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Article in *Environmental Engineering Science* · August 2013

DOI: 10.1089/ees.2012.0348

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## Critical Review of Desalination Concentrate Management, Treatment and Beneficial Use

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Received: September 1, 2012

Accepted in revised form: April 15, 2013

### Abstract

Desalination of seawater, brackish water, and reclaimed water is increasingly utilized worldwide to augment and diversify fresh water sources. The lack of economically and ecologically feasible concentrate management options, however, is a major barrier to widespread implementation of desalination, in particular at inland sites. This paper critically reviews strategies and technologies for concentrate management, including disposal, treatment, and beneficial use. Development of energy-efficient, cost-effective, and environmentally benign concentrate management systems is critical if desalination is to become a major part of a sustainable water future. This paper examines the limitations and advantages of a range of concentrate management tools, including emerging and novel technologies for minimization of concentrate volume, enhancement of water recovery, removal of organic contaminants, and recovery of valuable products and energy.

**Key words:** desalination; concentrate disposal; concentrate treatment; energy recovery; membrane processes; salt recovery; water recovery

### Introduction

THE DIFFICULTY IN MEETING the increasing demand for new freshwater resources has motivated many municipalities and water utilities to explore the desalination of seawater, brackish waters, and reclaimed water as alternative water supplies (Xu *et al.*, 2009; IDA, 2012). Desalination processes can remove most dissolved solutes (inorganic and organic) from impaired water. Two classes of desalination processes are currently employed: thermal-based and membrane-based. Thermal-based technologies, which have been used since the inception of seawater desalination and are widely used in the Middle East and the Caribbean, include multistage flash evaporation, multiple effect distillation, and vapor compression distillation. These technologies are used primarily where salinity is high (>35 g/L) and inexpensive energy is available (*e.g.*, Middle East, co-located power plants). Membrane-based technologies, including nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED), and electrodialysis reversal (EDR), are used in the majority of plants outside the Arabian Gulf region and in almost all recently constructed desalination facilities (IDA, 2012).

Desalination processes separate feed water into product and concentrate (also known as retentate, brine, or reject) streams. Concentrate management and disposal, especially for inland applications, is currently one of the most challenging issues associated with water desalination. Disposal methods depend on concentrate quantity and quality, permitting requirements, geography and geology (*e.g.*, accessibility to ocean or sewer, appropriate geological formation for deep well injection, land availability), costs, and potential environmental impacts.

Converting concentrate from a waste to a resource through treatment and beneficial use may minimize both costs and environmental impacts. This paper critically reviews concentrate management strategies, treatment technologies and beneficial uses, with the goal of identifying key barriers that need to be overcome for a broader use of desalination processes, especially for inland applications.

### Discussion

#### *Concentrate quantity and quality*

The quantity and quality of desalination concentrate depends on source water quality, pretreatment, desalination processes implemented, and water recovery (*i.e.*, ratio of permeate flow and feed flow). As water recovery increases,

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the concentration of dissolved solutes in the concentrate stream may exceed the solubility of sparingly soluble salts (e.g.,  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{SiO}_2$ , and  $\text{BaSO}_4$ ) and precipitation can occur. These precipitates along with colloids, organic matter, and bacteria can foul membrane and system surfaces, reducing process efficiency and limiting water recovery (Xu *et al.*, 2010; Yu *et al.*, 2010; Tang *et al.*, 2011). Typically, acid, scale inhibitors, and disinfectants are added to the feed or concentrate streams to reduce scaling and fouling, and to enhance water recovery (Van der Bruggen *et al.*, 2003). These additions increase the quantity and composition of materials in the concentrate stream.

Water recovery is also limited by the osmotic pressure of the highly concentrated brines, causing trans-membrane pressure to exceed design tolerance of the membrane and associated system components. Currently, the typical water recovery of seawater reverse osmosis (SWRO) systems varies between 40% and 50%, limited by the trans-membrane pressure (Matsumoto *et al.*, 2001; Gorenflo *et al.*, 2007). This means that ~50–60% of the feed stream is wasted as concentrate. Brackish water reverse osmosis (BWRO) desalination plants typically operate at recoveries of 75% to 85% (Younos, 2005; Sethi *et al.*, 2009), but occasionally some plants operate at only 50–60% due to scaling or energy saving considerations (Cress, 1999; Ahmed *et al.*, 2001). When using ED and EDR, water recovery of brackish water and reclaimed water can increase to 85–95%, depending on feed water quality (Broens *et al.*, 2004; Reahl, 2006).

Table 1 summarizes typical water recovery and quality for different water classifications. The potential for concentrate volume reduction is high for inland desalination facilities because of limited disposal options and the need of additional water supplies. However, higher recoveries lead to higher desalination costs. For example, very high recoveries, such as greater than 97%, can be achieved using thermal processes; the technologies are energy intensive and cost inhibitive. Between 85% and 97% recovery could be considered as practical and potentially achievable for reclaimed water and BWRO, while avoiding significant corresponding increases in costs (Sethi *et al.*, 2006). This is essentially the goal of emerging and promising technologies for recovery enhancement and concentrate minimization. During desalination processes, the

amount of contaminants could increase by 4–10 times and potentially reaching toxic level in concentrate. These contaminants (e.g., nitrate, naturally occurring radioactive materials, arsenic, and other heavy metals introduced by natural dissolution of rocks, agricultural runoff, and mining activities) also require treatment before discharge or beneficial use.

#### *Concentrate management strategies*

Concentrate management strategies include surface water discharge, sewer discharge, deep well injection, evaporation ponds, land application, and thermal processes for zero liquid discharge (ZLD) or near-ZLD. The benefits and challenges of the different concentrate management options are summarized in Table 2. Traditional concentrate disposal strategies are limited by environmental impacts, lack of dilution of the receiving water bodies, and by the required physical footprint. The problems associated with brine disposal options limit the implementation of desalination processes, especially when considering the enhancement of urban water infrastructure portfolios. Therefore, the selection of a concentrate management strategy needs to consider the costs, environmental impacts, complexity of permitting and regulations, site requirements and footprint, energy use, reliability, ease of implementation, and operation of the processes involved (Voutchkov, 2011).

#### *Concentrate treatment for improvement of water recovery, minimization of volume, and reduction of contaminants*

**Technologies.** Technologies have been proposed for concentrate treatment that relies less on dilution by discharge or requiring large physical footprints. Thus, these processes could be viable options to be used in urban settings to diversify available freshwater resources through desalination. Even highly concentrated brines consist mostly of water (e.g., ~94% for SWRO brine). Extracting this water can enhance sustainability in three ways: it provides an additional freshwater resource, decreases the volume of waste to dispose of, and it facilitates the precipitation and extraction of valuable salts from the concentrate. A number of technologies have been studied to

TABLE 1. SUMMARY OF WATER CLASSIFICATION BASED ON SALINITY, TYPICAL WATER RECOVERY, AND POTENTIAL FOR CONCENTRATE VOLUME REDUCTION

<i>Water classification and typical TDS range</i>	<i>Typical water recovery</i>	<i>Concentration factor</i>	<i>Range of concentrate quality</i>	<i>Potential for water recovery improvement</i>
Reclaimed water				
TDS 300–1000 mg/L (TOC 5–15 mg/L)	80–85%	5–6.67	TDS 1500–6670 mg/L (TOC 25–90 mg/L)	High
Brackish water <sup>a</sup>				
TDS 500–1000 mg/L	80–90%	5–10	TDS 2500–10,000 mg/L	High
TDS 1000–5000 mg/L	75–85%	4–6.67	TDS 4000–33,000 mg/L	High
TDS 5000–15,000 mg/L	50–80%	2–5	TDS 10,000–75,000 mg/L	Moderate due to high salinity in concentrate
Sea water				
TDS 30,000–40,000 mg/L	40–50%	1.67–2	TDS 60,000–80,000 mg/L	Low due to convenient ocean disposal option

<sup>a</sup>Feed water TDS of current brackish water reverse osmosis plants is typically less than 15,000 mg/L. TDS, total dissolved solids; TOC, total organic carbon.

TABLE 2. COMPARISON OF CONCENTRATE MANAGEMENT OPTIONS

<i>Concentrate management options</i>	<i>Advantages and benefits</i>	<i>Challenges and uncertainties</i>
<b>Surface water discharge</b> to rivers, lakes, ocean, or estuary via a dedicated outfall, or power plant outfall, or blending with wastewater	<ul style="list-style-type: none"> <li>• Used for facilities of all sizes</li> <li>• Cost effective</li> </ul>	<ul style="list-style-type: none"> <li>• Environmental implications due to the differences in salinity and major ion imbalance between concentrate and ambient surface waters, resulting in adverse impact on aquatic life</li> <li>• Stringent regulations, for example, National Pollutant Discharge Elimination System (NPDES)</li> <li>• Complex and costly permitting</li> </ul>
<b>Sewer discharge</b> to an existing wastewater treatment system	<ul style="list-style-type: none"> <li>• Commonly used for brackish water and wastewater facilities</li> <li>• Low energy use and costs</li> </ul>	<ul style="list-style-type: none"> <li>• Only feasible to small size facilities, limited by the hydraulic capacity of the sewer collection system and by the treatment capacity of the wastewater treatment plant receiving the discharge</li> <li>• May impact the operation of wastewater treatment plant and beneficial use of reclaimed water because of the concentrate salinity and specific constituents, such as sodium, chlorides, boron, and bromides in the blended stream due to their potential negative impact on microorganisms, plants, and soil.</li> </ul>
<b>Deep well injection</b> into a deep geological formation, that permanently isolates the concentrate from shallower aquifers that may be used as a source of drinking water	<ul style="list-style-type: none"> <li>• Suitable for inland facilities</li> </ul>	<ul style="list-style-type: none"> <li>• Typically expensive and often used in larger facilities</li> <li>• Require appropriate geological formation and confined saline water aquifer, not feasible for areas of elevated seismic activity or near geologic faults</li> <li>• Permitting is becoming more stringent because of greater perceived potential for leakage to, and contamination of nearby water supply aquifers</li> </ul>
<b>Evaporation ponds</b>	<ul style="list-style-type: none"> <li>• Suitable for inland and coastal facilities</li> <li>• Easy to implement and low maintenance</li> <li>• Economical if land is inexpensive</li> </ul>	<ul style="list-style-type: none"> <li>• Climate dependent</li> <li>• Large physical footprint</li> <li>• Regulatory permitting may be complicated</li> <li>• Limited to small flows</li> <li>• Need the control of erosion, seepage, and wildlife management</li> </ul>
<b>Land application</b> through percolation ponds, or beneficially used for irrigation of lawns, parks, golf courses, or crops	<ul style="list-style-type: none"> <li>• Relatively easy to implement and low costs</li> <li>• Beneficial use of concentrate</li> </ul>	<ul style="list-style-type: none"> <li>• Limited to irrigation of salt tolerant grass, trees, and plants</li> <li>• Limited to small facilities</li> <li>• Dependent on seasonal irrigation needs and climate</li> <li>• Limited by groundwater protection laws</li> <li>• Potential contamination of soil and groundwater</li> </ul>
<b>Thermal zero and near-zero liquid discharge</b>	<ul style="list-style-type: none"> <li>• Avoid a lengthy and tedious permitting process</li> <li>• Smaller environmental impact</li> <li>• Potential recovery of valuable salts</li> </ul>	<ul style="list-style-type: none"> <li>• Costly, capital and energy intensive</li> <li>• Disposal of the final brine or salt can be expensive</li> <li>• Large carbon footprint</li> </ul>

improve water recovery, reduce the volume of concentrate for disposal, and to remove contaminants before beneficial uses or discharge.

Alternative and emerging desalination technologies applicable to brines.

*Dewvaporation.* Dewvaporation is a humidification-dehumidification desalination process. Concentrate is

evaporated by heated air, and fresh water condenses as dew on a face of a heat transfer wall (Hamieh *et al.*, 2001; Hamed, 2005; Hamieh and Beckman, 2006; Beckman, 2008). Heat sources can be combustible fuel, solar, or waste heat. The tower unit is built of thin plastic films to avoid corrosion and to minimize capital costs. Because dewvaporation operates at atmospheric pressure, towers are relatively inexpensive; however, the footprint could be considerable.

Dewvaporation has been pilot tested using reclaimed water RO concentrate (Beckman, 2008) and produced water from oil and gas production (Godshall, 2006). Dewvaporation can reduce effluent disposal volumes by as much as 90% and generate high quality distilled water. However, volatile organic compounds in feed water can reduce the quality of the product water. Dewvaporation scaling potential is low because the evaporation occurs at the liquid-air interface and not on the heat transfer wall. Although much of the energy required is supplied by the energy released from vapor formation, energy demand is still a challenge. Using the average multiple effect value of 3.2, the heat needed for 1000 gallons (3785 L) 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 1000 gallons (Beckman, 2008) in addition to capital investment. The high energy demand makes the dewvaporation process not feasible for municipal applications if low grade heat is not available.

Commercial dewvaporation modules are available through Altela, Inc., which has designed, manufactured, and tested the AltelaRain<sup>SM</sup> systems based on the dewvaporation process for treatment of produced water generated during oil and gas exploration and production.

**Membrane distillation.** Membrane distillation (MD) is a thermally driven separation process that can utilize low-grade heat sources to facilitate mass transport through a hydrophobic, microporous membrane (Lawson and Lloyd, 1997; Hendren *et al.*, 2009; Qtaishat *et al.*, 2009; Cath, 2010). The driving force for mass transport is the vapor pressure gradient between the heated feed solution and the cooled distillate on the opposite side of the membrane. MD is capable of producing ultra-pure water at a lower cost than conventional distillation processes (Lawson and Lloyd, 1997; Hendren *et al.*, 2009; Qtaishat *et al.*, 2009; Cath, 2010). MD membrane materials include polytetrafluoroethylene (PTFE), polypropylene (PP), polyvinylidenedifluoride (PVDF), carbon nanotubes, and ceramic membranes (Cerneaux *et al.*, 2009; Dumée *et al.*, 2010; Gryta and Barancewicz, 2010; Singh and Sirkar, 2012). High water fluxes can be achieved with a feed temperature of 40 °C and even lower (Cath, 2010).

Theoretically, rejection for all nonvolatile solutes (including sodium, silica, boron, and heavy metals) is close to 100%; however, compounds more volatile than water will diffuse preferentially faster through the membrane (Cath *et al.*, 2004; Cath *et al.*, 2005a; Winter *et al.*, 2011). Recent studies showed that MD can desalinate highly saline streams, including seawater, concentrates, and produced water, and can successfully recover crystals from solutions under extreme conditions (Ji *et al.*, 2010). Martinetti *et al.* (2007) investigated the use of vacuum-enhanced direct contact membrane distillation (VEDCMD) in treating two brackish water RO concentrates with total dissolved solids (TDS) concentrations averaging 7500 and 17,500 mg/L. VEDCMD achieved water recoveries up to 81% from the brines. Total water recoveries (including initial RO recovery) were greater than 98% for the first brine and greater than 89% for the second. Both membrane scaling and the decrease in partial vapor pressure of water at higher feed concentrations can result in flux decline in MD (Martinetti *et al.*, 2007). Although flux could be recovered after chemical cleaning (Curcio *et al.*, 2010), frequent chemical cleaning is not sustainable due to high chemical demand and costs.

MD membranes are more chemically inert and resistant to oxidation than traditional RO and NF membranes, which allows for more efficient, chemically aggressive cleaning. However, the conductive heat loss through MD membranes is a major drawback that potentially impedes commercial development of the process (Cath, 2010). If low grade heat is available, high water recovery and low membrane fouling/scaling may potentially make MD an attractive alternative to desalination concentrate treatment at the municipal sectors, but long-term pilot-scale operation with real water is required to validate this hypothesis.

**Forward osmosis.** During forward osmosis (FO), water diffuses spontaneously from a stream of (relatively) low osmotic pressure (feed solution) to a hypertonic, very high osmotic pressure draw solution (McCutcheon *et al.*, 2006; Cath, 2010). Unlike RO and NF, FO systems do not require application of hydraulic pressure. FO membranes, traditionally cellulose acetate-based (Zhang *et al.*, 2010; Hancock *et al.*, 2011; Zhang *et al.*, 2011), are dense, nonporous barriers similar to RO membranes, but are composed of a hydrophilic active layer cast onto either a woven polyester mesh or a micro-porous support structure. New FO membranes are under development to increase water flux, reduce reverse salt transport, minimize internal concentration polarization, and decrease membrane fouling (Wang *et al.*, 2007; Chou *et al.*, 2010; Li *et al.*, 2011; Qiu *et al.*, 2011; Setiawan *et al.*, 2011; Tiraferri *et al.*, 2011; Wei *et al.*, 2011; Widjojo *et al.*, 2011; Yu *et al.*, 2011; Zhang *et al.*, 2011).

Typically, the FO draw solution is composed of NaCl, but other draw solutions (NH<sub>4</sub>HCO<sub>3</sub>, sucrose, nanoparticles, MgCl<sub>2</sub>, and other salts) have been examined (Cath *et al.*, 2006; McCutcheon *et al.*, 2006). During FO, the feed solution is concentrated, while the draw solution becomes more dilute. One prominent method for reconcentrating the draw solution is to utilize an RO subsystem (Cath *et al.*, 2006).

Recent studies have shown that synergistically coupling FO with RO creates an exceptionally robust, multibarrier system for treatment of highly impaired streams, such as municipal wastewater, concentrate from anaerobic digester, and RO concentrate (Cath *et al.*, 2005b; Cartinella *et al.*, 2006; Holloway *et al.*, 2007; Lundin, 2008; Martinetti *et al.*, 2009; Hancock *et al.*, 2011). FO membranes are capable of rejecting all particulate matter and almost all dissolved constituents (greater than 95% rejection of TDS). Unlike RO, fouling on FO membranes is not intensified by hydraulic pressure. FO foulants can be readily removed with cleaning (*e.g.*, increasing cross-flow velocity, osmotic backwashing) or with chemicals, and irreversible flux decline is minimal (Martinetti *et al.*, 2007). FO systems are capable of operating with feed TDS concentration ranging from 500 mg/L to more than 35,000 mg/L, and may achieve recoveries in excess of 96% when treating brackish water RO concentrates (Martinetti *et al.*, 2007). Occasional disposal of spent draw solution and addition of new solution may be required as sparingly soluble solutes and other membrane foulants slowly accumulate in the draw solution reconcentration loop (Hancock and Cath, 2009).

Recently, demonstration-scale FO systems operated in osmotic dilution mode have been developed for treatment of wastewater generated during oil and gas exploration (Hickbottom *et al.*, 2013). Laboratory testing results demonstrated that FO is an effective technology for treatment of desalination concentrate.

FO systems have shown a promising potential to treat difficult waters, including RO concentrate. As an emerging technology, there are needs to further improve the performance of FO membranes, develop cost effective techniques to re-concentrate draw solution, and improve the configuration of FO modules.

*Vibratory shear enhanced membrane filtration process (VSEP™).* The patented VSEP (New Logic Research) membrane filter pack consists of leaf elements arrayed as parallel membrane 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 (Shi and Benjamin, 2009).

VSEP has been used to treat high solids (dissolved and particulate) wastewaters, including those from dairy (Akoum *et al.*, 2004), livestock (Lee *et al.*, 2004), pulping (Huuhiilo *et al.*, 2001), and landfill operations (Zouboulis and Petala, 2008). VSEP was also tested for treatment of desalination concentrate (Madole, 2005; Subramani *et al.*, 2012). Lozier *et al.* (2007) conducted a pilot testing using VSEP RO and NF membranes to treat reclaimed water RO concentrate with TDS concentration higher than 2800 mg/L. The testing results showed that both membranes can reduce the volume of conventional RO system concentrate by up to 85% if a two-stage VSEP unit is implemented (Lozier *et al.*, 2007). VSEP recoveries exceeding 85% resulted in less than optimal operation of the unit (*e.g.*, decreased flux and high feed pressure), and with increased life cycle costs. Cleaning frequency is very high and not feasible, estimated to be twice per week (Shi and Benjamin, 2008).

Full-scale VSEP systems have been installed to treat various industrial wastewaters (New Logic Research).

**Hybrid processes.** Hybrid methods have been developed which combine unit processes to enhance water recovery of desalination concentrate. Many of these methods couple multiple membrane-based stages with intermittent biological treatment, chemical precipitation, or caustic addition (Gabelich *et al.*, 2007; Rahardianto *et al.*, 2007; Rahardianto *et al.*, 2010).

*Dual RO with intermediate softening.* Dual RO with chemical precipitation employs established technologies, such as lime soda softening and a second stage RO to treat primary RO concentrate. Sparingly soluble salts of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{SiO}_2$  are removed using chemical precipitation followed by media or membrane filtration. The secondary RO system can then continue the recovery of water before precipitation and fouling become a concern again. The combined recovery of such hybrid system was reported to be 95% or greater for brackish water feed water (Gabelich *et al.*, 2007).

The patented HERO™ (High Efficiency RO) technology uses weakly acidic cationic exchange resins to remove hardness and alkalinity, a degasification step to remove carbon dioxide from the concentrate, and intermediate caustic addition to increase the pH of the primary RO concentrate to above 10 (Mukhopadhyay, 1999). This allows for the secondary RO to operate at high recoveries. The negatively charged membranes tend to reject concentrated anions (*e.g.*,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ), and by operating above pH of 10, weakly acidic boric acid [ $\text{B}(\text{OH})_4^-$ ] is also rejected. The solubility of silica increases at

high pH, which allows for greater recovery rates when treating water that contains high concentrations of silica due to less silica precipitation on the membrane. The combined recovery of the process is estimated to be greater than 90% for brackish water, with typical target recovery rates of ~95% (Rahardianto *et al.*, 2007).

For carbonate-rich brackish water RO concentrate, air stripping  $\text{CO}_2$  from the solution increases the pH and precipitates solids (primarily  $\text{CaCO}_3$ ) (Hasson *et al.*, 2011). Aeration through a series of crystallizers precipitated at least 70% of the potential  $\text{CaCO}_3$ . With the secondary RO, the overall water recovery increased from 78% to 90%. Recoveries exceeding 95% can be anticipated for solutions of sufficiently high carbonate content (Hasson *et al.*, 2011).

These intermediate systems utilize established unit processes and require relatively less additional energy. They do, however, require additional chemicals, produce sludge, and require space for the reactors and chemical storage facilities.

*Dual RO with SPARRO: slurry precipitation and recycling RO.* In SPARRO, crystals, such as gypsum are added to the solution to induce precipitation of scaling compounds on seed crystals rather than on the membrane surface (Herrigel, 1980). Because the seed slurry is recirculated within the membrane system, the process requires a membrane configuration that will not plug, such as tubular membrane systems. The feed water is mixed with a stream of recycled concentrate containing the seed crystals and fed to the RO process. A hydro cyclone separator removes the crystals from the concentrate. The desired seed concentration is maintained in the reactor tank by controlling the rate of wasting from the separator. Overall recoveries with this process are estimated to be greater than 90% (Enzweiler, 2005).

A variation of this 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 (Enzweiler, 2005). The process was developed for an agricultural drainage water reclamation application and tested at bench scale. The process is known as double pass, preferential precipitation, RO process, or  $\text{DP}_3\text{RO}^\text{TM}$ . Although the TDS level in the agricultural drainage water is typically between 3000 to 12,000 mg/L, the recovery from a conventional RO system treating this water is reported to be limited to less than 50%, due to high calcium sulfate concentrations. The two-pass system is reported to be able to achieve a recovery of 92–96%. Calcium sulfate seeds in the first pass NF remove calcium sulfate and soften the water. The softened water is then treated by RO to meet the irrigation requirements (TDS concentration lower than 500 mg/L and sodium adsorption ratio lower than 4.0).

The benefit of SPARRO systems is increased RO recovery at relatively low energy costs. The systems do require tubular membranes (larger footprint) and additional chemicals.

*Electrodialysis (ED) and related processes.* ED processes have been used for several decades to remove ions from water for drinking water and wastewater treatment (Reahl, 2006; Strathmann, 2010). A conventional ED stack comprises a series of alternating cation and anion permselective membranes between a cathode and an anode. Cations are drawn toward the negatively charged cathode passing through the negatively charged cation exchange membrane and being rejected

by the positively charged anion exchange membrane. Similarly, anions are drawn toward the positively charged anode passing through the anion exchange membrane and being rejected by the cation exchange membrane.

EDR is a modified form of a conventional ED, performed by periodic reversal of the membrane stack direct current (DC) electric field to drive salt scale off the membranes before the scalants become permanently attached. DC field reversal reduces the need to feed either acid or antiscalant chemicals into the desalination process (Reahl, 2006).

ED and EDR systems have been proposed for the removal of salts from RO concentrate and for increasing overall water recovery. Pellegrino *et al.* (2007) tested a parallel RO/ED system in which hollow fiber RO membranes were placed as spacers between the ion exchange (IX) membranes of a pressurized ED cell. The ED unit continuously removes ions from the RO feed. This decreases the osmotic pressure and concentration polarization in the ensuing RO unit; thus, permitting increased recovery.

Reahl (1992) described a large EDR system for RO concentrate reclamation. A six-stage EDR system with a single train of EDR stacks reduced the TDS of RO concentrate from 4500 to 550 mg/L and recovered 83–86% of RO concentrate, resulting in an overall RO/EDR water recovery of 97%. Acid was added to the EDR feed and recirculating brine to reduce the Langelier Saturation Index from 3.6 to <1.8. Similarly, Turek *et al.* (2009) tested an RO-EDR system to treat a brackish groundwater RO concentrate with high scaling potential. This EDR system recovered 79% of the concentrate stream, improving overall recovery from 60% to 92%. Scaling was not observed despite the fact that the EDR unit operated at 360% calcium sulfate saturation and 2.3 Langelier Saturation Index.

These studies suggest that compared to the secondary RO processes described above, ED and EDR systems may require less pretreatment and are more tolerant of concentrate with high scaling potential. ED or EDR systems can also operate with a continuous free chlorine residual of up to 1 mg/L, which allows a better control of biofouling and more rigorous clean-in-place than secondary RO (Reahl, 2006).

Recently, a new modified form of ED, electrodialysis metathesis (EDM), was pilot-tested for treatment of RO concentrate (Bond *et al.*, 2011). The EDM process uses repeating unit comprising one diluate compartment, two concentrate compartments, one NaCl solution compartment, one regular anion exchange membrane, one regular cation exchange membrane, one monovalent selective anion exchange membrane, and one monovalent selective cation membrane. This unique configuration is designed to reduce the typical scalants in BWRO concentrate (*e.g.*,  $\text{CaSO}_4$  and  $\text{CaCO}_3$ ) by separating EDM concentrate into two streams of highly soluble salts: one containing sodium with anions and the other containing chloride with cations. EDM increased overall water recovery to over 99%. The treatment costs and energy demand of EDM were dependent on the TDS of the concentrate. Using an EDM before a crystallizer can reduce the costs of ZLD system significantly (Bond *et al.*, 2011).

However, it should be noted that the ED, EDR, or EDM are charge driven separation processes, and therefore, removal of organics, pathogens, and other nonionic substances by these processes is lower than in RO. For waters with higher total organic carbon (TOC) concentrations (*e.g.*, reclaimed and surface waters), the formation of disinfection byproducts during

chlorination may limit the use of ED or EDR product water for certain applications. Post-treatment, such as NF, ozonation, adsorption and biological treatment may be used to reduce the organic concentration in the product water. In addition, EDR requires electrical rectification and flow reversal, which means that additional valves and controllers are needed.

Removal of organic contaminants from municipal reclaimed water concentrate. Use of NF and RO membranes in processes to reclaim water for indirect potable water reuse from municipal wastewaters has increased substantially in recent years (Drewes *et al.*, 2005; Xu *et al.*, 2010). Many of the organics that are concentrated in these brines are of considerable concern and can hinder the beneficial use of reclaimed water concentrate. Contaminants of concern include nutrients (*e.g.*, ammonia, nitrate, and phosphorus), trace organic chemicals (*e.g.*, pesticides, personal care products, pharmaceutical products, and endocrine disruptors), effluent organic matter (*e.g.*, soluble microbial products, partially degraded organics), pathogens, and antiscalant chemicals.

Treatment trains to target removal of organic chemicals in concentrate must cope with two important factors: (1) concentrate organics are typically recalcitrant; at best they are only slowly transformed by conventional biological treatment processes; and (2) the water is very salty; the high ionic strength and some of the specific constituents can substantially impact process dynamics and rates. In the review of concentrate management, Pérez-González *et al.* (2012) summarized organics removal from reclaimed water concentrates, including coagulation, activated carbon adsorption, and several advanced oxidation processes. They noted that all reported systems had one or more of the following disadvantages: high chemical usage, intense energy consumption, and substantial capital cost.

Biological oxidation processes are often considered to be adversely affected by high ionic strength (WHO, 2007). Lay *et al.* (2010) reviewed the impact of salinity on the performance of bioreactors with the aim of understanding the effects on membrane bioreactors (MBRs). They described how physical-chemical salinity effects might affect bioreactor performance, and how microbial communities could adapt to these conditions to develop bioreactor systems that performed well at high salt concentrations.

Biological pretreatment methods using biological activated carbon (BAC) were only able to remove ~20% of TOC (Ng *et al.*, 2008). When combining with ozonation at an ozone dosage of 6.0 mg  $\text{O}_3$ /L with 20-min contact time, three times higher TOC removal was achieved as compared to using BAC alone (Lee *et al.*, 2009). This shows that peroxidation/biological treatment is a cost-effective method to treat RO brine by first breaking down highly refractory organic pollutants to simpler forms for better subsequent biodegradation.

Carbon adsorption of effluent organic matter in RO concentrate could achieve over 90% removal (Dialynas *et al.*, 2008; Zhou *et al.*, 2011). However, activated carbon mainly adsorbs organic fractions with small/medium molecular weight (MW) and exhibited lower affinity for large MW organics.

Dialynas *et al.* (2008) investigated the removal of organic carbon from the RO concentrate of an MBR effluent. Coagulation with alum removed up to 42% of dissolved organic carbon (DOC), while ferric chloride achieved higher removal (52%) at lower molar doses. However, coagulation using

ferric salts to treat RO concentrates from other secondary and tertiary effluents exhibited much lower DOC removal, only 26% and 5%, respectively (Westerhoff *et al.*, 2009; Zhou *et al.*, 2011).

Various oxidation processes have been studied for removing reclaimed water concentrate organics. Applying simple UV irradiation or  $\text{H}_2\text{O}_2$  oxidation did not remove DOC and the reclaimed water color (Zhou *et al.*, 2011). Individual oxidation processes, including photocatalytic oxidation, ozonation ( $\text{O}_3$ ), and sonolysis (SN) removed only a small fraction of DOC from raw RO concentrate, following the order of  $\text{SN} < \text{UVA}/\text{TiO}_2 < \text{UVC}/\text{TiO}_2 < \text{O}_3$ . Ozone treatment achieved the best removal efficiency of 22% and 90% for DOC and color, respectively. Increasing the energy input, catalyst dose, or reaction time produced only marginal improvements in the DOC removal efficiency (Zhou *et al.*, 2011).

During oxidation processes, DOC removal rates generally decreased as pH increased (Westerhoff *et al.*, 2010). The measured steady state  $\bullet\text{OH}$  radical concentration was higher at pH 5 than at pH 7. This lowered steady state concentration (and overall reactivity) was attributed to  $\bullet\text{OH}$  scavenging by bicarbonate ion. Scavenging by chloride (formation of  $\text{HOCl}$ ) has also been reported (Bagastyo *et al.*, 2011; Zhou *et al.*, 2011). The presence of chlorine in concentrates indicates the possibility of disinfectant byproduct formation (Agus *et al.*, 2009; Agus and Sedlak, 2010).

Research to date suggests that, in most situations, there is likely no simple and inexpensive procedure that effectively removes organics in RO concentrate. Multitrain systems designed with an understanding of the concentrate's chemistry are required.

### Beneficial use of concentrate

Finding beneficial uses for concentrates, or concentrate components, is essential if desalination processes are utilized to provide alternative water supplies for urban settings. Jordahl (2006) investigated the viability of beneficial and non-traditional uses of concentrate and identified a number of critically important site-specific considerations, including costs, climate, markets, regulatory issues, and ecological risks for beneficial use of concentrates.

**Recovery of valuable salts and byproducts.** The chemical components in the concentrate can be solidified and recovered for additional applications. It should be noted that the goal of these applications is to extract salts; water may not be recovered through the physical and chemical processes. In Israel, Mekorot Water Company owns and operates a dual purpose SWRO plant in Eilat that produces desalinated water and high-quality table salt (Ravizky and Nadav, 2007). The feed to the desalination plant is a blend of 80% seawater and 20% BWRO concentrate from adjacent BWRO plants. The concentrate from the SWRO plant is blended with seawater, and this stream is fed to a series of evaporation ponds, and thereafter to the salt processing factory of the salt company.

In Japan, ED is already used on a large scale to recover food-grade  $\text{NaCl}$  from seawater. Because of the preferential selectivity of monovalent ions over multivalent ions (*e.g.*,  $\text{Na}^+$  over  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$  over  $\text{SO}_4^{2-}$ ), special grade of monovalent permselective IX membranes were employed in ED stacks (Tanaka *et al.*, 2003). Tanaka *et al.* (2003) reported

that using ED to treat the concentrate from the SWRO plant as raw material for salt production might be more advantageous than using seawater for salt production, and save 20% of the energy. Davis (2006) used ED to treat SWRO concentrate to reduce the salinity of the reject stream before recycling to SWRO. The preconcentrated SWRO brine was used to extract salable sodium chloride, magnesium hydroxide and bromide.

ED can be combined with bipolar membranes (BMED) to produce acids and bases from desalination concentrate. In this process, mono-polar cation- and anion-exchange membranes are installed together with bipolar membranes in alternating series in an ED stack (Strathmann, 2010). Badruzzaman *et al.* (2009) conducted a bench-scale study that used BMED to produce mixed acid and mixed base streams from the concentrate of a wastewater reclamation plant. Chlorine was also produced by electrochlorination. The produced acids, bases, and hypochlorite could be directly used onsite. A preliminary economic evaluation indicated that this approach might be economically viable for inland wastewater reuse facilities that utilize RO membranes and have limited options for concentrate disposal.

A primary technical challenge for BMED development is the limited stability of current ion-exchange membranes in strong acids and bases and the precipitation of multivalent ions in the flow stream from basic bipolar membrane stack. The concentrate might require an extensive pretreatment. In addition, the acid and base products may be contaminated by salt ions, which permeate the bipolar membrane, especially when high concentrations of acids and bases are required, the salt contamination is high (Strathmann, 2010).

Recently, Saltworks Technologies has developed a patented desalination process that uses thermo-ionic gradient to treat high salinity water. Thermo-Ionic process uses proprietary IX membranes in an arrangement resembling EDR. Unlike EDR, desalination is driven by the salt concentration gradient between a hypersaline solution and feed water. The hypersaline solution is produced in a special evaporative unit that operates at a temperature  $10^\circ\text{C}$  warmer than the ambient wet bulb temperature. Because the unit relies on salinity gradients for internal voltage generation, the net salt flux, or current density, is lower than EDR, requiring more membrane area. Saltworks Technologies has also partnered with SPX Cooling Technologies to develop an air-cooled tower that is able to achieve ZLD and harvest the precipitated salts (GWI, 2011). The potential footprint for the ZLD applications could be large.

For some concentrates, the chemical composition may require multiple stages of reaction and evapo-cooling in addition to conventional mineral and chemical processing steps to extract valuable salts. The patented SAL-PROC<sup>TM</sup> process uses sequential or selective extraction to recover beneficial salts from inorganic saline waters (*e.g.*, irrigation drainage, produced water and RO concentrate) (Geo-Processors USA, Inc.). Jibril and Ibrahim (2001) were able, at a laboratory scale, to produce sodium bicarbonate ( $\text{NaHCO}_3$ ), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) from concentrated  $\text{NaCl}$  solutions by first ammoniating the solution, and then bubbling  $\text{CO}_2$  through the brine.

Recovery of salts offers the potential for revenue generation (offsetting costs) and near ZLD. One possible use of the salt is for winter de-icing of roads. According to the 2012 United States Geological Survey Mineral Commodity Summaries



(USGS, 2012), about 21.7 million metric tons of salt were consumed nationally for this purpose in 2010–2011. And ~22% of the salt was imported for consumption. The salt generated from the desalination concentrate can be used to supplement the deficiency of salt demand in the United States, and generating a revenue of \$32 per ton as rock salt or \$8 per ton as salt in brine (USGS, 2012). Assuming an average seawater salinity of 30 g/L, a rough estimate results in the salt production of 2.07 million tons per year from a 50 million gallons per day (189 million liters per day) desalination plants, ~10% of the salt consumed for winter de-icing in the United States. This means that too much salt may be generated from desalination plants for this purpose. Also, the impact of contaminants in the salt and the costs of salt transport need to be evaluated. In the United States, most desalination plants are in warmer areas such as in California, Texas, Florida, and Arizona where de-icing is most often not needed. Transportation may become a big economic hurdle for disposal of salt.

**Energy recovery from concentrate.** There is a substantial chemical energy difference between highly saline (e.g., seawater, brackish water, desalination concentrate) and lower salinity waters (e.g., river water, municipal wastewater). Mixing equal volumes (1 m<sup>3</sup>) of seawater (~0.5 M) and a fresh river water (~5 mM) releases the equivalent of ~0.5 kWh (Ramon *et al.*, 2011). This chemical energy difference may be converted into useful electricity through the use of selective membranes that act as semipermeable barriers. Several techniques capturing this energy have been investigated, including pressure-retarded osmosis (PRO) that uses water-permeable membranes similar to RO membranes, or reverse electrodialysis (RED) that uses ion-selective membranes (Post *et al.*, 2007; Turek and Bandura, 2007; Długołęcki *et al.*, 2008; Achilli *et al.*, 2009; Długołęcki *et al.*, 2009; Veerman *et al.*, 2009b; Achilli and Childress, 2010; Veerman *et al.*, 2010; Ramon *et al.*, 2011; Chou *et al.*, 2012).

Experimental and modeling work has been conducted to investigate the conversion efficiency of these membrane-based technologies. In PRO, the power density (W per unit membrane area) depends primarily on membrane properties and structure, hydraulic and osmotic pressure gradients across the membrane, and hydraulic conditions of the membrane cell/module. For example, thin film composite membrane improvements increased power production from a river/ocean water mix from 0.1 to 3.5 W/m<sup>2</sup> with a potential of 5 W/m<sup>2</sup> (Gerstandt *et al.*, 2008). In the same study, asymmetric cellulose acetate membranes power production ranged from 0.5 to 1.3 W/m<sup>2</sup>. There has been significant progress made recently in PRO technology. For seawater and diluted solution (0.55 M vs. 5 mM), the current PRO systems have been reported to produce 5–6 W/m<sup>2</sup> for a similar solution river/ocean water mix. At this level, PRO systems may be economical (Ramon *et al.*, 2011). First cut calculations suggested that PRO systems utilizing desalination concentrates could generate up to 15 W/m<sup>2</sup> (Ramon *et al.*, 2011), making the process even more economically attractive.

For the RED process, studies have reported that homogeneous IX membranes generate a higher power density than heterogeneous IX membranes (Długołęcki *et al.*, 2008; Veerman *et al.*, 2009a; Długołęcki *et al.*, 2010). The highest power density reported was 1.2 W/m<sup>2</sup> for artificial river water and

seawater (1 and 30 g/L NaCl; 0.02 and 0.5 M) using commercial Fumasep (FAD and FDK) and Selemion (AMV and CMV) membrane combinations (Veerman *et al.*, 2009a). When applying the RED process at larger, more practical scale (50 cells stack), a power density of 0.93 W/m<sup>2</sup> was obtained with the same river-seawater matrix (Veerman *et al.*, 2009b). Cell electrical resistance and hydrodynamic conditions affect power density, and efficiency improves at lower current densities (Veerman *et al.*, 2009a).

Experimental and modeling results suggest that PRO has more potential than RED for recovering salinity-gradient energy (Ramon *et al.*, 2011). Currently, salinity-gradient energy production appears to be neither economically feasible nor technically attractive when compared with other technologies. If membranes improve and fossil fuel prices increase, salinity-gradient power may become an attractive energy source in the future.

Recently, a novel “mixing entropy battery” (MEB) was developed at Stanford University (Mantia *et al.*, 2011) to recover salinity-gradient energy. The battery charges when flushed with freshwater and discharges when flushed with seawater. The cathode material (Na<sub>2</sub>Mn<sub>5</sub>O<sub>20</sub>) has high energy density, low cost, and is environmentally benign; the anode is made of an Ag/AgCl composite. The energy recovery of MEB may be higher than either PRO or RED; it is estimated that for a seawater/river water mix, MEB could recover 74% of the energy versus ~50% for PRO or RED.

Conversion of salinity-gradient sources to electric power has particular merit if seawater desalination concentrate waste stream can be used before discharge, because the energy stored in the concentrate is much higher than in seawater. However, substantial research is needed to improve the energy conversion efficiencies, mitigate biofouling and scaling of membranes and electrodes during operation with concentrate, and evaluate the cost effectiveness.

Solar energy ponds are another approach to capture and use solar energy from concentrate. They use salinity gradients to trap energy in the deeper, denser (high TDS) layer of the pond. The economic feasibility of using solar ponds to provide heat for a thermal desalination facility is dependent on climate condition, stage capacity, and salinity level. For arid and semi-arid areas with high solar radiation intensities, high ambient temperature most of the year, and availability of high concentration brine, solar ponds could be a feasible technology for water desalination. For example, a theoretical simulation estimated that coupling a 3000 m<sup>2</sup> solar pond with multistage multieffect desalination unit was able to provide an annual average production rate of 4.3 L/min distilled water using high concentration brine extracted from the Dead Sea in Jordan (Saleh *et al.*, 2011). The maximum heat extraction rate is 191.2 kW. Based on this study, solar pond for thermal desalination near the Dead Sea appears to be a feasible and appropriate technology for developing community villages around the valley of Jordan by providing fresh water needed for drinking, irrigation, and other needs.

Another research that used Libya as a case study found that solar ponds combined with multistage flash evaporation would require a large footprint, about 73–185 m<sup>2</sup> per m<sup>3</sup>/day capacity, depending on the storage zone temperature, peak clipping days, and performance ratio (Agha, 2009). At the current fossil fuel prices, solar desalination is not competitive given the high costs for the large pond area. A large quantity

of salt is required to construct a solar pond, about 146 acre-ft ( $180,000 \text{ m}^3$ ) of 10,000 mg/L TDS concentrate to construct one acre ( $1223 \text{ m}^3$ ) of solar pond with gradient and storage layers of 5 feet (1.5 m) (SJVDIP, 1999). It infers that solar pond is not feasible to recover heat from brackish water concentrate with lower salinity.

## Conclusions

As the number of desalination plant installations grows, concentrate management is facing increasing scrutiny due to larger concentrate flows, limited disposal options, and cumulative environmental impacts. More stringent discharge regulations and increased public concerns over adverse environmental impacts and energy footprints also make disposal more difficult, and complicate the permitting process. These issues are particularly acute in arid areas where desalination can present an attractive option to enhance the supply of unconventional freshwater. This paper evaluated a variety

of technologies for the improvement of water recovery, removal of contaminants, and recovery of valuable salts and energy from the concentrate. A guidance flowchart of concentrate management strategies is illustrated in Fig. 1.

Currently thermal processes using brine concentrator and crystallizer are considered mature industrial technologies to achieve ZLD or near ZLD of concentrate from low to high salinity; however, at high costs and intensive energy demand. The use of secondary membrane technologies, such as RO and ED or EDR with intermediate treatment has been pilot tested and demonstrated effective to improve water recovery of concentrate with low and moderate salinity by additional 10% to 20% depending upon the source water quality. These technologies are innovative combinations of commercial technologies and can be employed at full-scale in the near future. To achieve equivalent overall recovery, economic analysis indicated that these hybrid configurations could save 20% to 40% of costs compared to conventional RO and thermal processes (Sethi *et al.*, 2009). Emerging

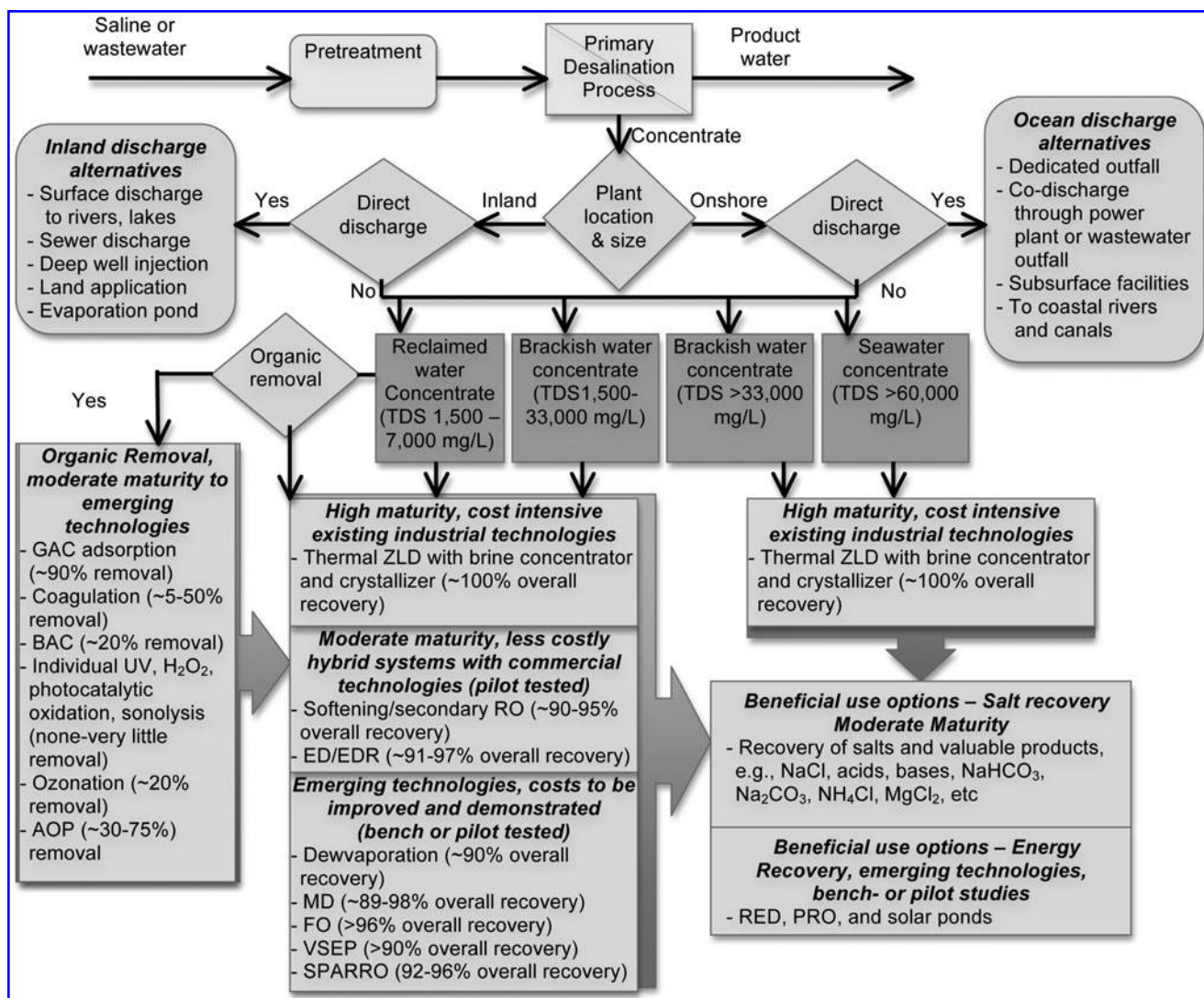


FIG. 1. Decision diagram of concentrate management strategies. AOP, advanced oxidation processes; BAC, biological activated carbon; ED, electrodialysis; EDR, electrodialysis reversal; FO, forward osmosis; GAC, granular activated carbon; MD, membrane distillation; PRO, pressure-retarded osmosis; RED, reverse electrodialysis; RO, reverse osmosis; TDS, total dissolved solids; ZLD, zero liquid discharge.

technologies may offer enhanced recovery, but they also face the challenges as conventional membrane systems, such as membrane fouling and scaling for MD and VSEP, and high energy demand for dewvaporation. FO is a promising alternative technology for desalination and concentrate management, but it is limited by the osmotic pressure gradient between feed and draw solution, and the economics and configuration need further improvement. Salt recovery has significant benefits to extract valuable resources from the waste stream, and can bring revenues to offset desalination costs. The quality, market, and transportation of the recovered salts need thorough assessment. Energy conversion from desalination concentrate is an emerging research area but is not economically competitive to traditional energy sources yet.

### Acknowledgments

The authors are grateful for the support from the National Science Foundation under Cooperative Agreement EEC-1028968, "Ultra-Deepwater and Unconventional Natural Gas and Other Petroleum Resources Research and Development Program" as part of the Research Partnership to Secure Energy for America program administered by the U.S. Department of Energy's National Energy Technology Laboratory, and the Water Research Foundation. The authors would also like to thank Drs. Nathan Hancock (Oasys Water, Inc.), Sandeep Sethi (Carollo Engineers), Robert S. Raucher (Stratus Consulting Inc.), Mike Mickley (Mickley & Associates), and Nikolay Voutchkov (Water Global Consulting), for technical discussions and assistance.

### Author Disclosure Statement

No competing financial interests exist.

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