation/reduction reactions, which consist of two half-reactions: the oxidation reaction in which a substance loses or donates electrons, and a reduction reaction in which a substance accepts or gains electrons. Oxidation and reduction reactions will always occur together since free electrons cannot exist in solution and electrons must be conserved [23]. Oxidants commonly used in water treatment applications include chlorine, chlorine dioxide, permanganate, oxygen, and ozone. The appropriate oxidant for a given application depends on many factors including raw water quality, specific contaminants present in the water, and local chemical and power costs [23]. Chemical oxidation is well established, reliable, and requires minimal equipment [24]. Oxidation can be employed to remove organics and some inorganic compounds like iron and manganese from produced water. The removal or oxidation rate may be controlled by applied chemical dose and contact time between oxidants and water.

No pretreatment is required for oxidation. Solid separation post-treatment might be required to remove oxidized particles. Chemical metering pumps are required for dosing. Some equipment may be required to generate the oxidant on-site. Chemical costs may be high. A summary of the oxidation assessment is provided in Table 7.

Table 7. Oxidation Assessment

Criteria	**Description/Rationale**
Industrial status	Chemical oxidation is well established, reliable, and requires minimal equipment. Used to remove COD, BOD, organic, and some inorganic compounds like iron and manganese.
Feed water quality bins	Applicable to all TDS bins, independent of salt type and concentration.
Product water quality	Depends on type of oxidant used
Production efficiency (recovery)	100% recovery.
Infrastructure considerations	Chemical metering equipment is required.
Energy consumption	Energy usage usually accounts for approximately 18% of the total O&M for oxidation processes.
Chemicals	Chemical costs may be high.
Life cycle	Critical components of the oxidation process are the chemical metering pumps. Chemical metering equipment can have a life expectancy of 10 years or greater.
O&M considerations	Periodic calibration and maintenance of chemical meter pumps is required.
Overall costs	Capital costs can be near to $0.01/gpd, O&M costs can be approximately $0.05/kgal (>$0.01/bbl)
Pre-and post treatment	No pretreatment or post-treatment is required for oxidation.
Concentrate management or waste disposal	No waste is generated from oxidation processes.
Note: 1 barrel = 42 US gallons	

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Settling

Settling can be achieved using a pond or a basin. In this process, particulates are removed by gravity settling. Settling ponds require a large footprint and environmental mitigation to protect wildlife. Settling ponds will most likely be used in combination with other treatment processes. There are no chemical requirements but chemicals can be used to enhance sedimentation. Infrastructure requirements include liners. Settling ponds are used to remove large particulates from water sources. The degree of particle removal and size of particles removed depends on the water detention time in the pond. A summary of the settling processes assessment is provided in Table 8.

Table 8. Settling Assessment.

Criteria	**Description/Rationale**
Industrial status	Settling is frequently employed for produced water at the full scale.
Feed water quality bins	There are no feed water restrictions to using settling as a treatment technology.
Product water quality	Depends on system design
Production efficiency (recovery)	Water volume may be lost due to evaporation depending on the residence time and configuration of the settling basin.
Infrastructure considerations	A large footprint is required for settling. The volume required depends on the hydraulic residence time required for the desired level of contaminant removal.
Energy consumption	None, unless pumping is required to get water to or from the settling basin.
Chemicals	No chemicals are required.
Life cycle	Long lifespan.
O&M considerations	Minimal.
Overall costs	Not available
Pre-and post treatment	No pretreatment required. Any necessary post treatment will be determined by the feed water quality and the target product water quality. Settling may be used as a unit process in a larger treatment train.
Concentrate management or waste disposal	The material that settles out of the feed water will require disposal.
Note: 1 barrel = 42 US gallons	

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Ultraviolet Disinfection

UV radiation disinfection is a popular form of primary disinfection because of its ease of use, no need of chemicals, and no formation of disinfection byproduct (DBP). Water is pumped through a UV reactor, which is equipped with an array of UV lamps providing disinfection dosages of 30-50 mJ/cm^2. As pathogens path through the reactor they are inactivated. They are exposed to the UV light for a predetermined period of time, depending on the desired level of disinfection. UV reactors are typically closed channel for potable water treatment and are installed in open channel for wastewater treatment. There are several types of UV lamps, with low pressure-high output (LPHO) and medium-pressure (MP) mercury vapor lamps being the most commonly used [24]. The lamps are housed inside of quartz lamp sleeves in the reactor to protect the lamp from breaking.

The mechanism of UV disinfection is inactivation through UV damage of the microorganism's DNA and/or RNA. Removal of suspended solids from the feedwater to UV is important to avoid shielding of microorganisms from the UV by suspended solids. This phenomenon is called "shadow effect". UV disinfection does not provide a disinfectant residual. Therefore, addition of chlorine or chloramine as a secondary disinfectant might be required [24].

Disinfection is typically the last treatment step in most water treatment facilities, most suspended solids and/or dissolved ions, if any, should have been removed prior to disinfection. No waste is generated in UV disinfection. UV equipment including lamps must be properly checked to ensure they are working according to technical specifications. The lamps age with time and require periodic replacement. A cleaning system must also be installed on the lamp sleeves, because the sleeve itself reacts with compounds in water and would decrease the UV transmittance if they are not cleaned [24]. A summary of the UV radiation assessment is provided in Table 9.

Table 9. Ultraviolet Disinfection.

Criteria	Description/Rationale
Industrial status	Not widely used for produced water treatment. May be best applied as a polishing step for produced water after other treatment processes.
Feed water quality bins	Applicable to all TDS bins. May not be suitable for highly turbid water.
Product water quality	Inactivation of microbial contaminants. 90 to 99% inactivation efficiency depending on UV intensity.
Production efficiency (recovery)	100% water recovery.
Infrastructure considerations	UV requires a treatment chamber or area in which the water will be "dosed" with UV exposure.
Energy consumption	3-25 kWh; 0.5-3 kW/mgd for LPHO
Chemicals	None.
Life cycle	Lamp life is approximately 5,000 to 8,000 hours.
O&M considerations	Minimal operator involvement, approximately 5 hours per month. Periodic cleaning and lamp replacement is required.
Overall costs	High capital cost. EPA estimated costs are $0.13/gpd.

Table 9. Ultraviolet Disinfection.

Criteria	**Description/Rationale**
Pre-and post treatment	Will require pretreatment to remove high concentrations of particulates, manganese, calcium, iron, and magnesium, which may decrease the effectiveness of the UV. No post treatment required.
Concentrate management or waste disposal	None.
Note: 1 barrel = 42 US gallons	

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Microfiltration/Ultrafiltration

Microfiltration (MF) has the largest pore size (0.1-3 μm) of the wide variety of membrane filtration systems. Ultrafiltration (UF) pore sizes range from 0.01 to 0.1 μm. In terms of pore size, MF fills in the gap between ultrafiltration and granular media filtration. In terms of characteristic particle size, MF range covers the lower portion of the conventional clays and the upper half of the range for humic acids. This is smaller than the size range for bacteria, algae, and cysts, and larger than that of viruses. MF is also typically used for turbidity reduction, removal of suspended solids, *Giardia,* and *Cryptosporidium*. UF membranes are used to remove viruses, color, odor, and some colloidal natural organic matter [25]. Both processes require low trans-membrane pressure (1-30 psi) to operate, and both are now used as a pretreatment to desalination technologies such as reverse osmosis, nanofiltration, and electrodialysis, but cannot remove salt themselves [24].

MF membranes can operate in either cross-flow separation as shown in Figure 4 and also dead-end filtration where there is no concentrate flow. There are also two pump configurations, either pressure driven or vacuum-type systems. Pressure driven membranes are housed in a pressure vessel and the flow is fed from a pump. Vacuum-type systems are membranes submerged in non-pressurized tanks and product water is extracted by a vacuum pump on the product side. Typical recoveries can range from 85% to 95% [23]. Flux rates range from 20 to 100 gpd/ft^2 (gfd) depending on the application. Backwash is usually used to clean the membranes and it is carried out for short durations (3 to 180 seconds) in relatively frequent intervals (5 min to several-hour) [23]. The frequency and duration of backwash depend on the specific application. A clean in place (CIP) can also be performed as a periodic major cleaning technique. Typical cleaning agents are sodium hypochlorite, citric acid, caustic soda, and detergents. They can be initiated manually, and automatically controlled. CIP is initiated when backwashing and chemically enhanced backwash are not effective in restoring desirable performance [24].

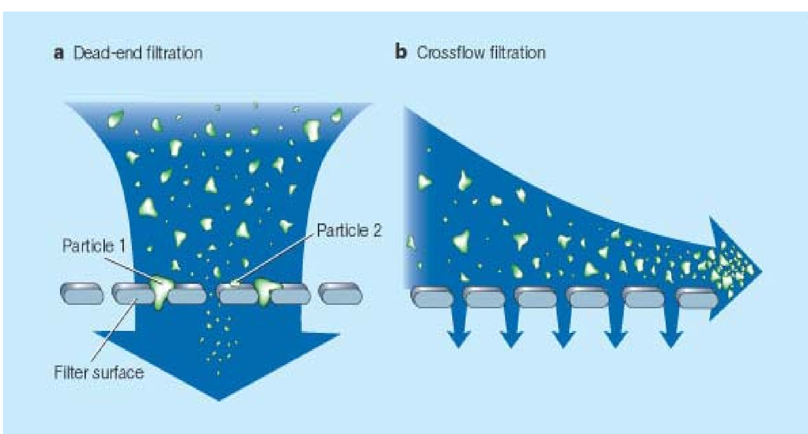

Figure 4. Dead-end filtration versus cross-flow filtration (Source: [26]).

Factors affecting membrane selection are:

- Cost
- Percent recovery
- Percent rejection
- Raw water characteristics
- Pretreatment

Factors affecting performance are:

- Raw water characteristics
- Pressure
- Temperature
- Regular monitoring and maintenance

A self-backwashing 100 µm strainer is often necessary to protect the membranes and moderate particulate loading. Depending on the raw water quality, a coagulant may be added to form pin-sized floc and help improve rejection [24].

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Ceramic MF/UF membrane

Ceramic ultrafiltration and microfiltration membranes are made from oxides, nitrides, or carbides of metals such as aluminum, titanium, or zirconium [27]. Ceramic membranes are much more resilient than polymeric membranes and are mechanically strong, chemically and thermally stable, and can achieve high flux rates. Typically, a tubular configuration is used with an inside-out flow path, where the feed water flows inside the membrane channels and permeates through the support structure to the outside of the module. These membranes are typically comprised of at least two layers, a porous support layer and a separating layer, see **Figure 5** [28].

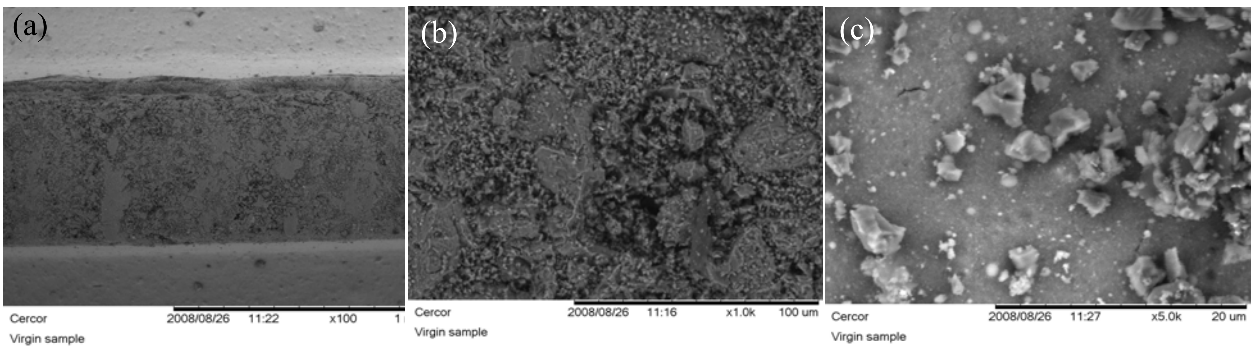

Figure 5. SEM micrographs of ceramic membrane (a) SEM of membrane support and membrane separating layer (100x), (b) SEM of membrane support (1000x), and (c) SEM of membrane separating layer (5000x).

Ceramic membranes are capable of removing particulates, organic matter, oil and grease, and metal oxides. Ceramic membranes alone cannot remove dissolved ions and dissolved organics. Pre-coagulation, injection of a chemical coagulant upstream from the membrane, improves removal efficiencies of dissolved organic carbon and smaller particulates. As with conventional ultrafiltration and microfiltration, a strainer or cartridge filter is necessary as pretreatment for ceramic membranes.

Numerous research studies have been conducted on using ceramic membranes to treat oil-containing wastewater and produced water [29-33]. These research studies have shown that ceramic membranes perform better than polymeric membranes on oil-containing waters. Ceramic membranes have also been employed commercially to treat oil produced water [34]. Ceramic membranes are employed as part of a large treatment train consisting of multiple unit process at the Wellington Water Works to treat oilfield produced water.

Energy requirements for ceramic membranes are lower than those required for polymeric membranes. Infrastructure requirements for ceramic membranes are similar to other membrane processes and include a break tank for the feed water, a feed pump, a rack for holding the membrane modules, a chemical metering system if necessary, a tank for the filtrate water and a pump and valves for the backwash and cleaning systems.

Ceramic membranes have a higher capital cost than polymeric membranes. The use of ceramic membranes is increasing as more research and pilot studies are conducted. The capital cost of ceramic membranes will continue to decrease as they become a more widely used technology. Ceramic membranes do require frequent backwashes; backwash waste will require disposal. If ceramic membranes are operated in a cross-flow mode, then there will be a residual process stream to dispose of. An assessment of ceramic MF/UF membranes is provided in Table 10.

Table 10. Ceramic MF/UF Membrane Assessment

Criteria	**Description/Rationale**
Industrial status	Ceramic membranes have been used extensively in industrial water treatment, including oil-containing wastewaters. Ceramic membranes are currently being used in a full-scale facility in Wellington, Colorado to treat oilfield produced water [34]. Many research studies have been performed which show that ceramic membrane are a viable treatment for produced water [29-33]. Many companies manufacture and sell ceramic membrane products in a variety of sizes, materials of construction, and geometric configurations.
Feed water quality bins	Applicable to all TDS bins, independent of salt type and concentration. High iron concentrations can be problematic, causing irreversible membrane fouling.
Product water quality	Product water is free of suspended solids. DOC removal is approximately 10%. Nearly all non-dissolved organic carbon removed.
Production efficiency (recovery)	Ceramic MF/UF membranes can be operated in dead-end or crossflow filtration mode, therefore, recoveries can range from 90% to 100%.
Infrastructure considerations	A feed tank, feed pump, coagulant dosing pump, and rack structure for holding the membrane modules is required for installation of a ceramic membrane plant.
Energy consumption	Not available.
Chemicals	Pre-coagulation may be used to enhance contaminant recovery. Doses usually range from 1 to 5 mg/L depending on water quality and the type of coagulant used. Common coagulants include polyaluminum chloride, ferric chloride, and aluminum sulfate. Chemical enhanced backwash may be used which would require the use of acidic and alkaline chemicals. Periodic chemical cleaning is required. Acids, bases, surfactants, and oxidants are commonly used.
Life cycle	Ceramic membranes are believed to have a lifespan much longer than polymeric membranes. Expected lifespan is >10 years.
O&M considerations	Ceramic membranes should be backwashed periodically and chemical cleaning is required at one week to a 3-month intervals depending on the feed water quality.
Overall costs	No capital or O&M costs are available at this time for ceramic membranes. Contact vendor for more information.
Pre-and post treatment	Straining or cartridge filtration is required as pretreatment to ceramic membrane systems. Coagulation can also be used as a pretreatment. Downstream processes may be required for desalination or polishing depending on feed water quality and finished water quality goals.
Concentrate management or waste disposal	Backwash waste requires disposal or recycling to a different part of the treatment plant. Chemical waste is generated during periodic cleanings. If the membranes are operated in crossflow mode, then the reject stream will require disposal or further treatment.
Note: 1 barrel = 42 US gallons	

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Polymeric MF/UF membrane

Polymeric MF/UF membranes are made from materials like polyacrylonitrile (PAN) and polyvinylidene (PVDF). Because there is a large market for polymeric ultrafiltration membranes, there are many vendors and suppliers for these membranes. They are also relatively inexpensive. Typically, package systems are purchased and installed by the vendor.

An important consideration for polymeric MF/UF membranes is integrity testing to ensure that the membrane is not damaged and is operating properly. Typically, the filtrate turbidity is monitored to give a rough indication of membrane integrity. Membrane integrity can be tested through a pressure decay test. In this test, pressurized air is applied to the membranes at a pressure less than would cause the air to flow through the membrane, and the pressure decay is measured. Regular monitoring of membrane performance is necessary to ensure the membrane system is operating at the most effective loading rate and backwash regime. Membrane life is typically estimated at 7+ years with manufacturer warranties covering 5 years in municipal applications.

Waste includes pretreatment waste, backwash flow, retentate flow (if applicable), and CIP waste. Waste streams are either discharged to the sewer or treated if discharging to surface waters. Waste streams being discharged to surface waters are typically processed for turbidity removal through settling ponds or other treatment systems. CIP waste is neutralized and usually combined with the rest of the waste. A summary assessment of polymeric MF/UF membranes is provided in Table 11.

Table 11. Polymeric MF/UF Membrane Assessment

Criteria	**Description/Rationale**
Industrial status	Polymeric membranes are used extensively in the municipal water treatment industry.
Feed water quality bins	Applicable to all TDS bins, independent of salt type and concentration.
Product water quality	Product water is free of suspended solids. DOC removal is approximately 10%. Nearly all non-dissolved organic carbon removed.
Production efficiency (recovery)	85% to 100% depending on feed water quality and mode of operation (dead-end vs. crossflow).
Infrastructure considerations	A feed tank, feed pump, coagulant dosing pump, and rack structure for holding the membrane modules are required.
Energy consumption	Not available.
Chemicals	Pre-coagulation may be used to enhance contaminant recovery. Doses usually range from 1 to 5 mg/L depending on water quality and the type of coagulant used. Common coagulants include polyaluminum chloride, ferric chloride, and aluminum sulfate. Chemical enhanced backwash may be used which would require the use of acidic and alkaline chemicals. Periodic chemical cleaning is required. Acids, bases, surfactants, and oxidants are commonly used.
Life cycle	7 years or longer.
O&M considerations	Integrity monitoring is required.
Overall costs	Capital cost for polymeric ultrafiltration systems vary based on the size of the plant and feed water quality. Approximate capital costs will be near $1 - $2/gpd ($0.02 to $0.05/bpd) and O&M costs approximately $1 to $2/kgal ($0.02 to $0.05/bbl).

Table 11. Polymeric MF/UF Membrane Assessment

Criteria	**Description/Rationale**
Pre-and post treatment	Straining or cartridge filtration is required as pretreatment to ceramic membrane systems. Coagulation can also be used as a pretreatment. Downstream processes may be required for desalination or polishing depending on feed water quality and finished water quality goals.
Concentrate management or waste disposal	Backwash waste requires disposal or recycling to a different part of the treatment plant. Chemical waste is generated during periodic cleanings. If the membranes are operated in crossflow mode, then the reject stream will require disposal or further treatment.
Note: 1 barrel = 42 US gallons	

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REVIEW AND ASSESSMENT OF DESALINAITON TECHNOLOGIES

Pressure Driven Membrane Technologies

Pressure driven membrane processes utilize hydraulic pressure to overcome the osmotic pressure of the feed solution and force pure water (called permeate) to diffuse through a dense, non-porous membrane [35]. The residual feed stream (sometimes called retentate, concentrate, or reject) is concentrated during the process and typically requires disposal. An illustration of the process is shown in Figure 6. Additional treatment technologies may be employed to further concentrate the concentrate stream towards zero liquid discharge (ZLD). Solutions of higher total dissolved solids (TDS) concentrations have greater osmotic pressures, and therefore require more hydraulic pressure to produce permeate. Practical limits are imposed on the process by pump energy and component manufacturing costs associated with operating at hydraulic pressures exceeding 1,000 psig. For this reason, pressure driven membrane processes are typically utilized for treatment of saline streams with TDS concentrations ranging from 500 to 40,000 mg/L; however, this technology has been utilized to treat water with 50,000 mg/L TDS [36].

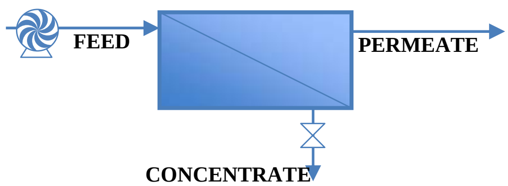

Figure 6. Schematic of a typical pressure driven membrane process. The concentrate stream may be further undergo additional desalination processes to produce more permeate and further concentrate this stream.

High-pressure membranes are typically employed in spiral-wound configurations (

Figure **7**) with membrane materials composed of an asymmetric polyamide or polypiperazine amid active layer and a polysulfone micro-porous support in a thin film composite (TFC) structure (

Figure **7**). Mesh spacers are installed in both the feed channel and permeate collection channels of the membrane module. Feed spacers are required to enhance hydrodynamic turbulences in the channel, which diminishes concentration polarization. Concentration polarization is a phenomenon where the feed solution becomes more concentrated at the feed-membrane interface, which results from the preferential diffusion of pure water through the membrane. A permeate spacer is required to provide mechanical support to the permeate collection channel.

Reverse osmosis (RO) and nanofiltration (NF) are examples of pressure driven membrane processes. RO and NF are proven, widely utilized treatment technologies for desalination of both seawater and brackish water [37]. Globally, RO seawater desalination technologies dominate global seawater desalination with a 58% share of the market and growing [38].

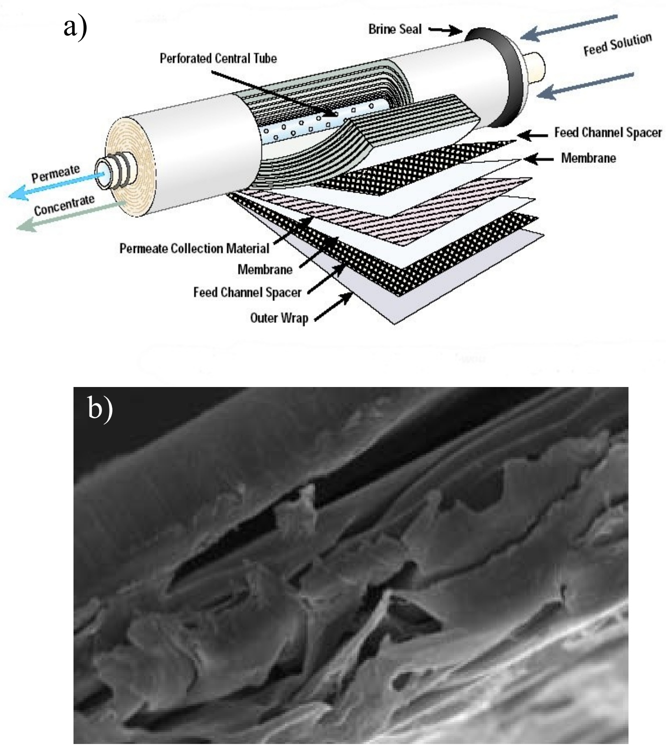

Figure 7. RO membrane construction. (a) A typical spiral wound high pressure membrane element and (b) SEM cross section view of an asymmetric RO membrane.

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Seawater Reverse Osmosis

Seawater RO (SWRO) membrane systems are most applicable for feed streams up to 47,000 mg/L TDS, i.e., seawater level % [37]. SWRO typically employs dense, highly selective TFC membranes that are capable of rejecting contaminants as small as 0.0001 µm. Systems that utilize SWRO may achieve high rejection of monovalent and multivalent ions and molecules, and metals. SWRO membranes are designed to achieve NaCl rejections in excess of 99% [37]. Other inorganic compounds such as silica and boron are rejected to a lesser extent and frequently require additional treatment considerations (such as increasing the pH of the RO feed stream to pH 10 or above). Rejection of organic compounds in SWRO ranges from very high rejections (greater than 99.7%) to very low rejections (<20%) depending on the organic compound's chemical structure and feed solution physicochemical parameters [39]. Because of the high molecular weight of radionuclides, the removal of these compounds is higher than 99%. Water recovery during SWRO is frequently restricted to 30-60% because of limitations resulting from the relatively high osmotic pressure of the feed stream [40, 41].

Membrane fouling and scaling is a primary concern when operating RO systems. SWRO frequently requires pretreatment to remove organic foulants, and may require the addition of scale inhibitors to condition feed water prior to contact with the membranes. Constituents of primary concern for all pressure driven membrane processes include organic acids, metal oxides, and sparingly soluble salts (e.g. $CaSO_4$, CaF_2, and $BaSO_4$). When appropriate design considerations are employed, SWRO systems are capable of operating with moderate chemical, energy, and maintenance demands.

The utilization of energy recovery devices to recycle hydraulic pressure within the RO system can substantially reduce energy costs. RO processes also easily automated and are relatively simple to operate. SWRO is a moderately robust technology that consistently delivers permeate water devoid of most inorganic constituents. RO membrane systems may be deployed on a trailer-mounted skid, as shown in

Figure **8**, which is highly mobile and modular. SWRO technology has one of the smallest footprints of all the technologies considered in this report. Depending on the chemical composition of the RO feed water, system failure may occur with changing feed water quality. Low recoveries associated with SWRO generate relatively large volumes of concentrated reject water. Residual management costs may be substantial.

RO systems have been previously employed for various types of produced water treatment. Early pilot studies were conducted without consideration for adequate pretreatment; subsequently the RO membranes were irreversibly damaged by foulants [42, 43]. Later, systems with rigorous pretreatment trains were employed with RO as a final desalination stage. One study was conducted at an oil field produced water facility in Bakersfield, CA (2001). The feed water was characterized as an NaCl dominated. The pilot system was constructed with a 100 m pre-filter leading to a polymeric UF membrane and followed by NF and RO. The system was operated for six months and produced 20 gpm of permeate over a period of more than 1,700 hours of operation [44]. Another early study was conducted in the Placerita Canyon Oil Field, CA in 2000; however, little detail is available on the specifics of testing conditions and system configuration [45]. Recently, numerous companies with water treatment expertise have begun developing high-pressure membrane based treatment systems. Many of these systems will be discussed in the hybrid membrane systems and commercial technologies sections of this report. A summary of the technical assessment for SWRO is listed in Table 12.

Figure 8. Trailer mounted membrane testing skid used at AQWATEC, CSM (Source: [46]).

Table 12. Summary of technical assessment of SWRO.

Criteria	**Description/Rationale**
Status of technology	Mature and robust technology for seawater desalination. Has been employed for produced water treatment. Reports from various producers in the CBM produced water field indicate that many RO pilot studies failed, but this is largely the result of insufficient process integration and poor pretreatment.
Feed water quality bins	Most applicable for TDS ranging from 20,000 to 47,000 mg/L, and water containing monovalent (Na, Cl), divalent (Mg, Ca, Ba, SO_4), multi-valent (Fe*, Mn*) electrolytes, and radionuclides. Also applicable for specific classes of organic compounds
Product water quality	SWRO permeate quality is dependent on feed water salinity and operating conditions. Typically, product water TDS ranges from 100 to 400 mg/L (>99.4% rejection), ammonia rejection is approximately 80%, boron rejection is typically less than 50% when operating at neutral pH.
Recovery	Product water recovery is between 30% and 60%.
Energy use	With energy recovery device, SWRO requires 11-16 kWh/kgal (0.46-0.67 kWh/bbl) of energy to power the system's high-pressure pumps [47].
Chemical use	Scale inhibitor and caustic may be required for process control to prevent scaling or fouling. Chemical cleaning rates depend on feed water quality. Cleaning will typically occur after certain design specifications are exceeded, and may require the use of NaOH, Na_4EDTA, HCl, $Na_2S_2O_4$, or H_3PO_4
Expected lifetime of critical components	Depending on operating conditions, SWRO membranes will require replacement within 3 to 7 years
Infrastructure considerations	SWRO requires minimal operational footprints compared to thermal desalination technologies, and can be highly automated SWRO skids are highly mobile.

Table 12. Summary of technical assessment of SWRO.

Criteria	**Description/Rationale**
O&M considerations	Monitoring and control required for feed pH, flow rates, TDS, turbidity, as well as vessel pressures. System automation lessens demands on skilled labor, however a skilled technician is required to perform routine system maintenance. Level of flexibility: High sensitivity to organic and inorganic constituents in the feed water. Level of robustness: TFC membranes have high pH tolerance, but cannot be exposed to feed temperatures in excess of 113 °F (45 °C) Level of reliability: SWRO systems operate semi-continuously with automated, short duration chemical rinse or osmotic backwashing cycles. Types of energy required: electrical.
Capital and O&M costs	Capital costs vary from $3 to $7/gpd (or $125 to $295/bpd), depending on various factors including size, materials of construction and site location. Operating costs are highly dependent upon energy price and feed water TDS, and approximately $2/kgal (or $0.08/bbl).
Pretreatment of feed water	All high-pressure membrane technologies require extensive pretreatment to mitigate harmful water quality constituents that will otherwise foul or scale the membrane. Particular attention should be given to hydrophobic organic compounds and sparingly soluble salts. The silt density index (SDI) of the feed stream should not exceed 3-5.
Post-treatment of product water	Product water may require pH stabilization or remineralization. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with permeate.
Concentrate management or waste disposal	No special concentrate treatment is required. Due to the relatively low recovery rates of 30% to 60%, moderately large amounts of concentrated brine are generated. SWRO operations are commonly located near oceans, which allows them to dispose of the brine by pumping it back into the ocean through diffusers.
Applicability for produced water treatment	Excellent - with appropriate pretreatment technologies
Note: 1 barrel = 42 US gallon (*): Assuming that ion is in a reduced (un-oxidized) state	

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Brackish Water Reverse Osmosis

BWRO membranes are designed to achieve moderately high rejection of dissolved constituents (>94% NaCl), and are most efficient when employed for the treatment of feed water containing TDS concentrations between 500 and 25,000 mg/L. BWRO generally may achieve water recoveries up to 85%. BWRO membranes generally reject metals and divalent ions to a high degree, and have similar limitations as SWRO for organics removal. Pretreatment for BWRO is similar to SWRO, and requires careful management to control organic fouling and inorganic scaling.

Operational costs for BWRO are reduced compared to SWRO because the hydraulic pressure required to overcome the osmotic pressure of the feed water is lower, and fewer membranes are required to achieve similar production rates. BWRO systems are equally matched with SWRO systems when other parameters are considered, including robustness, reliability, flexibility, mobility, modularity, and footprint. The higher recovery of BWRO over SWRO reduces concentrated brine generation and disposal costs.

Available scientific literature suggests that BWRO membranes have been previously tested on CBM produced water at the bench-scale [48, 49]. One study [48] examined the potential of harvesting iodide from produced water, and performed other experiments to determine the fouling potential and effective cleaning protocols for BWRO and NF membranes. Seven different membranes (four BWRO membranes, and three NF membranes) were investigated in the study. Feed water was obtained from a natural gas production facility in Eastern Montana and was characterized as brackish groundwater (5,200 mg/L TDS) dominated by NaCl.

A second bench-scale study [49] was conducted with both CBM produced water (sourced from Walsenburg, Colorado) and oil produced water (sourced from Wellington, Colorado). The purpose of this study was to determine the relative effectiveness of BWRO and NF membranes for treatment of produced water. Three membranes were tested in the investigation, one BWRO, and two NF membranes. The CBM produced water had 650 mg/L TDS and was dominated by sodium (no anion composition was given). A summary of the technical assessment for BWRO is listed in Table 13.

Table 13. Summary of technical assessment of BWRO

Criteria	Description/Rationale
Status of technology	Mature and robust technology for brackish desalination in the municipal water treatment sector. Laboratory scale studies have been conducted for oil and gas produced water.
Feed water quality bins	Most applicable for TDS ranging from 500 to 25,000 mg/L, and water containing monovalent (Na, Cl), divalent (Mg, Ca, Ba, SO_4), multivalent electrolytes (Fe, Mn), and radionuclides. Also applicable for specific classes of organic compounds.
Product water quality	BWRO permeate quality is dependent on feed water salinity and operating conditions. Typically, product water TDS ranges from 100 to 1,500 mg/L, ammonia rejection may range from 60% to 80%.
Recovery	Product water recovery is between 60% and 85%.
Energy use	BWRO will require less energy than equivalent SWRO systems for a specific feed water quality. BWRO requires approximately 0.5 to 3 kWh/kgal (0.02-0.13 kWh/bbl) of energy to power the system's high-pressure pumps.

Table 13. Summary of technical assessment of BWRO

Criteria	Description/Rationale
Chemical use	Scale inhibitor and caustic may be required for process control to prevent scaling or fouling. Chemical cleaning rates depend on feed water quality. Cleaning will typically occur after certain design specifications are exceeded, and may require the use of NaOH, Na_4EDTA, HCl, $Na_2S_2O_4$, or H_3PO_4.
Expected lifetime of critical components	Depending on operating conditions, BWRO membranes will require replacement within 3 to 7 years.
Infrastructure considerations	BWRO requires an equivalent footprint when compared to SWRO, and a minimal operational footprint compared to thermal desalination technologies. As with SWRO, BWRO can be automated, and mobile.
O&M considerations	Monitoring and control required for feed pH, flow rates as well as vessel pressures. System automation lessens demands on skilled labor, however a skilled technician is required to perform routine system maintenance. Level of flexibility: High sensitivity to organic and inorganic constituents in the feed water. Level of robustness: TFC membranes have high pH tolerance, but cannot be exposed to feed temperatures in excess of 113 °F (45 °C). Level of reliability: BWRO systems operate semi-continuously with automated, short duration chemical rinse or osmotic backwashing. Types of energy required: electricity.
Capital and O&M costs	Capital costs vary from $0.8 to $4/gpd (or $35 to $170/bpd), depending on various factors including size, materials of construction and site location. Operating costs are approximately $0.70/kgal (or $0.03/bbl). Moderate reductions in energy costs can be obtained by implementing energy recovery subsystems.
Pretreatment of feed water	All high-pressure membrane technologies require extensive pretreatment to mitigate harmful water quality constituents that will otherwise foul or scale the membrane. Particular attention should be given to hydrophobic organic compounds and sparingly soluble salts. The silt density index (SDI) of the feed stream should not exceed 5.
Post-treatment of product water	Product water may require pH stabilization or remineralization. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feed water with permeate.
Concentrate management or waste disposal	No special concentrate treatment is required. Moderate recovery rates of 50% to 85% generate modest amounts of concentrated brine. BWRO operations are commonly located inland and the concentrated brine typically requires deep well injection.
Applicability for produced water treatment	Excellent - with appropriate pretreatment technologies.
Note: 1 barrel = 42 US gallon	

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Nanofiltration

NF membranes are commonly utilized in brackish groundwater desalination for municipal water supplies [37]. Some pilot-scale studies have utilized a NF membrane subsystem to pretreat water before treatment with RO membranes [44]. NF membranes are designed to reject contaminants as small as 0.001 µm. This allows NF to achieve high rejection of divalent ions, metals (>99% of $MgSO_4$), and radionuclides. NF is best suited for softening applications and removal of most metals; this indicates that the product stream from conventional NF systems will tend to have higher SAR than the feed stream. Organic compounds are removed to varying extents with NF membranes [50]. The nominal TDS range for NF applications is between 1,000 and 35,000 mg/L (by using two stage NF process developed at Long Beach Water Department [51]). Water recovery ranges from 75-90%, but may require application of scale inhibitors or extensive pretreatment depending on feed water quality.

The energy required for NF membranes to perform separation is less than that required for SWRO or BWRO; while maintenance, robustness, reliability, flexibility, mobility, modularity, and operational footprint of NF membrane systems are equivalent to those of RO processes.

NF membranes have been investigated on both pilot- and bench-scale for treatment of produced water [44, 48, 49]. The pilot-scale study [44] is discussed in the SWRO section of this report. Two bench-scale studies examined the treatment of CBM produced water with BWRO and NF membranes, and are discussed in the BWRO section of this report. A summary of the technical assessment for NF is listed in Table 14.

Table 14. Summary of technical assessment of NF

Criteria	**Description/Rationale**
Status of technology	Mature and robust technology for water softening and metals removal in various sectors of the industrial and municipal water treatment sectors. Has been employed for produced water treatment.
Feed water quality bins	TDS applicability range is highly dependent on feed solution composition, but may range from 500 to 25,000 mg/L. Most useful for treatment of water with divalent (Mg, Ca, Ba, SO_4) electrolytes, multivalent metals (Fe, Mn), and radionuclides. Also applicable for specific classes of organic compounds.
Product water quality	NF permeate quality is dependent on feed water composition and operating conditions. High rejection (>99%) of larger divalent ions and metals with moderate rejection (<90%) of monovalent salts is expected.
Recovery	Product water recovery is between 75% and 90%.
Energy use	NF requires less energy than equivalent RO based systems for a similar feed water quality. Approximately 2 kWh/kgal (0.08 kWh/bbl) of energy is required to power the system's high-pressure pumps [52].
Chemical use	Scale inhibitor and caustic may be required for process control to prevent scaling or fouling. Chemical cleaning rates depend on feed water quality. Cleaning will typically occur after certain design specifications are exceeded, and may require the use of NaOH, Na_4EDTA, HCl, $Na_2S_2O_4$, or H_2O_2.
Expected lifetime of critical components	Depending on operating conditions, NF membranes will require replacement within 3 to 7 years.

Table 14. Summary of technical assessment of NF

Criteria	**Description/Rationale**
Infrastructure considerations	NF requires an equivalent footprint when compared to BWRO, and a minimal operational footprint compared to thermal desalination technologies. As with other pressure driven processes, NF can be highly automated, and have excellent mobility.
O&M considerations	Monitoring and control required for feed pH, flow rates as well as vessel pressures. System automation lessens demands on skilled labor, however a skilled technician is required to perform routine system maintenance. Level of flexibility: High sensitivity to organic and inorganic constituents in the feed water. Level of robustness: TFC membranes have high pH tolerance, but cannot be exposed to feed temperatures in excess of 113 °F (45 °C). Level of reliability: NF systems operate semi-continuously with automated, short duration chemical rinse or osmotic backwashing cycles. Types of energy required: electrical.
Capital and O&M costs	Capital costs vary from $0.8 to $4/gpd (or $35 to $170/bpd), depending on various factors including size, materials of construction and site location. Operating costs are assumed similar to BWRO, approximately $0.70/kgal (or $0.03/bbl). Moderate reductions in energy costs can be obtained by implementing energy recovery subsystems.
Pretreatment of feed water	All high-pressure membrane technologies require extensive pretreatment to mitigate harmful water quality constituents that will otherwise foul or scale the membrane. Particular attention should be given to hydrophobic organic compounds and sparingly soluble salts.
Post-treatment of product water	Product water may require remineralization to restore SAR values. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with permeate.
Concentrate management or waste disposal	No special concentrate treatment is required. Relatively high recovery rates of 75% to 90% generate minor amounts of concentrated brine.
Applicability for produced water treatment	Poor – NF is inappropriate as a standalone technology. NF processes will remove >99% of hardness, and will have substantially lower removal of Na and Cl ions, thus SAR is maximized in the product stream.
Note: 1 barrel = 42 US gallon	

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Electrochemical Charge Driven Membrane Process

Electrodialysis / Electrodialysis Reversal

Electrodialysis (ED) and electrodialysis reversal (EDR) are electrochemical charge driven separation processes in which dissolved ions are separated from water through ion permeable membranes under the influence of an electrical potential gradient. Ion exchange membranes, fabricated from ion exchange polymers, have the ability to selectively transport ions with a positive or negative charge and reject ions of the opposite charge. An ED stack consists of a series of anion exchange membranes (AEM) and cation-exchange membranes (CEM) arranged in an alternating mode between anode and cathode (**Figure 9**). The positively charged cations migrate toward the cathode, pass the cation-exchange membrane, and rejected by the anion-exchange membrane. The opposite occurs when the negatively charged anions migrate to the anode. This results in an alternating increasing ion concentration in one compartment (concentrate) and decreasing concentration in the other (diluate). The EDR process is similar to the ED process, except that it also uses periodic reversal of polarity to effectively reduce and minimize membrane scaling and fouling, thus allowing the system to operate at relatively higher recoveries.

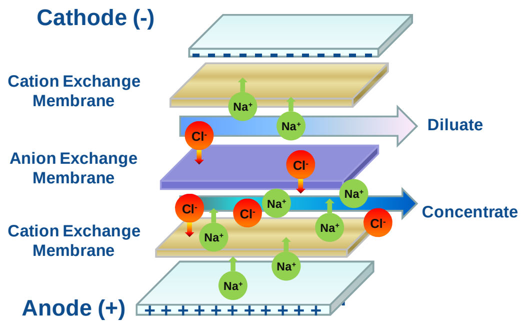

Figure 9. Schematic diagram of an ED stack.

The efficiency of ion transfer is determined by the current density and the residence time of the solutions within the membrane cells. The membrane selectivity decreases with increasing ion concentrations. EDR and ED processes are typically used in desalination of brackish water (up to about 8,000 mg/L TDS for EDR) and not seawater. This is because the cost of these processes increases substantially with increasing salinity or TDS concentration.

The efficiency of ED or EDR is limited by several factors such as fouling/scaling, current efficiency, counter effects of co-ion transport, osmosis, and diffusion. Organic fouling can occur in the diluate compartments due to precipitation of large negatively charged anions on the anion exchange membranes. Sparingly soluble inorganic salts (e.g., $CaSO_4$, $CaCO_3$) and multivalent ions (e.g., iron and manganese) can also scale the cation exchange membranes by precipitation and fixation. This can reduce the ED efficiency by neutralizing or reversing the fixed charges in the membranes. This can be avoided by pretreatment of the feedwater with processes such as filtration for suspended solids, softening or pH lowering, and addition of antiscalant into the concentrate compartments.

Depending on feedwater chemistry, water recovery in ED and EDR can be between 70 and 90%. ED membranes are not as susceptible to degradation by chlorine; therefore, dosing a small amount of chlorine to the feed water can control biological growth in the system. These features enable ED and EDR to treat surface and wastewaters having high concentrations of organic materials and microorganisms without significant fouling. EDR system is able to operate with maximum silt density index (SDI) of 15 compared to 5 for RO [53, 54]. A disadvantage of ED and EDR is its limited removal of non-charged constituents, including organics molecules, silica, boron, and microorganisms.

ED and EDR have been successfully used at a number of municipal water and wastewater treatment plants to desalinate brackish water and reclaimed water [55, 56]. Laboratory experiments have been conducted to investigate the application of ED in treatment of produced water at Argonne National Laboratory (ANL) and Gas Technology Institute (GTI) [56]. Moon et al. [57] used a laboratory ED prototype to treat CBM produced waters collected from the Powder River basin production field near Sheridan, Wyoming. The produced water was sodium bicarbonate type with TDS in the range of 1000-2000 mg/L. Preliminary results indicated water recovery of more than 90%. Energy consumption was in the range of 0.14 to 0.20 kWh/lb NaCl equivalent removed. 92% removal of dissolved solids was achieved [57]. At a scale of treatment exceeding 0.336 MGD (8,000 bbl/day) produced water, total costs were estimated to be below 15 cents per barrel for a treatment train that includes 5 μm cartridge filter, ED to reduce electro-conductivity (EC) and sodium levels, and stabilization of the product water stream with limestone to increase calcium concentrations and to decrease SAR values from over 50 to below 4 [58].

Sirivedhin et al. [59] tested the ability of ED to treat low- and high salinity produced waters at laboratory scale. Synthetic water was used to simulate produced water qualities in CO, TX, and WY (TDS in the range of 4,000-5,000 mg/L, sodium bicarbonate type, and sodium bicarbonate/sodium sulfate type waters), UT (63,000 mg/L, sodium chloride type), and OK (97,000 mg/L, sodium chloride type). ED treatment is more cost-effective and energy-efficient when treating low TDS water (e.g. TDS 4,000-5,000 mg/L). The power required to treat the high TDS water was approximately 23 times higher than that required to treat the low TDS water. While energy costs are likely to preclude using ED to treat concentrated produced water, the technology shows promise for treatment of relatively clean produced water such as CBM water.

Frac Water Inc. developed mobile treatment units using patent pending High Efficiency ED (HEED) treatment process for treating CBM produced water and reusing it in well fracturing [60]. The mobile treatment units treated produced water with TDS concentrations ranging from 11,400 to 27,000 mg/L and sulfates from 4,000 to 14,000 mg/L [61]. Pretreatment included cartridge filtration to remove particulate matter, carbon filters to remove organic matter, and weak acid cation exchange resins to remove hardness and iron. The ED treatment recovered 80-90% of the brackish water. The HEED™ stack configuration required up to 40% less membrane area that resulted in more than 70% increase in energy efficiency [62]. The product water quality met the requirements for the basic gel fracturing fluids.

The drawbacks of the system are high treatment cost and membrane fouling. The membranes should be regularly washed or cleaned in place with dilute acid and alkali solutions to restore performance when required. A summary of the technical assessment of ED and EDR is listed in **Table 15**.

Table 15. Summary of technical assessment of ED and EDR

Criteria	Description/Rationale
Status of technology	Mature and robust technology for seawater and brackish water desalination and wastewater reclamation. Have been tested for produced water treatment at laboratory-scale.
Feed water quality bins	Cost effective to TDS < 8,000 mg/L, and treat all types of water chemistry makeup.
Product water quality	Product water quality depends on ED stages, can achieve over 90%. Poor removal of non-charged substances such as organics, silica, boron, and microorganisms.
Recovery	Product water recovery is between 80% and >90%.
Energy use	Energy consumption was in the range of 0.14–0.20 kWh/lb NaCl equivalent removed [57].
Chemical use	Scale inhibitor and acid may be required for process control to prevent scaling. Periodic chemical cleaning is typically conducted using acid, caustic, EDTA, disinfectant, or other antiscaling chemicals.
Expected lifetime of critical components	ED membrane lifetime is estimated 4-5 years.
Infrastructure considerations	No special infrastructure requirement, need housing or shed.
O&M considerations	Levels of monitoring and control: current, voltage, TDS, pH, flow rates, membrane integrity. High level of skilled labor required; the operation of ED and EDR is more complicated than RO membranes. Level of flexibility: fairly flexible to varying water quality. Level of robustness: modest to withstand harsh conditions. Level of reliable – requires periodic chemical cleaning and maintenance. Types of energy required – electricity.
Capital and O&M costs	Total costs are site specific and depend on feed water TDS. For CBM produced water treatment (TDS 1000 – 2000 mg/L), costs were estimated to be under $3.6/kgal (15 cents per barrel) for a 0.34 MGD (8,000 bbl/day) treatment train [58].
Pretreatment of feed water	Pretreatment requires removal of particles and other scaling and fouling substances through filtration, pH adjustment, and addition of antiscalant.
Post-treatment of product water	Product water needs remineralization for SAR adjustment, and disinfection.
Concentrate management or waste disposal	Concentrate needs disposal.
Applicability for produced water treatment	Excellent for the produced water application.
Note: 1 barrel = 42 US gallon	

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Electrodeionization

Electrodeionization (EDI) is a commercial desalination technology that combines ED and conventional IX technologies. It is used for the production of ultra-pure deionized water, especially in the semiconductor industry. The principle of the process is illustrated in Figure 10. A mixed-bed ion exchange resin or fiber is placed into the diluate cell of a conventional electrodialysis cell unit [63].

The function of the IX resins is to increase the conductivity in the substantially non-conductive water. At very low salt concentrations, the feed solution water is dissociated at the contact region of the cation- and anion-exchange resin beds, generating protons and hydroxyl ions that further replace the salt ions in the resins. The final result is completely deionized water as a product. The IX resins are regenerated via water splitting under current. The process can be performed continuously without chemical regeneration of the IX resin [63], and reduce the energy consumption when treating very diluted solutions [64].

The main disadvantage of the EDI process is the relatively poor current utilization. For industrial wastewater treatment, the precipitation of divalent metal hydroxide in EDI stack is a serious problem as a result of metal ions reacting with hydroxide ions present in the EDI stack. With current EDI stack configurations, EDI has not shown potential for treatment of produced water and beneficial use. EDI is not likely to be selected for treatment of CBM produced water due to high energy consumption compared to other membrane processes.

No further assessment was conducted on EDI because of the limited information in the literature and its poor potential application in produced water treatment.

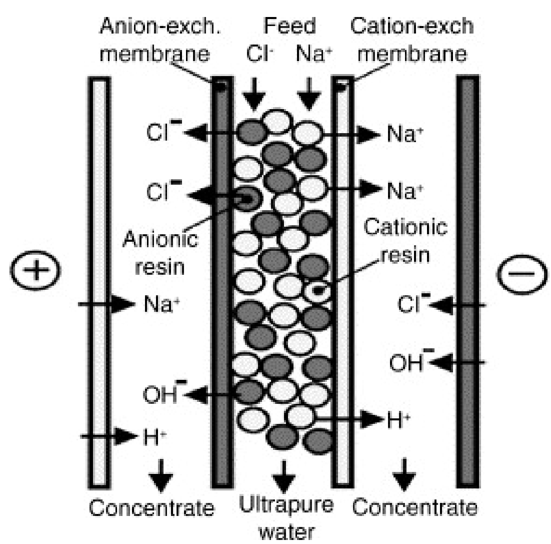

Figure 10. Production of ultrapure water with EDI technology (Source: [63]).

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Thermally Driven Membrane Process

Membrane Distillation

Membrane distillation (MD) is a novel thermally driven membrane separation process that utilizes a low-grade heat source to facilitate mass transport through a hydrophobic, microporous membrane. The driving force for mass transfer is a vapor pressure gradient between a feed solution and the distillate, and is the only membrane process that can maintain process performance (I.e., water flux and solute rejection) almost independently of feed solution TDS concentration. MD is most likely capable of producing ultra-pure water at a lower cost compared to conventionally distillation processes. Membrane materials commonly employed for MD include polytetrafluorethylene (PTFE), polypropylene (PP), and polyvinylidenedifluoride (PVDF). MD membranes may be packaged in either flat-sheet or hollow-fiber configurations.

MD may be operated in four basic configurations: direct contact MD (DCMD), vacuum (VMD), air gap (AGMD), and sweeping gas (SGMD) [65]. Of these four configurations, DCMD and AGMD are the most likely to be deployed as either treatment or post-treatment for CBM produced water. During DCMD a warm feed stream flows on one side of the hydrophobic, micro-porous membrane, while a cooler aqueous solution flows counter-currently on the opposite side of the membrane. Molecules of water evaporate and diffuse through the pores of the membrane. Upon contact with the cold distillate solution on the product side of the membrane the vapor condenses and is assimilated into the distillate solution. AGMD works on a similar principle as DCMD; however, instead of a cooler distillate stream the permeate side of the membrane contains an air gap and a cold plate. As water vapor diffuses through the membrane it enters the quiescent air gap and condenses on the cold plate. A general illustration of the principles of DCMD and AGMD is shown in **Figure 11**.

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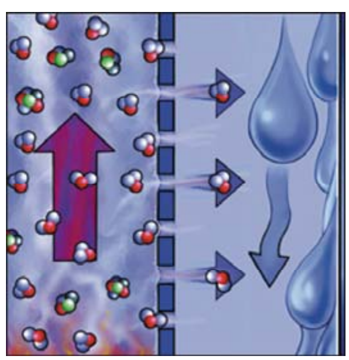

Figure 11. Generalized illustration of the principles of MD. A warm feed stream containing various non-volatile solutes and water flow on the left side of the membrane. Water vapor diffuses through the membrane and condenses in a cold distillate on the right (Source: [66]).

There is no documentation presently available that indicates that MD has been used for produced water treatment in the past. MD is an effective desalination technology because it is capable of treating feed waters with TDS concentration in excess of 35,000 mg/L. Theoretical rejection for all non-volatile solutes (including Na, SiO_2, B, and heavy metals) is 100%;

however, compounds with higher volatility than water, such as BTEX and other organic compounds, will diffuse preferentially faster through the membrane. As a standalone process MD may be capable of achieving similar water recoveries as BWRO. Recovery may be improved to greater than 80% when coupled with crystallizer technologies to reduce scaling [67].

For pretreatment, MD processes require a pre-filter to screen out large particles and the complete removal of any surfactants present in the feed stream. If surfactants are present in the MD feed stream they will wet the hydrophobic pores of the MD membrane and cause pore flooding, which results in a substantial reduction in membrane solute rejection. Chemical demands for MD processes are similar to that required for pressure-driven membrane processes, however foulants and scale layers are more easily removed from the membrane because they are not physically compacted onto the membrane surface. MD requires that the feed solution temperature be elevated beyond that of the permeate side of the membrane; yet, a large temperature gradient is not required to facilitate high mass transfer. The temperature gradient can be as low as 20 °C [65]. The required temperature gradient may be harvested from low-grade waste heat generated from compressors, pumps, etc. and does not represent a significant operational cost.

System maintenance is similar to that of pressure driven processes, and may require occasional system downtime to remove mineral scales or foulants. One benefit of MD is that the membranes are more chemically inert and resistant to oxidation than traditional RO and NF membranes, which allows for more efficient, chemically aggressive cleaning. The membrane module, recirculation pumps, and potentially a cooling system are the only components required for MD operations. The simplicity of MD process components means that they require little supervisory oversight. Membrane modules for MD have not undergone extensive optimization and may require larger footprints than a pressure driven system with equivalent capacity.

MD is an extremely flexible technology for most variations in feed water quality and quantity; however, the introduction of any surfactant into the feed solution will adversely affect the process. As with many membrane technologies, MD modules can be readily integrated on mobile platforms and are highly modular. A summary of the technical assessment for MD is listed in Table 16.

Table 16. Summary of technical assessment of MD

Criteria	**Description/Rationale**
Status of technology	Emerging thermally driven membrane technology, not previously employed for CBM produced water treatment.
Feed water quality bins	TDS application range is controlled by the presence of sparingly soluble salts. Yet, recent studies have demonstrated that scaling is not a major problem. Feed water TDS of 500 mg/L to greater than 50,000 mg/L is possible, and studies have demonstrated that more than 70,000 mg/L feed streams can be processes [68]. MD has 100% theoretical rejection of all non-volatile solutes.
Product water quality	MD distillate/condensate quality is equal to that of distilled water from thermally driven processes (TDS 2 to 10 mg/L). All solutes with higher volatility than water (such as ammonia) will preferentially diffuse into the product water.
Recovery	Product water recovery is between 60% and 95% [69].

Table 16. Summary of technical assessment of MD

Criteria	Description/Rationale
Energy use	MD is a thermally driven process and therefore it requires some energy input. However, the process only requires a moderate temperature gradient to operate. This allows for the system to function by harvesting waste heat from other processes or onsite compressors, pumps, etc.
Chemical use	Scale inhibitor and caustic may be required for process control to prevent scaling or fouling. Chemical cleaning rates depend on feed water quality. Cleaning will typically occur after certain design specifications are exceeded, and may require the use of NaOH, Na_4EDTA, or HCl.
Expected lifetime of critical components	Depending on operating conditions, MD membranes are likely to require replacement within 3 to 7 years.
Infrastructure considerations	MD processes have not enjoyed the same level of intensive research and development as pressure driven processes, as such the membrane modules are not yet optimized. This results in a larger footprint than an equivalent capacity RO or NF system. Because of its larger footprint, MD systems have reduced mobility when compared to pressure driven processes.
O&M considerations	Monitoring and control required for fluid temperature, flow rates, and membrane integrity. System automation lessens demands on skilled labor, however a skilled technician is required to perform routine system maintenance. Level of flexibility: High sensitivity to surfactants, hydrophobic organic compounds may be difficult to remove from the membrane. Level of robustness: MD membranes, especially PTFE based, are highly resistant to pH, oxidants, and irreversible flux decline. Level of reliability: MD systems operate semi-continuously with short duration chemical rinses. Types of energy required: electrical (if no source of waste heat is available).
Capital and O&M costs	Capital costs were estimated for a 1 MGD (24,000 bpd) DCMD plant to be \$3.34/gpd (or \$0.15/bpd), with operating costs estimated to be \$1.40/kgal (or \$0.06/bbl) [70].
Pretreatment of feed water	Removal of any constituents that may wet the hydrophobic, micro-porous pores of the MD membrane is required for efficient process performance.
Post-treatment of product water	Product water may require remineralization and pH stabilization. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feed water with distillate/condensate.
Concentrate management or waste disposal	No special concentrate treatment is required. High theoretical water recovery rates approaching 100% generate minor amounts of concentrated brine.
Applicability for produced water treatment	Moderate to good - Appropriate pretreatment is required to remove surfactants from the feed stream, and membrane modules are not yet optimized for water treatment in any sector.
Note: 1 barrel = 42 US gallon	

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Osmotically Driven Membrane Processes

Forward Osmosis

Forward osmosis (FO) is an osmotically driven membrane process. During FO, water diffuses spontaneously from a stream of low osmotic pressure (the feed solution) to a hypertonic (draw) solution having a very high osmotic pressure. Unlike RO and NF, FO systems operate without the need for applying hydraulic pressure (

Figure **12**). The membranes used for this process are dense, non-porous barriers similar to RO and NF membranes, but are composed of a hydrophilic, *cellulose acetate* active layer cast onto either a woven polyester mesh or a micro-porous support structure.

Typically, the FO draw solution is composed of NaCl, but other draw solutions composed of NH_4HCO_3, sucrose, and $MgCl_2$ have been proposed [71]. During FO the feed solution is concentrated while the draw solution becomes more dilute. Figure 13 illustrates a generic industrial scale application of FO, which requires the continuous reconcentration of the draw solution for sustainable system operation. One prominent method for reconcentrating the draw solution is to utilize an RO subsystem; this configuration will be discussed in Hybrid FO/RO systems.

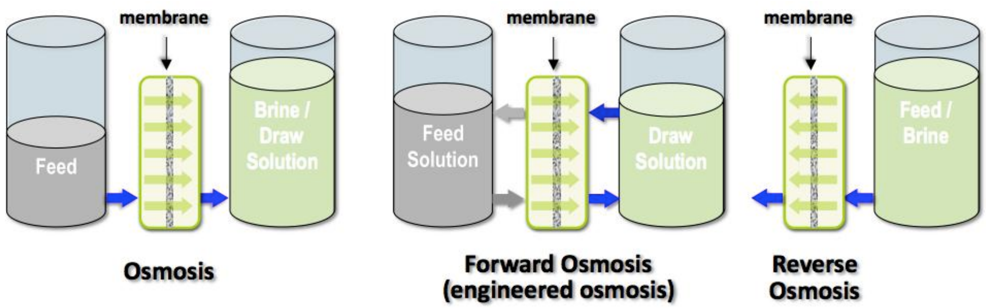

Figure 12. Water diffusion in FO and pressure driven membrane processes (RO and NF). For FO, ΔP is approximately zero and water diffuses to the more saline side of the membrane. For RO and NF, water diffuses to the less saline side due to hydraulic pressure (ΔP>Δπ).

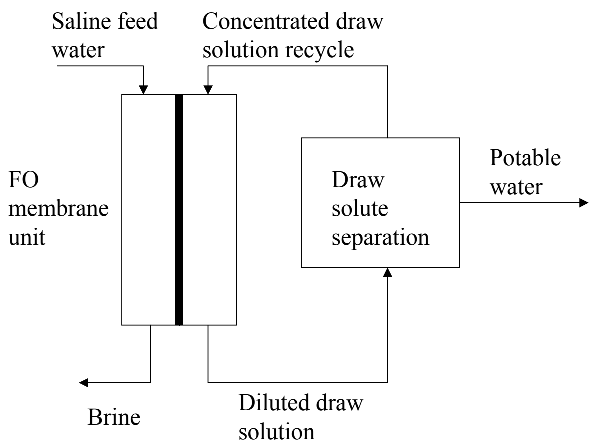

Figure 13. Schematic of a generic FO system for desalination.

FO membranes are capable of rejecting all particulate matter and almost all dissolved constituents (greater than 95% rejection of TDS). These attributes also allow FO to achieve very high theoretical recoveries while minimizing energy and chemical demands. An additional benefit of FO is that the process occurs spontaneously, without the need for applied hydraulic pressure. The hydraulic pressure applied in pressure driven membrane processes is responsible for compacting foulants onto the membrane, which substantially intensifies irreversible flux decline. Fouling layers that accumulate on FO membranes may be readily removed with cleaning (e.g., increasing cross-flow velocity, osmotic backwashing) or with chemicals, and irreversible flux decline is minimized [67, 72].

FO processes are capable of operating with feed TDS ranging from 500 mg/L to more than 35,000 mg/L, and may achieve recoveries in excess of 96% when treating brackish water [67]. FO membranes may be packaged in flat sheet or spiral-wound configurations. These packages allow for relatively small process footprints, but are still not optimized to the extent of pressure driven processes.

Osmotically driven membrane processes have not yet been tested on produced waters. However, multiple lab scale experiments have been conducted with FO, and have utilized feed water supplies ranging from seawater and brackish water to municipal and industrial wastewater [67, 73-76]. FO has also been employed in a pilot and full-scale studies with industrial and municipal wastewaters, but the FO process was coupled with RO to reconcentrate the draw solution (see Hybrid FO/RO systems). A summary of the technical assessment for FO is listed in Table 17.

Table 17. Summary of technical assessment of FO

Criteria	Description/Rationale
Status of technology	Emerging osmotically driven membrane technology. FO has not been previously employed for produced water treatment.
Feed water quality bins	TDS application range is controlled by the osmotic pressure differential between the feed solution and draw solution. The TDS range is between 500 mg/L to greater than 35,000 mg/L. FO has equivalent solute rejection performance to existing pressure driven processes for monovalent and divalent electrolytes, metals, and organics.
Product water quality	The product of FO is a diluted draw solution (typically composed of NaCl). To obtain pure water from the process a secondary system is required to extract pure water from the draw solution, and to reconcentrate the draw solution. This is typically accomplished with RO. FO membranes have similar solute rejection as NF (>90% TDS, >80% ammonia, low rejection of boron).
Recovery	Product water recoveries have exceeded 96% in hybrid RO/FO systems.
Energy use	FO is an osmotically driven process that occurs spontaneously without the need for substantial energy input. The process requires only enough power to circulate the draw solution and feed solution across the FO membrane.

Table 17. Summary of technical assessment of FO

Criteria	**Description/Rationale**
Chemical use	Scale inhibitor and caustic may be required for process control to prevent scaling or fouling. Chemical cleaning rates depend on feed water quality. Cleaning will typically occur after certain design specifications are exceeded, and may require the use of NaOH, Na_4EDTA, or HCl.
Expected lifetime of critical components	Depending on operating conditions, FO membranes are likely to require replacement within 3 to 7 years.
Infrastructure considerations	FO processes have not enjoyed the same level of intensive research and development as pressure driven processes, as such the membrane modules are not yet optimized. This results in a larger footprint than an equivalent capacity RO or NF system. Because of its larger footprint, FO systems may have reduced mobility when compared to pressure driven processes.
O&M considerations	Monitoring and control required for flow rates and membrane integrity. System requires very little oversight, however a skilled technician is required to perform routine system maintenance. Level of flexibility: Extremely flexible technology, with sensitivity to low and high pH streams. Level of robustness: FO membranes are highly resistant to irreversible flux decline. Level of reliability: FO systems operate semi-continuously with short duration physical or chemical cleanings. Types of energy required: electrical (to power low pressure circulation pumps).
Capital and O&M costs	Capital costs are unknown.
Pretreatment of feed water	A prefilter is required to remove large debris; antiscalant may be required for high recovery operation.
Post-treatment of product water	Diluted draw solution requires further separation to produces pure water and reconcentrate the draw solution for reuse.
Concentrate management or waste disposal	No special concentrate treatment is required. Relatively high recovery rates exceeding 96% (for hybrid RO/FO systems) generate very minor amounts of concentrated brine.
Applicability for produced water treatment	Moderate to good - FO may provide excellent pretreatment for adjacent processes, but FO membranes are not yet available for commercial installations.
Note: 1 barrel = 42 US gallons	

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Hybrid Membrane Technologies

Numerous methods have been proposed to enhance recovery and minimize concentrated brine volume generation resulting from membrane desalination processes. Many of these methods couple multiple stages of membrane-based treatment processes with intermittent chemical precipitation or caustic addition. These processes include: dual NF, Dual RO with chemical precipitation, Dual RO with softening pretreatment with high pH operation (High Efficiency RO (HERO™)), and Dual RO with Slurry Precipitation and Recycling RO (SPARRO). Other membrane hybrid processes include novel combinations of RO with other established or novel membrane technologies. These include coupling FO with RO and coupling RO with ED.

Dual RO with chemical precipitation

Dual RO with chemical precipitation is a physical-chemical method for enhancing recovery of conventional RO processes through treatment and minimization of concentrate. The process employs established technologies such as lime soda softening and a second stage RO [77-79]. As illustrated in Figure 14, this approach is based on treatment of the concentrate from a primary RO system using a physical-chemical process, followed by subsequent treatment in a secondary RO system. The chemical treatment step utilizes precipitation to remove calcium, magnesium, and other sparingly soluble salts, and is followed by filtration (e.g., media filtration or membrane filtration) for removing solids carryover from the precipitation process. The secondary RO system is then operated at a higher TDS, and requires higher pressures compared to the primary RO system. The combined recovery of the process is reported to be 95% or greater for brackish water.

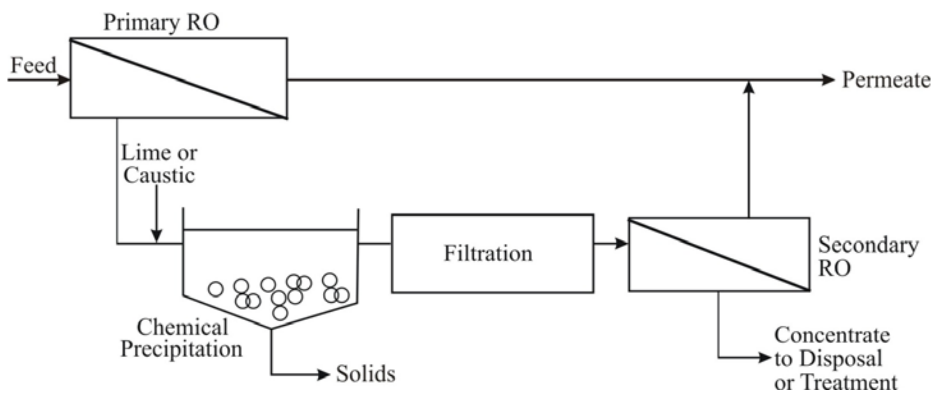

Figure 14. Dual RO with intermediate chemical precipitation.

The positive attributes of this technology include the application of established unit processes and relatively low additional energy requirements. Negative attributes include additional chemicals, production of sludge from the chemical precipitation process, and footprint and costs of chemical feed and storage facilities.

This approach has recently been pilot tested at the Metropolitan Water District of Southern California [77]. A dual RO configuration with intermediate chemical precipitation has also been recently pilot tested at the Southern Nevada Water Authority [80]. This treatment process has not yet been utilized for CBM produced water. A summary of the technical assessment for a dual RO with chemical precipitation is listed in Table 18.

Table 18. Summary of technical assessment of dual RO with chemical precipitation

Criteria	**Description/Rationale**
Status of technology	Pilot tested at municipal desalination plants. Not previously employed for CBM produced water treatment.
Feed water quality bins	TDS application range is 1,000 mg/L and 35,000 mg/L. High removals of monovalent and divalent ions, metals, and organics is expected. System is likely to achieve additional silica removal through co-precipitation.
Product water quality	Treatment process permeate quality is dependent on feed water salinity and operating conditions. Pilot studies report 94% rejection of TDS.
Recovery	Product water recovery is estimated to exceed 90%.
Energy use	No data is currently available.
Chemical use	Chemical demand of lime ($Ca(OH)_2$) or caustic soda (NaOH) will depend on water chemistry and the quantity of calcium and magnesium targeted for removal. Chemical cleaning rates depend on feed water quality. Cleaning will typically occur after certain design specifications are exceeded, and may require the use of NaOH, Na_4EDTA, or HCl.
Expected lifetime of critical components	No data is currently available.
Infrastructure considerations	This treatment process will require a substantially larger footprint that conventional RO systems. Chemical storage and sludge dewatering facilities will be required, in addition to a second bank of RO elements. System mobility is reduced compared to conventional RO systems. Filtration system and chemical storage components are the primary factors in limiting mobility.
O&M considerations	Monitoring and control required for flow rates, chemical dosing, and RO element pressure. System may require substantial oversight to ensure proper operation of the primary RO stage brine management systems. Level of flexibility: May have moderate sensitivity to organic and inorganic constituents in the feed water. Level of robustness: TFC membranes have high pH tolerance, but cannot be exposed to feed temperatures in excess of 113 °F (45 °C). Level of reliability: RO systems operate semi-continuously with automated, short duration chemical rinse or osmotic backwashing cycles. Types of energy required: electrical.
Capital and O&M costs	Costing figures are unknown.
Pre-treatment of feed water	All high-pressure membrane technologies require extensive pretreatment to mitigate harmful water quality constituents that will otherwise foul or scale the membrane. The feed stream to the second RO stage requires chemical precipitation and filtration prior to contact with the RO membranes.
Post treatment of product water	Product water may require pH stabilization or remineralization. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with permeate.

Table 18. Summary of technical assessment of dual RO with chemical precipitation

Criteria	**Description/Rationale**
Concentrate management or waste disposal	No special concentrate treatment is required. Relatively high recovery rates exceeding 90% generate very minor amounts of concentrated brine.
Applicability for produced water treatment	Good to excellent - the limiting criteria is chemical cost, availability, and disposal considerations.
Note: 1 barrel = 42 US gallons	

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Dual RO with softening pretreatment and high pH operation (HERO™: High Efficiency RO)

This patented technology [81] consists of a hardness and alkalinity removal step, a degasification step to remove carbon dioxide, and intermediate caustic addition to increase the pH of the RO feed water. This technology was developed to produce water of exceptionally high purity for the micro-electronics industry.

For municipal brackish water, the process combines a two-phase RO process with chemical pretreatment of primary RO, intermediate ion exchange treatment of primary RO concentrate, and high pH operation of secondary RO [82]. The approach is illustrated in Figure 15. The (secondary) RO step operates as a "high-efficiency" system due to ion exchange pretreatment and high pH operation.

The concentrate of the primary RO is treated in weakly acidic cationic (WAC) exchange resins. The carbon dioxide from the concentrate is stripped and the pH is increased with caustic to above 10. This allows for the secondary RO to operate at high recoveries. Operating the negatively charged membranes at a high pH is reported to allow better removal of both weakly ionized anions as well as the strongly ionized species. The solubility of silica is increased at high pH, which allows for greater recovery rates when treating water that contains high concentrations of silica. The combined recovery of the process is estimated to be greater than 90% for brackish water, with typical target recovery rates of approximately 95%.

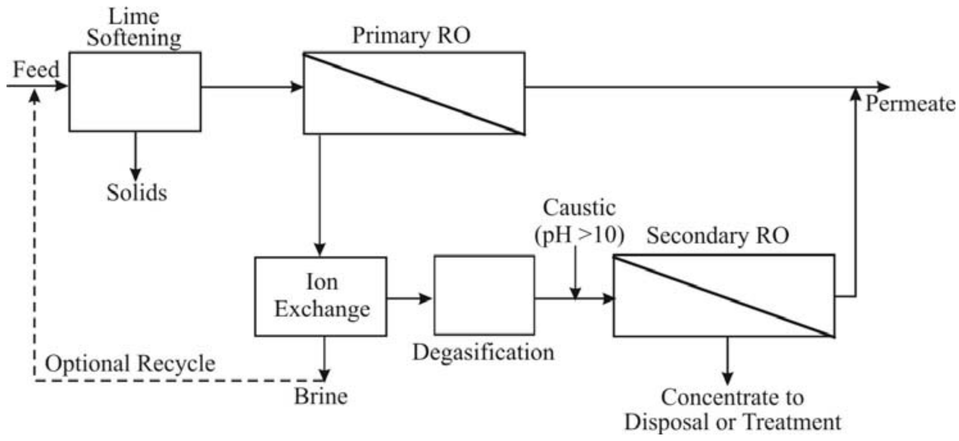

Figure 15. Schematic of a dual RO system that incorporates a softening pretreatment and intermediate high pH operation (High Efficiency RO (HERO™)).

The HERO™ system has been utilized to enhance recovery of surface water (Colorado River water) during desalination [79]. Raw water feed characteristics included relatively low feed solution TDS of 950 mg/L, dominated by sodium and SO_4 with the presence of other constituents including SiO_2, B, Ca, Ba, Mg, and HCO_3. Results demonstrated that recoveries of 95% to 98% were achievable with the HERO™ system. A demonstration scale facility at the Arlington Valley Power Station in Arizona was constructed [83]. The facility is designed to treat 2.4 MGD of cooling tower blow down that contains 10,000 mg/L of TDS and is saturated with SiO_2. A summary of the technical assessment for a dual RO with chemical precipitation is listed in Table 19.

Table 19. Summary of technical assessment of dual RO with softening pretreatment and high pH operation (High Efficiency RO (HERO™))

Criteria	Description/Rationale
Status of technology	Technology has undergone lab-scale testing on surface water, and demonstration-scale testing on cooling water blowdown. Variations of this process have been employed by commercial vendors for produced water treatment (e.g., CDM).
Feed water quality bins	The estimated TDS application range is between 500 mg/L and 10,000 mg/L. Moderately high removals of monovalent and divalent ions, metals, and organics is expected. System is likely to achieve additional silica and boron removal with high pH operation.
Product water quality	Treatment process permeate quality is dependent on feed water salinity and operating conditions. Lab-scale studies report 94% rejection of TDS.
Recovery	Product water recovery is estimated to exceed 90%.
Energy use	Energy requirements are estimated to be between 11and 19 kwh/m^3 (0.48 to 0.80 kWh/bbl)
Chemical use	Chemical cleaning rates depend on feed water quality. Cleaning will typically occur after certain design specifications are exceeded, and may require the use of NaOH, Na_4EDTA, or HCl. IX process will require regeneration with strong acid, likely H_2SO_4 or HCl.
Expected lifetime of critical components	No data is currently available.
Infrastructure considerations	This treatment process will require a substantially larger footprint that conventional RO systems. Chemical storage and sludge dewatering facilities will be required, in addition to a second bank of RO elements. System mobility is reduced compared to conventional RO systems. Lime softening and IX system along with chemical storage components are the primary factors in limiting mobility.
O&M considerations	Monitoring and control required for flow rates, chemical dosing, IX resin regeneration, and RO element pressure. System may require moderate oversight to ensure proper operation of the primary RO stage brine management systems. Level of flexibility: May have moderate sensitivity to organic and inorganic constituents in the feed water. IX resin requires regeneration. Level of robustness: TFC membranes have high pH tolerance, but cannot be exposed to feed temperatures in excess of 113 °F (45 °C). Level of reliability: RO and IX systems operate semi-continuously with automated, short duration chemical rinses or osmotic backwashing cycles (for RO). Types of energy required: electrical.
Capital and O&M costs	Capital costs are estimated to be $4.6/gpd ($195/bpd), while operation and management costs are approximated at $3.5/kgal ($0.14/bbl).
Pre-treatment of feed water	Process will require coagulation and pre-filtration to remove suspended solids prior to lime softening. Other pretreatment options including antiscalant and acid addition may be required. The feed stream to the second RO stage requires chemical precipitation and filtration prior to contact with the RO membranes.

Table 19. Summary of technical assessment of dual RO with softening pretreatment and high pH operation (High Efficiency RO (HERO™))

Criteria	Description/Rationale
Post treatment of product water	Product water will require pH stabilization or remineralization. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with permeate.
Concentrate management or waste disposal	No special concentrate treatment is required. Relatively high recovery rates exceeding 90% generate very minor amounts of concentrated brine. Sludge from the sedimentation basin will require dewatering and landfill application.
Applicability for produced water treatment	Good to excellent - the limiting criteria is regenerant cost, availability, and disposal considerations.
Note: 1 barrel = 42 US gallons	

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Dual RO with SPARRO: Slurry Precipitation and Recycling RO

In SPARRO, specific crystals are added to feed water to aid in precipitation of scaling compounds in a membrane application. For example, Gypsum crystals are used to precipitate calcium sulfate. The concept of adding crystals to feed water in tubular RO membrane systems for preferential precipitation and the concept of recycling the seeded slurry were first patented in 1980 [84].

Seed crystals are added to the water in a tubular RO membrane system and the scaling compounds are precipitated on the seed crystals instead of on the membrane. The seed crystals serve as preferential growth sites for calcium sulfate and other calcium salts and silicates, which begin to precipitate as their solubility products are exceeded during the concentration process within the membrane tubes.

The slurry of seed crystals is recirculated in the RO system and the precipitates are removed from the system in a controlled fashion. Because the seed slurry is recirculated within the membranes, the process is confined to the use of a membrane configuration that will not plug, such as tubular membrane systems.

Another patent was later awarded that focused on the methodology of determining adequate seed crystal concentration in the preferential precipitation systems [85]. A series of pilot tests were also performed by Resources Conservation Company (RCC) based on the original patented technology ([84, 85]. Subsequently, there have been other tests of the technology based on the concept of adding seed crystals to a tubular membrane configuration. Two variations of the further testing are discussed below. The first approach is illustrated in Figure 16 [86].

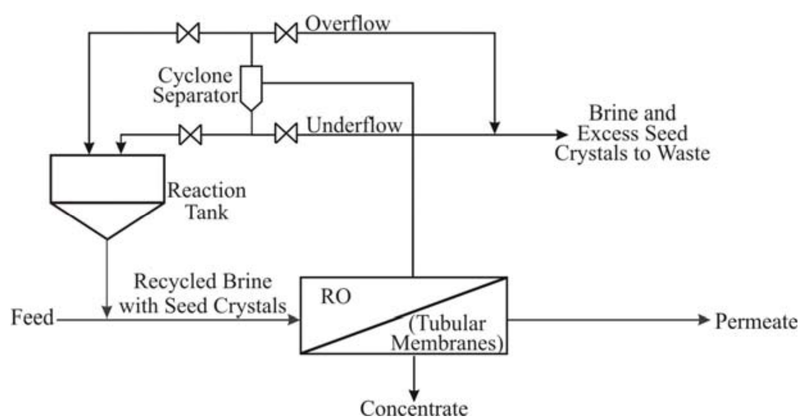

Figure 16. Schematic of Seeded Slurry Precipitation and Recycle RO (SPARRO).

The water to be desalted is mixed with a stream of recycled concentrate containing the seed crystals and fed to the RO process. The concentrate with seed crystals is processed in a cyclone separator to separate the crystals, and the desired seed concentration is maintained in a reactor tank by controlling the rate of wasting the upflow and/or underflow streams from the separator. The combined recovery of the process is estimated to be greater than 90%.

The positive attributes of this technology include relatively low energy costs. Negative attributes include requirement of tubular RO membranes, larger footprint for tubular membranes, and additional chemicals. This approach has been tested at pilot scale in South Africa, at the East

Rand Proprietary Mines [86]. A pilot testing of this approach for concentrate treatment tested at the Eastern Water Municipal District in California [87].

Another variation of the seeded slurry approach involves a two-pass process, with the first pass employing a tubular NF system with seeded slurry recycle and the second pass employing a spiral wound RO system [88]. The process was developed for an agricultural drainage water reclamation application and tested at bench scale. The process, known as double pass, preferential precipitation, reverse-osmosis process, or DP_3RO^{TM}, is proprietary and in the process of applying for patent.

Although the TDS level in the agricultural drainage water is typically between 3,000 to 12,000 mg/L, the recovery of a conventional RO system treating this water is reported to be limited to less than 50%, due to the high levels of calcium sulfate concentrations. The two-pass system is reported to be able to achieve a recovery of 92-96%. The first pass NF uses calcium sulfate seeds in a seeded slurry recycle configuration and provides removal of calcium sulfate and softening in general. The softened water is then treated with RO to meet the irrigation requirements (TDS < 500 mg/L and sodium adsorption ratio < 4.0).

Other positive attributes of this technology include increased RO recovery in an agricultural drainage water application. Negative attributes include requirement of tubular NF membranes, larger footprint for tubular membranes, a two-pass system (and associated energy and costs), and additional chemicals. This approach has been tested at bench-scale using drainage water from the Panache Drainage District in California [88]. A summary of the technical assessment for a slurry precipitation and recycling RO system is listed in Table 20.

Table 20. Summary of technical assessment of slurry precipitation and recycling RO (SPARRO).

Criteria	Description/Rationale
Industrial status	Pilot-scale testing on impaired water from a mining operation. No previous utilization for CBM produced water treatment.
Feed water quality bins	The estimated TDS application range is between 500 mg/L and 10,000 mg/L. Moderately high removals of monovalent and divalent ions, metals, and organics is expected.
Product water quality	Treatment process permeate quality is dependent on feed water salinity and operating conditions. Pilot-scale studies report 94% rejection of TDS.
Production efficiency (recovery)	Product water recovery is estimated to exceed 94%.
Infrastructure considerations	This treatment process will require a substantially larger footprint that conventional RO systems. Chemical storage and reaction vessel facilities will be required, in addition to a second bank of RO elements. System mobility is reduced compared to conventional RO systems.
Energy consumption	Energy requirements are estimated to at 18.2 kWh/kgal (0.77 kWh/bbl)
Chemicals	The system requires a continuous feed of seeding material. Chemical cleaning rates depend on feed water quality. Cleaning will typically occur after certain design specifications are exceeded, and may require the use of NaOH, Na_4EDTA, or HCl.
Life cycle	No data is currently available.

Table 20. Summary of technical assessment of slurry precipitation and recycling RO (SPARRO).

Criteria	Description/Rationale
O&M considerations	Monitoring and control required for flow rates, chemical dosing, and RO element pressure. System may require substantial oversight to ensure proper operation of integrated system. Level of flexibility: May have moderate sensitivity to organic and inorganic constituents in the feed water. Level of robustness: TFC membranes have high pH tolerance, but cannot be exposed to feed temperatures in excess of 113 °F (45 °C). Level of reliability: RO systems operate semi-continuously with automated, short duration chemical rinses or osmotic backwashing cycles (for RO). Types of energy required: electrical.
Overall costs	Capital costs are estimated to be $4.7/gpd ($199/bpd), while operation and management costs are currently unknown.
Pre-and post treatment	Process will require coagulation and pre-filtration to remove suspended solids prior contact with the slurry reaction chamber to ensure optimal operation. Other pretreatment options including antiscalant and acid addition may be required. Product water may require pH stabilization or remineralization. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with permeate. The feed stream to the second RO stage requires chemical precipitation and filtration prior to contact with the RO membranes.
Concentrate management or waste disposal	No special concentrate treatment is required. Relatively high recovery rates exceeding 90% generate very minor amounts of concentrated brine.
Applicability for produced water treatment	Good to excellent - the limiting criteria is sludge disposal and chemical reagent availability.
Note: 1 barrel = 42 US gallons	

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FO-RO Hybrid System

During FO the feed solution is concentrated while the draw solution becomes more dilute. For the process to be sustainable on an industrial scale, the draw solution requires continuous reconcentration. One prominent method for reconcentrating the draw solution is to utilize an RO subsystem. Reconcentration with RO is a viable option because the draw solution does not contain high levels of sparingly soluble salts or foulants. Recent studies have shown that synergistically coupling FO with RO creates an exceptionally robust, multi-barrier system for treatment of highly impaired streams [69, 75, 89-91]. A system diagram is shown in
Figure **17**.

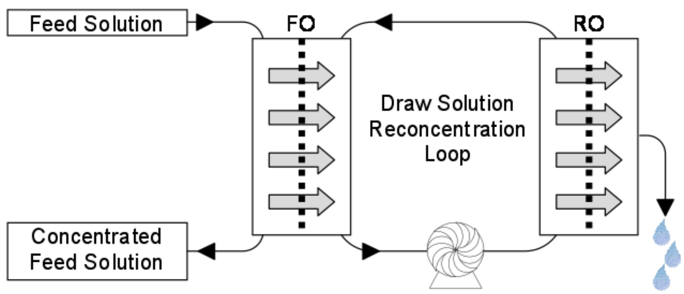

Figure 17. Schematic drawing of a hybrid FO-RO system. Impaired feed water contacts one side of the forward osmosis. Water diffuses form the feed solution into the draw solution. An RO system is then employed to reconcentrate the draw solution and produce pure water permeate.

Hybrid FO-RO systems have undergone pilot-scale testing at the Denver Water Recycling Facility with a feed source consisting of secondary and tertiary effluents [91]. Full-scale testing of a hybrid FO-RO system was completed at a landfill in the Pacific-Northwest of the United States [76]. During full-scale testing the system was employed to treat landfill leachate. Additional pilot scale testing is planned to occur in a brackish water desalination facility in southern California during the summer of 2010.

The physical limit on the applicable TDS range for this process is the requirement that the draw solution have a higher osmotic pressure than the impaired feed water stream, and that the osmotic pressure of the draw solution is not prohibitive for reconcentration by RO. These limitations indicate that FO-RO systems are most applicable for a feed water TDS ranging from 500 mg/L to 35,000 mg/L. An FO-RO system provides two significant barriers, in the form of two dense, non-porous membranes, which allows for the system to treat highly impaired water with high rejection of solutes. The FO membrane will act to reject most contaminates in the feed water, including scale forming minerals, most organic compounds, and microorganisms. Employing a SWRO membrane for the RO stage will ensure high NaCl rejection (exceeding 99.7%) [69, 91]. The estimated water recovery for an FO-RO system is in excess of 96% [69].

FO membrane elements are not yet optimized and therefore require a larger operational footprint to achieve a similar water recovery to an RO system of equivalent production capacity. FO-RO systems may be deployed in highly portable, trailer mounted membrane skids, and are highly modular. An FO-RO system requires a stable source of electrical energy to operate. System cleaning is highly dependant on feed water quality; however, the FO membrane in highly resistant to membrane fouling and scaling. Mechanical cleaning of FO membrane modules has been shown to be a highly efficient method for restoring membrane performance without the need for chemicals [72]. However, chemical cleaning and the addition of scale inhibitors may be required for both the FO and RO subsystems depending on feed water quality.

The service life of an FO-RO system is currently unknown, however RO membrane elements will likely require replacement within 3 to 7 years of operation [36]. Industrial scale FO-RO systems would be highly automated systems, and would require relatively little supervisory oversight. The FO subsystem is capable of treating highly variable feed water qualities and protects the RO membrane modules from harmful membrane foulants. The system would require few major maintenance periods; however, the system would need to undergo brief, routine backwashing and mechanical cleanings several times each day. Optimization is underway. The FO component of an FO-RO system provides excellent pretreatment capabilities, while the concentrated brine generated from the RO system is continuously recycled in the system. The most significant waste stream that will require either further treatment or disposal is the concentrated feed stream. Additionally, the FO draw solution may require infrequent disposal and addition of a new draw solution as sparingly soluble solutes and other membrane foulants slowly accumulate in the draw solution reconcentration loop [92]. A summary of the technical assessment for an FO-RO system is listed in Table 21.

Table 21. Summary of technical assessment of hybrid FO-RO system.

Criteria	Description/Rationale
Industrial status	One pilot-scale test on secondary effluent from a municipal wastewater treatment plant. No previous utilization for CBM produced water treatment.
Feed water quality bins	The estimated TDS application range is between 500 mg/L and 35,000 mg/L. High removals of monovalent and divalent ions, metals, and organics is expected.
Product water quality	Treatment process permeate quality is dependent on feed water salinity and operating conditions. Pilot-scale studies report greater than 99% rejection of TDS in RO permeate.
Production efficiency (recovery)	Product water recovery is estimated to exceed 96%.
Infrastructure considerations	This treatment process will require a larger footprint that conventional RO systems. Chemical storage will be required, in addition to a FO membrane bank. System mobility is reduced compared to conventional RO systems.
Energy consumption	Energy requirements are estimated between 5.68 to 11.36 kWh/kgal (0.24 to 0.48 kWh/bbl) [91].
Chemicals	Chemical cleaning rates depend on feed water quality. Cleaning will typically occur after certain design specifications are exceeded, and may require the use of NaOH, Na_4EDTA, or HCl.
Life cycle	No data is currently available for hybrid system; however, RO elements will likely require replacement between 3 and 7 years of operation.

Table 21. Summary of technical assessment of hybrid FO-RO system.

Criteria	Description/Rationale
O&M considerations	Monitoring and control required for flow rates, chemical dosing, and RO element pressure. System may require substantial oversight to ensure proper operation of integrated system. Level of flexibility: Highly flexible to alterations in feed water quality. Level of robustness: TFC membranes have high pH tolerance, but cannot be exposed to feed temperatures in excess of 113 °F (45 °C). FO membranes are typically composed of *cellulose acetate* and are more resistant to oxidants that TFC membranes, but less resistant to low or high pH operation. Level of reliability: RO systems operate semi-continuously with automated, short duration chemical rinses or osmotic backwashing cycles (for RO). FO systems may operate semi-continuously with short duration, high flow rate mechanical cleanings. Types of energy required: electrical.
Overall costs	Capital costs for FO-RO systems are currently unknown.
Pre-and post treatment	Process may require pretreatment options including antiscalant and acid addition. Product water may require pH stabilization or remineralization. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with permeate. The concentrated feed stream may require additional post treatment or disposal consideration.
Concentrate management or waste disposal	No special concentrate treatment is required. Relatively high recovery rates exceeding 96% generate very minor amounts of concentrated brine.
Applicability for produced water treatment	Moderate to good – FO provides an excellent pretreatment option for the RO stage; however, FO membrane modules are not yet optimized for use in CBM produced water treatment.
Note: 1 barrel = 42 US gallons	

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Dual NF

In this approach the concentrate from a primary NF process is employed as the feed solution for an additional NF stage. The second NF stage produces additional permeate that enhances the recovery of the overall process. This technology is currently under consideration for municipal brackish water desalination projects, including an ongoing study at the Irvine Ranch Water District (IRWD) in California. Recoveries of 92% are achieved in the primary NF system of the IRWD dual NF system, however the challenge water contains relatively low levels of sparingly soluble salts [36]. Currently, the concentrate from the full-scale primary NF system is being sent to a pilot skid comprised of a secondary NF system. Overall recoveries of about 98% have been obtained [93]. More challenging feed water, such as water with high hardness, would likely force the dual NF system to operate with an intermediate chemical precipitation stage, such as dual RO with chemical precipitation. This intermediate chemical precipitation stage would allow for the removal of sparingly soluble salts that are near their saturation limit, and would otherwise lead to severe scaling of the secondary NF.

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Thermal Technologies

In distillation processes, energy is used to heat feed water that evaporates and then condenses to become purified water. Distillation technologies were traditionally used for large seawater desalination plants until the 1980s. In the past few decades the development of membrane separation processes such as RO and NF made them the technology of choice for most seawater and brackish water desalination; this is largely due to the higher energy requirements of conventional thermal desalination processes. Thermal separation processes are still employed in places where waste heat is readily available from power plants or other industries; this is particularly relevant in the Persian Gulf, where the cost of energy is relatively lower.

Thermal separation technologies that are used for desalination include multi stage flash (MSF) distillation, multiple effect distillation (MED), and vapor compression distillation (VCD) [94]. In MSF, the feed water is heated, the pressure is lowered, and the water "flashes" into steam. This process constitutes one stage of a number of stages in series, each operating a lower temperature and pressure [95]. In MED, the feed water passes through a number of evaporators in series. Vapor from one series is subsequently used to evaporate water in the next series. The VCD process involves evaporation of feed water, compression of the vapor, and then recovering the heat of condensation to evaporate more feed water. Some distillation plants are hybrids of more than one desalination technology, such as MED-VCD [96]. The waste product from these processes is a solution with high salt concentration. By using hybrid thermal technologies, zero liquid discharge can be achieved through brine concentrator and crystallizer.

Membrane systems typically have advantages over thermal processes. These include lower energy consumption, lower capital cost, and smaller physical footprint. However, feed water to membrane systems requires extensive pretreatment, and the processes are not applicable to very high salinity water (e.g., above seawater level of approximately 47,000 mg/L TDS). Recent innovations in materials, chemical additives for scale and corrosion control, and process engineering make thermal processes more attractive and competitive in certain applications, particularly for achieving zero liquid discharge and treating highly contaminated water. Besides distillation technologies, new thermal separation technologies such as freeze-thaw and dewvaporation have been developed for desalination of water.

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Multi stage flash

The multi stage flash (MSF) distillation process is based on the principle of flash evaporation in which water is evaporated by reducing the pressure as opposed to raising the temperature with additional heat/energy. In MSF the heated feed water flows into a stage with lower pressure and immediately boils or flash into steam [94]. The high efficiency of the MSF process is achieved by preheating new feed water through capturing of the heat of condensation in each flash chamber or stage.

A simplified schematic of an MSF seawater desalination plant is shown in Figure 18. The incoming seawater passes through the heating stage(s) and is preheated in the heat recovery/condenser sections of each subsequent stage. After passing through the last heat recovery section, and before entering the first stage, the feed water is further heated to the boiling temperature of the first stage in the brine heater using externally supplied energy or steam. This raises the feed water to its highest temperature, after which it is passed through the stages where flashing takes place. The vapor pressure in each of these stages is controlled so that the heated brine enters each chamber at the superheated conditions associated with the temperature and pressure of each stage (each lower than the preceding stage) to induce instantaneous boiling/evaporation [97].

The fresh water is produced by condensation of the steam, which is collected at each stage. The desalinated water produced by the MSF process contains typically 2–10 mg/L TDS, and requires remineralization through post-treatment process [98][99].

The range of recoveries for conventional MSF desalting process is limited to approximately 10-20% for seawater [94].

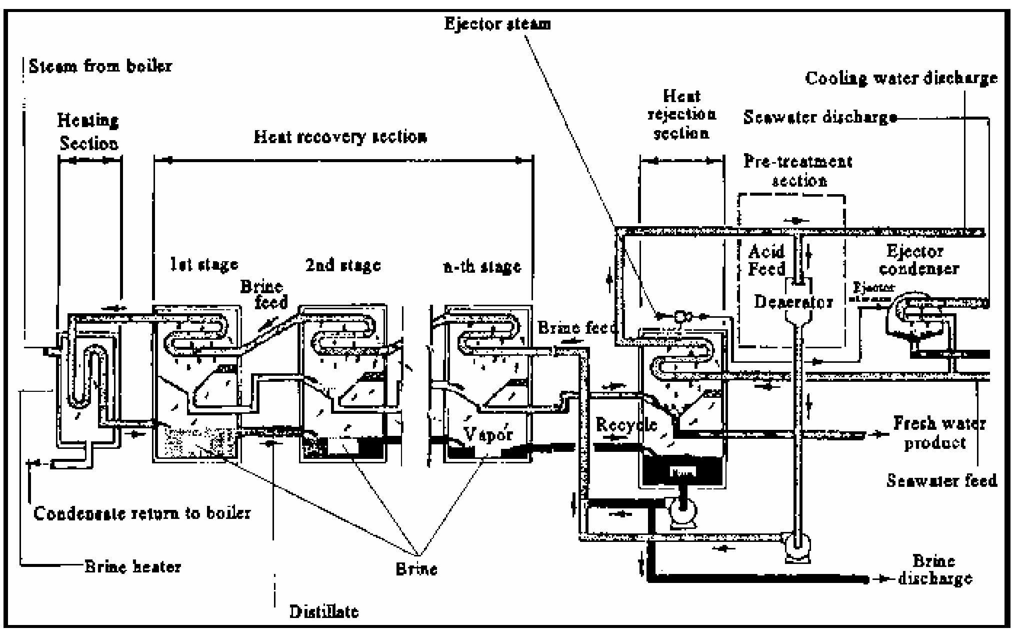

Figure 18. Simplified schematic of MSF seawater desalination plant (Source: [97]).

According to the Global Water Intelligence (GWI) report, MSF had a market share of more than 60% of the worldwide desalination capacity in 2003 and decreased to 34% by the end of 2005 due to the competition of membrane technologies [38]. MSF can be applied to a wide range of feed water quality bins including produced water. MSF often requires centralized design and construction of large-scale plants.

Formation of scale on heat transfer surfaces is a major operating problem in thermal desalination processes. It impedes the rate of heat transfer rates on condensing and heat transfer surfaces, and will consequently reduce the distiller performance. The majority of MSF plants are currently using scale inhibitors such as phosphonates or polycarboxylic and polymaleic acids in conjunction with mechanical sponge ball cleaning to control alkaline scale formation [96]. Acid cleaning may be required if scale formation is not controlled by using the scale inhibitors and mechanical cleaning.

Well designed and operated, some MSF distillers have been in service for more than 20 years, and are expected to exceed 30 years [96]. This increases the cost effectiveness of process. A summary of the technical assessment of MSF is listed in Table 22.

Table 22. Summary of technical assessment of MSF.

Criteria	**Description/Rationale**
Industrial status	Mature and robust technology for seawater and brackish water desalination. Can be employed for produced water treatment.
Feed water quality bins	Usually applicable to a high TDS range to 40,000 mg/L, and all types of water chemistry makeup.
Product water quality	Product water quality for MSF plants is typically very high (TDS 2-10 mg/L), with little variation due to feed or concentrate salt content.
Production efficiency (recovery)	Product water recovery is between 10% and 20% [94].
Infrastructure considerations	The infrastructure considerations or constraints are large physical plant size. The technology relies on the availability of low-pressure steam, either by dedicated generation or by cogeneration arrangements with adjacent power plants. The MSF plants have low mobility.
Energy consumption	In addition to the 11 to 21 kWh/kgal (0.45-0.9 kWh/bbl) of energy required for electricity, the thermal energy needs for a MSF distillation plant is estimated at 0.8 million Btu/kgal (about 80 kWh/kgal or 3.35 kWh/bbl) [95]. Consequently, the total energy needs for MSF are between 70 and 112 kWh/kgal (or 3.35-4.70 kWh/bbl) [95] [100].
Chemicals	Scale inhibitor and acid may be required for process control to prevent scaling. Corrosion control is achieved via pH control. Annual cleaning is typically conducted using acid, EDTA, or other antiscaling chemicals.
Life cycle	Typically 20 years, although most plants built in the 1970's and 1980's are still in operation with expected life of over 30 years.

Table 22. Summary of technical assessment of MSF.

Criteria	Description/Rationale
O&M considerations	Levels of monitoring and control required for feed pH, flow rates as well as steam and vessel pressures. High level of skilled labor required, however lower than equivalent membrane plants. Level of flexibility: easy to adapt to highly varying water quality; not flexible for varying water flow. Level of robustness: high ability of the equipment to withstand harsh conditions. Level of reliable: typical plants operate continuously, with shutdown only for planned maintenance once per year (6-8 weeks) [97]. Types of energy required: thermal and electricity.
Overall costs	Capital costs vary from \$6–8.6/gpd (or \$250-360 per bpd), depending on various factors including size, materials of construction and site location [98]. As a non-modular form of construction, the economy of scale can reduce the cost for larger plants, assuming ready site access for marine transportation. Operating costs are approximately \$3/kgal (or \$0.12/bbl), and total unit costs are \$4.4/kgal (or \$0.19/bbl) [98]. Significant reductions in energy costs can be realized from cogeneration arrangements where cheap, low-pressure steam is available.
Pre-and post treatment	One of the advantages of MSF compared to membrane technologies is that the general operation requires less rigorous pretreatment and feed conditioning. Feed water requires screens and rough filtration to remove large suspended solids. Since the elevated process temperatures will automatically sterilize the water, there is no need to add biocides once the water enters the MSF units. Product water needs stabilization because of the low TDS level. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with the distillate.
Concentrate management or waste disposal	No special concentrate treatment is required. Due to the typically low recovery rates of 25 to 30%, large amounts of concentrate are generated.
Applicability in produced water treatment	Good for high TDS produced water treatment. MSF often requires centralized design and construction of large-scale plants.
Note: 1 barrel = 42 US gallons	

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Multi effect distillation

The basic principle of a multi effect distillation (MED) system is to apply sufficient energy to bring the feed water to its boiling temperature and then to deliver the additional energy needed for the heat of vaporization to transform a portion of the saline water to steam. The final step is to condense the process steam as pure water.

A "single stage" operation is very energy intensive. Multiple vessels can be used to make the process more efficient by operating the vessels (or effects) at successively reduced pressures to promote boiling at lower temperatures, and thus achieving multiple boiling and evaporation cycles, without the addition of more heat. Typically, 8 to 16 effects may be used in MED to minimize the energy consumption. A schematic of a conventional MED system using steam as a heat source, with four effects is illustrated in Figure 19. The feed water is distributed on the outside of the evaporator tubes in a thin film to promote rapid boiling and evaporation. Steam is condensed on the colder inside surface. The vapor produced in each effect is used to heat the feed water in the next effect. The following are the energy consuming components of an MED process:

- Steam of sufficient pressure to drive evaporation in the first stage.
- Energy for vacuum systems to reduce the boiling pressure in the downstream effects (if operated at low temperatures).
- Energy to pump the feed through the heat exchangers to the evaporator(s), to re-circulate the brine within each evaporator stage and to pump the condensate and brine through the heat recovery for exiting the system.
- Cooling water to condense the steam from the final stage.

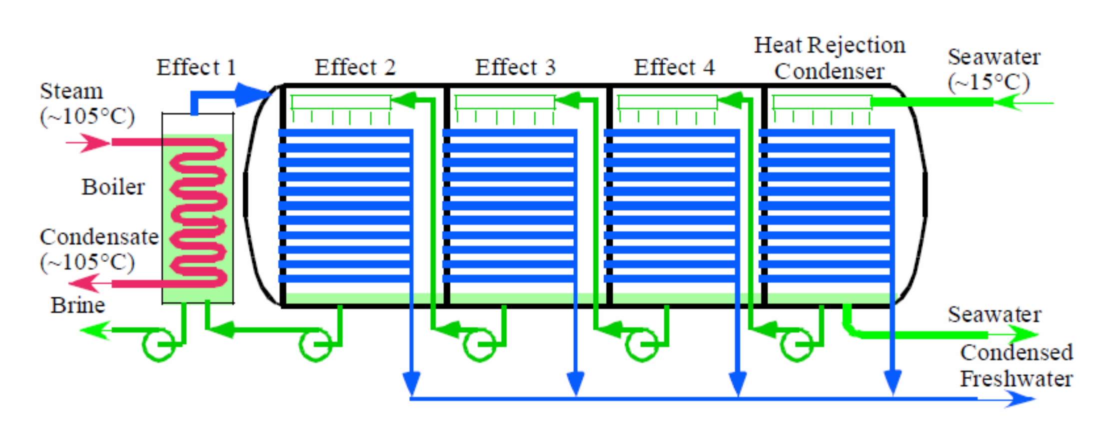

Figure 19. Schematic of a conventional MED system using steam as a heat source (Source: [101]).

Energy efficiencies may be gained through combination of the evaporator systems with available low-pressure or waste steam/heat sources and by the addition of efficiency enhancement devices to a conventional MED system.

Although the MED is an older technology than the MSF, it has not been extensively utilized for water production as MSF because of scaling problems associated with old designs. Recently, considerable improvements in MED systems have been introduced to reduce the undesirable characteristics (e.g., low heat transfer rate and high rates of scale formation) of the old MED submerged tube evaporators. Falling film evaporators such as vertical tube evaporator (VTE) and the horizontal tube evaporator (HTE) of new MED plants have a number of distinct advantages [96]. They provide higher overall heat transfer coefficients and low specific heat transfer surface area compared to MSF desalination systems. They do not employ recycling; thus they are based on the once through principle and have low requirements for pumping energy.

MED process has recently made substantial progress for small thermal desalination plants. According to the GWI report, MED had a market share of 6.9% of the worldwide desalination capacity by 2005 [38]. The largest MED unit was commissioned in Layyah desalination plant in Sharjah (UAE) in 2001. It consists of two MED units each with a capacity of 6 MGD (143,000 bbl per day) [96].

Like MSF, MED can be applied to a wide range of feedwater quality, including produced water. MED also offers the possibility of reducing plant size and footprint. The range of recoveries for conventional MED desalting process is limited to 20-35% for seawater, and 67% for stacked vertical tube design [94]. A summary of the technical assessment of MSF is listed in Table 23.

Table 23. Summary of technical assessment of MED.

Criteria	**Description/Rationale**
Industrial status	Mature and robust technology for seawater and brackish water desalination. Can be employed for produced water treatment.
Feed water quality bins	Applicable to a wide TDS range, and all types of water chemistry makeup.
Product water quality	Product water quality for MED plants is typically very high, with little variation due to feed or concentrate salt content.
Production efficiency (recovery)	Product water recovery is between 20% and 35% for horizontal and vertical tube design, and 67% for stacked vertical tube design [94].
Infrastructure considerations	Infrastructure considerations are similar to MSF, and MED units are of smaller capacity.
Energy consumption	The power consumption of an MED plant is significantly lower than that of an MSF plant, and the performance ratio of the MED plant is higher than MSF plant. The electrical consumption is 11 kWh/kgal (0.48 kWh/bbl) [98]. The power energy consumption of MED is in the range of 31-45 kWh/kgal (1.3-1.9 kWh/bbl) [100].
Chemicals	Scale inhibitor and acid may be required for process control to prevent scaling. Corrosion control is achieved via pH control. Annual cleaning is typically conducted using acid, EDTA, or other antiscaling chemicals.
Life cycle	Typically 20 years. Operational experience of the MED plants operating since 1970’s and 1980’s in Middle East revealed that the specified performance has been consistently satisfied and no major problems have been experienced [96].

Table 23. Summary of technical assessment of MED.

Criteria	Description/Rationale
O&M considerations	Levels of monitoring and control required for feed pH, flow rates as well as steam and vessel pressures. High level of skilled labor required, however lower than equivalent membrane plants. Level of flexibility: easy to adapt to highly varying water quality; not flexible for varying water flow. Level of robustness: high ability of the equipment to withstand harsh conditions. Level of reliable: typical plants operate continuously, with shutdown only for planned maintenance once per year. Types of energy required: thermal and electricity.
Overall costs	Because energy consumption of MED is lower than MSF, the overall cost is less than MSF. Capital costs vary from $6–8/gpd (or $250-330 per bpd), depending on various factors including size, materials of construction and site location [98]. As a non-modular form of construction, the economy of scale can reduce the cost for larger plants, assuming ready site access for marine transportation. Operating costs are approximately $2.6/kgal (or $0.11/bbl), and total unit costs are $3.8/kgal (or $0.16/bbl) [98].
Pre-and post treatment	Similar to MSF, MED requires less rigorous pretreatment and feed conditioning as compared to membrane treatment. Product water needs stabilization because of the low TDS level. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with the distillate.
Concentrate management or waste disposal	No special concentrate treatment is required. Due to the typically low recovery rates of 20-35%, large amounts of concentrate (65-80%) are generated.
Applicability in produced water treatment	Good for high TDS produced water treatment. MED often requires centralized design and construction of larger plants.
Note: 1 barrel = 42 US gallons	

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Vapor Compression Distillation

In vapor compression distillation (VCD) systems, mechanical (mechanical vapor compression or MVC) or thermal (thermo vapor compression or TVC) compression of the vapor provides the heat for evaporation. The process compresses the vapor generated within the unit itself. The mechanical compressor is usually electrically or diesel driven. Thermal compression uses high-pressure steam. Compression raises the pressure and temperature of the vapor so that it can be returned to the evaporator and used as a heat source.

A schematic of a VC system using steam as a heat source, with four effects stages is illustrated in Figure 20. Water vapor is drawn from the evaporation chamber by a compressor and except for the first stage the vapor is condensed on the outsides of tubes in the same chambers. The heat of condensation is used to evaporate a film of saline water applied to the insides of the tubes within the evaporation chambers. The low temperature VCD is a simple, reliable, and efficient process. Having a high capacity compressor allows operation at temperatures below 70°C, which reduces the potential for scale formation and corrosion [99].

The VCD process is generally used for small-scale desalination units; ranging from 0.026 to 0.79 MGD (1,100 - 18,000 bbl per day). The power consumption of larger units is approximately 30 kWh/kgal of product water (1.3 kWh/bbl) [99]. The VCD process is well established and is used for seawater desalination as well as treating produced water and RO concentrate (i.e., brine concentrator application) in a near-zero liquid discharge (ZLD) application. VCD units are often used for resorts, industries, and drilling sites where fresh water is not readily available.

Vapor compression allows higher water recovery compared to conventional MSF and MED; the range of recoveries for conventional VCD is 40% for seawater [94]. To achieve ZLD, VCD can work as a crystallizer and the energy demand for concentrate evaporation and crystallization is 100-250 kWh/kgal (4.2 to 10.5 kWh/bbl) [102]. A summary of the technical assessment of VC is listed in Table 24.

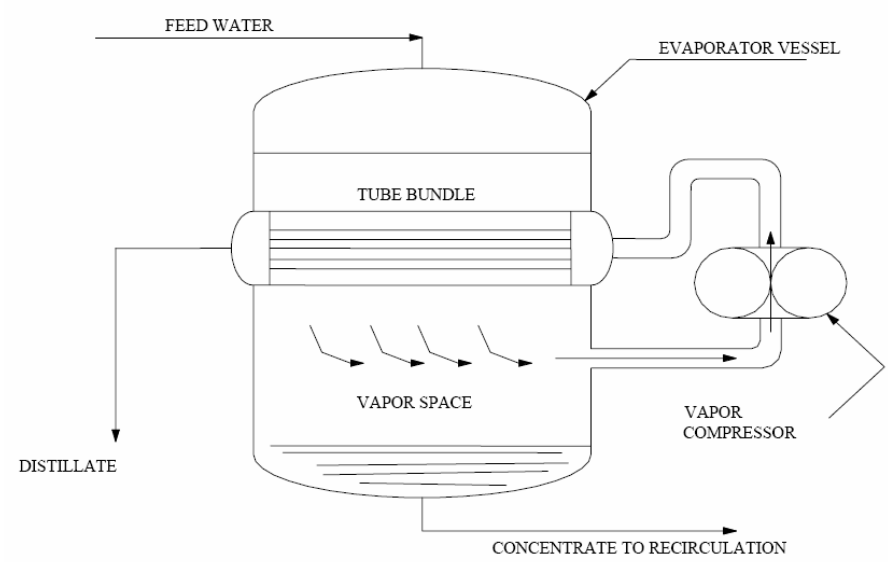

Figure 20. Simplified schematic of a VCD unit (Source: [94]).

Table 24. Summary of technical assessment of VCD.

Criteria	Description/Rationale
Industrial status	Mature and robust technology for seawater and brackish water desalination. Various enhanced VC technologies have been employed for produced water treatment.
Feed water quality bins	Applicable to high TDS water > 40,000 mg/L, and all types of water chemistry makeup.
Product water quality	Product water quality for VC plants is typically very high, with little variation due to feed or concentrate salt content.
Production efficiency (recovery)	Product water recovery is approximately 40% for desalination; for ZLD, VC works as a crystallizer and achieve high recovery.
Infrastructure considerations	Infrastructure considerations are similar to MSF and MED units, but VCD units are of small scale.
Energy consumption	The power consumption of a VCD plant is significantly lower than that of MSF and MED plants. For desalination, the power energy consumption of large VC plant is approximately 30 kWh/kgal (1.3 kWh/bbl) of product water [99]. The electricity consumption is 26.5 kWh/kgal (1.1 kWh/bbl) for MVC [98]. To achieve zero-liquid discharge, the energy demand for concentrate evaporation and crystallization is about 100 to 250 kWh/kgal (4.2 to 10.5 kWh/bbl) [102].
Chemicals	Scale inhibitor and acid may be required for process control to prevent scaling. Corrosion control is achieved via pH control. Annual cleaning is typically conducted using acid, EDTA, or other antiscaling chemicals.
Life cycle	Typically 20 years, although longer life may be expected with the selection of better materials of construction, that is, alloys with high corrosion resistance.
O&M considerations	Levels of monitoring and control required for feed pH, flow rates as well as steam and vessel pressures. High level of skilled labor required. VCD, especially MVC is a more complex system and adds to the O&M skill level required. Level of flexibility: easy to adapt to highly varying water quality; not flexible for varying water flow. Level of robustness: high ability of the equipment to withstand harsh conditions. Level of reliable: typical plants operate continuously, with shutdown only for planned maintenance once per year. Types of energy required: thermal and electricity.
Overall costs	The capital costs depend on various factors including size, materials of construction and site location. The operating costs depend on the purpose of plant; the costs to achieve ZLD are significantly higher than desalination because of energy costs. Significant reductions in energy costs can be realized from cogeneration arrangements where low pressure steam is available. Capital costs of MVC for seawater desalination vary from $3.3–6/gpd (or $140-250 per bpd), depending on various factors including size, materials of construction and site location [98]. Operating costs are approximately $1.8/kgal (or $0.075/bbl), and total unit costs are $1.9/kgal (or $0.08/bbl) for seawater desalination [98].

Table 24. Summary of technical assessment of VCD.

Criteria	Description/Rationale
Pre-and post treatment	VC requires less rigorous pretreatment and feed conditioning as compared to membrane treatment. Product water needs stabilization because of the low TDS level. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with the distillate.
Concentrate management or waste disposal	No special concentrate treatment is required. For ZLD, generated mixed solids need waste disposal.
Applicability in produced water treatment	Excellent for high TDS produced water treatment and ZLD.
Note: 1 barrel = 42 US gallons	

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Multi Effect Distillation – Vapor Compression Hybrid

Both multiple-effect distillation (MED) and vapor compression evaporation (VCD) are state of the art technologies that have been employed for many years in desalination of seawater and brackish waters. More recently, hybrid MED-VCD has been employed to treat produced water (see more detailed discussion in commercial thermal technology processes). The combination of the two techniques to enhance the desalination process is frequently mentioned as a means of enhancing thermal desalination by reducing both capital and operating costs. This technology is favorable for replacing some of the older MSF plants. There is not much innovation in the design of such hybrids, but there are some complexities associated with the integration of the two processes. The advantages gained from combining the processes include:

- Increased production
- Expansion of capacity of existing MED units
- Enhanced energy efficiency

For desalination, power consumption of MED-TVC plants is approximately 7.57 kWh/kgal (0.32 kWh/bbl) and there are no requirements to recirculate large quantities of brine [96]. The combination of high performance ratio and low power consumption results in lower overall energy costs.

In the 1982, six MED-TVC distillers were operated in different remote sites of Abu Dhabi (UAE); each had a rated production capacity of 1.2 MGD [96]. Veolia Water Systems (France) installed an 11.1 MGD MED-VC system in Layyah (Sharjah, U.A.E.), which is claimed to have an energy efficiency of 50% over conventional systems. A barge mounted MED-MVC hybrid was built in Germany and shipped to Saudi Arabia. The advantage of such a system design and delivery method is that it minimizes local construction costs and shortens the interval between purchase and startup. A summary of the technical assessment of MED-VCD is listed in Table 25.

Table 25. Summary of technical assessment of MED-VCD.

Criteria	**Description/Rationale**
Industrial status	Mature and robust technology for seawater and brackish water desalination. Has been employed for produced water treatment.
Feed water quality bins	Applicable to high TDS range, and all types of water chemistry makeup.
Product water quality	Product water quality for MED-VCD plants is typically very high.
Production efficiency (recovery)	Product water recovery is between 30% and 45% for seawater desalination. GE brine concentrator and crystallizer can increase water recovery to 75-85% [103].
Infrastructure considerations	The infrastructure considerations or constraints are similar to that of MSF. Sufficient land must be available to accommodate the large plant footprint. The availability of low-pressure steam, either by dedicated generation or by cogeneration arrangements with adjacent power plants is essential. If using MVC, the system's high the electrical demand must be considered.
Energy consumption	For desalination, power consumption of MED-TVC plants is only around 7.57 kWh/kgal (0.32 kWh/bbl) [96]. To achieve zero-liquid discharge, the energy demand for concentrate evaporation and crystallization is about 100 to 250 kWh/kgal (4.2 to 10.5 kWh/bbl) [102].

Table 25. Summary of technical assessment of MED-VCD.

Criteria	Description/Rationale
Chemicals	Scale inhibitor and acid may be required for process control to prevent scaling. Corrosion control is achieved via pH control. Annual cleaning is typically conducted using acid, EDTA, or other antiscaling chemicals.
Life cycle	Typically 20 years, although longer life may be expected with the selection of better materials of construction, that is, alloys with high corrosion resistance.
O&M considerations	Levels of monitoring and control required for feed pH, flow rates as well as steam and vessel pressures. High level of skilled labor required. VCD, especially MVC is a more complex system and adds to the O&M skill level required. Hybrid designs of the two different technologies further add to the O&M complexity compared to the individual processes. Level of flexibility: easy to adapt to highly varying water quality; not flexible for varying water flow. Level of robustness: high ability of the equipment to withstand harsh conditions. Level of reliable: typical plants operate continuously, with shutdown only for planned maintenance once per year. Types of energy required – thermal and electricity.
Overall costs	Capital cost of MED-TVC is approximately \$6/gpd (\$250 per bbl per day) [98]. The costs may vary depending on various factors including size, materials of construction and site location. Operating costs are dependent upon energy consumption. Significant reductions in energy costs can be realized from cogeneration arrangements where low pressure steam is available.
Pre-and post treatment	MED-VC requires less rigorous pretreatment and feed conditioning as compared to membrane treatment. Product water needs stabilization because of the low TDS level. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with the distillate.
Concentrate management or waste disposal	No special concentrate treatment is required. For ZLD, generated mixed solids need waste disposal.
Applicability in produced water treatment	Excellent for high TDS produced water treatment and ZLD. Maybe economical to large flow rate and not applicable to point source of produced water wells.
Note: 1 barrel = 42 US gallons	

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Freeze/Thaw Evaporation (FTE®)

The freeze/thaw evaporation is a water treatment process that combines freezing and thawing cycle with conventional evaporation technology [104]. A schematic diagram of FTE® is shown in Figure 21. When the ambient air temperature is below 32 °F (0 °C), the saline water (feed water) is sprayed or dripped onto a freezing pad to create an ice pile. Relatively pure ice crystals form and an unfrozen solution (brine) containing elevated concentrations of the dissolved constituents drains from the ice. The runoff can be diverted to a brine storage facility or back to the feed water storage facility for recycling. When the temperatures rise, the ice melts and the runoff from the freezing pad is highly purified water that can be diverted to a treated water storage facility for beneficial uses or surface discharge.

During warm months, the FTE system is operated as a conventional evaporation facility. During months with subfreezing (<32 °F) temperatures, a large ice pile is created by spraying the water to be treated in a shallow pit, and the natural freeze–thaw process takes over. FTE® allows water treatment and disposal on a continuous basis.

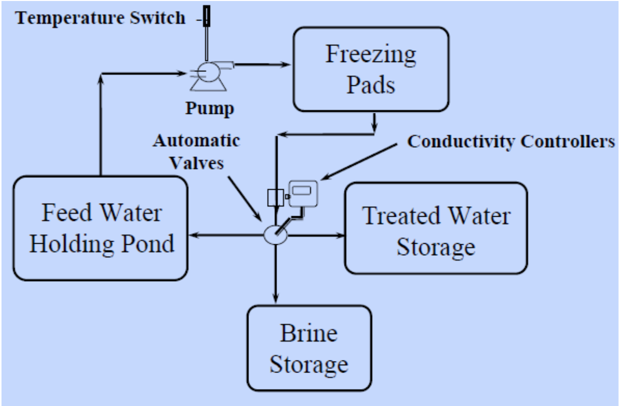

Figure 21. Schematic of Freeze/Thaw Evaporation (FTE®) (Source: [104]).

FTE® processes were developed by the Energy & Environment Research Center (EERC) and B.C. Technologies, Ltd. (BCT), in 1992 [105]. Field-scale FTE testing of CBM produced water treatment started in 1995. Between 1995 and 2001, three commercial-scale FTE® plants were deployed to simultaneously remove salts, organics, and heavy metals from wastewaters generated in natural gas production fields in New Mexico and Wyoming [105]. Industrial partners in these operations included Amoco Production Company, McMurry Oil Company, Crystal Solutions, and Gas Research Institute. Results from these field tests confirm both the process economic viability and its potential to produce usable, quality treated water from oil and natural gas produced water. As of 2003, two FTE plants continued to operate commercially in Wyoming: one in the Jonah gas field south of Pinedale and the other in the Red Desert near Wamsutter (Figure 22). The treatment capacity of those plants is more than 40,000 gallons a day (950 bbl/day) [105].

Figure 22. Photo of FTE® Field Performance in Wamsutter, Wyoming (Source: [104]).

The FTE® facility in the Great Divide Basin of WY was originally constructed and operated by Crystal Solutions (CS) (1999-2003) and is now owned by Samson Resources Company and operated by CS. The initial nominal plant capacity (1999-2002) was 500 bbl/day, and current plant capacity (2003 to present) is 1,000 bbl/day. Approximately 1.8 million bbl of produced water have been treated at the facility to date [104].

The FTE® process has been proven in commercial operations to be capable of treating a broad variety of wastewater, and of removing over 90% of produced water constituents [104], including total suspended solids (TSS), total dissolve solids (TDS), total recoverable petroleum hydrocarbons (TRPH), volatile organic compounds (VOC), semi-volatile organic compounds, and heavy metals. However, the FTE® process is not capable of treating wastewater having more than 5% methanol. The FTE® operation performance during wintertime is shown in Table 26. A technical assessment of FTE® process is summarized in Table 27.

Table 26. FTE® operation in the Great Divide Basin of Wyoming in winter 2001-2002. (Source: [104])

	Volume (bbl)	TDS (mg/L)	TPH (mg/L)
Feed	102,440	9,790	39.1
Brine	38,119	44,900	63.2
Treated Water	52,356	1,000	3.1
Sub. + Evap.	11,965		

Table 27. Summary of technical assessment of FTE®.

Criteria	**Description/Rationale**
Industrial status	Mature and robust technology for produced water treatment and disposal.
Feed water quality bins	As an evaporation process, the applicable feedwater TDS could be >40,000 mg/L. Produced water with high methanol concentration cannot be treated.
Product water quality	Product water quality is moderate with TDS in the range of 1000 mg/L [104]. The FTE® process can remove over 90% of the following types of produced water constituents: TSS, TDS, TRPH, volatile and semi-volatile organic compounds, heavy metals.
Production efficiency (recovery)	Product water recovery is approximately 50% during wintertime. No water can be recovered during other seasons as the process works as a conventional evaporation pond.

Table 27. Summary of technical assessment of FTE®.

Criteria	Description/Rationale
Infrastructure considerations	The FTE® process does not require infrastructure or supplies that limit its use. However, the FTE® process has several inherent features that severely limit it application ([104]): • The FTE® process requires a climate with a substantial number of days with temperatures below freezing. • The FTE® process requires a significant amount of land – 35 acres for a 1,000 bbl facility. • The FTE® process requires proper hydro-geologic setting including favorable soil conditions, locations of legal waters and characteristics of near surface aquifers.
Energy consumption	Not available.
Chemicals	No chemicals
Life cycle	Expected 20 years.
O&M considerations	Low level of monitoring and control. Low level of skilled labor required. High level of flexibility: easy to adapt to highly varying water quality and quantity. High level of robustness. High level of reliability. Types of energy required – electricity.
Overall costs	The FTE® process economics are strongly application and location specific. In most of Wyoming, a 42,000 gal/day (1,000 bbl/day) facility will require total installed capital costs of $1.75 to 2.0 million for a turnkey operation and annual operating expenses range from $0.031 to 0.042/kgal ($0.75 to $1.00/bbl). Thus, using the FTE® process in most of Wyoming, produced water total amortized produced water treatment costs range from $0.062 to 0.079/kgal ($1.50/bbl to $1.87/bbl): with amortized capital costs range from $0.75/bbl to $0.87/bbl assuming 15% rate of return on capital and 20 year plant life [104].
Pre-and post treatment	The FTE process requires minimal pre-treatment of produced water. For example the pretreatment at the Samson Resources facility in the Great Divide Basin of WY is limited to removal of product oil and tank bottoms using two 400 bbl gun-barrel oil-water separators. In CBM applications, pretreatment would not be necessary if product oil is not present in the water. Post-treatment will depend on the product water quality and beneficial use applications or discharge standards.
Concentrate management or waste disposal	The FTE® process generates waste streams: oil from the oil water separators (if present), and concentrated brine. Currently, the brine is allowed to passively evaporate in evaporation ponds. Long-term plans are to allow the concentrate to evaporate to a solid at the end of the facility operation and dispose of the material in a permitted landfill.
Applicability in produced water treatment	Excellent for ZLD of produced water, may be limited by land availability and climate conditions.
Note: 1 barrel = 42 US gallons	

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Dewvaporation – AltelaRain^SM Process

Dewvaporation is a process that involves humidification-dehumidification desalination. It reduces the energy costs by using counter-current heat exchange technology. Feedwater is evaporated by heated air, which condenses as fresh water on the opposite side of a heat transfer wall. The energy needed for evaporation is partially supplied by the energy released during condensation. Heat sources can be combustible fuel, solar, or low-grade heat from various resources. The tower unit is built of thin plastic films to avoid corrosion and to minimize equipment costs. Towers are relatively inexpensive because they operate at atmospheric pressure.

Altela, Inc. has designed, manufactured, and tested several AltelaRain^SM prototype systems based on the dewvaporation process. A schematic of the AltelaRain^SM process is shown in Figure 23. Three full-scale AltelaRain^SM ARS-4000 systems have been deployed at natural gas wells in the San Juan Basin near Farmington, NM [106]. The ARS-4000 system can process approximately 4,000 gallons per day (100 bbl/day) of produced water with salt concentrations in excess of 60,000 mg/LTDS.

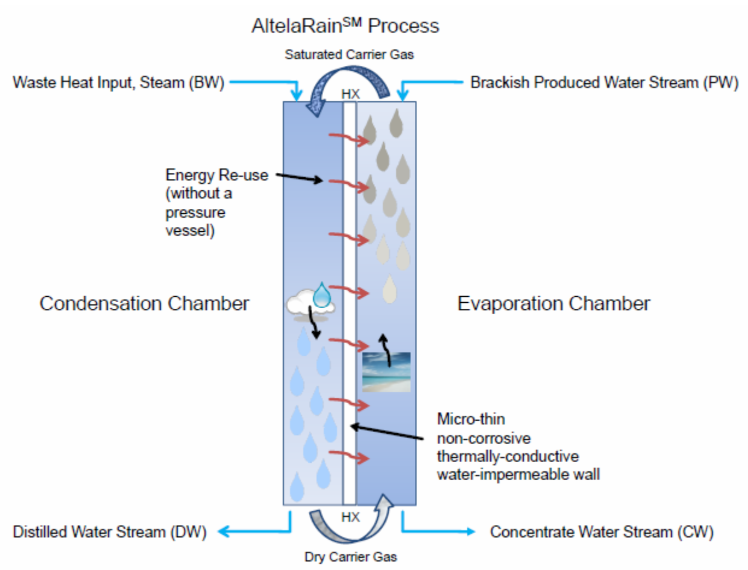

Figure 23. Schematic of AltelaRain^TM process (Source: [107]).

AltelaRain^SM System can reduce effluent disposal volumes by as much as 90%. Because the treated water stream is distilled water, the AltelaRain^SM produces very high quality water. In one test the TDS concentration of produced water was reduced from 41,700 mg/L to 106 mg/L and chloride concentration was reduced from 25,300 mg/L to 59 mg/L [108]. Similarly, benzene concentration was reduced from 450 µg/L to non-detectable following AltelaRain^SM treatment [108].

The AltelaRain^SM technology requires no special infrastructure, supplies, or consumables for its unattended operation. It requires only regular 110V electricity (from either a generator or solar panels), making it a water treatment alternative at remote wells where no high power grid is available. Dewvaporation operates primarily from low-grade heat source that generates steam at atmospheric pressure. It can come from a variety of sources, such as industrial waste heat, or well-site gas. At locations where either waste heat or waste gas is not readily available, steam can be generated using a small natural gas-fired boiler. Altela currently operates three systems in such remote locations that both the electricity and heating needs are satisfied by using natural gas from the well that produces the water [106].

Like other evaporative processes, the energy consumption of the dewvaporation system is high. In a report published by the U.S. Bureau of Reclamation [109], the authors provided the following estimate of energy consumption and cost for a dewvaporation system:

- Electrical cost for pumps and fans: $0.05 per 1,000 gallons (0.5 kWh per 1,000 gallons at ¢10 cents per kWh) [109].
- Other energy cost: using the average multiple effect value of 3.2, the heat needed for 1,000 gallons of distillate production would be 2.6 million BTUs (764 kWh heat). At a natural gas cost of ¢80 per therm, the operating cost would be $20.85 per 1,000 gallons. If waste heat or solar heat were available, the operating cost would reduce to the electrical cost of pumps and fans [109].

A technical assessment of the AltelaRain^SM process is summarized in Table 28.

Table 28. Summary of technical assessment of AltelaRain^SM process.

Criteria	Description/Rationale
Industrial status	Full-scale application for produced water treatment.
Feed water quality bins	Applicable to TDS up to 40,000 - 60,000 mg/L, and a broad variety of water chemistry makeup.
Product water quality	Product water quality is very high with TDS in the range of 20-100 mg/L [106, 108]. The process also has high removal rate of heavy metals, organics, and radionuclides.
Production efficiency (recovery)	Product water recovery is approximately 90%.
Infrastructure considerations	No special infrastructure, supplies, or consumables for its unattended operation. Energy requirements include 110V electricity (from either a small generator or solar panels), and thermal (either from industrial waste heat, well-site flash gas, or using a small natural gas-fired boiler).
Energy consumption	Altela, Inc. claims that electricity requirement is low because the system operates at ambient pressures and low temperature [106, 108]. The AltelaRain system yields energy costs that are approximately only 30% of comparable ambient pressure distillation/evaporation processes. The 'Multiple-effect' energy savings are comparable to that achieved by pressure distillation methods such as MVC.
Chemicals	No chemicals.
Life cycle	No data available.
O&M considerations	Low level of monitoring and control. Low level of skilled labor required. High level of flexibility: easy to adapt to highly varying water quality and quantity. High level of robustness. High level of reliability. Types of energy required –electricity and thermal.
Overall costs	Not available. The Altela reported the cost structure associated with building, installing, maintaining, and servicing the system is lower than the escalating costs associated with traditional produced water hauling and reinjection.

Table 28. Summary of technical assessment of AltelaRain[SM] process.

Criteria	Description/Rationale
Pre-and post treatment	Require no pre-treatment. Screens (>300 micron) are required if debris present in produced water to protect the pumps and valves in the incoming lines. Product water needs remineralization because of the low TDS level. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with the distillate.
Concentrate management or waste disposal	The current 10% brine stream is transported off the well site and then either injected into a disposal well or evaporated/stored in large ponds.
Applicability in produced water treatment	Excellent for produced water application. Like other evaporative processes, high energy-consumption might be a limiting factor for its applicability if no waste heat or cheap energy sources are available.
Note: 1 barrel = 42 US gallons	

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Alternative Technologies

Ion exchange process

In ion exchange (IX), removal of specific ions or compounds from a stream is facilitated by the exchange of a pre-saturated ion with the target ions on an IX resin. Contaminant cationic solutes such as calcium, magnesium, barium, strontium, and radium are removed by cation exchange resins, and anionic solutes such as fluoride, nitrate, fulvates, humates, arsenate, selenate, chromate, and anionic complexes of uranium may be removed by anion exchange resins [110]. Recent research also suggests that IX may be employed to remove boron from RO permeate [111]. IX is a well-developed process and is commonly applied to drinking water treatment for hardness removal, but is increasingly being studied for the removal of radionuclides and nitrates [110, 112].

IX resins are typically composed of synthetic resins or activated alumina. These resins are characterized as either strong or weak and may be acidic or basic in nature. Acidic ion exchange resins are utilized to remove unwanted cations from solution. Examples of frequent chemical reactions for IX in strong and weak acid resins and in basic IX resin are shown below:

$$2(R-SO_3H)+Ca^{2+}\rightarrow(R-SO_3)_2Ca+2H^+ \text{ (strong acid resin)}$$

$$2(R-COOH)+Ca^{2+}+2HCO_3^-\rightarrow(R-COO)_2Ca+H_2O+CO_2 \text{ (weak acid resin)}$$

$$(R-NH_3OH)+HCl\rightarrow(R-NH_3Cl)+H_2O \text{ (basic resin)}$$

IX resins are typically manufactured to have readily reversible reactions, which allows for the IX resin to be regenerated once its adsorptive capacity is exhausted. The IX resin's adsorptive capacity is exhausted when the target ion reaches a prescribed breakthrough concentration in the IX product water. To achieve high purity water quality, many conventional IX processes are operated with mixed beds to achieve removal of both cations and anions. Regeneration occurs by flooding the IX resin with a solution that is highly concentrated with the pre-saturated ion. During standard operation an IX bed may treat between 300 to 300,000 bed volumes (BV) before requiring regeneration, depending on the adsorptive capacity of the resin and the feed water quality [110]. Regeneration typically requires 2 to 20 BV of rinse water (generally less than 2% of the product water) to restore the adsorptive capacity of the IX resin [110].

IX systems are typically installed in fluidized, packed bed configurations. IX is an established water treatment technology that is utilized for municipal drinking water treatment, wastewater treatment, and CBM produced water treatment (especially in the Powder River Basin) [110, 113]. The operational footprint for most IX processes includes packed resin beds (sometimes referred to as columns) and onsite regenerant and cleaning chemical storage. The type of regenerant chemicals depends on the characteristics of the IX resin employed and may be include solution of H_2SO_4, HCl, NaOH, Na_2CO_3, or NaCl.

Typically, IX processes operate with minimal energy demand and may require only electricity for pumping fluids under low hydraulic pressure. Operation and management considerations for IX include occasional disinfection of IX resin with NaOCl or H_2O_2. Careful management of the feed stream is also necessary to ensure that fouling agents such as suspended solids, scale forming materials (e.g., $CaSO_4$), and oxidized metal are not present in the feed water. Additionally, many IX resins are sensitive to free chlorine oxidation. IX processes must also be carefully managed to reduce osmotic shock and mechanical abrasion of IX resin, which will lead to physical loss of the resin [114].

Operating costs for standard IX processes vary greatly with feed water quality and loading rate. An economic feasibility analysis conducted by DowEX (Dow Chemical Company, Midland, MI) estimated that IX, after a conventional pretreatment (e.g., coagulation, flocculation, and sedimentation), could be used to treat surface water to a quality of less than 1 µS/cm in conductivity. The costs for IX vary between $1.9-2.6/kgal ($0.08-0.11/bbl) at 220 gpm (5 bbl per minute) and $1.0-1.7/kgals ($0.04-0.07/bbl) at 880 gpm (21 bbl per minute). At the lower flow rate, operating costs account for ~70% of the total cost with regenerants, raw water, labor and maintenance making the most significant contributions. At 880 gpm, operating costs increase to ~80% [115].

Waste disposal needs of IX processes include the need to neutralize and dispose of spent IX regenerant solution. These solutions typically represent a very low volume of wastewater, but may be highly saline and require additional treatment to limit disposal costs. Product water from IX processes may require SAR adjustment [19]. A summary of the technical assessment for general IX processes is shown in Table 29.

Table 29. Summary of technical assessment of IX processes.

Criteria	Description/Rationale
Industrial status	Large industrial operations including utilization for CBM produced water treatment in the Powder River Basin.
Feed water quality bins	The average TDS application range is between 500 mg/L and 7,000 mg/L. Depending on selection of IX resin, high removals of monovalent and/or divalent ions and possibly metals is expected.
Product water quality	Treatment process permeate quality is dependent on feed water salinity and operating conditions. >93% rejection of target ions is achievable.
Production efficiency (recovery)	Product water recovery is dependent on IX resin regeneration needs, but recovery typically exceeds 98%.
Infrastructure considerations	This treatment process has a highly variable operational footprint, and may be sized for single-family point-of-use systems up to large municipal drinking and wastewater treatment plants. Regenerant storage will be required, in addition to other cleaning chemicals. Systems may be highly mobile, however certain systems may require the use of heavy machinery to relocate.
Energy consumption	Energy requirements are minimal and may only include pumping costs. This makes IX one of the least energy intensive processes with an energy demand that may be as low as 1.5 kWh/kgal (0.07 kWh/bbl) assuming a 200 gpm flow rate, 5 m pumping head, an 80% efficient pump.

Table 29. Summary of technical assessment of IX processes.

Criteria	Description/Rationale
Chemicals	Chemical cleaning rates depend on feed water quality and IX resin adsorptive capacity. Resin regeneration will typically occur after certain product water quality specifications are exceeded. Regenerant solutions may require the use of HCl, H_2SO_4, NaOH, Na_2CO_3, or NaCl. Additional chemical disinfection may be required to mitigate biofouling and will typically consist of H_2O_2 or NaOCl cleaning solutions.
Life cycle	The average lifespan for anion exchange resins is about 4 to 8 years, while cation exchange resins may perform for 10 to 15 years [114].
O&M considerations	Monitoring and control required for flow rates, product water quality and resin regeneration. System will likely require minimal supervisory oversight. Level of flexibility: Low to moderate flexibility depending on resin type. Level of robustness: IX processes are highly sensitive to fouling from organic materials and suspended solids. Care should be exercised to limit exposure of IX resin to oxidized metals and sparingly soluble mineral salts. Acid cation resins should not be exposed to feed temperatures in excess of 120 °C, while base anion resins are limited to 100 °C or lower. Level of reliability: IX systems may operate semi-continuously with automated, short duration resin regeneration cycles. Other IX systems may operate continuously for 10-20 hours and require several hours of downtime during regeneration. Types of energy required: electrical.
Overall costs	The costs for IX vary between $1.9-2.6/kgal ($0.08-0.11/bbl) at 220 gpm (5 bbl per minute) and $1.0-1.7/kgals ($0.04-0.07/bbl) at 880 gpm (21 bbl per minute). At the lower flow rate, operating costs account for ~70% of the total cost with regenerants, raw water, labor and maintenance making the most significant contributions. At 880 gpm, operating costs increase to ~80% [115].
Pre-and post treatment	Process will require pretreatment options including suspended solids, oxidized metals, and scaling mineral removal. Product water may require pH stabilization or remineralization. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feed water with product water.
Concentrate management or waste disposal	The spent resin regeneration solution will require neutralization. Relatively high recovery rates exceeding 98% generate very minor amounts of concentrated brine.
Applicability for produced water treatment	Excellent – Treatment well suited for specific applications.
Note: 1 barrel = 42 US gallons	

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Capacitive deionization (CDI) & Electronic Water Purifier (EWP)

Capacitive deionization (CDI) is an emerging desalination technology. The Lawrence Livermore National Laboratory (LLNL) started studying CDI in the late 1980s. In CDI, ions are adsorbed onto the surface of porous electrodes by applying a low voltage electric field, producing deionized water (Figure 24). Liquid is flowing between the high surface electrode pairs having a potential difference of 1.0-1.6 Volt DC. The negative electrodes attract positively charged ions such as calcium, magnesium, and sodium, and the positive electrodes attract negatively charged ions such as chloride, nitrate, and silica. The major mechanisms related to the removal of charged constituents during water treatment are physisorption, chemisorption, electrodeposition, and/or electrophoresis. Unlike ion exchange, no additional chemicals are required for regeneration of the electrosorbent in this process. Adsorbed ions are desorbed from the surface of the electrodes by eliminating the electric field, resulting in the regeneration of the electrodes. The efficiency of CDI strongly depends on the surface property of electrodes such as their surface area and adsorption properties [116].

There are a variety of electrode materials and configurations to enhance the CDI performance. The LLNL developed and optimized carbon aerogel materials, which are ideal electrode materials because of their high electrical conductivity, high specific surface area, and controllable pore size distribution [117]. Shiue et al. improved the CDI efficiency by using spiral wound electrodes (activated carbon coated on titanium foil) cartridge [118]. Atlas developed the Electronic Water Purifier (EWP), which is a hybrid CDI and electrodeionization (CDI-EDI) technology using activated carbon electrodes that has a coating and a conductive material [119].

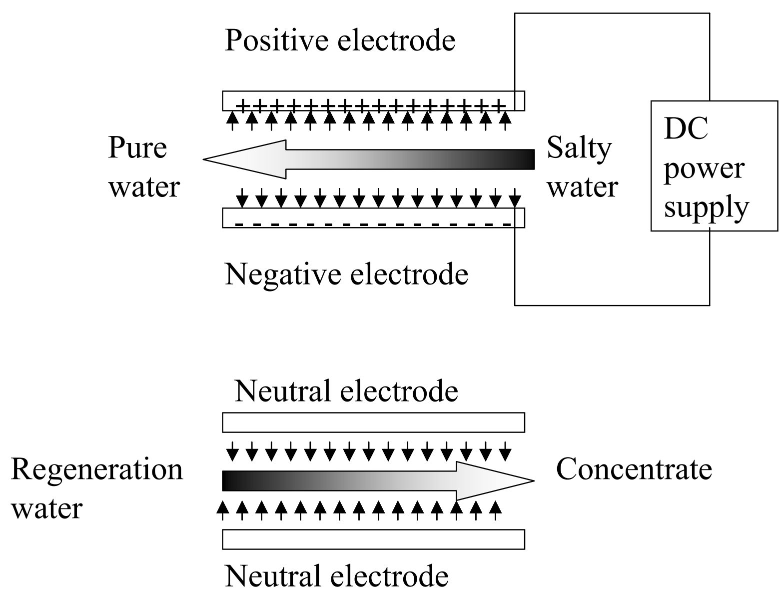

Figure 24. Schematic of Capacitive Deionization (CDI).

Previous studies have shown that CDI technology is cost competitive to RO at low TDS range (<3,000 mg/L) due to the high cost of CDI modules with increased feed water TDS level [116, 119, 120]. Xu et al. (2008) conducted a pilot-scale testing of produced water treatment at a sandstone gas production field in Montana using two industrial capacitive deionization technology (CDT^{TM}) aquacells developed by CDT, Inc., Dallas, TX. For the development of cost-effective CDI system, the capacitance of carbon aerogel have to be improved while production cost should be reduced. Long regeneration time and carry-over of ions following regeneration limit the efficiency of treatment of highly saline water and decrease the production recovery [116]. The laboratory and field-testing during treatment of sandstone produced water indicated that CDI exhibited much less fouling/scaling propensity compared to RO/NF [116]. CDI required a simple cartridge filtration as pretreatment, and no electrode deterioration was observed during both laboratory and field-testing of produced water.

Atlas tested the Electronic Water Purifier (CDI-EDI) for CBM produced water treatment in the Atlantic Rim (Washakie Basin), Carbon County, Wyoming [119]. A picture of the EWP unit is shown in Figure 25. The system is mounted in a 6’x8’x8’ (WxLxH) container, and can be transported easily to different sites. The test was conducted with feed flows of 5 gpm (1000 bbl/day) and with two 5-gpm systems in series. Solids were filtered using a 30-micron filter. The field testing results are summarized in Table 30. The technical assessment of the EWP produced water treatment technology is summarized in Table 31.

Table 30. Field testing results of treating CBM produced water (Source: [119])

Feed Conductivity	2,500 mg/L
Purified Effluent	270 mg/L
Estimated Feed SAR	24
Estimated Product SAR	3
Purification average	90%
Recovery	85%
Power Consumption	4.0 kWh/kgal (0.17 kWh/bbl)

Figure 25. Electronic Water Purifier Pilot Test--250 BPD (Source: [119]).

Table 31. Summary of technical assessment of EWP process.

Criteria	**Description/Rationale**
Industrial status	Emerging technology. Have been pilot tested in Atlantic Rim for CBM produced water treatment 10, 000 gal/day (250 bbl/day).
Feed water quality bins	Cost competitive for water with TDS <3,000 mg/L. Has been applied to medium TDS range (<6,000 mg/L). CDI is applicable to all types of water chemistry makeup.
Product water quality	Product water quality depends on treatment time. EWP can achieve 90% TDS removal. CDI has poor removal of uncharged substances such as boron and organics.
Production efficiency (recovery)	Product water recovery is approximately 80%.
Infrastructure considerations	Very low infrastructure requirement. Small footprint and mobile.
Energy consumption	The power consumption of CDI depends on the amount of salt removed. For example, to achieve 88-89% removal, the energy consumption of EWP is 4 kWh/kgal (0.17 kWh/bbl) for 2,500 mg/L TDS feed water, and 18 kWh/kgal (0.76 kWh/bbl) for 6,000 mg/L TDS water [119].
Chemicals	No chemicals required.
Life cycle	Expected 10 years.
O&M considerations	Low levels of monitoring and control. Low level of skilled labor required. High level of flexibility. High level of robustness. High level of reliability. Types of energy required: electricity or gas. Can be run by 3 kW diesel, propane generator also available.
Overall costs	Over a 10-year span the total cost of capital and operations is estimated $0.05 per barrel of water processed [119].
Pre-and post treatment	Minimal pretreatment such as cartridge filter.
Concentrate management or waste disposal	20% brine needs deep well injection or crystallizer for ZLD, and generated solid solids need waste disposal.
Applicability in produced water treatment	Good for treatment of produced water with TDS<3,000 mg/L.
Note: 1 barrel = 42 US gallons	

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Gas Hydrates

Gas hydrates are crystalline water-based solids that physically resemble ice. However, instead of the closed crystalline lattice structure of ice, gas hydrates have open lattice structure with a cavity that traps non-polar molecules (typically gases). A photograph of a gas hydrate is shown in Figure 26. The hydrogen bonded water molecules essentially form a cage structure that traps gases including CH_3, H_2S, and CO_2. An illustration of a gas hydrate is also shown in Figure 26. As with the freeze-thaw technology, when water crystallizes, it tends to exclude impurities (such as dissolved salts and suspended solids) from the crystalline matrix. Stable gas hydrates are naturally formed at moderately high pressures (10-13 MPa) and relatively low temperatures (0-10 °C) at natural gas seeps within marine sediments [121]. The formation and subsequent processing of gas hydrates produce three streams: a pure water stream, natural gas, and concentrated brine.

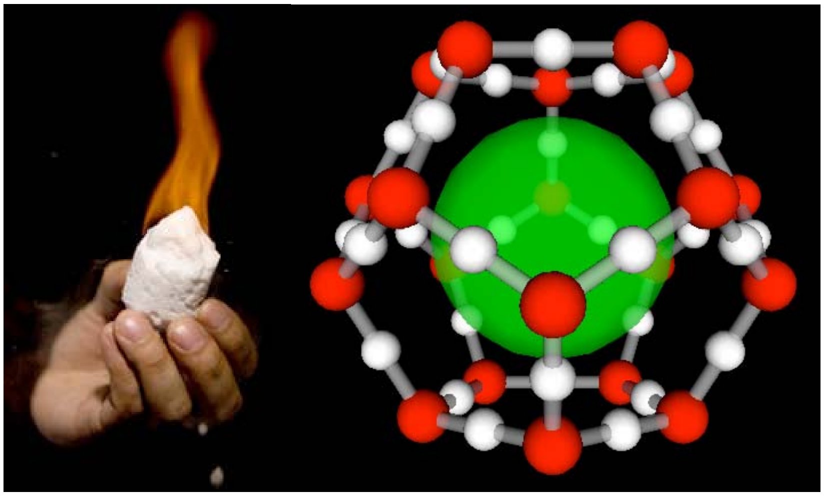

Figure 26: The physical and chemical appearance of gas hydrates. Methane liberated from a solid gas hydrate (left) (Source: [122]). Open crystalline 'cage' structure of a gas hydrate with a green polar molecule 'trapped' inside (right) (Source: [123]).

A collaborative research initiative conducted by BC Technologies in conjunction with Oak Ridge National Laboratory (ORNL) and the International Petroleum and Environmental Consortium seeks to evaluate the effectiveness of forming gas hydrates in-situ at the well head for produced water treatment and management. The study is in its last year and is currently undergoing field demonstrations of an unspecified scale. Prior to the field demonstration, pilot-scale experiments were performed with flowrates of 1,050 to 2,100 gpd (25 to 50 bpd) on feed water with similar chemistry to that identified in the Greater Green River Basin [124]. These experiments demonstrated that the pilot system could recover 50-60% of the hydrates in a single pass; yet, of the hydrates recovered, only 23-29% of the feed water volume is converted to pure water. The feed water is reported to be composed of a TDS concentration that is greater than 10,000 mg/L, but is not likely to be greater than 35,000 g/L. No further data is currently available to assess the technical merits and limitations of this technology.

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Evaporation

Evaporation ponds use the natural water cycle driven by solar energy to evaporate water. Depending on the produced water quality, the ponds may be lined to prevent concurrent subsurface infiltration of the water. In other geologic settings, the ponds may be placed on natural confining layers such as bentonite rich clay soils, or exposed shales that prevent the downward migration of the groundwater [19]. If the evaporation pond is constructed solely for evaporative loss (no infiltration), the ponds are generally designed to be broad shallow pools that maximize the surface area allowing for increased evaporation rates. Once the water has evaporated, the salt sludge is either left in place or removed and hauled offsite for disposal. This disposal method can be expensive due to the large surface area required and the associated land and impermeable liner costs [125]. Regulatory requirements, ecological impacts, and possible concentration of trace elements to toxic levels may determine the design, construction, and operation of evaporation ponds.

Evaporation ponds can be a viable option in relatively warm, dry climates with high evaporation rates, level terrain, and low land costs. They are typically economical and employed only for smaller concentrate flows. Evaporation rates can be enhanced by spraying the water through nozzles. However, this practice can lead to salt damage to soil and vegetation due to drifting. Therefore, misting towers are not currently recommended as a management practice [11]. Produced water can be managed at small onsite evaporation ponds or can be sent offsite to commercial facilities that employ large evaporation basins. Examples of commercial evaporation facilities can be found in Colorado, New Mexico, Utah, and Wyoming [1].

Solar energy ponds are special type of evaporation alternatives that focus on capturing solar energy with the goal to use it beneficially. The approach uses salinity gradients to trap energy in the lower, higher density layer of the concentrate in the pond. The solar energy penetrates the upper, less concentrated layers. The lower, heated layer does not rise due to the higher concentration and density and the absence of convection, and thus reaches significantly high temperatures. The energy trapped in this layer is extracted and can be used to generate electricity. Solar ponds have some concentrate volume-reducing properties but they are not a concentrate management process [126].

ALL Consulting investigated the potential of using evaporation ponds in some of the areas of interest for CBM development [19]. For example, the Powder River Basin (PRB) of Montana and Wyoming and the San Juan Basin of Colorado, evaporation rates between 28 and 40 in/yr have been historically recorded, while areas in Utah have evaporation rates between 40 and 52 in/yr. The Gulf Coast region of Louisiana and Texas has average evaporation rates between 48 and 70 in/yr. Thus in the areas where future CBM development is expected to occur, the potential exists for evaporation to result in a significant amount of managed water loss. Although some portions of these states have considerable annual evaporation, seasonal variations should be taken into account.

The contaminants in produced water such as selenium, oil, and other hydrocarbons may pose potential problems to migratory waterfowl. Covering ponds with netting helps to avoid this problem [57]. The technical assessment of evaporation ponds for produced water disposal is summarized in Table 32.

Table 32. Summary of technical assessment of evaporation ponds.

Criteria	**Description/Rationale**
Industrial status	Industrialized technology. Have been used for produced water management.
Feed water quality bins	From low TDS range 2,000 mg/L to high TDS >40,000 mg/L.
Product water quality	Not applicable.
Production efficiency (recovery)	Concentrate management technology. All water is evaporated and hence "lost" to atmosphere
Infrastructure considerations	Large land area requirements. Landscape and topography are important in siting the location of an evaporation pond. Clay or synthetic liners are required. Monitoring wells or boreholes are required. Siting, designing, and constructing the ponds should consider minimizing the volume of water that is able to enter the pond from natural runoff or flooding.
Energy consumption	Only energy requirement is pumping of concentrate to the pond.
Chemicals	No chemicals required.
Life cycle	Depending on the projected oil/gas development
O&M considerations	Minimal; only mechanical equipment used is pumps. Other items may include liner repairs and monitoring.
Overall costs	Capital costs are highly variable and dependent on location. There is little economy of scale, and method is most competitive for small flows.
Pre-and post treatment	None except sludge disposal if pond has been designed for periodic sludge removal (hazardous sludge would require proper handling, treatment, and disposal).
Concentrate management or waste disposal	Pond may be designed for either sludge accumulation throughout life of ponds with capping at the end of useful life, or for periodic sludge removal and disposal.
Applicability in produced water treatment	Excellent for disposal of produced water, more economical and competitive to small flows.
Note: 1 barrel = 42 US gallons	

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Wind Aided Intensified Evaporation (WAIV)

The WAIV is a relatively new technology that was developed to be used in conjunction with evaporation ponds. It uses wind to promote evaporation and to reduce the overall surface area of the ponds. The concentrate is sprayed over vertical transport surfaces to reduce the pond footprint. The hydrophilized evaporation surfaces can consist of woven nettings, or non-woven geo-textiles, or tuff (vocanic rock) arranged in trays. Studies indicate that the WAIV method intensifies the evaporation process to about 10 times that of regular evaporation ponds [127]. The footprint of the WAIV ponds can be much smaller than a typical evaporation pond. The approach is illustrated in Figure 27.

This technology was tested in Israel, and it is likely that it can be used in similar conditions of low humidity and high temperatures in CBM development areas. The US Bureau of Reclamation tested this technology and identified that the dripping nozzles would salt up and clog. This required cleaning of the nozzles on a regular basis [126].

Lesico CleanTech manufactures the WAIV evaporation technology [128]. The technical assessment of the WAIV for produced water disposal is summarized in Table 33.

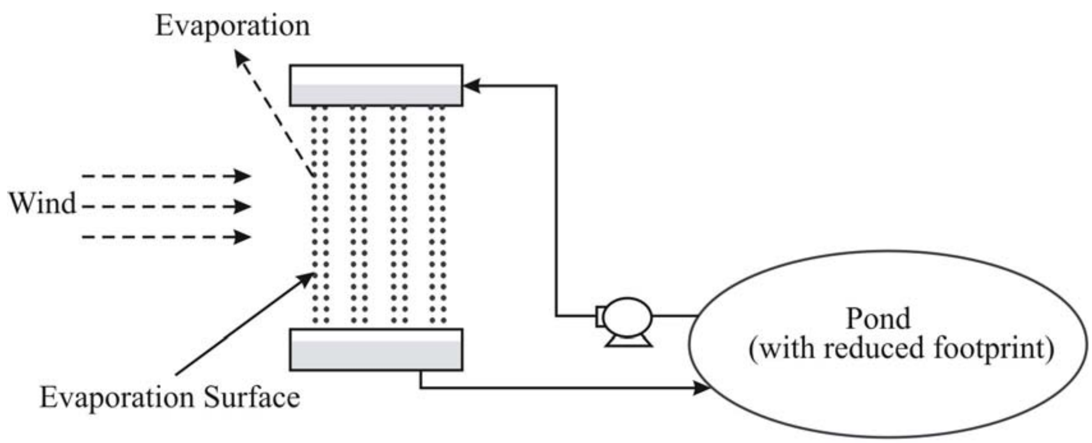

Figure 27. Schematic of Wind Aided Intensified Evaporation (WAIV) Process (Source: [93]).

Table 33. Summary of technical assessment of WAIV evaporation ponds.

Criteria	**Description/Rationale**
Industrial status	Emerging technology, pilot tested in Israel. Have not been used for produced water management.
Feed water quality bins	Applicable to high TDS water >20,000 mg/L.
Product water quality	Not applicable.
Production efficiency (recovery)	Concentrate management technology. All water is evaporated and hence "lost" to atmosphere.
Infrastructure considerations	Compact and modular system. Due to enhanced evaporation using vertically stacked surfaces, the area requirements are significantly reduced compared to evaporation pond. Area reported to be reduced about 10 times.
Energy consumption	No data available. Overall, energy consumption would be higher than for evaporation pond since additional pumping energy would be required.
Chemicals	Acid for cleaning of the evaporation surfaces.
Life cycle	No data available, expected to depend on the projected oil/gas development.
O&M considerations	No data available. Expected to be greater than for evaporation pond since more pumping, mechanical frames, and evaporation surfaces are used.
Overall costs	No cost information is reported. In general, O&M costs are expected to be higher as compared to evaporation pond, though comparison of capital costs is unknown, except that, aside from the wind parameter, capital costs for WAIV would be location independent while pond costs are highly variable and dependent on location.
Pre-and post treatment	None except sludge disposal if pond has been designed for periodic sludge removal (hazardous sludge would require proper handling, treatment, and disposal).
Concentrate management or waste disposal	Pond may be designed for either sludge accumulation throughout life of ponds with capping at the end of useful life, or for periodic sludge removal and disposal.
Applicability in produced water treatment	Good candidate for disposal of produced water. More economical and competitive for small flows.
Note: 1 barrel = 42 US gallons	

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Commercial Thermal Processes

GE: Evaporative produced water treatment and steam generation using MVC evaporators

Steam injection is becoming a common method to enhance oil recovery during oil production. Thermal technologies have been used to treat produced water while generating steam for extracting heavy oil. Conventional produced water treatment and steam generation system often includes a warm or hot lime softener followed by a filtration system to reduce silica, calcium, and magnesium concentration in de-oiled produced water (Figure 28). The hardness and iron are further removed through a weak acid cation (WAC) IX process to ensure the sound operation of the steam generator. Once-Through Steam Generators (OTSGs), driven by natural gas, have been used to produce approximately 80% quality steam (80% vapor, 20% liquid) for injection into a well to fluidize the heavy oil [129]. In most cases, the OTSG blowdown is disposed by deep well injection. This stream can also be further concentrated with a ZLD brine concentrator and crystallizer, producing a dry solid for disposal. Some of the OTSG blowdown can be recycled to the softener system, but as the solids are cycled up in the system, the OTSG's maintenance needs are increased.

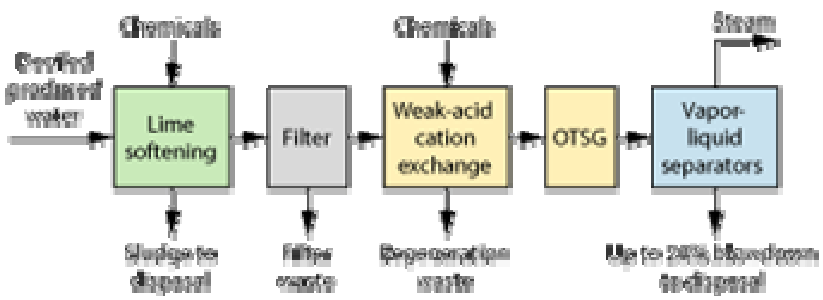

Figure 28. Conventional produced water treatment and steam generation system (Source: [129]).

The more recent Steam-Assisted Gravity Drainage (SAGD) method requires 100% quality steam for injection. The use of OTSG for SAGD applications requires a series of vapor-liquid separators to produce the requisite steam quality. As an alternative to traditional produced water treatment and steam generation system, GE developed an evaporative produced water treatment process using mechanical vapor compression (MVC) evaporators for supplying high quality steams to SAGD. The heat transfer coefficient for the vertical-tube, falling-film MVC evaporators is higher than for traditional evaporators, offering improved evaporation efficiency and energy savings. This arrangement, in conjunction with a proprietary brine distribution system, allows evaporation to occur with reduced fouling by keeping surfaces perpetually wetted (Figure 29). By using the MVC system, produced water treatment system is much simplified as shown in Figure 30.

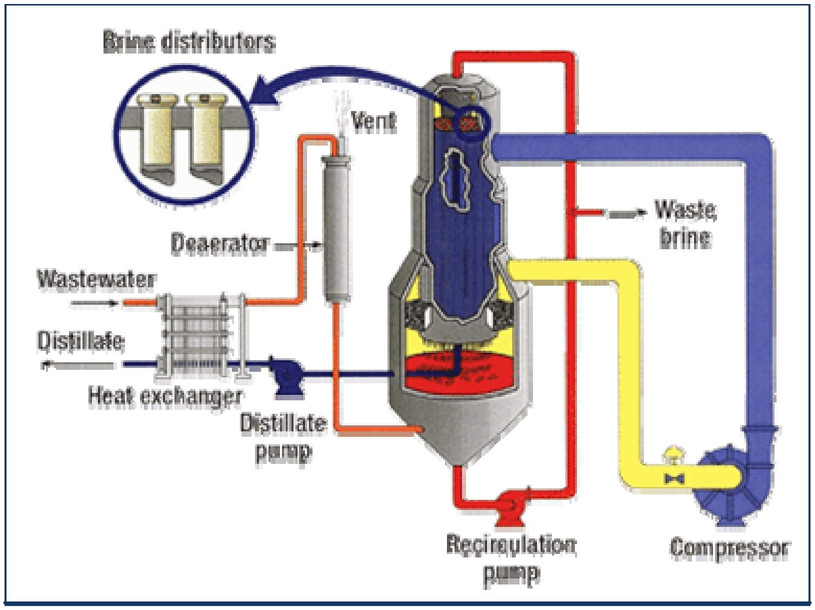

Figure 29. A schematic of a vertical-tube, falling-film MVC evaporator (Source: [129]).

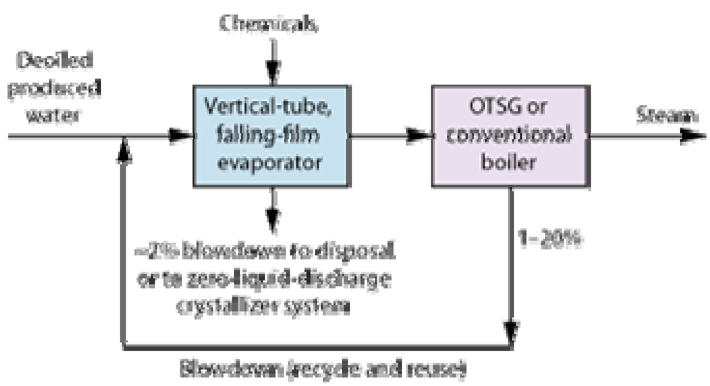

Figure 30. The vertical-tube, falling-film MVC evaporation system for produced water treatment and steam production (Source: [129]).

De-oiled produced water enters a feed tank where the pH is adjusted. The wastewater is pumped to a heat exchanger that raises its temperature to a boiling point. Hot, de-aerated feed enters the evaporator sump, where it combines with the recirculating brine slurry. The slurry is pumped to the top of a bundle of heat transfer tubes. As the brine flows down the tubes, a small portion evaporates and the rest falls into the sump to be recirculated (Figure 29). The vapor travels down the tubes with the brine and is drawn up through specially designed mist eliminators on its way to the vapor compressor. Compressed vapor flows to the outside of the heat transfer tubes, where its latent heat is given up to the cooler brine slurry falling inside. As the vapor loses heat, it condenses as distilled water. The distillate is pumped back through the heat exchanger, where it gives up sensible heat to the incoming wastewater. A small amount of the brine slurry is continuously blowdown from the evaporator to control density [129].

The OTSG or drum boiler blowdown can be recycled to the evaporator feed, eliminating the need to dispose of this waste stream without affecting recovered water quality. The evaporator blowdown is disposed via deep well injection or treated further by a crystallizer to eliminate all liquid waste. The crystallizer produces a dry cake material for disposal ([129]).

Evaporative produced water treatment was tested in 1999, and was initially used by Japan Canada Oilsands and PetroCanada, respectively. The blowdown from the OTSG steam separators was effectively processed by an evaporator and crystallizer combination in a ZLD system. Today, there are about 16 produced water evaporators operating or under construction in nine plants in Alberta, Canada and other regions ([129]).

As compared to the conventional oil produced water treatment, the evaporative produced water treatment exhibits a number of advantages [130]. These include:

- Evaporators de-couple the produced water system from the boiler feed system, increasing boiler reliability
- Lower capital, operating, and lifecycle costs compared to traditional method
- Eliminates traditional produced water treatment systems (WLS or HLS, WAC, etc.)
- Minimizes softener sludge and other waste streams requiring disposal
- Minimizes chemical use, cost, storage, and handling
- May reduce amount of de-oiling equipment
- Reduces maintenance materials and labor
- Reduces ZLD system size by 80% (if ZLD is required)

Although fouling severity and frequency have been minimal in operating produced water evaporators, there is a risk that severe fouling could limit steam production. The traditional approach eliminates this risk [129]. Due to the high energy-consumption and economical scale of treatment plant, the thermal technologies are more competitive for high TDS water and centralized treatment systems. The technical assessment of the evaporative produced water treatment technology is summarized in Table 34.

Table 34. Summary of technical assessment of GE – evaporative produced water treatment using MVC evaporators.

Criteria	Description/Rationale
Industrial status	Mature and robust technology. Have been used for oil produced water treatment and steam generation.
Feed water quality bins	Applicable to a wide TDS range (<100,000 mg/L TDS), and all types of water chemistry makeup.
Product water quality	Product water quality for MVC is high, with little variation due to feed or concentrate salt content [129].
Production efficiency (recovery)	Product water recovery is approximately 98%. 2% blowdown can be disposed via deep well injection or treated by a crystallizer to ZLD.
Infrastructure considerations	Infrastructure considerations are similar to MSF and MED units.

Table 34. Summary of technical assessment of GE – evaporative produced water treatment using MVC evaporators.

Criteria	**Description/Rationale**
Energy consumption	The power consumption of MVC evaporator is 70 kWh/kgal of distillate produced (2.94 kWh/bbl) [129]. A typical produced water evaporator will consume 60-65 kWh/kgal of distillate. The higher consumption of the GE MVC evaporator is that the system was designed to have a crystallization device downstream and, therefore, the cycles of concentration are higher than would otherwise be required. The higher cycles of concentration increase the vapor compressor electrical consumption to overcome the associated increase in boiling point of the brine within the evaporator. Electrical consumption of less than 60 kWh/k gal can be achieved by modifying the evaporator configuration [129].
Chemicals	Scale inhibitor and acid may be required for process control to prevent scaling. Corrosion control is achieved via pH control. Annual cleaning is typically conducted using acid, EDTA, or other antiscalant.
Life cycle	Expected 30 years.
O&M considerations	Levels of monitoring and control: required for feed pH, flow rates as well as steam and vessel pressures. High level of skilled labor required. MVC is a complex system and adds to the O&M skill level required. Level of flexibility: easy to adapt to highly varying water quality but not flexible for varying water flows. Level of robustness: high ability of the equipment to withstand harsh conditions. Level of reliable: typical plants operate continuously, with 99% on-stream availability. Types of energy required – electricity and gas.
Overall costs	Economic comparisons of produced water treatment approaches are site specific and detailed conclusions will vary. However, there is a consensus in the industry that the majority of new SAGD facilities will use evaporative treatment methods, with a minority continuing to utilize traditional methods.
Pre-and post treatment	MVC requires minimal pretreatment such as de-oiling, pH adjustment, and deaeration.
Concentrate management or waste disposal	2% brine needs deep well injection or crystallizer for ZLD, and generated solid solids need waste disposal.
Applicability in produced water treatment	Excellent technology for produced water with high TDS and near ZLD disposal, more applicable to centralized system and large flow rate.
Note: 1 barrel = 42 US gallons	

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Aquatech: Mechanical Vapor Compression (MVC) Technology

Aquatech International Corporation develops membrane/thermal technologies to address the needs of diverse industries, including power, oil and gas, mining, and metals. Aquatech offers diverse products that encompass various water and wastewater treatment technologies under the WATER*TRAK*™ umbrella. It includes RO, RECOMAX™, HERO™ and UF (both tubular and hollow fiber), IX, electrodeionization, media filters, and activated carbon filters. Aquatech uses MVC technology to provide high recoveries to minimize the requirement for fresh water such as for the Canadian Tar Sands by allowing efficient reuse of oilfield produced water (Source: www.aquatech.com).

No enough data allow a technical assessment for Aquatech MVC technology. However, it is expected to be similar to the GE MVC technology as shown in Table 34.

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Aqua-Pure - Mechanical Vapor Recompression (MVR) Evaporation

The NOMAD systems are designed and built by Aqua-Pure Ventures Inc., based in Calgary, Alberta, Canada, and operated by Granbury-based Fountain Quail Water Management. This MVR evaporation NOMAD system is an energy efficient process that uses a very compact welded cassette heat exchanger with a plate-and-frame construction and a rising-film design. With this design, boiling occurs on a wet surface, minimizing scale deposition that occurs in conventional thermal technologies.

For frac flowback water treatment, feedwater is first dosed with flocculants to coagulate/flocculate the suspended solids and organic matters. The wastewater is then passed through an inclined plant mechanical separator to remove formed flocs. The effluent from the separator is pumped to the Aqua-Pure MVR evaporator unit to remove dissolved solids (Figure 31). A compressor is used to add the energy required to boil water. The feed water passes through two preheat exchangers where heat is absorbed from the distillate and concentrate products leaving the system. The feed then passes into a recirculation loop where concentrate circulates through an evaporator exchanger and a vapor / liquid separator. A portion of the concentrate is boiled to steam in the evaporator exchanger and separated from the liquid in the separator vessel.

The manufacturer claims that the MVR evaporation can recycle up to 85% of frac flowback water into distilled water. With a lower contamination level in the feed water, the system could achieve a 90% to 95% recovery of distilled water [131]. The treated water is stored in tanks for future reuse.

The system is skid mounted. The footprint of the MVR system NOMAD 2000 is similar to that of a traditional MVR evaporator—about 2,500 square feet for a daily output of 84 kgal (2,000 barrels) of distilled water and 21 kgal (500 barrels) of concentrated brine. The system consists of three modules, each 11.5 feet wide and 12.5 feet high [131]:

- A pre-treatment module 40 feet long, weighing 25,000 pounds.
- An evaporator module 37 feet long, weighing 42,000 pounds.
- A compressor module 30 feet long, weighing 96,000 pounds.

The system also includes interconnecting pipes and electrical connections, and a 50-kW generator. It needs no external source of electric power. It draws natural gas directly from the well to run the compressor and to drive the generator, which produces electricity to power the pumps, instruments, and controls. Figure 32 shows a close view of the Aqua-Pure unit operating by Devon Energy Corporation near Decatur, Texas.

A summary of the technical assessment of Aqua-Pure MVR Evaporation process based on the information provided in the manufacturer's website is listed in Table 35.

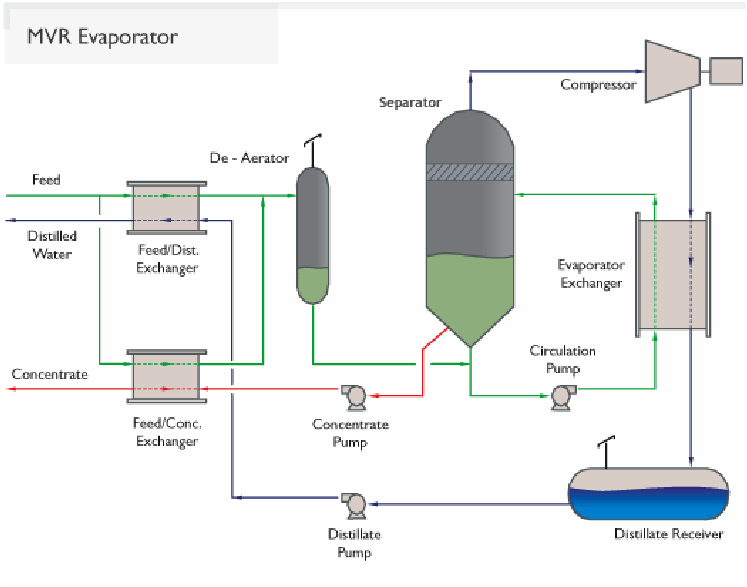

Figure 31. Schematic of the Aqua-Pure MVR Evaporator (Source: [131]).

Figure 32. Closer view of the Aqua-Pure unit (Source: J. Veil, Argonne National Laboratory).

Table 35. Summary of technical assessment of Aqua-Pure MVR Evaporation process.

Criteria	**Description/Rationale**
Industrial status	Pilot-scale field-testing for frac water treatment.
Feed water quality bins	Applicable to TDS <80,000 mg/L, and a broad variety of water chemistry makeup.
Product water quality	Product water quality is very high with TDS in the range of 10 mg/L [132]. Trace amounts of volatile hydrocarbons may present.
Production efficiency (recovery)	Product water recovery is between 60 and 90%, depending on feed water quality (Source: NOMAD 2000 Factsheet).

Table 35. Summary of technical assessment of Aqua-Pure MVR Evaporation process.

Criteria	Description/Rationale
Infrastructure considerations	No special infrastructural requirement as the unit is skid-mounted. The footprint of NOMAD 2000 is 2,500 square feet. Require gas or electricity as power.
Energy consumption	The energy consumption should be comparable to the pressure distillation methods such as MVC, about 30 kWh/kgal (1.3 kWh/bbl) of product water. Operational energy use is 466 KW for the NOMAD 2000 unit.
Chemicals	Flocculants for coagulation and flocculation. Similar to other thermal technologies, scale inhibitor and acid may be required for process control to prevent scaling. Corrosion control is achieved via pH control. Annual cleaning is typically conducted using acid, EDTA, or other antiscaling chemicals.
Life cycle	Typically expected 20 years, although longer life may be expected with the selection of better materials of construction, that is, alloys with high corrosion resistance [93].
O&M considerations	Low level of monitoring and control required for feed pH, flow rates as well as steam and vessel pressures. High level of skilled labor required to operate MVR evaporators. High level of flexibility: easy to adapt to highly varying water quality and quantity. High level of robustness: high ability of the equipment to withstand harsh conditions. High level of reliability: scale removal requires a two-man crew in one or two work shifts, less than with a traditional MVR evaporator. Types of energy required – Gas or electricity.
Overall costs	According to Devons, the cost to treat frac water is $79.6/kgal ($3.35/bbl), about 68% more than the $47.6/kgal ($2/bbl) cost if post-fracing water is simply disposed of [133]. Devon has continued to study the Aqua-Pure process for its potential payoffs in the future, both in the Barnett Shale region and elsewhere. They are gaining valuable experience with the technology and can work on improving its efficiency and lowering the cost (Source: John Veil, Argonne National Lab). In the Barnett Shale region, natural gas is plentiful, and can be readily obtained as a fuel source to operate the technology. In other applications, such as treating produced water from oil wells, natural gas may not be an affordable energy source (Source: John Veil, Argonne National Lab).
Pre-and post treatment	Require pre-treatment to remove suspended solids and organic matter. Product water needs remineralization because of the low TDS level. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with the distillate. Post-treatment may also include carbon adsorption or oxidation if organic substances are present in product water.
Concentrate management or waste disposal	Solids collected in the separator need a filter press for dewatering and disposal. The brine stream needs transported off the well site and then injected into a disposal well or evaporated/stored in large ponds.
Applicability in produced water treatment	Good candidate technology for produced water with high TDS and near ZLD disposal, more applicable to centralized system and large flow rate.
Note: 1 barrel = 42 US gallons	

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212 Resources - Mechanical Vapor Recompression (MVR) Evaporation

Similar to Aqua-Pure MVR evaporation process, 212 Resources developed and operates transportable, skid-mounted "pods" that deployed at drill site to process frac flowback water for reuse (www.212resources.com). The treatment train consists of a number of process elements (Figure 33), including:

- Collection and gravity settling of solids
- Course filtration and material management
- Heated oil/water separation to recover immiscible hydrocarbons
- Vapor compression, turbulent flow, high velocity flash evaporation to recover brine and distilled water
- Steam distillation integrated with the evaporator for recovery of methanol and other miscible hydrocarbons with advanced UV and carbon filtration polishing
- The units are powered by natural gas from the local site or from external electrical hook-ups

Its core technology is a patented VACOM technology (http://www.vacomllc.com/) that combines mechanical vapor recompression with turbulent flow heat exchange technology. The Vacom vapor compression, flash evaporation system is applicable for high TSD waters from deep-well, hydraulic fracing, natural gas wells, deep coalbed methane wells, and other oil and gas produced waters. 212 Resources' system is able to recover oil, methanol, total dissolved solids, minerals, and metals from water that are associated with drilling and production.

212 Resources has a contract to build a large plant in Wyoming for treatment of frac flowback water and produced water from natural gas fields [134]. In May 2008, 212 Resources announced that the company had signed a contract with Denver-based Delta Petroleum Corporation for managing its flowback and produced water in the Colorado Vega field. This ten year service contract involves multiple 212 Resources "pods" and is similar to the work being done in Wyoming, except that the treated water will be discharged off-site (the Wyoming project water is reused for drilling) [135]. 212 Resources has also been planning testing in the Barnett Shale [133, 136].

There are similarities in the Aqua-Pure (or Fountain Quail) and 212 Resources systems: both can be powered by on-site natural gas and both use evaporation and distillation technologies. The 212 Resources system uses a different method of heat transfer, allowing the machines to handle higher TDS (110,000 mg/L) than the Aqua-Pure (TDS 80,000 mg/L). Although 212 Resources' pods are transportable, they resemble a miniature recycling plant in an enclosed building when assembled. The size of a pod is 40'x60'. The Aqua-Pure's NOMAD system serves as a transportable and modular technology with a 20'x60' footprint. A summary of the technical assessment of the 212 Resources' process is listed in **Table 36**.

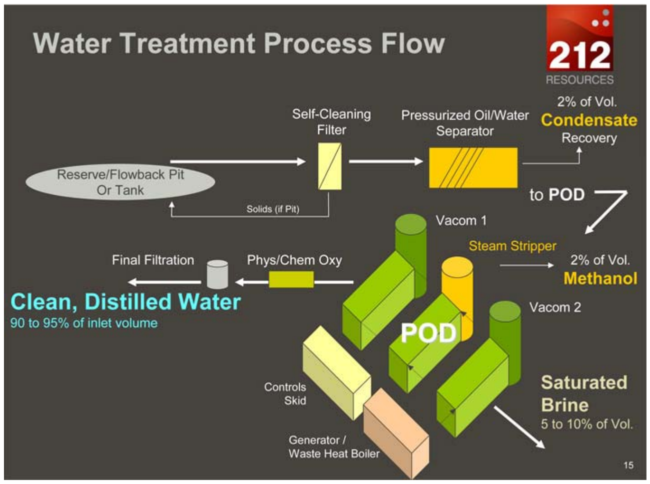

Figure 33. Schematic of the 212 Resources water treatment system (Source: [137]).

Table 36. Summary of technical assessment of the 212 Resources water treatment system.

Criteria	Description/Rationale
Industrial status	Full-scale application for frac water treatment in Wyoming and Colorado.
Feed water quality bins	Applicable to TDS <110,000 mg/L, and a broad variety of water chemistry makeup.
Product water quality	Similar to other MVR technology, product water quality is expected high with TDS in the range of 10-100 mg/L. Trace amounts of volatile hydrocarbons present in desalted water can be removed by carbon filtration.
Production efficiency (recovery)	Product water recovery is between 90 and 95%, depending on feed water quality.
Infrastructure considerations	No special infrastructural requirement as the unit is skid-mounted. The footprint of pods is 40'x60'. Require gas or electricity as power.
Energy consumption	The energy consumption is expected to be comparable to the pressure distillation methods such as MVC, about 30 kWh/kgal (1.3 kWh/bbl) of product water.
Chemicals	Similar to other thermal technologies, scale inhibitor and acid may be required for process control to prevent scaling. Corrosion control is achieved via pH control. Annual cleaning is typically conducted using acid, EDTA, or other antiscaling chemicals.
Life cycle	Typically expected 20 years, although longer life may be expected with the selection of better materials of construction, that is, alloys with high corrosion resistance [93].
O&M considerations	High level of monitoring and control required for feed pH, flow rates as well as steam and vessel pressures. High level of skilled labor required to operate MVR evaporators. High level of flexibility: easy to adapt to highly varying water quality and quantity. High level of robustness: high ability of the equipment to withstand harsh conditions. High level of reliability. Types of energy required: Gas or electricity.

Table 36. Summary of technical assessment of the 212 Resources water treatment system.

Criteria	**Description/Rationale**
Overall costs	The cost of treating the frac flowback water is not reported. However the costs persuaded the industry to employ the technology to treat the frac water. It is assumed that the cost of 212 Resources technology is competitive to the Aqua-Pure process. Besides, the recovered oil and methanol can bring additional profits.
Pre-and post treatment	Pre-treatment includes settling and filtration to remove suspended solids and organic matter. Product water includes UV and carbon filtration to remove miscible hydrocarbons. Remineralization or blending may be required depending the application of product water.
Concentrate management or waste disposal	The solids collected in the separator need a filter press for dewatering, and then disposal. The brine stream needs transported off the well site and then injected into a disposal well or evaporated/stored in large ponds.
Applicability in produced water treatment	Excellent technology for produced water with high TDS and near ZLD disposal, more applicable to centralized system and large flow rate.
Note: 1 barrel = 42 US gallons	

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AGV Technologies: Wiped Film Rotating Disk (WFRD)

AGV Technologies, Inc. (AGV) developed a new Wiped Film Rotating Disk (WFRD) system for produced water treatment. The WFRD is a vapor-compression distillation technology that can also operate in the MED mode if thermal energy is available [138]. The WFRD system uses rotating disks as heat transfer surfaces. A thin microfilm layer of input water (produced water) is applied to the outside surface of the rotating disk. Superheated vapor in the cavity of a disk condenses on the inside surface. A slight temperature difference across this disk allows heat to flow from the condensing liquid to the evaporating fluid, driving evaporation and recycling of the latent heat of evaporation. This evaporated vapor moves to the next disk assembly (effect) and is condensed, providing the energy to evaporate more feed water [138]. A schematic for a five-effect WFRD unit operating in the vapor compression mode is illustrated in Figure 34.

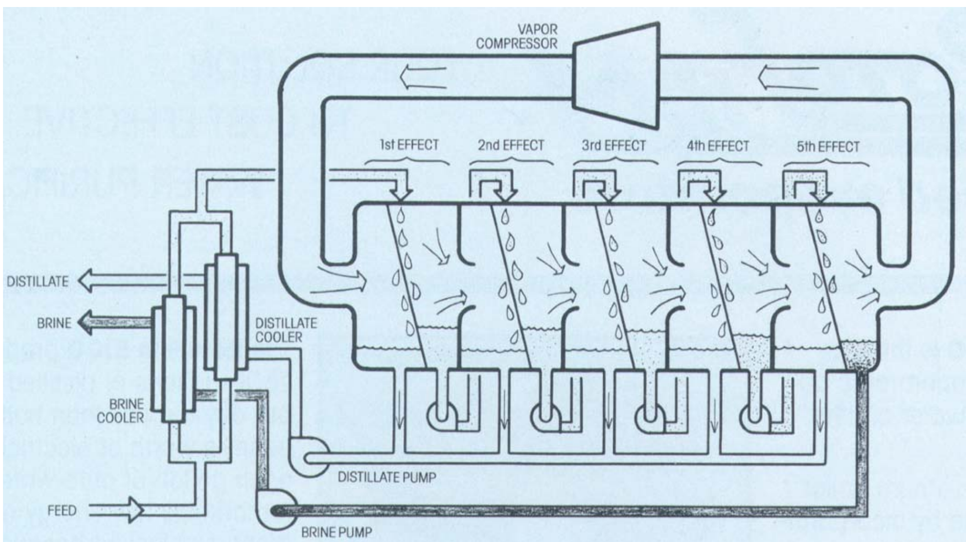

Figure 34. Schematic flow diagram for a five-effect WFRD unit operating in the vapor compression mode with each slanted line representing the rotor in each of the five effects [138].

AGV Technologies claims that the WFRD is designed to improve heat transfer efficiency and reduce scaling and fouling [138]. Resistance to heat flow in distillation is determined by the thickness of the liquid layer on the evaporation and condensation surfaces. The WFRD design minimizes this thickness; resulting in very thin condensate and feed films on the heat transfer surfaces. The WFRD technology achieves a heat transfer coefficient of 25 kW m^{-2} $°C^{-1}$.

In 2004, the WFRD technology was tested using CBM production water collected from two sources – the Powder River Basin (Northeast Wyoming / Southeast Montana, with TDS 1,068 mg/L) and the San Juan Basin (New Mexico, with TDS 23,000 mg/L). Produced water from each source was treated using a prototype WFRD test unit; a single effect system with two 24-inch disk sets. It was configured to operate at an 8 to 1 brine recycle ratio and an evaporator temperature of 122 °F. The system is capable of producing a maximum of 2.6 gal per hour. Each run processed 5 gallons of produced water with recovery rate of 90%. The AGV technology removed 99% of the TDS from both raw produced waters without any adjustments, pretreatment, or additional equipment. TOC was reduced by 86% for the San Juan samples and 70% for the Powder River samples. While the percentage reduction for some inorganic constituents and TOC resulting from WFRD processing was less in the Powder River samples, the levels measured in Powder River recovered water were very low [138].

Currently, AGV Technologies, Inc. is developing the PW-600 – the first commercial AGV product. It will be available for installation in oil and gas production and produced water disposal facilities. The PW-600 system is designed to process 25 kgal (600 barrels) of produced water per day. Initial PW-600 units are electrically powered. Waste heat, cogeneration, and renewable energy powered models will be available.

The WFRD system has been proved promising through the short-term laboratory testing. Long-term testing would be required to demonstrate its performance and efficiency in production field. The assessment summarized in **Table 37** is based on test operation of the prototype system and results presented in the 2004 Final Report "Improving Produced Water Quality for Coal Bed Methane. Prepared by AGV Technologies, Inc. for RPSEA" [138].

Table 37. Summary of technical assessment of the WFRD distillation system.

Criteria	Description/Rationale
Industrial status	Emerging technology in produced water treatment. Has been previously employed for CBM produced water treatment at bench-scale (capacity 2.6 gallons per hour). Currently the vendor, AGV Technologies, Inc. is developing a commercial unit treating 600 bpd of produced water.
Feed water quality bins	Applicable to TDS range from 1000 to 23, 000 mg/L.
Product water quality	TDS rejection 99%; TOC rejection 70- 86%; ammonia rejection low.
Production efficiency (recovery)	Product water recovery is approximately 90%.
Infrastructure considerations	No special infrastructural requirement as the unit is skid-mounted. The system requires housing or shed. Energy sources could be gas, electricity, thermal, and renewable energies.
Energy consumption	Not available.
Chemicals	It is expected that scale inhibitor and acid may be required for process control to prevent scaling. Corrosion control is achieved via pH control. Annual cleaning is typically conducted using acid, EDTA, or other antiscaling chemicals.
Life cycle	Not available.
O&M considerations	High level of monitoring and control required for feed pH, flow rates as well as steam and vessel pressures. High level of skilled labor required to operate distillation system. High level of flexibility: easy to adapt to highly varying water quality and quantity. High level of robustness: high ability of the equipment to withstand harsh conditions. High level of reliability.
Overall costs	Not available. AGC Technology estimates that the operational cost of processing produced water with the WFRD will be approximately 30% of that for the distillation systems ($0.67/bbl). If powered with thermal energy from a methane-fired boiler, the operating cost would be reduced 45% compared with the electrically powered WFRD. A cogeneration configuration results in a 67% cost reduction compared with electrically powered WFRD configuration.

Table 37. Summary of technical assessment of the WFRD distillation system.

Criteria	**Description/Rationale**
Pre-and post treatment	Pre-treatment might includes settling and filtration to remove suspended solids and organic matter. Product water includes UV and carbon filtration to remove miscible hydrocarbons. Remineralization or blending may be required depending the application of product water.
Concentrate management or waste disposal	The 10% brine stream needs disposal, such as deep well injection or using solar ponds.
Applicability in produced water treatment	Similar to other thermal technologies, the WFRD is a good candidate to treat high salinity produced water.
Note: 42 gallons in a barrel.	

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Intevras Technologies, LLC: Evaporative Reduction and Solidification (EVRAS) units

Intevras Technologies, LLC, a Texas privately held company, has developed a thermal method for brine treatment called EVRAS (Evaporative Reduction and Solidification). The EVRAS™ system is a patented technology that utilizes low-grade waste heat to concentrate and/or crystallize large volume wastewater streams.

The EVRAS technology employs an evaporative process similar to a cooling tower that relies on water temperature, surface area, and airflow. Produced water evaporates during the process into the atmosphere. The EVRAS™ "crystallizers" allow total evaporation, resulting in precipitated solids. The solid waste residue is then removed for disposal, re-cycling, or resale (salts) in other markets.

The EVRAS system overcomes the scaling problems on heat exchangers through the use of (i) flexible films as the surface media for the air and brine contacting process, and (ii) two step heat transfer process employing an intermediary heat transfer liquid. A schematic of the EVRAS process is illustrated in Figure 35.

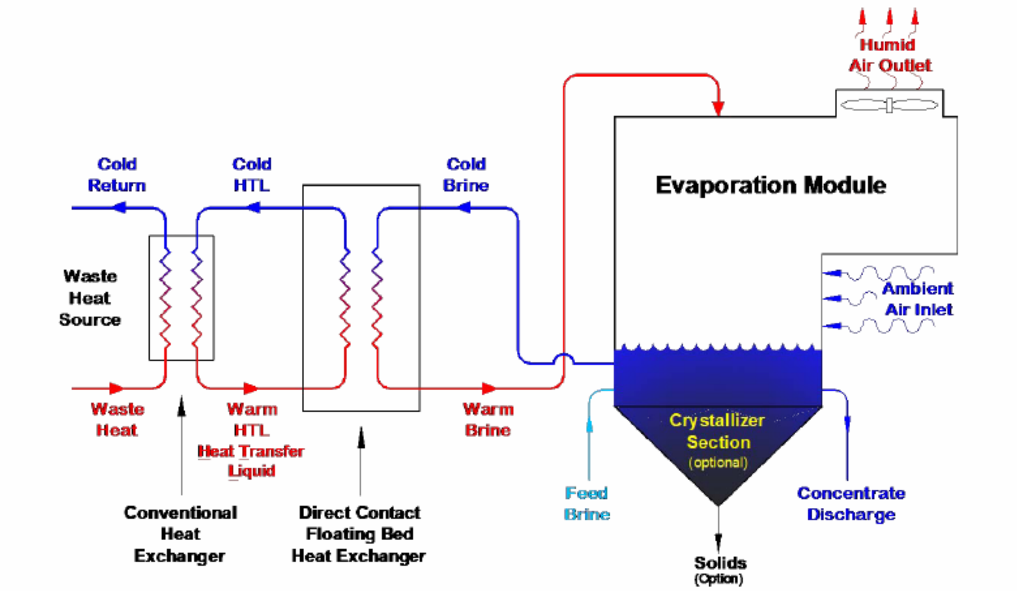

Figure 35. Schematic of EVRAS process for brine treatment (Source: [139]).

The EVRAS system is being tested in produced water field for brine volume minimization. For example, as part of a joint pilot project with the City of Fort Worth, Chesapeake Energy is studying the EVRAS system as a potential way to reduce the amount of produced water being injected into saltwater disposal wells in the Barnett Shale. A picture of the EVRAS system is shown in Figure 36. Using the heat generated by natural gas compressor stations (an energy source that would typically being wasted), the system filters and then evaporates a portion of the produced water into atmosphere. Early estimates indicate that approximately 50 kgal (1,200 barrels) of fresh water can be evaporated out of 126 kgal (3,000 barrels) of concentrated saltwater, resulting in smaller volume to be injected [140].

According to the technical information provided in the website of Intevras Technologies, the advantages of the EVRAS system include:

- Use of low temperature waste heat
- TDS insensitive
- Corrosion resistant and minimal scaling problems
- Simplicity in operation and minimal maintenance: operating at atmospheric pressure
- No blow-down or discharge

The EVRAS process is an evaporative system and no fresh water is recovered from produced water. The EVRAS fits with compression stations to use the waste heat. Without waste heat available onsite, the process is energy intensive and may not be feasible for CBM produced water treatment. The EVRAS system does not have multiple effects; therefore, the energy consumption is intense. Also, the vendor claim that the EVRAS system is suitable to treat large volume of waste streams and it may not be feasible to treat point source of CBM produced water with varying flow rates. The assessment summarized in Table 38 is based on the information provided in the website of Intevras Technologies, LLC (www.intevras.com).

Figure 36. Picture of an EVRAS system to evaporate a portion of produced water from natural gas drilling in Barnett Shale [140].

Table 38. Summary of technical assessment of the EVRAS evaporative system.

Criteria	**Description/Rationale**
Industrial status	Proven technology in various industries. For example, the technology has been employed in California for waste disposal of brines generated with the production of oil and gas. It is also being tested for reducing the produced water volume during natural gas drilling in the Barnett Shale (field testing, capacity unknown). Intevras Technologies, LLC, owns the patent of the technology.
Feed water quality bins	The technology is not sensitive to the level and type of brine. The process has been employed with saturated feed waters at TDS level of 310,000 mg/L [141].
Product water quality	No product water.

Table 38. Summary of technical assessment of the EVRAS evaporative system.

Criteria	**Description/Rationale**
Production efficiency (recovery)	Not applicable.
Infrastructure considerations	No special infrastructural requirement. The system requires no housing or shed. Energy can be waste heat. Waste heat sources of 85 °F or higher are generally recommended.
Energy consumption	Not available.
Chemicals	The use of chemicals is expected to be minimal because of low scaling and fouling potential on heat exchangers.
Life cycle	Not available.
O&M considerations	Low level of monitoring and control. Low level of skilled labor required to operate the system. High level of flexibility: easy to adapt to highly varying water quality. High level of robustness: high ability of the equipment to withstand harsh conditions. High level of reliability.
Overall costs	Not available.
Pre-and post treatment	Minimal pre-treatment, might includes settling and filtration to remove suspended solids and organic matter.
Concentrate management or waste disposal	The concentrated brine stream, or solids needs disposal. The salts may be used for industrial applications.
Applicability in produced water treatment	The technology may be a candidate for ZLD of high salinity produced water. May not be cost effective to low water flow.
Note: 1 barrel = 42 US gallons	

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Total Separation Solutions: SPR – Pyros

Total Separation Solutions, LLC (TSS) developed a new PYROS™ system for heating and evaporation of produced water. Fluid is pumped into the PYROS™ system, heated to evaporation temperatures, and concentrated. The byproduct of the process is clean steam that is condensed into fresh water by heating the incoming fluid. A methodology the TSS proposed for produced water treatment is shown in Figure 37.

The PYROS™ system includes cross-flow filtration modules to remove suspended solids from produced water and frac flowback waters. Cross-flow filtration using sintered metal tubes allows the continuous operation without replacing filters. The PRROS™ is part of a modular system. TSS, LLC claims that the complete PYROS™ system does not require any additional services. The modular skid design and small size allows it to be installed at the point of source of produced water to eliminate excessive trucking costs [142].

The core technology of the PYROS™ system is ShockWave Power™ reactor (SPR™). Fluid is delivered into a SPR™ reactor, where it is passed over the generator's spinning cylinder. The specific geometry of the holes in the cylinder, clearance between the cylinder, and the housing and rotational speed create pressure differences within the liquid where cavitation bubbles form and collapse. These collapsing microscopic bubbles generate shock waves that are used to heat, concentrate, and mix the fluid. The result is the conversion of mechanical energy into heat energy. In the SPR™ reactor, there are no heat transfer surfaces; therefore, scaling is not a problem. Additionally, there is an ultrasonic cleaning effect that occurs on the metal surfaces inside the SPR™ as the shockwaves are generated within narrow clearances. This cleaning effect, in conjunction with a negative temperature difference between metal and liquid, results in scale-free heating.

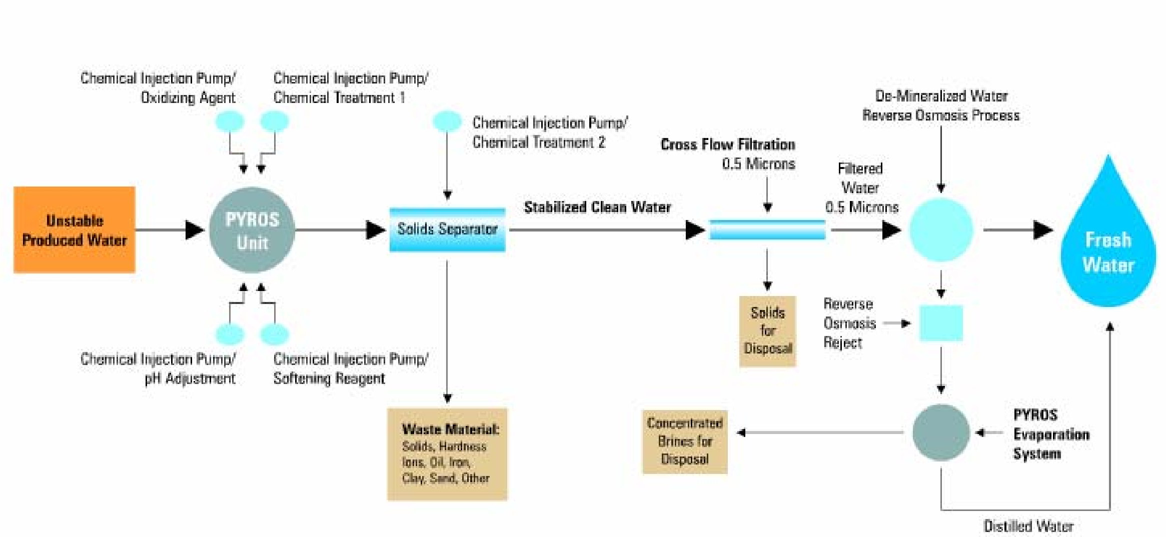

Figure 37. Schematic of PYROS system for produced water treatment (Source: [142]).

TSS technology has been used to process more than 10,000 bbl of frac water per day for an operator in the Haynesville Shale. The assessment summarized in Table 39 is based on the information provided on the website of TSS.

Table 39. Summary of technical assessment of the PYROS evaporative system.

Criteria	Description/Rationale
Industrial status	SPR is a proven technology in heating fluid. It is a new technology for produced water treatment. It has been employed to treat frac water in Haynesville Shale, 10,000 bpd. TSS owns the patent of the technology in oil and gas field.
Feed water quality bins	The technology is not sensitive to the level and type of brine. It is expected to treat high TDS water.
Product water quality	High product water quality, volatile compounds can present in product water (steam).
Production efficiency (recovery)	The PYROS 4 system evaporates up to 5000 bbl of water, and generates 5000 pounds of steam per hour, that is 6.8% water recovery (through steam), and 93.2% as concentrate.
Infrastructure considerations	Modular skid, SPR skid 8.5 x 14 feet.
Energy consumption	The system consumes 33 gallons of diesel per hour.
Chemicals	The use of chemicals is highly dependent upon the water quality. The chemical consumption of SPR reactor is expected to be minimal because of low scaling and fouling potential on heat exchangers.
Life cycle	Not available.
O&M considerations	Low level of skilled labor required to operate the system. High level of flexibility: easy to adapt to highly varying water quality.
Overall costs	Not available.
Pre-and post treatment	Pre-treatment might include chemical precipitation, settling, and filtration to remove iron and manganese, suspended solids and organic matter.
Concentrate management or waste disposal	The concentrated brine stream needs disposal or reuse.
Applicability in produced water treatment	The technology may be a candidate for treatment of high salinity produced water.
Note: 1 barrel = 42 US gallons	

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Commercial IX Processes

EMIT: Higgins Loop

EMIT Higgins Loop technology is the most widely utilized IX process for CBM produced water treatment. EMIT currently has 18 operating treatment units in Wyoming, Montana, and Colorado. 17 of the operating treatment units are located in the Powder River Basin, while one system is located in the southern most area of the Greater Green River Basin [143]. These treatment units have a reported treatment capacity of 336,000 to 1,176,000 gpd (8,000-28,000 bpd) [144].

The Higgins Loop operates as a continuous countercurrent ion exchange contactor for liquid phase separations of ionic components, primarily sodium. The unique aspect of the Higgins Loop is that it performs resin regeneration continuously during the process, with minimal need for system downtime during regeneration. The IX contactor consists of a vertical cylindrical loop that contains a packed bed of resin separated into four operating zones by butterfly or "loop" valves. These operating zones are illustrated in Figure 38, and include pulsing (‘A’), regeneration (‘B’), adsorption (‘C’), and backwashing zone (‘D’). Each zone functions as a separate vessel.

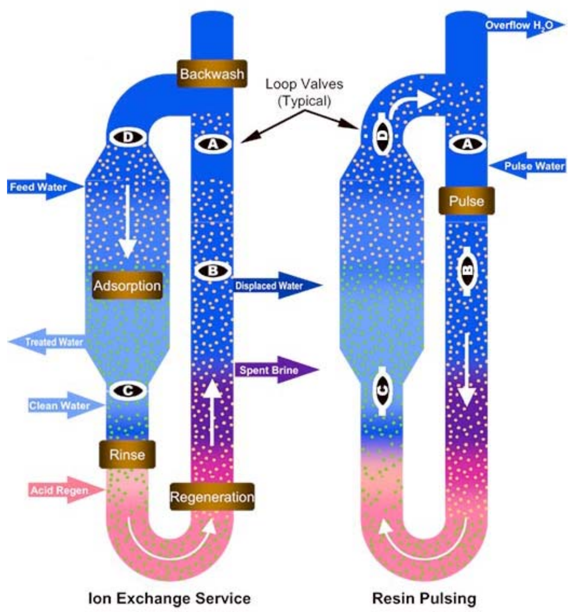

Figure 38. Schematic of the EMIT Higgins Loop IX contactor. Process diagram shows flow during normal operation (ion exchange service) and during resin regeneration (resin pulsing).

Produced water containing high concentration of sodium is fed into the adsorption zone of the Higgins Loop. There, it contacts strong acid cation resin, which accepts Na and other cations in exchange for hydrogen ions. Data from field trials indicates sodium removal of 97% [45]. In the lower section of the Higgins Loop, resin saturated with sodium is regenerated with a 4.11 M HCl solution (representing 1-10% of the treated volume) [143, 144]. This generates a small to moderate concentrated NaCl brine stream, which is typically disposed of by Class I or II deep injection wells. Regenerated resin is rinsed with water prior to reentry into the adsorption zone to remove acid from its pores. As resin in the upper layer of the adsorption zone becomes loaded with sodium, the flows to the Higgins Loop are momentarily interrupted. This allows advancement of the resin bed (pulsing) through the loop in the opposite direction of liquid flow. Liquid flows are restarted after resin pulsing is complete [143, 144].

Higgins Loop technology is best suited for feed water containing 3,500 mg/L TDS and dominated by $NaHCO_3$ [143]. Emit Higgins Loop model 3012 is built on two skids with a total footprint of 220 ft^2, while the more popular model 6024 ships on three skids and has a total footprint of 450 ft^2 [145].System setup requires a large crane (shown in Figure 39), but is otherwise relatively mobile.

Figure 39. Installation of EMIT Higgins Loop system in the Powder River Basin (Source: [145]).

Electric power consumption is estimated between 4.96 to 12.4 kWh/kgal (0.21 to 0.52 kWh/bbl) [144]. Public data concerning operational costs is unavailable at this time, however this costs will likely be similar to conventional IX processes as described in Table 29. System life cycle and IX resin life are also not reported, however EMIT claims that the system is able to operate with greater than 98% runtime [143]. Field testing data shows that the Higgins Loop is able to achieve 98% reduction SAR values, but may not treat TDS to an acceptably low level for discharge of product water with current NPDES regulations [45, 143]. Further post-treatment may be necessary. A summary of the technical assessment for the EMIT Higgins Loop IX process is shown in Table 40.

Table 40. Summary of technical assessment of EMIT Higgins Loop IX process.

Criteria	**Description/Rationale**
Industrial status	18 installations currently treating CBM produced water in the Powder River Basin and Greater Green River Basin. EMIT systems are capable of treating 336,000 to 1,176,000 gpd (8,000 to 28,000 bpd).
Feed water quality bins	The reported optimal feed water quality for the process is a $NaHCO_3$ dominated feed with 3,500 mg/L TDS.
Product water quality	Treatment process permeate quality is dependent on feed water salinity and operating conditions. >97% rejection of Na is achievable, with additional removal of Mg, Ba, and HCO_3.
Production efficiency (recovery)	Product water recovery is dependent on IX resin regeneration needs, but recovery typically exceeds 99%.

Table 40. Summary of technical assessment of EMIT Higgins Loop IX process.

Criteria	Description/Rationale
Infrastructure considerations	This treatment process has operational footprint that varies from 220 ft^2 to 450 ft^2. System is reported to be skid based, and highly mobile.
Energy consumption	Energy requirements are estimated at 4.96 to 12.4 kWh/kgal (0.21 to 0.52 kWh/bbl).
Chemicals	Chemical cleaning rates depend on feed water quality and IX resin adsorptive capacity. Resin regeneration will typically occur after certain product water quality specifications are exceeded. The regenerant solution is composed of 4.11 M HCl. Additional chemical disinfection may be required to mitigate biofouling and will typically consist of H_2O_2 or NaOCl cleaning solutions.
Life cycle	Strong acid cation exchange resins may perform for 10 to 15 years [114].
O&M considerations	Monitoring and control required for flow rates, product water quality and resin regeneration. System will likely require minimal supervisory oversight. Level of flexibility: Low flexibility for treating feed water with alternative dominant feed solute or high organic loading. Level of robustness: IX processes are highly sensitive to fouling from organic materials and suspended solids. Care should be exercised to limit exposure of IX resin to oxidized metals and sparingly soluble mineral salts. Acid cation resins should not be exposed to feed temperatures in excess of 120 °C. Level of reliability: The Higgins Loop operates with an automated, short duration resin pulsing cycle to maintain IX resin productivity. Types of energy required: electrical.
Overall costs	Capital costs are unknown. Operations cost are most influenced by the market cost of HCl acid.
Pre-and post treatment	Process will require pretreatment options including suspended solids, oxidized metals, and scaling mineral removal. Product water may require pH stabilization or remineralization. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feedwater with product water. The concentrated feed stream may require additional post treatment or disposal consideration. Current practice is disposal by Class I or II injection wells.
Concentrate management or waste disposal	The spent resin regeneration solution will require neutralization. Relatively high recovery rates exceeding 99% generate very minor amounts of concentrated brine.
Applicability for produced water treatment	Excellent – Treatment well suited for specific feed water constituents (primarily $NaHCO_3$), and widely utilized in the Powder River Basin. Process requires substantial chemical input in the form of IX resin regenerant, and is best suited for centralized treatment in areas with good transportation infrastructure.
Note: 1 barrel = 42 US gallons	

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Drake: continuous selective IX process

Drake Water Technologies, LLC is a Montana based company that has developed a patented IX process with minimal waste production [146]. The Drake system is designed to perform targeted removal of monovalent cations, especially sodium for SAR reduction, and is designed as a three-phase, continuous fluidized bed system. Though it is not recorded explicitly, it is likely that the Drake system utilizes a strong acid cation exchange resin. A system schematic is shown in Figure 40. System design includes a continuous circuit for dosing (22), loading (42 – fluidized bed rector), separating (16), and regenerating (14) the ion exchange media. The system's primary patent claim is that it moderates resin and feed solution contact time by rotary valves (18 and 20) to reduce exchange of divalent ions.

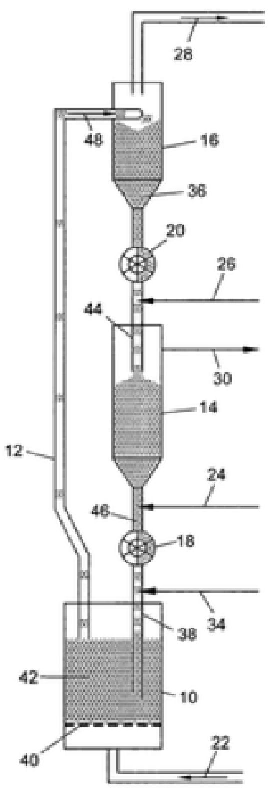

Figure 40. Drake: continuous selective IX process. Schematic taken from US patent [146].

The Drake system is in its third stage of pilot testing at a Willow Creek installation near Gillette, Wyoming in the Powder River Basin [147]. The third-generation Drake IX system is designed to treat 361,000 gpd (8,600 bpd) [144]. Pilot testing was conducted on a feed water with approximately 1,000 mg/L TDS; however, the process may be capable of treating water with marginally higher salinity. Recent pilot testing results indicate a sodium removal of 93%. System recovery is reported to be greater than 97% [147]. System reject is composed of highly concentrated Na_2SO_4, which may be dried and further concentrated in evaporation ponds to produce a commercial grade Na_2SO_4.

A Drake IX system is estimated to require two acres of surface area, which includes a one acre Na_2SO_4 collection impoundment [144]. The system may be deployed as small, modular shed that is capable of being towed on a trailer. In addition to a standard IX system, this process also requires two 16,800 gal (400 bbl) water tanks and a 4,400 gal (105 bbl) H_2SO_4 regenerant tank [147]. Pre-treatment technologies may be required to remove resin foulants from the raw water supply. Energy requirements are not explicitly stated, but are likely to be slightly less than that required for the EMIT Higgins Loop system. Additional operation and management considerations may be inferred from the overall operation of IX processes. A technical assessment for the Drake IX process is summarized in **Table 41**.

Table 41. Summary of technical assessment of the Drake IX process.

Criteria	Description/Rationale
Industrial status	Pilot scale operations for CBM produced water treatment in the Powder River Basin. The current Drake system is designed to treat 361,000 gpd (8,600 bpd).
Feed water quality bins	The system has been tested with 1,000 mg/L TDS feed water dominated by $NaHCO_3$.
Product water quality	Treatment process permeate quality is dependent on feed water salinity and operating conditions. 93% rejection of Na ions is reported.
Production efficiency (recovery)	Product water recovery is dependent on feed water quality and IX resin regeneration needs, but recovery with ideal feed water is reported as 97%.
Infrastructure considerations	This treatment process is reported to require a surface area of approximately 2 acres (87,000 ft^2). Individual systems may be highly mobile, however further construction may be necessary to provide increased protection from the elements.
Energy consumption	Energy requirements are minimal for most IX processes. No values are reported for the Drake system, but they may be inferred to be less than that required by the Higgins Loop.
Chemicals	Chemical cleaning rates depend on feed water quality and IX resin adsorptive capacity. H_2SO_4 regenerant is required to restore the IX resin's adsorptive capacity. Additional chemical disinfection may be required to mitigate biofouling and will typically consist of H_2O_2 or NaOCl cleaning solutions.
Life cycle	Cation exchange resins may perform for 10 to 15 years [114].
O&M considerations	Monitoring and control required for flow rates, product water quality and resin regeneration. System will likely require minimal supervisory oversight. Level of flexibility: System is optimized to remove Na ions, but will achieve moderate removal of divalent cations and metals. Level of robustness: IX processes are highly sensitive to fouling from organic materials and suspended solids. Care should be exercised to limit exposure of IX resin to oxidized metals and sparingly soluble mineral salts. Acid cation resins should not be exposed to feed temperatures in excess of 120 °C. Level of reliability: No information is provided on system up time. Types of energy required: electrical.
Overall costs	No data provided.

Table 41. Summary of technical assessment of the Drake IX process.

Criteria	Description/Rationale
Pre-and post treatment	Process will require pretreatment options including suspended solids, oxidized metals, and scaling mineral removal. Product water is not likely to require remineralization. It may be necessary to blend small amounts of filtered and sterilized feedwater with product water.
Concentrate management or waste disposal	Relatively high recovery rates exceeding 97% generate very minor amounts of concentrated brine. The concentrated Na_2SO_4 regenerant stream may be further concentrated to produce a commercial grade salt.
Applicability for produced water treatment	Excellent – Treatment well suited for specific applications, specifically feed water dominated by $NaHCO_3$. Process may require substantial chemical input in the form of IX resin regenerant, and may be best suited for centralized treatment in areas with good transportation infrastructure.
Note: 1 barrel = 42 US gallons	

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Eco-Tec: Recoflo® compressed-bed IX process

A Canadian based company, Eco-Tec Inc. has developed two compressed bed IX systems that offer lower operational footprint, faster regeneration, and increased throughput compared to conventional IX processes. The compressed bed systems are an extension of conventional packed bed IX processes. The Eco-Tec systems are differentiated by one system that has two separate compressed-bed columns for anion and cation removal, and a second system with three separate compressed-bed columns that contain a primary cation bed and anion bed followed by a polishing cation bed. The ion exchange resin employed by the Recoflo® process is composed of fine mesh resins that are reported to increase exchange kinetics [148, 149]. A photograph of the two-bed system is shown in **Figure 41**.

Figure 41. Eco-Tec Recoflo® compressed bed IX system. Of the two cylindrical beds pictured, one is loaded with cation exchange resin and the other with anion exchange resin. Each column houses 3 to 6 inches of ion exchange resin [148].

Eco-Tec Recoflo® systems have been employed to treat copper electrolyte solutions, recover nickel salts, recover metals from process solutions, and purify alternative fuels [150]. Recently, Eco-Tec was awarded a service contract for a Marathon installation in the Powder River Basin (WY) [151]. The system is designed to treat 1.5 MGD (36,000 bpd) produced water.

The Recoflo® system is designed to operate with a short duration run time of 30 minutes followed by a seven minute regeneration period. Eco-Tec claims that operating the system in this manner increases the access to most exchange sites on the resin, which increases exchange rates for both the IX and regeneration process [149]. The system requires both H_2SO_4 and NaOH to regenerate the cation and anion IX resins, respectively. Recoflo® compressed beds are more mobile than conventional IX processes and the Higgins Loop. A schematic of a full treatment train with two, skid-mounted three-bed systems operating in parallel is shown in **Figure 42**. A summary of the technical assessment for the Eco-Tec Recoflo® compressed-bed IX process is shown in Table 42.

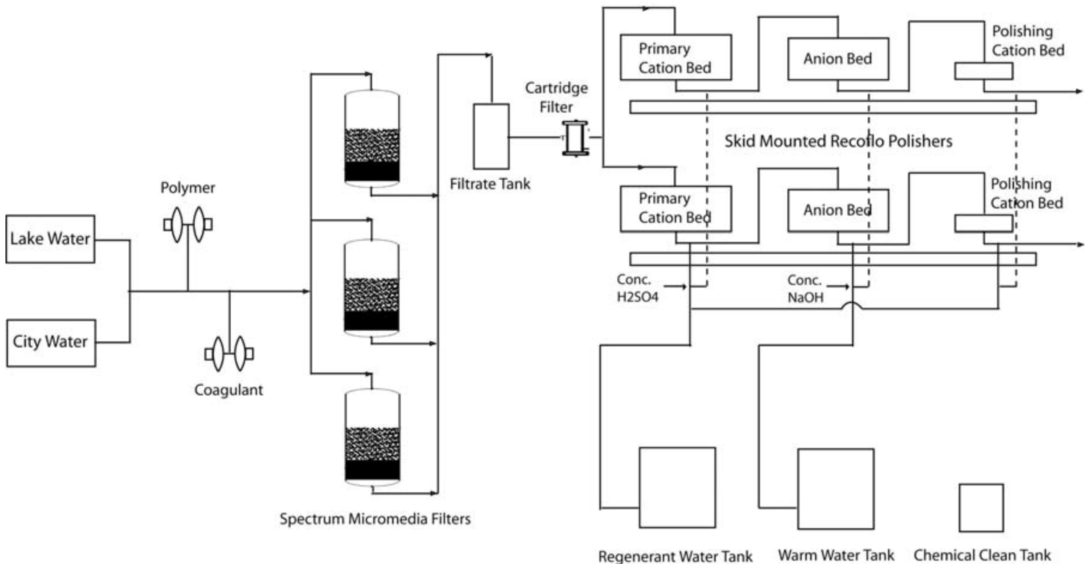

Figure 42. System schematic with two three-bed Eco-Tec Recoflo® process operating in parallel. Note that pretreatment is required to remove resin foulants from the feed stream [148].

Table 42. Summary of technical assessment of the Eco-Tec Recoflo® compressed-bed IX process.

Criteria	Description/Rationale
Industrial status	Pilot scale operations for CBM produced water treatment in the Powder River Basin. The current Eco-Tec system is designed to treat 1.5 Mgd (36,000 bpd).
Feed water quality bins	Current installations of the Eco-Tec system have been in the microelectronics industry. The system is utilized primarily as a polishing step for water that is already of high purity. No data is currently available on the CBM produced water that the system is operating with in the PRB.
Product water quality	Treatment process permeate quality is dependent on feed water salinity and operating conditions. >90% rejection of Na, Mg, Ca, and SO_4 ions is expected, in addition to significant metals removal.
Production efficiency (recovery)	No data is provided regarding overall process production efficiency.
Infrastructure considerations	Eco-Tec's Recoflo® system is designed to utilize a smaller operational footprint that conventional IX processes, however no data is available to specify the exact footprint of the system. Individual systems may be highly mobile; however, further construction may be necessary to provide increased protection from the elements.
Energy consumption	Energy requirements are minimal for most IX processes. No values are reported for the Eco-Tec system, but they may be inferred to be less than that required by the Higgins Loop.

Table 42. Summary of technical assessment of the Eco-Tec Recoflo® compressed-bed IX process.

Criteria	Description/Rationale
Chemicals	Chemical cleaning rates depend on feed water quality and IX resin adsorptive capacity. H_2SO_4 and NaOH regenerant solutions are required to restore the IX resin's adsorptive capacity. Additional chemical disinfection may be required to mitigate biofouling and will typically consist of H_2O_2 or NaOCl cleaning solutions.
Life cycle	Cation exchange resins may perform for 10 to 15 years, while anion exchange resins may last for only 4 to 8 years [114].
O&M considerations	Monitoring and control required for flow rates, product water quality and resin regeneration. System will likely require minimal supervisory oversight. Level of flexibility: Specifics on the treatment process' capabilities is unknown, however the system may require considerable IX resin regeneration for feed water with higher TDS. Level of robustness: IX processes are highly sensitive to fouling from organic materials and suspended solids. Care should be exercised to limit exposure of IX resin to oxidized metals and sparingly soluble mineral salts. Level of reliability: System is marketed with the stipulation of 30 minute on-stream followed by 7 minutes of regeneration. Types of energy required: electrical.
Overall costs	No data provided.
Pre-and post treatment	Process will require pretreatment options including suspended solids, oxidized metals, and scaling mineral removal. Product water is may require remineralization. It may be necessary to blend small amounts of filtered and sterilized feedwater with product water.
Concentrate management or waste disposal	IX processes tend to have high recovery, however the Eco-Tec system may have lower recovery due to its IX resin regeneration needs.
Applicability for produced water treatment	Excellent – Treatment well suited for specific applications, may provide exceptional post-treatment capabilities for selective ion removal (e.g., boron or radionuclides).
Note: 1 barrel = 42 US gallons	

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Catalyx Fluid Solutions/RGBL IX Process

RGBL acquired the rights to an IX process developed by Catalyx Fluid Solutions. The Catalyx system is a patented IX process that was designed to minimize waste during resin regeneration (wasting only 25-50% for each regeneration cycle) and rinse water according to manufacturer information [152]. The Catalyx system was designed for the removal of sodium (by ion exchange) and bicarbonate (through off gassing of CO_2), with the ion exchange chemical reaction:

$$Na^{+} + HCO_3^{-} + R_{H^{+}} \rightarrow R_{Na^{+}} + H_2O + CO_2 \uparrow$$

Waste minimization is facilitated by the use of three tanks that are responsible for shuffling regenerant and rinse waters of various qualities during IX resin regeneration cycles. During the onset of a regeneration cycle, acidic regenerant utilized from the previous regeneration cycle is first processed through the packed bed of resin in a counter-current direction and wasted. A second tank containing acidified rinse water from the previous regeneration cycle is then processed through the packed bed and recollected in the first tank. The third tank contains rinse (product) water, which is employed to flush any remaining regenerate out of the packed bed. Once the rinse water is processed through the IX bed it is collected in the second tank. The third tank is refilled with product water during normal operation of the system [152].

Only trivial technical literature, and no field piloting results are available to discuss the broader merits and limitations of this technology.

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Commercial Membrane Processes

CDM Produced Water Technology

CDM has developed a process for treating produced water containing TDS levels up to 20,000 mg/L. The technology is not specific for coal bed methane (CBM) produced water and has been pilot tested with tight sands produced water in the Piceance Basin and with CBM produced water in the Powder Rive Basin. CDM is also marketing the technology for treating flow-back water from subsurface hydraulic fracturing.

The treatment process is comprised of a train of different technologies in series to meet site-specific treatment goals (**Figure 43**). The specific processes included in the treatment train are dictated by the feed water quality and the desired product water quality. Some of the technologies that may be utilized include: advanced filtration, weak acid cation IX softener, UV disinfection, low pressure RO, antiscalant addition, seawater/high pressure RO, evaporation, and crystallization. The feed stream is kept anoxic to minimize oxidation of iron and other metals, and to reduce the fouling potential of the water. Depending on the feed water quality, the process can achieve more than 97% recovery. A computer program was developed that assists in selecting the required technologies and predicts the performance and scale formation within the system based on feed water quality.

The pretreatment for the process consists of media filers, and polymeric hollow fiber UF membranes to remove particulates, silt, oil, grease, coal fines, clay, and bacteria. The filtration system is backwashed using RO permeate. A weak acid cation (WAC) IX softener is used to reduce hardness and other metals. The resin is regenerated using hydrochloric acid. The water is then disinfected using UV. The calcium and magnesium-rich WAC regeneration solution is combined with the filter backwash and is either treated separately or combined with the product streams from the membrane processes and discharged, depending on the scenario and the feed water quality.

After pretreatment, low-pressure reverse osmosis (capable of achieving 85% recovery) is employed. The train size and type of membrane employed is tailored based on the feed water quality. An antiscalant (~10 mg/L) is added to the concentrate stream to stabilize the silica and to prevent scale formation in the next high-pressure RO stage. The second RO stage consists of high-pressure or seawater RO membranes that can achieve 80% water recovery. The RO permeate is combined with the low-pressure RO permeate for discharge or beneficial use. The concentrate, approximately 2 to 3% of the initial feed volume, is either disposed of as a waste, or can be treated for ZLD.

Because many produced waters contain high levels of sodium and low levels of divalent ions, the sodium adsorption ratio (SAR) may be too high even after treatment for the water to be put to beneficial use. In these cases, a limestone bed is used to add calcium to the water and lower the SAR.

Some produced water applications may require ZLD because brine disposal is not feasible or is too expensive. For ZLD applications, the concentrate from the second stage RO is fed to an evaporator. Evaporators are very energy intensive and therefore the energy for the evaporator can be obtained from natural gas waste heat from a compressor at the well field. The distillate from the evaporator is combined with the RO permeate streams for discharge or for other beneficial uses. The residuals from the evaporator can be either concentrated brine or solids. Depending on feed water quality and discharge permits, filter backwash stream and WAC regeneration brine can be blended with the product water streams (low and high pressure RO and evaporation) before discharge.

The CDM process has been pilot tested with CBM produced water feed from the Powder River Basin and with tight sands gas produced water from the Piceance Basin. The CBM produced water contained emulsified oil and grease, particulates, and silt. Sodium bicarbonate was the dominant salt. The tight sands gas produced water contained 438 mg/L oil and grease, and 119 mg/L silica. No operational data was available for either test site.

The following cost estimates were presented based on the pilot testing experience in the Powder River Basin: $0.14/bbl or $3.33/1000 gal (not including energy or brine disposal), $0.08/bbl or $1.90/1000 gal for brine disposal. Cost estimates were not provided for the pilot test on tight sands produced water.

The following water quality issues affecting pretreatment were identified: silt, suspended solids, oil coated particles, and coal fines. Water quality issues affecting the RO processes include: calcium harness, iron, barium, silica, and microbial fouling. CDM found that for CBM produced water, sodium bicarbonate solubility is the limiting factor for further increasing the system recovery. In order to accommodate changing water volumes, modular systems can be designed to treat volumes from 5,000 bbl/day (200,000 gpd or 145.8 gpm) to 20,000 bbl/day (840,000 gpd or 583 gpm) with additional units added or removed, as necessary. A technical assessment of the CDM process is summarized in Table 43.

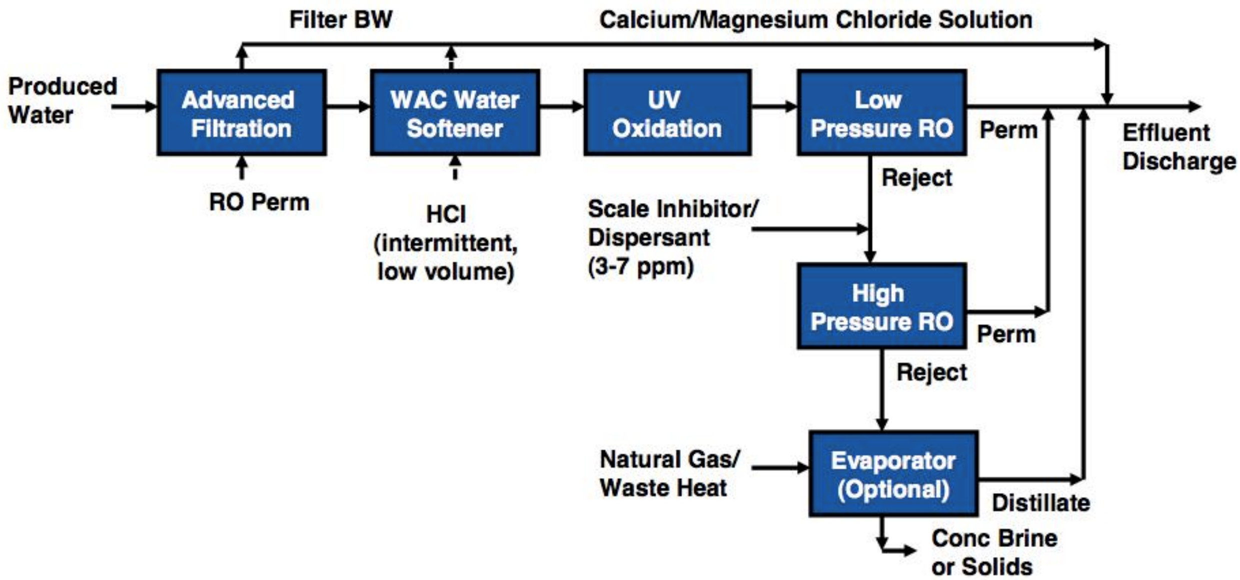

Figure 43. CDM produced water treatment technology: process diagram.
(http://ipec.utulsa.edu/Conf2008/Manuscripts%20&%20presentations%20received/Kimball_24.pdf).

Table 43. CDM Process Assessment.

Criteria	Description/Rationale
Status of technology	This process has been tested on a coal bed methane application in the Powder River Basin. It has also been tested on a tight sands water applications in the Piceance Basin. No commercial installations exist at the time of publication of this document.
Feed water quality bins	≤ 40,000 mg/L TDS.
Product water quality	The system can be tailored by adding and removing unit processes to meet different product water criteria.
Recovery	Depends on feed water quality and unit processes used. Water recovery may range from 50% to greater than 90%.
Energy use	Highly dependent on the number and type of unit processes used. No information available.
Chemicals use	Highly dependent on the number and type of unit processes used. No information available.
Expected lifetime of critical components	Membrane replacement will be necessary every 5 to 10 years depending on the applications. Other system components will have a life expectancy of 10 to 20 years.
Infrastructure considerations	The CDM process comes as a package solution. Site preparation is required.
O&M considerations	This process will most likely require large amounts of energy and chemicals.
Capital and O&M costs	None available. Contact manufacturer.
Pretreatment of feed water	The CDM process is designed to be a standalone technology that includes all necessary pretreatment technologies.
Post treatment of product water	The CDM process is designed to be a standalone technology that includes all necessary post treatment technologies.
Concentrate management or waste disposal	See fact sheets for individual processes. Waste depends on specific system components used.
Note: 1 barrel = 42 US gallons	

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Veolia Water Solutions and Technologies: OPUS™ – optimized pretreatment and separation technology

N.A. Water Systems, a Veolia Water Solutions and Technology company, designed the OPUS™ system. OPUS™ is a proprietary optimized pretreatment and unique separation process for desalination of water with high concentrations of sparingly soluble solutes (e.g., SiO_2, $CaSO_4$, and $Mg(OH)_2$), organics, and boron. The system is able to achieve high recovery with high purity product water through the use of extensive pretreatment processes prior to water contacting both IX and RO sub-systems. A system schematic is shown in Figure 44.

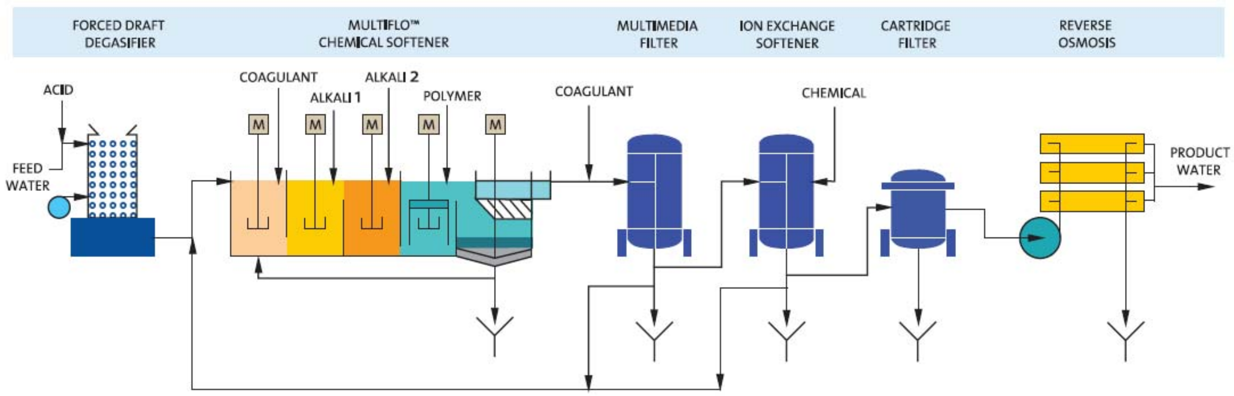

Figure 44. Process schematic of Veolia Water Solutions and Technologies: OPUS™ CBM produced water treatment system (Source: [153]).

The process first performs acidification and degasification of the raw feed water. This is followed by an aggressive, conventional coagulation, flocculation, and high-rate plate settler sedimentation process, which is termed Multiflo™ chemical softening in the OPUS™ literature [153]. After this step, the feed stream should be devoid of nearly all high-molecular-weight organic molecules and oxidized metals (particularly iron and manganese). Additionally, colloidal silica is partially removed by co-precipitation. Decant from the sedimentation basin is then filtered by a packed-bed media filtration column, which removes any microflocs and most suspended solids that did not settle out in the plate settlers. The media filter may also achieve additional removal of low to medium molecular weight hydrophobic organic molecules, including any remaining oil and grease.

Filtrate from the media filter is then processed through a mixed, packed-bed IX column for further water softening and removal of microorganisms. A cartridge filter is then employed to remove any IX resin or any remaining suspended solids prior to contact with the RO membranes. The water is then pressurized and treated by BWRO membranes at an elevated pH. Operating the RO elements under this condition reduces the fouling propensity of silica and increases the rejection of both silica and boron.

In April of 2008 the OPUS™ system was field tested at a steam-enhanced oil production site in San Ardo, CA. The tested OPUS™ system was designed to treat 2.1 MGD (50,000 bpd) of water with high boron, silica, and organics concentrations [154]. Water recovery for the OPUS™ is described by the manufacturer as high, and may be equivalent to that of other high recovery RO systems that operate with elevated pH. OPUS™ product literature indicates removals for TDS of 99.6%, TOC of 99%, silica of 99.9%, and boron of 99.4% [154]. Sodium removal is not indicated, however it may be considered similar to that for BWRO processes.

The product literature makes little mention of system mobility; however, it is possible that the entire system could fit in several cargo trailers. No data is provided on the system footprint or energy consumption. The Mutliflo™ pretreatment component requires significant chemical input in the form of acids (possibly HCl or H_2SO_4), coagulants (potential chemicals include $Fe_2(SO_4)_3$ and Alum), alkali compounds (likely $Ca(OH)_2$), and polymer aids (candidates include polyDADMAC or PAC) [110]. Additional chemical demand is created by the IX regenerant solution that may require both acid and base regenerants, as well as base chemicals required to increase the pH of the RO feed water.

OPUS™ literature does not present a life cycle assessment of the system; however, BWRO membranes are known to have a 3 to 7 year lifespan and IX resin typically requires replacement after 5 to 10 years [36, 114]. The OPUS™ system likely requires substantial process automation and control. Moderate operator oversight may be required, especially for management of the Multiflo™ pretreatment system.

OPUS™ represents a highly flexible and robust treatment process and can operate with highly variable feed water quality. With proper management the system likely requires minimal down time and maintenance. Cost figures related to capital, and operating costs are not reported. The system generates concentrated brine and IX regenerant that require disposal and may require chemical stabilization. Sludge is generated during the pretreatment process and requires disposal in landfills. A technical assessment of the Veolia Water Solutions and Technologies: OPUS™ – optimized pretreatment and separation technology is summarized in Table 44.

Table 44. Summary of technical assessment for Veolia Water Solutions and Technologies: OPUS™ – optimized pretreatment and separation technology.

Criteria	Description/Rationale
Industrial status	System has undergone field trials at a steam-enhanced oil production field in San Ardo, CA.
Feed water quality bins	The estimated TDS application range is between 500 mg/L and 10,000 mg/L. High removals of monovalent and divalent ions, metals, and organics is expected. System is likely to achieve additional silica and boron removal with high pH operation.
Product water quality	Treatment process permeate quality is dependent on feed water salinity and operating conditions. Product literature reports >99% rejection of TDS and most multivalent solutes. System is likely to achieve >94% removal of Na based on typical BWRO performance.
Production efficiency (recovery)	Product water recovery is estimated to exceed 90%.
Infrastructure considerations	This treatment process will require a substantially larger footprint that conventional RO or IX systems. Substantial chemical storage and sludge dewatering facilities will be required. System mobility is reduced compared to conventional RO systems. Mutliflo™ pretreatment process along with chemical storage components is the primary factors in limiting mobility.
Energy consumption	Energy requirements are unknown.

Table 44. Summary of technical assessment for Veolia Water Solutions and Technologies: OPUS™ – optimized pretreatment and separation technology.

Criteria	**Description/Rationale**
Chemicals	Multiflo™ pretreatment system will require multiple chemical compounds to operate and include acids, bases, hydrolyzing metal coagulants, and polymer based coagulants. Examples of these chemicals are provided in the main body of this report. Chemical cleaning rates depend on feed water quality. Cleaning will typically occur after certain design specifications are exceeded, and may require the use of NaOH, Na_4EDTA, or HCl. IX process will require regeneration with strong acid, likely H_2SO_4 or HCl.
Life cycle	No data is currently available.
O&M considerations	Substantial monitoring and control required for flow rates, chemical dosing, IX regeneration, and RO element pressure. System may require moderate oversight to ensure proper operation of the primary RO stage brine management systems. Level of flexibility: Highly flexible system that may readily adapt to changes in feed water quality. Level of robustness: TFC membranes have high pH tolerance, but cannot be exposed to feed temperatures in excess of 113 °F (45 °C). Level of reliability: RO and IX systems operate semi-continuously with automated, short duration chemical rinses or osmotic backwashing cycles (for RO). Types of energy required: electrical.
Overall costs	Capital costs are unknown.
Pre-and post treatment	Product water will require pH stabilization or remineralization. This may be achieved by lime bed contacting or by blending small amounts of filtered and sterilized feed water with permeate.
Concentrate management or waste disposal	No special concentrate treatment is required. Relatively high recovery rates exceeding 90% generate very minor amounts of concentrated brine. Sludge from the sedimentation basin will require dewatering and landfill application.
Applicability for produced water treatment	Excellent – Treatment provides robust pretreatment to limit foulant loading on high-pressure membranes.
Note: 1 barrel = 42 US gallons	

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New Logic Research: V✧SEP® - Vibratory Shear Enhanced Membrane Filtration

The patented V✧SEP® technique was developed by New Logic International in California. The V✧SEP® membrane filter pack consists of leaf elements arrayed as parallel discs and separated by gaskets. The shear waves produced by the membrane vibration cause solids and foulants to be lifted off the membrane surface and remixed with the bulk material flowing through the membrane stack (Figure 45). This high shear processing exposes the membrane pores for maximum throughput that is typically between 3 and 10 times the throughput of conventional cross-flow systems [155]. Compared to conventional RO systems, V✧SEP® is not limited by the solubility of minerals or the presence of suspended solids. It can be used in the same applications as crystallizers or brine concentrators and is capable of high water recoveries of up to 90% [156]. The V✧SEP® system can be configured to employ either RO or NF membranes in a single-stage or multiple-stage arrangement. The configuration depends on feed water quality, water quality goals of the V✧SEP® permeate, and targeted water recovery.

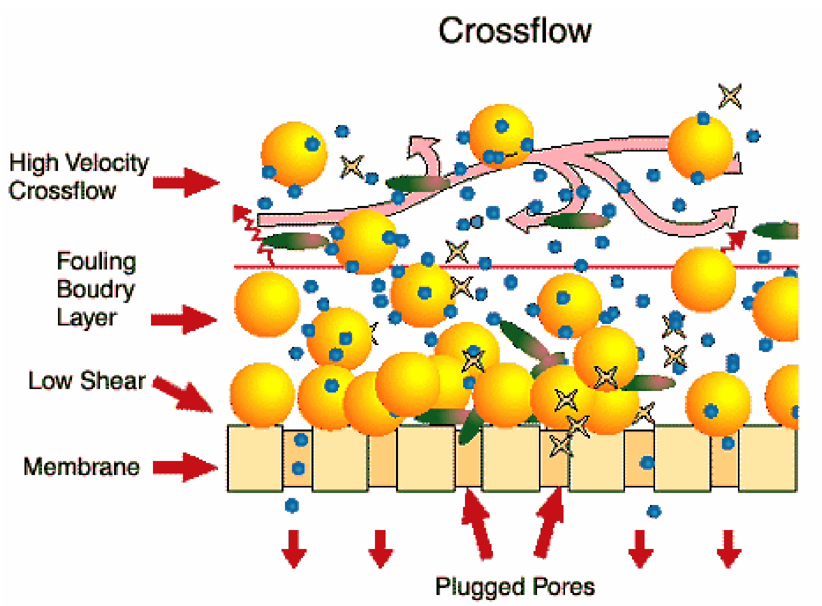

Figure 45. Fouling reduction mechanisms of V✧SEP® (Source: [155]).

The manufacturer claims that the V✧SEP® process has several advantages over conventional membrane process [157]. These include:

- Minimal pretreatment: Because of high shearing energy at the membrane surface and near the pores, colloidal fouling and concentration polarization are greatly reduced. The use of pretreatment to prevent scale formation is not required.
- Low fouling and scaling potential: Sinusoidal shear waves from the membrane surface help to repel approaching particles and colloids; thus, reduce fouling and scaling potential.
- High permeate flux: The throughput rates of V✧SEP® are 5-15 times higher. The sinusoidal shear waves propagating from the membrane surface act to hold suspended particles above the membrane surface allowing free transport of the liquid through the membrane.

- Low energy consumption: High flux, and minimized membrane scaling and fouling make V✧SEP® very energy efficient (0.27 kWh/kgal filtrate).
- Small footprint: The V✧SEP® membrane system has a vertical plate-and-frame configuration, where hundreds of membrane leafs are stacked on top of each other. This results in a very small horizontal footprint of the unit. As much as 2000 square feet (185 m^2) of membrane is contained in one V✧SEP® module with a footprint of 4x4 ft.

The combined advantages make V✧SEP® an attractive technology for treatment of produced water. New Logic has been testing V✧SEP® for produced water treatment - both onshore and offshore. Test were conducted in California, the North Sea, Latin America, and Alberta's Oil Sands [158]. Several produced water projects are listed in Table 45.

Table 45. V✧SEP® produced water projects.

Produced water type	Location	MGD	bbl/day
CBM Produced Water	Utah	0.72	17143
Offshore Produced Water	Santa Maria, CA	0.86	20571
Oil Produced Water	Santa Maria, CA	0.22	5143
Oil Produced Water	Bakersfield, CA	12.24	291429
Produced Water	Kuwait	1.44	34286
Offshore Produced Water	Peru	0.05	1200
Note: 1 barrel = 42 US gallons			

In 2006, the first full-scale V✧SEP® system was selected to create steam quality water from oilfield produced brine at a BreitBurn Energy facility in Santa Barbara, California. BreitBurn implements steam flooding in the process and is using steam generators in the operations to enhance oil production. Re-injection of produced water into the source formations was the method of disposal. After on-site trials, BreitBurn determined that the V✧SEP® system provided a cost-effective solution capable of removing the contaminants and providing the needed boiler feed water; thus, eliminating the need for expensive pretreatment and chemical usage.

The BreitBurn produced water is high in alkalinity, silica, sodium, carbonate, and TOC. The feed to the VSEP® contains 25,900 mg/L TDS and 870 mg/L hardness. The TOC was mostly made up of paraffins, waxes, and asphaltenes that are colloidal materials that do not readily separate using conventional methods. Asphaltenes tend to adsorb at water-in-crude oil interfaced to form a rigid film surrounding the interface. A schematic drawing of the BreitBurn treatment process is shown in Figure 46. The treatment employs both NF and RO membranes. The final permeate, after two stages of filtration, has a non-detectable concentrations of hardness and water quality that is suitable for boiler feed water. The V✧SEP® process achieved an overall recovery of 70% of the oil produced water as clean boiler feed water.

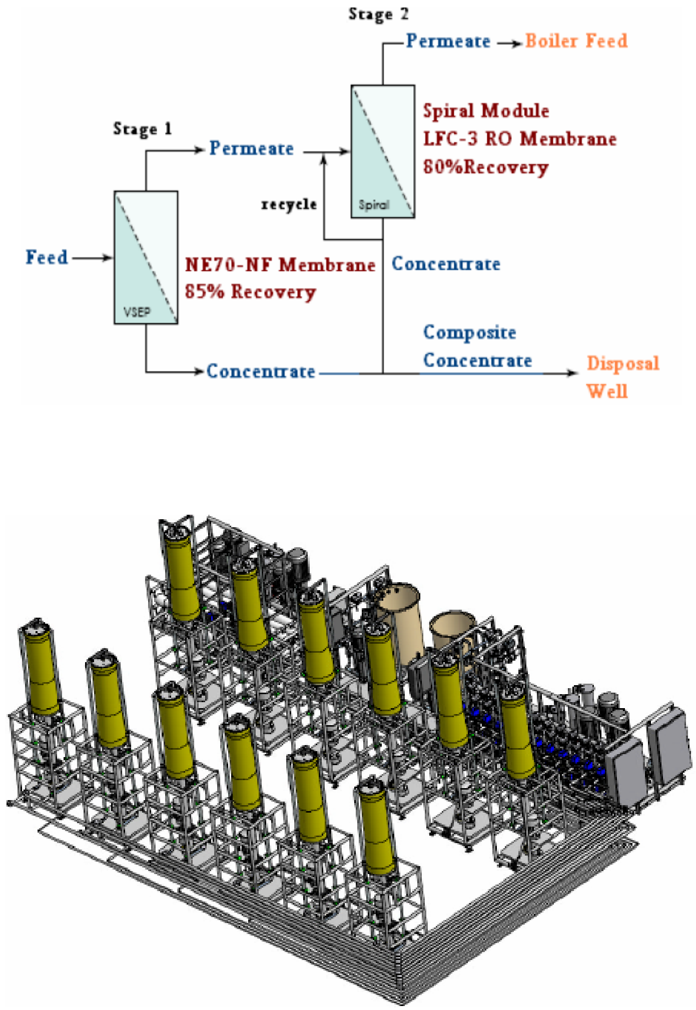

Figure 46. Schematic of the BreitBurn treatment process of oil produced water.

The V✧SEP® process has proven effective in treating high solids water. The V✧SEP® may not be economical for CBM produced water that has less solids and can be treated by conventional membrane processes. A technical assessment of the V✧SEP® treatment process is summarized in Table 46. Data is based on the information provided on the website of the manufacturer.

Table 46. Summary of technical assessment of V✧SEP® process.

Criteria	Description/Rationale
Industrial status	Full-scale application for produced water treatment (offshore and onshore)
Feed water quality bins	Applicable to TDS <30,000 mg/L, and a broad variety of water chemistry makeup.
Product water quality	Similar to other membrane technology, product water quality depends on the molecular cut-off of the membrane. High water quality can be expected by using RO membranes.
Production efficiency (recovery)	Product water recovery is between 70 and 90%, depending on feed water quality.
Infrastructure considerations	Require up to 17' in ceiling clearance. The V✧SEP® units are vertical and compact. The footprint of a 2000 SF of membrane unit is 4'x4', and can be installed into a container with a volume of about 15 Cubic Feet. Require gas or electricity as power.
Energy consumption	The energy consumption is low, and reported 0.27 kWh/kgal of product water [157].
Chemicals	No chemical requirement for pretreatment. Chemicals are required for membrane cleaning.
Life cycle	As an emerging technology, no life cycle is reported. Due to high sheer force, shorter membrane lifetime may be expected as compared to conventional membranes.
O&M considerations	High level of monitoring and control required. High level of skilled labor required to operate V✧SEP® process. High level of flexibility: easy to adapt to highly varying water quality and quantity. The level of robustness and reliability need to be demonstrated through long-term operation. Types of energy required: electricity.
Overall costs	The capital and construction costs of V✧SEP® are site specific. For produced water/bilge water treatment, the V✧SEP® system power consumption is estimated $0.31/kgal (based on 0.05 $/kWh electricity cost); the system maintenance & cleaning is about $0.37/kgal [157].
Pre-and post treatment	No or minimal pre-treatment such as settling, prescreen, or cartridge filtration to remove suspended solids and organic matter. Depending on product water quality, remineralization or blending may be required.
Concentrate management or waste disposal	The brine stream needs transported off the well site and disposal.
Applicability in produced water treatment	Excellent technology for the produced water application, may not be economical for CBM water application due to high energy consumption and less solids in water.
Note: 1 barrel = 42 US gallons	

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Eco-Sphere: Ozonix™

Eco-Sphere has developed a semi-truck trailer-mounted, advanced oxidation system that is primarily marketed for the treatment and reuse of frac flow-back water, but may have merit for oil and gas produced water treatment. The packaged system first employs settling tanks and a large mesh particle filter to screen out particles and large suspended solids, respectively. Decanted feed water is then pumped into a reaction vessel and is flash mixed with supersaturated ozonated water. The ozone is decomposed into hydroxyl radicals by ultrasonic transducers, which readily oxidizes metals, decomposes soluble and insoluble organic compounds and microorganisms. Ultrasonic transducers also induce cavitations among the dissolved ozone bubbles, which act to induce shearing of larger particles and decreases particle flotation times. The reaction vessel also employs two electrodes to facilitate precipitation of hard salts from the influent. Aluminum sulfate is then dosed into the solution to facilitate particle coagulation. The ozonated, coagulated water is then passed through a centrifuge to remove all oxidized material. Activated carbon cartridge filter are then utilized to remove any remaining organic compounds or suspended solids from the solution. RO membranes are employed as a final step to remove monovalent and divalent inorganic solutes [159, 160].

A proof-of-concept pilot study was conducted with the Ozonix™ system in the Woodford Shale Play in November of 2008 [160]. Newfield Exploration Mid-Continent, Inc. tested the process on frac flowback water from a field near Coalgate, OK. The frac flowback water was characterized as having an influent TDS of 14,000 mg/L (dominated by chloride, sodium, and potassium), TSS constituting of 65 mg/L, TOC of 65 mg/L, total oil and grease of 14 mg/L, barium concentration of 35 mg/L, total BTEX of 38 µg/L, and radionuclide counts (reported as gross alpha) of 264 pCi/L. The system was housed in a large mobile trailer and was used to treat 100 bph (4,200 gph) of frac flowback water for 12-14 hours per day for two weeks. A third party consultant group was hired to provide quality assurance and quality control for the study. A 220 kW electrical energy generator was utilized to power the system during field trials. Assuming a 13-hour workday, this equates to 2,860 kWh of energy consumed to treat 1,300 bbl (54.6 kgal) of water. Based on these calculations, the specific energy consumption per bbl of water treated is 2.2 kWh/bbl (52 kWh/kgal). The manufacturer claims that purified water recovery may exceed 75%, and only 1% of the initial bulk volume needing disposal. The resulting waste stream is likely disposed of in class I or II injection wells. No mention is made of solids disposal issues related to the initial solids separation and centrifuge processes. Chemical requirements are reported to include aluminum sulfate and antiscalant. The pilot system required three people to operate; however, the manufacturer estimates that only two operators would be required with further process automation. A technical assessment of the Ozonix treatment process is summarized in Table 47.

Table 47. Summary of technical assessment for Eco-Sphere: Ozonix™ process.

Criteria	**Description/Rationale**
Industrial status	Pilot scale study with frac water flowback in the Woodford Shale Play of eastern Oklahoma. System piloted for 2 weeks and treated 4,200 gph (100 pbd).
Feed water quality bins	System was tested with highly challenging feed water. TDS of 14,000 mg/L, presence of dispersed oils, over 1,000 mg/L of total hardness, and presence of barium.
Product water quality	Pilot study reports 99.1% TDS rejection, and 97% removal of BTEX compounds.

Table 47. Summary of technical assessment for Eco-Sphere: Ozonix™ process.

Criteria	Description/Rationale
Production efficiency (recovery)	Pilot study reports purified water recovery approaching 75%. Vendor claims a 1% waste stream for disposal, with the rest of the solution being retained for reuse as frac water.
Infrastructure considerations	Operational footprint of pilot study system is reported as being 'roughly' the size of a frac tank.
Energy consumption	The energy consumption is estimated at 52 kWh/kgal (2.2 kWh/bbl)
Chemicals	Chemical requirements include aluminum sulfate for coagulation and scale inhibitors for RO subsystem.
Life cycle	Life cycle information is not yet available.
O&M considerations	Commercial system is expected to require two-fulltime operators. High level of flexibility: easily adapts to highly varying water quality and quantity. Highly robust pretreatment process. Reliability needs to be demonstrated through long-term operation. Types of energy required: electrical.
Overall costs	Operational and capitol costs are not specified by vendor.
Pre-and post treatment	All pretreatment requirements are already integrated into the system. Remineralization and water stabilization may be required for RO permeate stream.
Concentrate management or waste disposal	Any remaining brine stream will require disposal through injection.
Applicability for produced water treatment	Excellent – Treatment provides robust pretreatment to limit organic and hard salt loading on high-pressure membranes.
Note: 1 barrel = 42 US gallons	

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GeoPure Water Technologies, LLC

The GeoPure desalination process is a combination of pre-treatment, UF, and RO. These three treatment steps are operated in series to treat a wide range of produced water compositions and produce clean water that may then be discharged or reused. This technology was specifically developed for the desalination of oil and gas produced waters. Pilot scale systems have been tested in Texas A&M laboratories and at 12 field locations throughout Texas. The manufacturer [161] claims to have purified produced waters containing up to 50,000 mg/L TDS, but does not cite any specific studies. Depending on raw water quality, this process employs various pretreatment processes to remove dispersed oil, suspended solids, or dissolved hydrocarbons. The pretreated water is then further purified with polymeric UF and RO. The UF system provides a final barrier to suspended solids (such as colloids) prior to the RO subsystem.

GeoPure Water Technologies, LLC performed a field test of its commercial desalination unit in the Barnett Shale Play of central Texas in 2006 [162, 163]. In this field trial, frac flowback water was treated at a feed rate of 210,000 gpd (5,000 bpd). The feed water from this field trial also contained 4,200 mg/L TSS, 170 mg/L Fe, and 940 mg/L Ba. After coagulation/flocculation, the water was treated with GeoPure's UF and RO units. Influent and RO permeate TDS concentrations were 15,000 and 190 mg/L, respectively, corresponding to 98.7% TDS rejection. When including the coagulation/flocculation pretreatment process, total treatment costs were estimated to average $0.94 per barrel.

A second field trial was conducted at a CBM well field in Western Wyoming [162, 164]. The GeoPure treatment process was tested with CBM produced water containing corrosion inhibitor, alcohols, and surfactants. Other feed water parameters include a feed TDS of 9,700 mg/L (dominated by NaCl) and 41 mg/L of dissolved hydrocarbons. 99% rejection of TDS was achieved. No electrical or other cost information was provided from this study.

GeoPure focuses on optimizing pretreatment technologies to protect its core UF/RO treatment processes from membrane foulants (especially dispersed oils). A technical assessment of the GeoPure treatment process is summarized in Table 48.

Table 48. Summary of technical assessment for GeoPure Water Technologies, LLC.

Criteria	**Description/Rationale**
Industrial status	Oil and natural gas related field trials have reportedly been conducted at 12 sites. Two summary documents from field trial experiences with frac flowback water in Texas and CBM produced water in Wyoming were located.
Feed water quality bins	The vendor reports treating water in excess of 50,000 mg/L TDS. Available field trial reports report treating water with TDS ranging from 9,700 to 15,000 mg/L. Frac flowback water constituted high concentrations of barium, dissolved hydrocarbons, and iron.
Product water quality	98-99% rejection of TDS was reported in available field-testing reports.
Production efficiency (recovery)	Product water recovery in one field test was reported to be 50%. 60-70% recovery is estimated for feed water of 7,000 and 17,000 ppm chlorides, respectively.

Table 48. Summary of technical assessment for GeoPure Water Technologies, LLC.

Criteria	**Description/Rationale**
Infrastructure considerations	Depending on the type of pretreatment needed, foot print size will vary. The average footprint will be larger than typical RO system on account of pretreatment needs such as chemical storage and settling basin for coagulation/flocculation. System mobility is reduced compared to conventional RO systems. Coagulation/flocculation is a contributing factor to lack of mobility.
Energy consumption	Energy consumption was not report for this system.
Chemicals	Chemical such as Alum or $FeCl_3$ or similar coagulants may be necessary for pretreatment. RO system may require scale inhibitor. Also, chemicals necessary for membrane cleaning would be similar to those reported previously for RO and UF.
Life cycle	No data is currently available
O&M considerations	System employs standard automation for RO and UF systems. System may require moderate oversight to ensure proper operation of the coagulation/flocculation sludge and RO brine management systems. Level of flexibility: Able to adapt to various feed water types on account of pretreatment options. Level of robustness: 60-day field test of semi-continuous operation showed no permanent fouling of the membranes. Level of reliability: UF and RO systems operate semi-continuously with automated, short duration chemical rinses or osmotic backwashing (for RO). Types of energy required: electrical.
Overall costs	Capital costs are unpublished, while operation and management costs for the Barnett Shale Trend study seen above were found to be $0.94/bbl.
Pre-and post treatment	pH adjustment and remineralization may be required.
Concentrate management or waste disposal	Concentrate treatment is required on account of relatively low recovery rate. Sludge from the sedimentation basin will require dewatering and landfill application.
Applicability for produced water treatment	Excellent – Multiple pretreatment options provide system with considerable flexibility.
Note: 1 barrel = 42 US gallons	

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Geo-Processors: Sal-Proc™, ROSP, and SEPCON

Sal-Proc™, linked RO – Sal-Proc (ROSP), and Saline Effluent to Products Conversion (SEPCON) are all treatment technologies developed by Geo-Processors USA, Inc. The Sal-Proc™ technology is at the heart of both ROSP and SEPCON systems, and is a patented technology. The process was designed to facilitate the sequential or selective precipitation and extraction of specific dissolved chemical compounds and salts from saline waters. Depending on the chemical composition of the saline feed stream, the process combines well established chemical reactions and process engineering with evapo-cooling and crystallization steps for selective salt recovery. A simplified flow diagram of this process is shown in **Figure 47**.

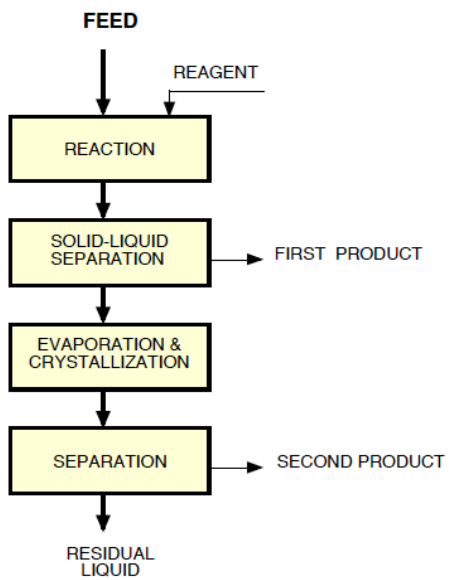

Figure 47: Process flow of Sal-Proc™ system (Source: [165]).

The final product of the Sal-Proc™ system is a refined chemical salt that may have commercial value; depending on feed water quality these salts may include $CaSO_4$, $Mg(OH)_2$, NaCl, $CaCl_2$, NaOH, $CaCO_3$, and Na_2CO_3 [166].

When the Sal-Proc technology is integrated with a RO treatment system, the combined system is termed ROSP. The combination of these processes enables the conversion of saline impaired water into fresh water and useful chemical compounds. ROSP systems may employ Sal-Proc™ as a pretreatment process for removal of sparingly soluble salts prior to contact with the RO membrane, or as post treatment to reduce brine disposal volume and cost [165].

Saline Effluent to Products Conversion (SEPCON) facilities are defined by Geo-Processors USA, Inc. as any installation that utilizes Sal-Proc™, or by natural extension, ROSP subsystems as part of their brine management strategy. A SEPCON demonstration and testing facility is currently under construction in California (2009). SEPCON systems are expected to have reduced operating costs with increased feed water throughput [165]. The number of possible system configurations that could utilize a Sal-Proc™ subsystem is too numerous to list; therefore, the remainder of this technology's technical summary focuses on the stand-alone Sal-Proc™ process.

The Sal-Proc™ system has undergone a sustained period of development and improvements including field trials, piloting, and public demonstrations. Sal-Proc™ systems have been employed at various installations with treatment capacities between 217,151 to 2,111,000 gpd (5,170 to 50,250 bpd). The Sal-Proc™ system has been tested on TDS concentrations ranging from 7,500 to 82,000 mg/L [165]. Silica crystallization and removal is not mentioned in any of the literature on the Sal-Proc™ technology, which may indicate that the system is not designed to treat silica-saturated water.

Designed to facilitate zero liquid discharge of concentrated saline brines, the Sal-Proc™ process has a theoretical recovery of 100%. However, the final 15% of water removed from a feed solution are not likely to be captured for beneficial use. Infrastructure requirements for Sal-Proc™ systems may be relatively high, and will likely require significant footprint to accommodate chemical reagent storage and product salt storage. The Sal-Proc™ is relatively mobile, and may be constructed to operate out of a cargo trailer. Sal-Proc™ is designed to be highly modular and readily integrated into other unit processes.

Energy requirements for the Sal-Proc™ system are unspecified. However, available data indicates that the system has a capital cost ranging from $2.3/gpd to $22.1/gpd ($96/bpd to $928/bpd), and an operations and management cost of roughly $3.9/kgal to $13.9/kgal ($0.16/bbl to $0.58/bbl) [165]. The literature does not provide any indication of serviceable lifetime for the process. This proprietary process requires chemical reagents to produce saleable salts, however the exact nature of these reagents is not reported with the exception of $Ca(OH)_2$ [167]. The process may also require cleaning chemicals, however no reference is made to this affect in the literature. Extensive monitoring and operator oversight may be required to optimize reagent dosing and recovered salt management. Minimal pretreatment is required to remove organic constituents and any micro constituents that may adversely effect the generation of saleable salts from the system. A summary of the technical assessment for the Sal-Proc™ process is shown in Table 49.

Table 49. Summary of technical assessment of Sal-Proc™ process.

Criteria	**Description/Rationale**
Industrial status	Full-scale application for produced water treatment in Queensland, Australia. System produces 21,600 tons of saleable chemicals per year [165].
Feed water quality bins	Applicable to TDS >7,500 mg/L.
Product water quality	As recovery is pushed towards zero liquid discharge (100%) the product water will become difficult to recover for beneficial use and of low quality.
Production efficiency (recovery)	Theoretical recovery is 100%.
Infrastructure considerations	Operational footprint may be relatively large to accommodate for chemical reagent and product chemical storage, as well as cleaning chemical storage. Individual Sal-Proc™ units may require a relatively low footprint equivalent to a cargo container.
Energy consumption	The energy consumption is currently unknown.
Chemicals	Chemicals may be required for pretreatment. SARO systems will likely require antiscalants. Chemical reagents, particularly $Ca(OH)_2$, required to facilitate chemical crystallization create significant chemical demand.
Life cycle	As an emerging technology, life cycle information is not yet available.
O&M considerations	High level of monitoring and control required. High level of skilled labor required to operate Sal-Proc™ process. High level of flexibility: easy to adapt to highly varying water quality and quantity. Highly robust process. Reliability needs to be demonstrated through long-term operation. Types of energy required: electrical.
Overall costs	The capital and construction costs of Sal-Proc™ systems are site specific. Cost estimates for capital cost of this process are $2.3/gpd to $22.1/gpd ($96/bpd to $928/bpd), and operations and management cost are roughly $3.9/kgal to $13.9/kgal ($0.16/bbl to $0.58/bbl).
Pre-and post treatment	No or minimal pre-treatment such as settling, prescreen, or cartridge filtration to remove suspended solids and organic matter. Salts may be selectively removed from the feed solution to produce water quality suitable for surface discharge.
Concentrate management or waste disposal	Any remaining brine stream will require disposal through injection.
Applicability for produced water treatment	Excellent – Capable of near zero liquid discharge operation, and may produce a marketable salt from the concentrated brine. Large chemical demand may limit application to centralized treatment facilities.
Note: 1 barrel = 42 US gallons	

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Post-treatment and Miscellaneous Treatment

SAR and Other Nutritious Minerals Adjustment

Some produced water and/or treated water such as RO product water have high sodium and low calcium and magnesium concentrations. High sodium concentrations in waters reduce the permeability of clay-bearing soil and adversely affect the soil structure. Water that lack secondary macronutrients such as calcium, magnesium, and sulfate can cause deficiency symptoms in crops that may need remediation by fertilization. Therefore, the water has to be properly treated to prevent adverse effects to distribution systems, soils, and crops.

Sodium adsorption ratio (SAR), along with pH, characterizes salt-affected soils. It is an easily measured property that gives information on the comparative concentrations of sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) in soil solutions. SAR is calculated using the following equation:

$$SAR = \frac{Na^+ (meq/L)}{\sqrt{\frac{(Ca^{2+} + Mg^{2+})(meq/L)}{2}}}$$

When the SAR rises above 12 to 15, serious physical soil problems arise and plants have difficulty absorbing water. **Table 50** and **Table 51** provide specific information on tolerance of plants and soils to SAR.

Table 50. Plants tolerance to SAR.

Tolerance	SAR of irrigation water	Crop
Very sensitive	2-8	Fruits, nuts, citrus, avocat
Sensitive	8-18	Beans
Moderately tolerant	18-46	Clover, oats, rice
Tolerant	46-102	Wheat, barley, tomatoes, beets, tall wheat grass, crested grass

Source: Extracted from the Australian Water Quality Guidelines for Fresh & Marine Waters (ANZECC)

Table 51. SAR Hazard of irrigation water

	SAR	Notes
None	< 3.0	No restriction on the use of recycled water
Slight to moderate	3.0 - 9.0	From 3 to 6 care should be taken to sensitive crops. From 6 to 8 gypsum should be used. Not sensitive crops. Soils should be sampled and tested every 1 or 2 years to determine whether the water is causing a sodium increase
Acute	> 9.0	Severe damage. Unsuitable.

High SAR water can be blended with other source waters for remineralization. There are also a variety of treatment methods that can be used to add hardness back to desalinated water [102]; these may include addition of lime or contact filtration through limestone (calcite or dolomite) filters. The addition of slaked lime (calcium hydroxide) to produced water can provide calcium and alkalinity (i.e., hydroxide alkalinity) as well as to adjust product water pH. When adding lime to water, it is important to consider that the solubility of calcium carbonate depends on pH, temperature, and ionic strength. Lime may not dissolve easily and may cause residual turbidity, which is a disadvantage of this approach.

It should be noted that adding calcium and magnesium to produced water does not reduce sodium, but changes the ratio of sodium to other salts. Although the SAR is decreased by adding hardness, the produced water becomes more saline with the sodium salt still dissolved in the water. This approach is not likely to work with CBM product water that is sodium bicarbonate type. The added hardness (calcium) will combine with carbonate from the CBM water and precipitate out as calcium carbonate (lime).

SAR treatment may require the addition of acid (e.g., H_2SO_4) to help degassing carbonate and dissolve the lime and produce the desired hardness concentration. Warm water however can slow down the rate of lime dissolution. This method is commonly used to add hardness and alkalinity to water to make it more stable and for corrosion protection.

Besides SAR adjustment of produced water, land irrigated by high SAR produced water can be treated with gypsum and other soil supplements between irrigation cycles (e.g., conducted by Williams [3]). The technical assessment of SAR adjustment and addition of other minerals for produced water disposal and reuse is summarized in Table 52.

Table 52. Summary of technical assessment of SAR adjustment and addition of other minerals.

Criteria	**Description/Rationale**
Industrial status	Industrialized technology. Have been used for produced water management.
Feed water quality bins	Not applicable.
Product water quality	Not applicable.
Production efficiency (recovery)	Not applicable.
Infrastructure considerations	No specific requirement.
Energy consumption	Energy requirement is low.
Chemicals	Chemicals required, such as lime, limestone, acid or other mineral salts, etc.
Life cycle	Same as treatment plant.
O&M considerations	Chemical handling.
Overall costs	Overall cost is low, and depending on the chemical used.
Pre-and post treatment	Not applicable.
Concentrate management or waste disposal	Not applicable.
Applicability in produced water treatment	Excellent for produced water treatment.
Note: 1 barrel = 42 US gallons	

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Constructed Wetlands

The development of constructed wetlands started approximately 40 years ago to exploit the biodegradation ability of plants [19]. Wetland treatment systems utilize natural filtration systems to remove suspended matter, organic matter, nutrients, metals, and certain pathogens. Constructed wetlands allow vertical and horizontal flow of water through the system. In vertical flow system (**Figure 48**) water flows through layers of soils and gravels. It is an aerobic process used primarily to remove organic matter and nutrients by natural bacteria in an aerobic environment.

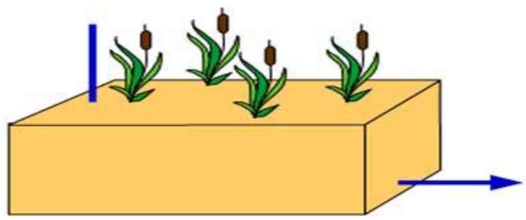

Figure 48. Vertical flow constructed wetland.

The horizontal flow constructed wetland system (**Figure 49**) is a facultative aerobic or anaerobic process, depending on the time and frequency of inundation, where water flows from one side of the system to the other. This type of constructed system is typically used to remove biological organic matter, to disinfect, to filter finely, and remove specifically by precipitation, ionic exchange, or adsorption [19].

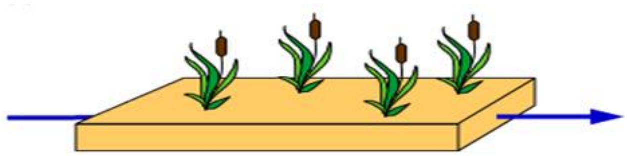

Figure 49. Horizontal flow constructed wetland.

Constructed wetlands also provide an approach to treat raw produced water or as post-treatment to further clean treated water. Research sponsored by Marathon Oil Company in 2000 involved construction of an artificial sedge wetland system to treat CBM produced water. The purpose of the project was to determine if constituents concentrated in CBM produced water, mainly SAR, iron, and barium, could be treated cost-effectively. The flowrate into the wetland system in that study was designed to be 30-40 gpm (approximately 1 bpm). Results after one year of operation indicated that the wetland system could effectively treat iron and possibly barium, but not change SAR. A report by Montana State University further supported these results, concluding "clean water is needed to supplement sodicity and saline treatment by vegetation and soil (Cited from All Consulting report, [168]).

Leon et al [169] proposed that for produced water with high chloride content, wetlands can be used as a natural evaporating system, in which halophyte plants uptake water and evapotranspire it, reducing water volume and the associated costs by effluents reinjection. For produced water with organic compounds content, wetlands are proposed to be used as treatment systems. Wetlands could be designed for specific desired results, depending on produced water quality and prevalent environmental conditions [169].

The advantage of the constructed wetland systems includes low construction and operation costs (Cooper, et al., 1996, cited from All consulting report [168]), approximately 1 to 2 cents/bbl. Kuipers estimated the constructed wetlands costs from 1 to 7 cents per barrel per day [170]. Constructed wetland systems are easy to maintain, but they have slow operation rate. The long-term use of artificial wetlands for organic removal treatment is 20 years and provides excellent wildlife habitat.

Constructed wetlands have several constraints on their usefulness: 1) Wetlands require a large amount of land per unit volume of water; 2) A sufficient supply of water is necessary to support the wetland; 3) The source and quality of wastewater may require pretreatment, in some agricultural and municipal cases wastewater must be pre-treated before entering a treatment wetland (Gopal, 1999, cited from [171]); and 4) Periodic release of captured contaminants during high flow periods or periods when vegetation decomposes may occur.

A limitation of wetlands in cold climates is that primary function may be minimal during winter months. A possible solution to this problem would be to spray the inflow water in the air. This would cause the fresh water to freeze (some would evaporate as well), and the remaining water would be more concentrated in respect to the salts [171].

For engineered wetlands, the change in TDS due to significant evapotranspiration is important to consider in a hot and dry climate [172]. Desalination process located downstream from the engineered wetland may be needed to reduce the TDS concentration to required effluent concentrations.

Various plant types have been studied and identified for salt tolerance and uptake, as well as for their quality as forage for livestock. A possible strategy to aid in processing CBM product water is to construct a wetland composed of a variety of halophytic plants which have dense fibrous root systems, uptake salts and sodium, can be used as forage, have high evapotranspiration and water use rates, or a combination of these traits.

Wetlands may have significant ecological and environmental impact. They provide areas that can be utilized by wetland birds and animals and aquatic life. Wetlands can also be utilized for livestock and wildlife watering purposes [170]. On the other hand, the contaminants in CBM produced water may affect fish and wildlife. For example, the research conducted by the USGS has demonstrated acute and chronic sodium bicarbonate toxicity to aquatic species. The CBM produced water discharges containing selenium in concentrations above 2 mg/L may cause bioaccumulation in sensitive species [173]. In addition, if the wetlands are constructed as part of direct discharge, they will change habitat from increased flows and increased erosion. Impacts to downstream users due to direct discharges would be higher with increased flows during traditional low flow periods and increased sedimentation from erosion. The technical assessment of constructed wetlands for produced water disposal is summarized in Table 53.

Table 53. Summary of technical assessment of constructed wetlands.

Criteria	Description/Rationale
Industrial status	Industrialized technology. Have been used for produced water management.
Feed water quality bins	In general < discharge limit if surface discharge applied. Salt concentration of water in which halophytic plants are grown ranged from 2 to 6 % (corresponding to 20,000 to 60,000 mg/L, EC 30 - 90 dS/m) [171].
Product water quality	Not applicable.
Production efficiency (recovery)	Variable, mainly discharge technology.

Table 53. Summary of technical assessment of constructed wetlands.

Criteria	Description/Rationale
Infrastructure considerations	Large land area requirements. Pipeline, monitoring wells or boreholes are required.
Energy consumption	Energy requirement is low. Water may need to be pumped to the wetlands.
Chemicals	No chemicals required.
Life cycle	Site specific, may be 20 years for organic matter decomposition.
O&M considerations	Annual operation and maintenance is assumed to consist of repairs to the piping and wetlands sediment removal requiring equipment for one week and 22.5 days labor [170].
Overall costs	Capital costs are highly variable and dependent on location. O&M cost is estimated $0.01-0.07/bbl [170].
Pre-and post treatment	May need treatment to remove certain contaminants.
Concentrate management or waste disposal	Sludge needs disposal if wetland has been designed for periodic sludge removal.
Applicability in produced water treatment	Excellent for produced water treatment and disposal.
Note: 1 barrel = 42 US gallons	

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Infiltration Ponds

Infiltration impoundment (aka holding pond, recharge pond) is a common method of handling CBM produced water. These impoundments are typically unlined; in some cases, the bottom surface of an impoundment area may contain key trench-type excavations or closely spaced boreholes to enhance infiltration. Evaporation also may be enhanced by atomizers placed on towers situated on floating islands, with spray from these units directed above the water surface only [174].

Infiltration ponds also have some treatment function to lower TDS by a settling removal mechanism or by water infiltration through a pre-fabricated pond liner. Nutrient uptake is also possible through various biological processes that could facilitate additional uses [19].

In Wyoming, approximately 3,000 infiltration ponds are either currently in use or are in the permitting stage [175]. Similar use of infiltration ponds in Montana is expected as CBM development expands. Infiltration ponds have several advantages. They are an inexpensive means of disposing of produced water, and allow more flexibility in pumping rates for the developer/operator. Also, the produced water, which comes from primary aquifers in the area, helps recharge the shallow ground-water system [175]. In areas with limited water supplies, this technology would be most applicable to increase declining groundwater systems to help supplement various water uses.

The use of recharge ponds to replenish depleted aquifers would be very site specific and would require extensive evaluation [19]. The infiltration ponds also have several potential disadvantages. The infiltrated water may not move vertically into the original deep aquifers, but rather tends to infiltrate to shallow zones or move laterally. As the sodium-bicarbonate water moves through the shallow weathered bedrock, a series of chemical reactions may increase the salt load in the water and detrimentally impact shallow aquifers or streams. Predicting changes in water quality is an integral part of permitting these ponds [175].

Researchers at the Montana Bureau of Mines and Geology are developing methods to assess proposed CBM infiltration pond sites and to test and calibrate those methods with field research. This will determine what criteria will be needed for the appropriate siting of infiltration ponds. The technical assessment of infiltration ponds for produced water disposal is summarized in Table 54.

Table 54. Summary of technical assessment of infiltration ponds.

Criteria	**Description/Rationale**
Industrial status	Industrialized technology. Have been used for produced water management.
Feed water quality bins	Meeting water recharge standards.
Product water quality	Improved quality through infiltration, including different removal rates of organic matter, suspended solids, nutrients and metals.
Production efficiency (recovery)	Variable and site specific. Water balance studies on existing reservoirs in Powder River Basin indicate that rates of infiltration range from 4 feet to more than 20 feet per year, depending on the soil type that underlies the impoundments [174]. In areas of sandy soil, the rate of infiltration may be considerably higher than 20 feet per year. An average rate of infiltration of 8 feet per year is assumed for the regional modeling analysis. This analysis estimated that 15% of the water that is discharged to impoundments would resurface and enter the surface drainage system. Of the remaining 85%, about 67% would infiltrate to recharge the shallow groundwater system, and the remaining 33% would evaporate [174].
Infrastructure considerations	Large land area requirements. Pipeline, monitoring wells or boreholes are required.
Energy consumption	Energy requirement is low; water may need to be pumped.
Chemicals	No chemicals required.
Life cycle	Depending on well development.
O&M considerations	Annual operation and maintenance is assumed to consist of repairs to the piping, pumps and clogged sediment removal.
Overall costs	Capital costs are variable and site specific. Typical cost was estimated \$0.01-0.02/bbl [170].
Pre-and post treatment	May need treatment to remove certain contaminants.
Concentrate management or waste disposal	Removed sludge needs disposal.
Applicability in produced water treatment	Excellent for produced water disposal.
Note: 1 barrel = 42 US gallons	

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Big Cat Energy Corporation: Aquifer Recharge Injection Device (ARID)

The aquifer recharge injection device (ARID) is a separation technology that allows for the production of natural gas from a coal seam without producing any water at the surface. In this system the producing well is also able to function as the disposal well for produced water. ARID consists of an aluminum mandrel that is installed between a producing coal seam and a stratigraphically higher saline aquifer. The cylindrical mandrel has several rubber o-rings that are used to seal the mandrel, like a plug in the borehole. The mandrel has four machined ports; these four ports are used for water and gas conveyance, a pump cable, and a transducer. A submerged pump is attached to the bottom of the mandrel with a pipe. Water is pumped from the bottom of the borehole the top of the mandrel plug. Water is then allowed to fill up the top of the plug and seep into a previously identified saline aquifer through perforations in the well casing. A watertight seal at the wellhead ensures that all of the water pumped from the producing zone is forced into the discharge aquifer. During pumping CBM gas accumulates in the headspace created between the mandrel and water level of the coal seam. This gas is recovered through the mandrel with a pipe that leads to a surface compression station. A schematic drawing of ARID is provided in Figure 50.

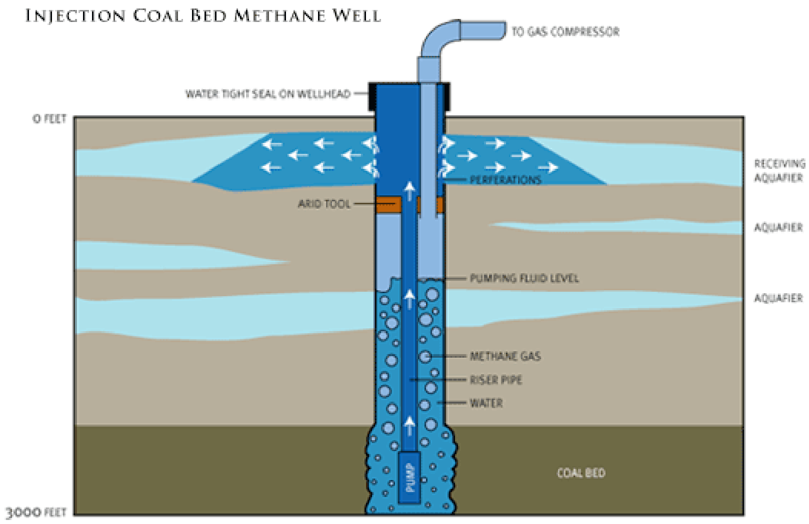

Figure 50. Operational diagram of the ARID process (Source: [176]).

The ARID system is being marketed for the Powder River Basin. Big Cat Energy Corp. claims that it will circumvent many of the NPDES regulations that make it difficult to produce out of the Montana portion of the basin. There are no published or verifiable reports on this process; however, the device is expected to undergo field trials in 2009 [177].

Beyond the Powder River Basin, this simple technology may be employed as a cost effective solution for management and disposal of very high TDS water (Bin 5). The limiting criterion is the presence of a *stratigraphically higher* aquifer that has similar natural water chemistry to that of the CBM produced water and the necessary assimilative hydraulic capacity. Trivial technical literature combined with the absence of field trial data makes it difficult to discuss the broader merits and disadvantages of this technology.

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Membrane Cleaning

Researchers at Texas A&M University have performed numerous experiments to elucidate the most effective cleaning chemicals to remove UF membrane foulants from the treatment of produced water with moderately high salinity and dissolved oil. The cleaning efficacy of nine unique micelle based cleaning solutions was tested on three separate polyvinyl diflouride (PVDF) polymeric UF membranes. Each unidentified UF membrane was subjected to six different bench-scale fouling scenarios with two different feed water flow rates and three different transmembrane pressures. Each of the cleaning solutions was developed with various types of alkylpolyglycoside derivatives and solid surfactants (such as alpha-olefin sulfonates) in the presence of various salt concentrations to achieve a desired oil and water solubility characteristic. The exact composition of the various cleaning solutions is not disclosed [178].

Experimental results from the Texas A&M study indicate that certain micelle based cleaning solutions may be tailored to provide improved cleaning efficacy over acid and base cleaning results from a previous study [179]. Burnett [178] reported a flux recovery ($J_{cleaned}/J_{uncleaned}$) ranging from 1.15 to 7.53, with an average of 2.73 and a standard deviation of 2.14 for the nine different cleaning solutions.

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ACRONYMS

AEM – Anion Exchange Membranes
AGMD – Air Gap Membrane Distillation
ARID – Aquifer Recharge Injection Device
bbl – Barrel (42 US gallon)
BOD – Biological Oxygen Demand
bpd – Barrels per day
bpm – Barrel per minute
BTEX – Benzene, Toluene, Ethylbenzene, and Xylene
BWRO – Brackish Water RO
CBM – Coalbed Methane
CDI – Capacitive deionization
CDT – Capacitive deionization technology
CEM – Cation Exchange Membranes
CIP – Clean In Place
COD – Chemical Oxygen Demand
DAF – Dissolved Air Flotation
DBP – Disinfection Byproduct
DCMD – Direct Contact Membrane Distillation
DGF – Dissolved Gas Flotation
DP_3RO^{TM} – Double Pass, Preferential Precipitation, Reverse-Osmosis process
ED – Electrodialysis
EDI – Electrodeionization
EDR – Electrodialysis Reversal
EVRAS – Evaporative Reduction and Solidification
EWP - Electronic Water Purification
FO – Forward osmosis
FTE – Freeze/Thaw Evaporation
gfd – Gallon per square foot per day
gpd – Gallon per day
gpm – Gallon per minute
HEED – High Efficiency Electrodialysis
$HERO^{TM}$ – High Efficiency RO
HTE – Horizontal Tube Evaporator
IGF – Induced Gas Flotation
IX – Ion Exchange
MD – Membrane Distillation
MED – Multiple Effect Distillation
MF – Microfiltration
MGD – Million Gallons per Day
MSF – Multi Stage Flash Distillation
MVR – Mechanical Vapor Recompression
NF – Nanofiltration
NOM – Natural Organic Matter
NPDES – National Pollutant Discharge Elimination System

OTSG – Once-Through Steam Generators
POTW – Publicly Owned Treatment Works
RO – Reverse osmosis
ROSP – Combined RO – Sal-Proc
SAGD – Steam-Assisted Gravity Drainage
SAR – Sodium Adsorption Ratio
SDI – Silt Density Index
SEM – Scanning Electron microscope
SEPCON – Saline Effluent to Products Conversion
SGMD – Sweeping Gas Membrane Distillation
SPARRO – Slurry Precipitation and Recycling RO
SPR – ShockWave Power™ reactor
SWRO – Seawater RO
TDS – Total Dissolved Solids
TFC – Thin Film Composite (membrane)
TOC – Total Organic Carbon
TRPH – Total Recoverable Petroleum Hydrocarbons
TSS – Total Suspended Solids
TVC – Thermo Vapor Compression
UF – Ultrafiltration
VCD – Vapor Compression Distillation
VMD - Vacuum Membrane Distillation
VOC – Volatile Organic Compounds
VTE – Vertical Tube Evaporator
WAIV – Wind Aided Intensified Evaporation
WFRD – Wiped Film Rotating Disk
ZLD – Zero Liquid Discharge