RECLAMATION
Managing Water in the West

Forward Osmosis Evaluation and Applications for Reclamation

Research and Development Office
Science and Technology Program

Final Report ST-2015-7911-01

U.S. Department of the Interior
Bureau of Reclamation
Research and Development Office

Mission Statements

The U.S. Department of the Interior protects America's natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

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

Final Report 2015-01-7911

Forward Osmosis Evaluation and Applications for Reclamation

Research and Development Office
Advanced Water Treatment

by

Julie Korak

and

Miguel Arias-Paic

REPORT DOCUMENTATION PAGE			*Form Approved* *OMB No. 0704-0188*
T1. REPORT DATE October 2015	**T2. REPORT TYPE** Research	**T3. DATES COVERED** October 2014 to September 2015	
T4. TITLE AND SUBTITLE Forward Osmosis Evaluation and Applications for Reclamation		**5a. CONTRACT NUMBERS** XXXR4524KS-RR4888FARD1401301	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER 7911 (S&T)	
6. AUTHOR(S) Julie Korak Miguel Arias-Paic		**5d. PROJECT NUMBER** 7911	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER 86-68190	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Julie Korak, Bureau of Reclamation Miguel Arias-Paic, Bureau of Reclamation		**8. PERFORMING ORGANIZATION REPORT NUMBER**	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Research and Development Office U.S. Department of the Interior, Bureau of Reclamation, PO Box 25007, Denver CO 80225-0007		**10. SPONSOR/MONITOR'S ACRONYM(S)** R&D: Research and Development Office BOR/USBR: Bureau of Reclamation DOI: Department of the Interior	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S) 2015-01-7911	
12. DISTRIBUTION / AVAILABILITY STATEMENT Final report can be downloaded from Reclamation's website: https://www.usbr.gov/research/			
13. SUPPLEMENTARY NOTES			

14. ABSTRACT *(Maximum 200 words)*

Forward osmosis (FO) is a separation technology that has garnered increased focus from the research community as a potential water treatment method. FO is a separation process driven by differences in osmotic pressure across a semi-permeable membrane. Water permeates from a solution with low osmotic pressure to high osmotic pressure without the application of a hydraulic driving force. Water permeates across the membrane until equilibrium is reached, and both feed and draw solutions have equal osmotic pressures. The product is a diluted draw solution and concentrated feed solution. FO applications range from osmotic dilution prior to desalination, water recovery from wastewater, fertigation, emergency water supply and treatment of high salinity brines. FO is generally most viable in the following scenarios: 1) highly fouling and scaling brines where increased water recovery is required, 2) highly saline solutions where other methods of water recovery become operationally unsuitable, 3) applications where multiple barriers are required for water recovery, and 4) situations where the draw solution can be directly used for beneficial purposes and 5) dilution of a high salinity feed stream with a low salinity waste stream.

15. SUBJECT TERMS

Forward osmosis, water treatment, desalination, fertigation, water reuse, osmotically driven membrane processes

16. SECURITY CLASSIFICATION OF: U			**17. LIMITATION OF ABSTRACT** U	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Miguel Arias-Paic
a. REPORT U	**b. ABSTRACT** U	**c. THIS PAGE** U		49	**19b. TELEPHONE NUMBER** 303-445-2132

S Standard Form 298 (Rev. 8/98)
P Prescribed by ANSI Std. 239-18

Forward Osmosis Evaluation and Applications for Reclamation

Peer Review Documentation

Project and Document Information

Project Name Forward Osmosis Evaluations and Applications for Reclamation WOID A752F

Document Forward Osmosis Evaluations and Applications for Reclamation Document date 10/2015

Peer Reviewer Steve Dundorf

Review Certification

Peer Reviewer: I have reviewed the assigned items/sections(s) noted for the above document   and believe them to be in accordance with the project requirements, standards of the profession,   and Reclamation policy.

Peer Reviewer _____*Stephen C Dundorf*_____ Date _____10/27/2015_____
                                            (Signature)

Disclaimer

Executive Summary

Forward osmosis (FO) is a separation technology that has recently garnered increased focus from the research community as a potential water treatment method. FO has been labeled as a low energy separation method with a range of potential applications (i.e., fertigation, emergency water supply, treatment of high salinity wastes, wastewater treatment, osmotic dilution of RO feed source, and RO pre-treatment). This report provides a review of FO research, in particular discussing the current state of membrane and draw solution technology, reviewing potential FO applications and commenting on the future potential of FO for each application.

FO is a separation process driven by differences in osmotic pressure across a semi-permeable membrane. Water permeates from a solution with low osmotic pressure to high osmotic pressure without the application of a hydraulic driving force. In theory, only water permeates from low (feed solution) to high (draw solution) osmotic pressure. Since membranes are semi-permeable, there may be some transport of dissolved species between both the draw and feed solutions. Membrane rejection (feed to draw solution) of NaCl is greater than 93% for FO membranes, so mass transport of solutes in this direction is usually neglected. Reverse salt flux (draw to feed solution) is a more important consideration, because it represents a loss of a process chemical and may lead to scaling on the feed solution side of the membrane. Water permeates across the membrane until equilibrium is reached, and both feed and draw solutions have equal osmotic pressures. The product is a diluted draw solution and concentrated feed solution. Unless there is a direct use for the diluted draw solution, a subsequent treatment step is required (i.e., reverse osmosis (RO)) to recover water with low salinity from the diluted draw solution. FO can be characterized as a low flux process ($<$ 10 L/m^2/hr for FO compared to 20-30 L/m^2/hr for RO) when cellulose triacetate membranes are used, which have similar salt rejections compared to RO membranes. Recent developments of polyamide thin film composite FO membranes exhibit higher fluxes (10-50 L/m^2/hr) but have lower salt rejection from the feed to draw solutions.

The FO process has been tested and implemented for a wide range of water treatment applications, where fouling and scaling aspects of conventional processes can be mitigated. Depending on the application, implementing FO may decrease operational power requirements. In recent years, improvements to FO systems, including draw solution testing and membrane material development, have allowed for increased flux while minimizing internal concentration polarization, improving energy requirements and fouling effects. Thermodynamically, it has been demonstrated that a two-step separation process (i.e., FO followed by RO) cannot be more energetically favorable than a direct separation step (i.e., solely applying RO). However, FO can be beneficial if another operational limitation (e.g., scaling or fouling) can be minimized. If water

recovery from a potential draw solution (e.g., seawater) is a treatment objective, then energy needs can be minimized by osmotic dilution of the draw solution.

Forward osmosis applications range from osmotic dilution prior to desalination, water recovery from wastewater, fertigation, emergency water supply and treatment of high salinity brines. This report reviews the current state of each application and evaluates the likelihood for future implementation. A brief summary is provided in Table E-1. Within this range of applications, FO is generally most viable in the following scenarios: 1) highly fouling and scaling brines where increased water recovery is required, 2) highly saline solutions where other methods of water recovery become operationally unsuitable, 3) applications where multiple barriers are required for water recovery, 4) situations where the draw solution can be directly used for beneficial purposes, and 5) dilution of a high salinity feed stream with a low salinity waste stream. The addition of other unit operations to the FO process requires scrutiny since increased energy of separation will be required, potentially making a hybrid FO-RO process more energy intensive than a conventional process. Based on the comprehensive literature review, it is evident that there is a substantial body of knowledge with process fundamentals and proof-of-concept studies. These studies that place the foundation for FO must expand to include investigations of practical and economically viable applications.

Table E.1—Summary of FO Applications and Outlook for Future Use

Application	Maturity of Technology	Potential for Improvement	Likelihood of Use Compared to Other Technologies	
			Currently	At full maturity
Fertigation	Bench scale tests only	Low	Low	Low
Emergency Water Supply	Commercially available	Low	Moderate	Low
Highly Saline Wastes	Bench and pilot scale tests	High	Moderate	High
Direct Wastewater Treatment	Bench Scale tests	Moderate	Low	Moderate
Osmotic dilution of saline water using impaired water	Bench and pilot scale	Moderate	Moderate	Moderate
Conventional Desalination Pre-treatment	Bench scale	Moderate	Low	Low

Contents

Figures

Tables

Acronyms and Abbreviations

A	pure water permeability
atm	atmosphere
B	solute permeability coefficient
BGW	brackish groundwater
DS	draw solution
$\Delta\pi$	osmotic pressure differential
C_M	molar concentration
CA	cellulose acetate
CTA	cellulose triacetate
ECP	external concentration polarization
FO	forward osmosis
FS	feed solution
ft^2	square feet
g/L	gram per liter
hr	hour
HTI	Hydration Technology Innovations
ICP	internal concentration polarization
J_w	water flux
K	solute resistivity
k	mass transfer coefficient
kg/ha/d	kilogram per hectare per day
L	liter
lbf	linear bed feet

LBL	layer-by-layer
$L/m^2/hr$	liter per square meter per hour
m^2	square meter
M_w	molecular weight
mg/L	milligram per liter
mg-N/L	milligram of nitrogen per liter
mL	milliliter
$mmol/m^2/hr$	millimole per square meter per hour
NF	nanofiltration
PRO	pressure retarded osmosis
$\pi_{D,b}$	bulk osmotic pressure in draw solution
$\pi_{F,b}$	bulk osmotic pressure in feed solution
π_{high}	high osmotic pressure
π_{low}	low osmotic pressure
RO	reverse osmosis
σ	reflection coefficient
TDS	total dissolved solids
TFC	thin film composite
TFN	thin film nanocomposite
UF	ultrafiltration
V	extraction volume

1.   Introduction

There is a constant effort to identify treatment technologies that allow for greater utilization of saline water sources (e.g., brackish groundwater, seawater, wastewater effluent) or for decreased costs in treating impaired water sources. Improved water treatment processes can offer opportunities to better utilize water sources with high salinity. Additionally, saline wastes (e.g., RO concentrate) can be minimized for decreased environmental impacts, transport and disposal costs. Advanced water treatment can also promote reuse or water recovery from industrial waste streams (e.g., landfill leachate, produced water).

Forward osmosis has been a popular research topic gaining particular interest in the past 5 years (figure 1) for the treatment of saline and industrial waste streams. Forward osmosis is an osmotically driven process by which water passes through a semipermeable membrane due to differences in osmotic pressure, not due to applied hydraulic pressure. As a result, this technology has been pitched as a low energy alternative to pressure driven processes. The objective of this report is to review the fundamentals of FO and provide a critical evaluation of potential applications for FO.
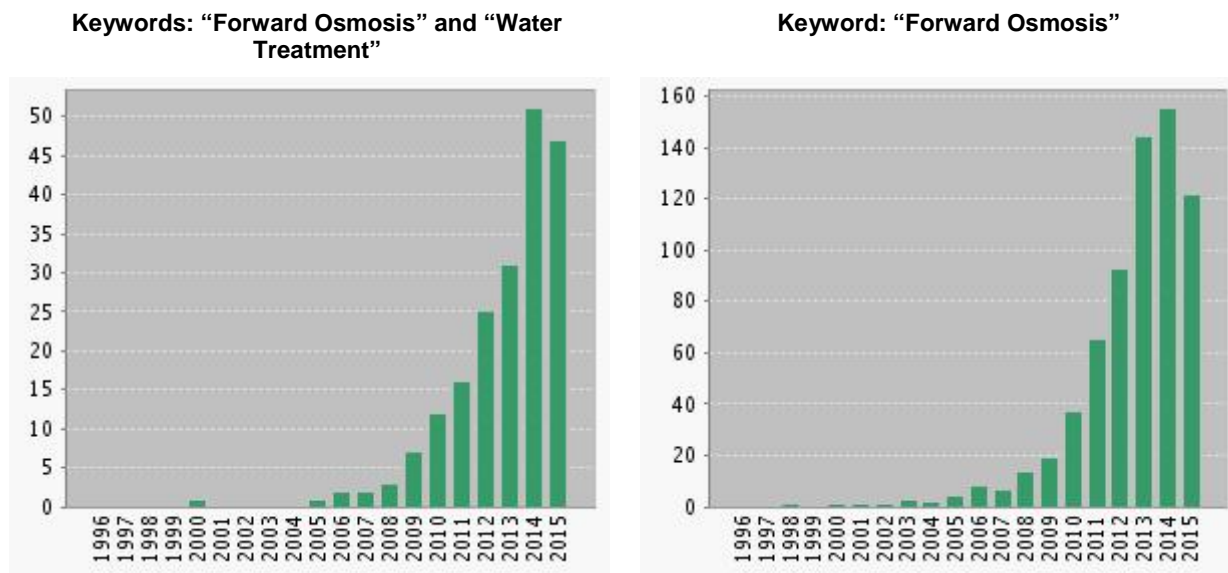
Figure 1.—Published articles by year with keywords from Web of Science. Accessed 8/10/15.

2.   Theory

Osmotic pressure differences drive the FO process. A semi-permeable membrane separates two solutions that have different osmotic pressures. The lower osmotic pressure (π_{Low}) feed solution (FS) is the stream from which the objective is to extract water. The draw solution (DS) has a high osmotic pressure (π_{Hi}) and is the stream that extracts the water from the FS. Without any externally applied hydraulic pressure, water flows from the FS to the DS. During this process, the FS becomes more concentrated and the DS becomes more dilute. Equilibrium is reached

when both the FS and DS have the same osmotic pressure at which point the driving force is zero. FO is usually coupled with additional treatment steps in order to produce water with low salinity. Once water has permeated from the FS to the DS, a subsequent treatment process recovers water from the DS. A common secondary treatment process is reverse osmosis to re-concentrate the draw solution and recover product water. The FO membrane orientation in Figure 2 with the active layer in contact with the FS is referred to as FO mode. If the active layer is in contact with the DS, the system is operating in pressure-retarded osmosis (PRO) mode.
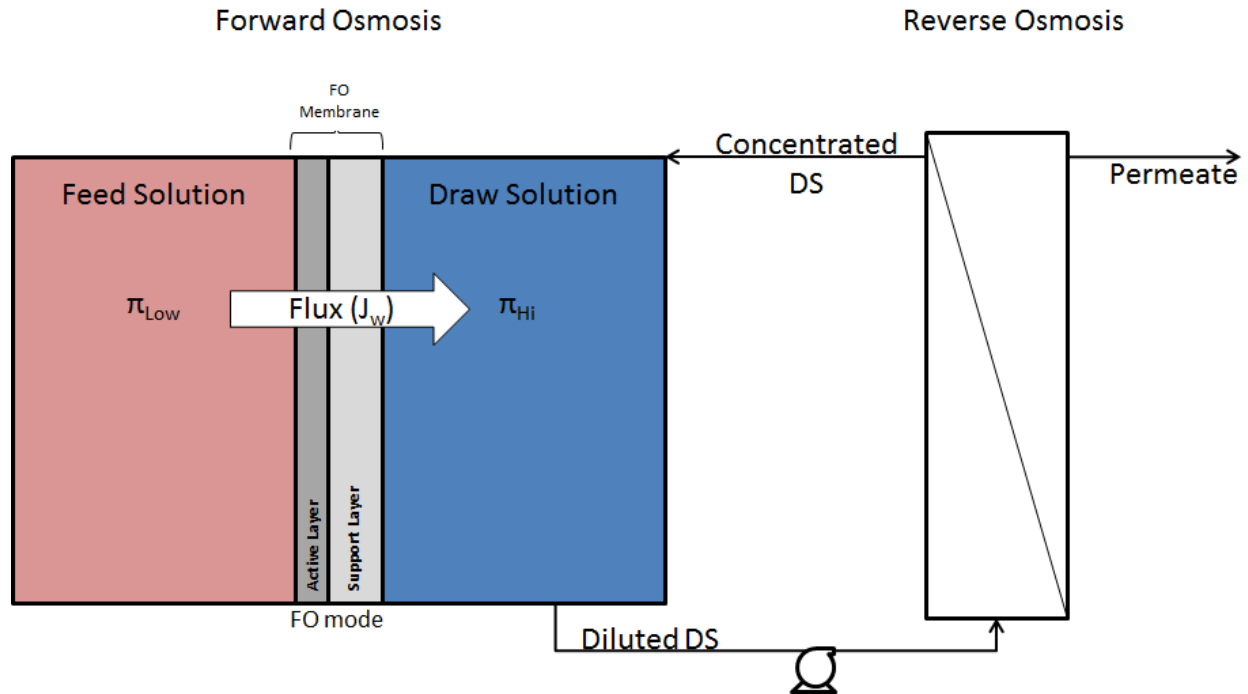
Figure 2.—Schematic of forwards osmosis with optional reverse osmosis to re-concentrate and recycle draw solution.

Flux across the membrane is controlled by differences in osmotic pressure between the draw and feed solutions. Osmotic pressure is a colligative property that is proportional to the molar concentration at low concentrations and can be non-linear at high concentrations. In an ideal case, a greater osmotic pressure difference between the FS and DS lead to a greater water flux across the membrane (Eqn. 1), where A is the water permeability constant and σ is the reflection coefficient.

$$J_w = A\sigma\Delta\pi$$

Eqn. 1

2.1   Concentration Polarization

Like reverse osmosis processes, FO processes may be affected by concentration polarization that cause deviations in the observed flux from those predicted simply based on osmotic pressure

differences (Eqn. 1). In reverse osmosis, *external* concentration polarization is the primary concern but FO is most affected by *internal* concentration polarization effects. Attempts to minimize concentration polarization and improve flux have motivated membrane materials research.

External concentration polarization (ECP) occurs when the solute concentration at the membrane interface results in a solute concentration that is different from the bulk concentration. *Concentrative* ECP occurs when solute accumulates on the feed solution side, increasing the concentration of solute [Cath et al., 2006; Gray et al., 2006; McCutcheon and Elimelech, 2006]. The concentration increase at the membrane interface relative to the bulk solution effectively decreases the osmotic pressure differential between the feed and draw solutions, decreasing the driving force and net flux of water through the membrane. *Dilutive* ECP occurs on the permeate side of the membrane due the water flux through the membrane. Low salinity water permeating through the membrane leads to a dilution of the draw solution solute at the membrane interface. Decreasing the solute concentration at the membrane decreases the osmotic pressure differential between feed and draw solutions - ultimately decreasing flux through the membrane.

ECP is most apparent in reverse osmosis systems due to high permeate flux. In FO systems, ECP can be neglected or minimized in many cases due to low permeate flux and controlling cross-flow velocity. Increasing the cross-flow velocity and turbulence at the membrane interface on both the draw and feed sides decreases ECP effects [Cath et al., 2006]. When the membrane is in FO orientation, the permeate flux is often sufficiently low to neglect ECP [McCutcheon and Elimelech, 2006]. In pressure retarded osmosis (PRO), water from a low salinity FS permeates through a membrane into a pressurized, high salinity DS. Permeate flux is higher initially but decreases rapidly due to ECP effects that cannot be neglected [McCutcheon and Elimelech, 2006].

Internal concentration polarization (ICP) is more important than ECP in FO [Lutchmiah et al., 2014; McCutcheon and Elimelech, 2006]. Internal concentration polarization occurs within the porous support layer of the asymmetric FO membranes when the solute concentration within the support layer differs from the bulk solution [Cath et al., 2006; Gray et al., 2006; McCutcheon and Elimelech, 2006]. When the membrane is oriented in FO mode (active layer on the feed solution side), water permeating through the membrane dilutes the draw solution solute concentration in the support layer, known as *dilutive* ICP. The osmotic pressure at the active layer interface therefore depends on the steady state balance between DS solutes diffusing towards the active layer and solute advection away due to permeate flux. This effective decrease in DS concentration at the active layer interface decreases the osmotic driving force between the FS and DS and decreases permeate flux [Gray et al., 2006; McCutcheon and Elimelech, 2006]. DS solutes with larger molecular weights lead to greater flux decline due to the decreasing diffusion coefficients with increasing molecular weight [Cath et al., 2006; Gray et al., 2006]. When the membrane is oriented in PRO mode (active layer facing the DS), a concentrative ICP occurs. Solute accumulates on the feed solution side in the porous support layer, which decreases osmotic pressure difference and flux [Cath et al., 2006; Gray et al., 2006]. Unlike ECP, ICP effects cannot be minimized by optimizing operational parameters such as cross-flow velocity [Lee et al., 1981]. One method of minimizing ICP effects is to operate with counter-current flow

to maintain a constant osmotic pressure differential across the length of the membrane [Cath et al., 2006].

The effects of ICP are seen by measuring the flux at different DS concentrations. Fundamental theory in the absence of any ECP or ICP effects would predict a linear relationship between DS concentration (osmotic pressure) and permeate flux (Eqn. 1). When the DS concentration is low, a linear relationship has been observed. At higher DS concentrations, there is a logarithmic relationship between DS osmotic pressure and flux (at constant FS osmotic pressure) [Cath et al., 2006; Gray et al., 2006; McCutcheon and Elimelech, 2006; Phuntsho et al., 2013b; Sahebi et al., 2015; Tan and Ng, 2010]. To operate in this ideal linear range, Zhao et al (2012) used DS concentrations of 0-0.15 M Na_2SO_4 for characterization purposes [Zhao et al., 2012]. At low DS concentrations where the flux is low, ICP effects are negligible and flux is proportional to DS osmotic pressure. Another artifact of ICP is that specific reverse solute flux increases as a result of ICP due to the increased solute concentration gradient across the active layer [Phillip et al., 2010].

Since the accumulation of solutes in the porous support layer depend on permeate flux, modeling the flux of a FO process is iterative. Loeb et al (1997) presented Eqn. 2 that describes the flux (J_w) as a function of the feed osmotic pressure (π_{low}), draw solution osmotic pressure (π_{hi}) and solute resistivity (K). Assuming that the osmotic pressure adheres to the van't Hoff equation (pressure linearly related concentration), Eqn. 3 and Eqn. 4 relate K for both dilutive (FO) and concentrative (PRO) ICP scenarios, where A is the pure water permeability, and B is the solute permeability coefficient of the active layer [Loeb et al., 1997]. Water flux is a function of osmotic pressure on both sides of the membrane and the resistance of solute diffusion in the membrane, K. The parameter K, in turn, depends on the water flux [Gray et al., 2006]. Other parameters, such as the membrane permeability constant, also depend on the osmotic pressure of the draw solution and membrane orientation [Cath et al., 2006]. K is inversely proportional to the solute diffusion coefficient [Gray et al., 2006; McCutcheon and Elimelech, 2006]. Practically, the differences between Eqn. 2 and 3 for the different membrane orientations affect the rate of flux decline. Initially, PRO operations usually exhibit higher initial fluxes, but flux decline is more rapid due to concentrative ICP effects [Tang et al., 2010].

$$J_w = K \ln \frac{\pi_{Hi}}{\pi_{Low}} \qquad \textbf{Eqn. 2}$$

$$K = \frac{1}{J_W} \ln \frac{B + A\pi_{Hi}}{B + A\pi_{Low} + J_W} \qquad \begin{array}{l}\textbf{Eqn. 3}\\ \text{Dilutive ICP}\end{array}$$

$$K = \frac{1}{J_W} \ln \frac{B + A\pi_{Hi} - J_W}{B + A\pi_{Low}} \qquad \begin{array}{l}\textbf{Eqn. 4}\\ \text{Concentrative ICP}\end{array}$$

In FO mode with the active layer facing the FS, the system experiences both dilutive ICP (DS side) and concentrative ECP (FS side). Assuming the membrane salt flux is negligible (B=0), the fundamental equations can be rearranged to yield an implicit relationship for J_w (Eqn. 5) incorporating both concentration polarization effects. A full derivation is given in McCutcheon and Elimelech (2006). Eqn. 5 demonstrates that increasing the bulk osmotic driving force ($\pi_{D,b}$ -

$\pi_{F,b}$) will yield diminishing increases of water flux and is self-limiting [McCutcheon and Elimelech, 2006].

$$J_W = A\left[\pi_{D,b}\,exp(-J_W K) - \pi_{F,b}\,exp\left(\frac{J_W}{k}\right)\right]$$ **Eqn. 5**

   A: pure water permeability coefficient
   $\pi_{D,b}$: osmotic pressure of DS in bulk solution
   $\pi_{F,b}$: osmotic pressure of FS in bulk solution
   K: solute resistivity
   k: mass transfer coefficient

The effects of concentration polarization have been quantified in literature following a couple of different approaches. From a fundamental perspective, several studies have quantitatively modeled the system following Eqn. 3-Eqn. 4 to empirically determine the solute resistivity [Gray et al., 2006; McCutcheon and Elimelech, 2006]. Others have taken a more applied approach by calculating a performance ratio, which is the ratio between the theoretical flux (based on osmotic pressure difference) and the observed flux [Phuntsho et al., 2013b]. Reported performance ratio values for applications with fertilizers as a draw solution are typically less than 40%, illustrating the large effect of concentration polarization [Phuntsho et al., 2013a, 2013b, 2012a, 2011].

3.   Operational and Sizing Considerations

Compared to other membrane separation processes, the operating characteristics dictating appropriate application of forward technology differ. For example, key considerations for sizing RO membranes and pumps are the water flow, feed osmotic pressure, target water recovery, membrane rejection, and scaling potential. Forward osmosis does not require a high pressure pump, instead using two low pressure circulation pumps for the FS and DS to minimize external concentration polarization. Membrane sizing is dictated by not only feed osmotic pressure but also the DS osmotic pressure, which is dependent on solute choice and concentration. Most importantly, an appropriate use of FO is largely dictated by the subsequent use of the diluted draw solution. Table 1 summarizes the main design considerations for FO systems, each of which are described in the following sections.

Table 1.—Main considerations for designing an FO process

Design Consideration	Impact
Membrane Material	• Flux • Concentration polarization • Cost • Membrane rejection (from FS to DS) • Reverse solute flux (from DS to FS), loss of draw solute
Membrane Orientation	• Flux • Fouling potential • Trade-off between flux and fouling potential • Concentration polarization
Draw Solution (Composition and Concentration)	• Determines osmotic pressure • Affects reverse solute flux and concentration polarization • Scaling potential • Dictates downstream processes for re-concentration or beneficial use of diluted draw solution
Cross flow velocity and flow regime	• External concentration polarization • Local osmotic pressure driving force

3.1 Membrane construction and orientation

FO membranes are asymmetrical and consist of two layers: active layer and support layer. The active layer is a semipermeable material with ideally a high salt rejection. The support layer consists of a porous layer that provides structural support for the active layer but no salt rejection. While the materials may be similar, the FO support layers are thinner than RO membranes due to the lower operating pressure [Cath et al., 2006]. The asymmetric design of FO membranes means that the orientation of the membrane has important implications. When the active layer is oriented towards the feed solution, this operation is referred to as FO mode. Conversely, orienting the active layer towards the draw solution is referred to as PRO mode. FO membranes have been developed using phase inversion, thin-film composite and layer-by-layer (LBL) synthesis [Qasim et al., 2015].

The most common materials for the active layer are cellulose (tri)acetate- and polyamide-based materials. Several review papers have provided comprehensive summaries of FO membranes [Cath et al., 2006; Lutchmiah et al., 2014]. Cellulose acetate membranes are most common as they have been produced commercially for longer than polyamide-based thin film composite (TFC) membranes. Hydration Technology Innovations began commercially producing TFC FO membranes in 2012. Compared to cellulose acetate (CA), TFC membranes have been shown to have higher fluxes and better rejection of trace organic contaminants due to increased negative surface charge despite greater pore sizes [Sukitpaneenit and Chung, 2012; Xie et al., 2014]. Porous FO membranes resembling UF and NF membranes have been shown to have high fluxes but are only applicable for applications where NaCl rejection is not important (e.g., oil-water separations) [Qi et al., 2015]. The active layer surface chemistry properties are important for solute flux across the membrane. The carboxyl groups on polyamide-based membranes can

6

promote cation diffusion through the membrane, especially at higher pH values through an ion exchange process [Arena et al., 2015; Lu et al., 2014]. Post-treatment to improve flux and rejection have been evaluated in several studies. Polyelectrolyte post-treatment of hollow fiber poly(amide-imide) membranes yielded a positive surface charge at environmental pH values that exhibited high pure water permeabilities (~2.2 L/m^2/hr) and high salt reject for divalent cations (MgCl$_2$) [Setiawan et al., 2011].

The composition of the support layer is important for balancing the material structural needs with hydrophilicity. The support layer provides the mechanical strength of the membrane but affects membrane performance due to internal concentration polarization. Increasing both porosity of the support layer and hydrophilicity improves membrane flux. CA membranes often have a polyester mesh as a support layer [Cath et al., 2006]. Polysulfone is a common support layer for TFC membranes [Qasim et al., 2015], but alternative materials, such as polyacrylonitrile [Ren and McCutcheon, 2015] and polyvinylpyrrolidone blended polyethersulfone [Yang et al., 2009], have been investigated.

Recently thin film nanocomposite (TFN) membranes that incorporate nanoparticles embedded in the active or support layer have been an active research area [Lau et al., 2015]. Example nanoparticle materials embedded include zeolites, multi-walled carbon nanotubes, silicon dioxide and titanium dioxide (TiO$_2$) [Lau et al., 2015]. Embedding a nanofiller in the active layer has resulted in increased water flux but decreased salt rejection [Emadzadeh et al., 2014; Lau et al., 2015; Tian et al., 2015]. Adding TiO$_2$ to the porous polysulfone support layer to increase hydrophilicity increased flux in FO mode by 87% but at the expense of increased reverse solute flux [Emadzadeh et al., 2014]. Tian et al (2015) added functionalized carbon nanotubes to the support layer to increase porosity and mechanical strength, which increased flux in both FO and PRO mode. Another study added boehmite nanoparticles to a cellulose acetate membrane and observed a threefold flux increase and similar reverse solute flux when less than 0.5 wt% boehmite was used [Zirehpour et al., 2015].

3.2   Draw Solute Selection

A range of draw solution solutes have been proposed for FO systems [Ge et al., 2013; Li and Wang, 2013] coupled with a variety of novel recovery methods [Luo et al., 2014]. The most common solutes are inorganic salts (e.g., NaCl, KCl, MgCl$_2$, Na$_2$SO$_4$, CaCl$_2$) and inorganic fertilizers (e.g., NH$_4$Cl, monoammonium phosphate, potassium dihydrogen orthophosphate) [Achilli et al., 2010; Phuntsho et al., 2013a, 2012a]. Additional broad categories of draw solutes include organic salts (e.g., sodium formate, sodium acetate and magnesium acetate) and synthetic materials (e.g., hydrophilic magnetic nanoparticles, polyelectrolytes, ionic liquids) [Cai et al., 2015; Ge et al., 2013; Li and Wang, 2013]. There appears to be some debate regarding whether the use of hydrogels as a solid draw agent should be classified as FO [Razmjou et al., 2013; H. Wang et al., 2014; Zhao, 2014]. Non-synthetic draw solutions, such as seawater [Cath et al., 2010; Hoover et al., 2011] and cooling water [Wang et al., 2014] have also been used.

3.2.1 Process driving force

Focusing on inorganic salt draw solutions, draw solution composition dictates several aspects of a FO system. Neglecting non-ideal concentration polarization effects, draw solute composition and concentration determine the driving force of the process. In general, osmotic pressure increases with solute concentration albeit non-linearly at higher concentrations typically used in FO applications. At a given concentration, osmotic pressure depends on the specific solute and its dissociated ions as osmotic pressure is a colligative property. At the same osmotic pressure, choice of draw solution solute affects the observed flux. For example, given the same osmotic pressure, the relative order of flux for different solutes was $KCl>Na_2SO_4>CaCl_2>MgSO_4>urea$ [Phuntsho et al., 2013b]. Differences can be attributed to the differences in dilutive ICP effects, which ultimately stem from differences in diffusivity [Gray et al., 2006]. Not only does solute selection affect the flux (or rate of water permeation), but the choice of solute also dictates the theoretical capacity for water extraction (i.e., volume of water that permeates at a given DS solute concentration). At a given FS TDS, the maximum water extraction per mass of draw solute depends on the solute. Small molecular weight solutes (e.g., NaCl) have a greater extraction capacity at equilibrium compared to larger solutes (e.g., $MgSO_4$), and extraction capacity increases exponentially as FS TDS decreases [Phuntsho et al., 2014a].

3.2.2 Concentration polarization and reverse salt flux

Draw solute size and charge affects concentration polarization and reverse solute flux. Flux will be dependent on solute diffusivity and potential for reverse solute flux. Dilutive internal concentration polarization occurs within the support layer when operating in FO mode. The extent of the concentration polarization, which ultimately decreases flux, depends on the solute size and diffusivity. Solutes with a greater molecular weight have lower diffusivities and lead to larger ICP effects and lower flux [Gray et al., 2006].

There is trade-off between minimizing both ICP effects and reverse solute flux, as both depend on solute size. Small solutes exhibit greater reverse solute flux. Solutes that are divalent exhibit lower reverse solute flux compared to monovalent ions, and hydrophobic solutes (e.g., urea) exhibit the greatest reverse flux [Phuntsho et al., 2013b]. Reverse solute flux can be quantified by several parameters. Some studies report the flux of draw solution ions (units of $mmol/m^2/hr$). Typical values for NaCl reverse solute flux with CTA membranes are 29-293 $mmol/m^2/hr$ [Alturki et al., 2013; Holloway et al., 2014; Phillip et al., 2010]. These values must always be put into the context of the application. The reverse solute flux depends on the draw solution concentration. Higher DS concentration leads to greater reverse flux [Alturki et al., 2013; Phillip et al., 2010]. Membrane type and orientation also affects RSF with TFC membranes exhibiting lower reported RSF compared to CTA membranes [Phuntsho et al., 2013b; Xie et al., 2014]. Reverse solute flux is usually greater in FO mode compared to PRO mode [Alturki et al., 2013]. Since reporting solute flux offers no context for the amount of draw solution solute lost per unit of water extracted, specific reverse solute flux is commonly reported [Lotfi et al., 2015]. This metric is the ratio of the reverse solute flux to the water flux to quantify mass (or moles) of

solute lost per volume of water permeated. Typical values for NaCl with a CTA membrane are 0.3-2 g/L [Cath et al., 2010; Phuntsho et al., 2013b; Sahebi et al., 2015]. Finally, an alternative metric, termed the reverse flux selectivity, has been defined as the inverse of the specific reverse solute flux and represents the volume of water extracted per mass of lost draw solute [Phillip et al., 2010]. The loss of draw solution solute is an important factor that affects operational costs of any system.

Selection of the draw solute can also determine scaling potential. Some reverse solute flux of the draw solute is unavoidable. If that solute reacts with other constituents of the feed solution, it can form a precipitate that leads to membrane scaling on the active layer (in FO mode). Phuntsho et al (2014) found that reverse flux of diammonium phosphate (a potential draw solute for fertigation applications) caused significant scaling upon reaction with magnesium in the FS. Loss of flux due to scaling increased with increasing draw solution concentration, demonstrating a trade-off between increasing the osmotic driving force and the scaling potential [Phuntsho et al., 2014b].

Ultimately, the choice of draw solute and concentration likely lies in the final use or recovery of the diluted draw solution [Luo et al., 2014]. Unlike hydraulic pressure driven processes, FO transports water from a feed stream to the draw solution, which has a higher salinity than the feed stream. For synthesized draw solutions, post-treatment to extract clean permeate usually relies on a downstream pressure-driven membrane separation process (e.g. RO) that is thermodynamically less energy efficient than direct desalination [McGovern and Lienhard, 2014; Shaffer et al., 2015]. A higher draw solution concentration may increase flux across the FO membrane, but a higher osmotic pressure may need to be overcome in a subsequent RO step. Some draw solutes, such as ammonium bicarbonate, require heating to decompose and strip the solution of the inorganic salt [McCutcheon et al., 2005; Qin and He, 2014]. Few applications (discussed in the following sections) present cases where the diluted draw solution has a direct beneficial use without requiring additional treatment to regenerate the draw solution. With all the recent emphasis on identifying novel draw solutes to improve FO energy efficiency, Shaffer et al (2015) argues that small inorganic salts are the best option. They create a high osmotic pressure without increasing viscosity, have high diffusivities to reduce ICP effects and have reduced reversed solute flux with new TFC-FO membranes [Shaffer et al., 2015].

4.   FO Applications

The aspects that set FO apart from other membrane driven processes suggest that FO may be best applied to niche applications. Compared to RO, NF and UF, FO yields lower fluxes that are driven by difference in osmotic pressure and are not dictated by energy input. Unlike other technologies, the primary design considerations for FO must take into consideration the chemistry of the feed solution and also that of the draw solution. The following sections summarize documented implementations of FO technology for different applications and evaluate their efficacy. Applications investigated include fertigation, emergency water supply, high salinity brine treatment, wastewater desalination and RO pre-treatment.

4.1   Fertigation

Fertigation is a potential application of FO that has garnered a lot of attention. Fertigation is a process where a soluble fertilizer is applied through irrigation. A concentrated solution of the intended fertilizer is used as the draw solution for the desalination of either brackish groundwater or seawater. The advantage of this process is that the diluted draw solution would not require post-treatment to re-concentrate the draw solution. This section reviews the current state of research and demonstrates that fertigation using FO does not efficiently recover brackish groundwater.

Choice of draw solute affects both the rate of water generation (flux) and the maximum amount of water that can be extracted via FO. Observed measurements for flux and water extraction capacity are summarized in Table 2. At a given molar concentration, different fertilizers produce different osmotic pressures, largely depending on the number of ions that dissociate. At the same osmotic pressure, however, small molecular weight solutes generate greater water flux [Phuntsho et al., 2011]. This trend is attributed to internal concentration polarization effects, which are decreased when a solute is small and has a high diffusivity. Blended fertilizers generate osmotic pressures that are not necessarily equal to the sum of the components and are often less [Phuntsho et al., 2012a]. The theoretical volume of water that a solute can extract depends on the solute molecular weight according to Eqn 6, where M_W is the molecular weight of the draw solute and C_M is the concentration of draw solute when its osmotic pressure equals that of the feed solution. Based on this equation, small molecular weight solutes have a larger extraction capacity [Phuntsho et al., 2013a, 2011]. Data from a study by Phuntsho et al (2013) is plotted Figure 4 for the solute that has the highest theoretical water extraction capacity (NH_4Cl) and the lowest extraction capacity ($Ca(NO_3)_2$). All other solutes tested (e.g., KCl and ammonium sulfate (SOA)) fell in between. Figure 4 shows that for a 1 M draw solution, there is a rapid decline in water extraction capacity with increasing feed osmotic pressure. Therefore, fertigation is best suited as a FS for brackish groundwaters with low osmotic pressures.

$$V = \frac{100}{M_W C_M} - 1 \qquad\qquad \textbf{Eqn 6}$$

Table 2.—Summary of fertigation studies and performance indicators

| Study	Feed Solution	Draw Solutions	Membrane	Reported Flux (L/m^2/hr)	Extraction Capacity (L$_{H20}$/kg$_{fertlilizer}$)	Ref
1	DI Water	9 solutes at 2M	CA	13-22.6	23-58 @ 14 atm DS 11-29 L @ 28 atm	[Phuntsho et al., 2011]
2	Synthetic BGW TDS= 4-27 g/L	11 solutes and 2 blends at 1 M	CTA	6-10 (Low TDS FS) 4-6 (High TDS FS)	120-311 (Low TDS) 15-43 (High TDS)	[Phuntsho et al., 2013a]
3	Synthetic BGW TDS= 7-27 g/L	6 solutes at 1 M	CTA	5-9	NA	[Phuntsho et al., 2014b]
4	10 g/L NaCl	$(NH_4)2SO_4$ $NH_4H_2PO_4$ up to 3 M	CTA	3-14	N/A	[Sahebi et al., 2015]
5	DI Water 5 g/L NaCl	Fertilizer blends at 1 M	CTA	5-13	N/A	[Phuntsho et al., 2012a]
6	Synthetic TDS=5-35 g/L	$NH_4H_2PO_4$, $(NH_4)_2HPO_4$ $(NH_4)_2SO_4$, $Ca(NO_3)_2 \cdot 4H_2O$ at 1-3 M	Polyamide hollow fiber	3-14	N/A	[Lotfi et al., 2015]
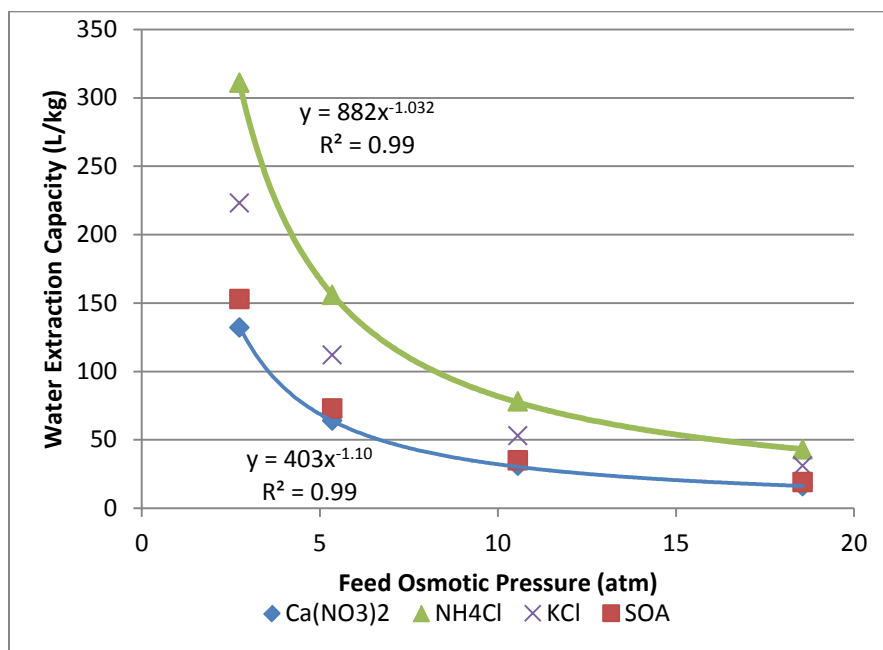
Figure 3.—Theoretical water extraction capacity for different draw solutes as a function of feed solution osmotic pressure for 1 M draw solutions. Data published in [Phuntsho et al., 2012b].

Draw solute selection has a large impact on reverse solute flux, which represents a loss of valuable fertilizer. Nutrients in a concentrated feed solution could pose problems for discharge due to nutrient loading and eutrophication potential in surface waters. Phuntsho et al (2011) evaluated 9 different solutes at a draw solution concentration of 2 M using DI water as the feed solution. This set-up allowed the quantification of reverse solute flux from the draw solution to the feed solution. Reverse flux ranged from 0.005-0.79 mmol/m^2/s [Phuntsho et al., 2011]. Reverse flux was greatest for solutes where both the cation and anion have a small hydrated diameter and are monovalent in charge (e.g., NH_4NO_3 and KNO_3). If one ion was divalent, reverse solute flux was significantly lower, because both ions migrate to maintain electroneutrality. Neutral compounds (e.g., urea) exhibited higher reverse solute fluxes likely due to a lack of electrostatic interactions.

In addition to water extraction capacity, the final fertilizer concentration is important for application. The higher the extraction capacity, the more dilute the final diluted draw solution, but often this diluted draw solution is still too concentrated to use directly for fertigation. Phuntsho et al (2013) reported that depending on the draw solute and osmotic pressure of the feed solution, dilution factors ranging from 4 to over 200 may be needed to achieve concentrations of 120-200 mg-N/L for application.

Case Study. Using the data published, a high level calculation was performed to determine the relative system size and water impact for a potential fertigation system. The case study is based on the following assumptions:

1. 1 acre is planted with tomatoes.
2. Bed spacing is 6 feet leading to 7300 linear bed feet (lbf) per acre with a wetting width of 1 foot (7300 ft^2 requiring targeted drip irrigation per acre cultivated) [Zotarelli et al., 2015].
3. Tomato crops require 2.6 kg/ha/day of nitrogen. This is an average value as needs vary with growing season [Imas, 1999].
4. Fertigation occurs every 3 days [Imas, 1999], dictating that the FO system must reach extraction capacity in 36 hours.
5. Nitrogen form (NH_4 to NO_3) is neglected due to lack of FO data.
6. Concentration at time of application is 150 mg-N/L [Imas, 1999], possibly requiring dilution of the diluted draw solution prior to application.
7. Source waters considered are brackish groundwaters with osmotic pressures between 4-17 atm

Based on these assumptions, the size of the system can be determined as a function of averaged flux for the two solutes with the highest (NH_4Cl) and lowest ($Ca(NO_3)_2$) extraction capacities. The best case scenario would be for a solute with a high extraction capacity and low osmotic pressure feed solution that would require minimal dilution to meet the required application concentration. In this case, the most productive combination would be NH_4Cl with the low salinity waters. Given the available data, the lowest reported feed solution osmotic pressure was 2.74 atm. At theoretical equilibrium, this diluted draw solution would require a dilution factor of 5.6 prior to application. The initial (highest) flux recorded for this combination was 11 L/m^2/hr, which would require a membrane area of 1.6 m^2. Due to decreased driving force as the DS dilutes and internal concentration polarization, the average flux over the course of 3 days will be much lower in which case the membrane area increases upwards of 9 m^2 (figure 5). For the solute with the lowest extraction capacity ($Ca(NO_3)_2$), the system would operate at lower fluxes as the highest recorded flux was only 5 L/m^2/hr. Even though the water flux using $Ca(NO_3)_2$ would be lower, the extraction capacity is also lower and equilibrium is reached at a higher concentration. As a result, the required system size to achieve equilibrium within the 3 day time period is smaller (figure 5). Since the $Ca(NO_3)_2$ draw solution is more concentrated at equilibrium, more dilution water is needed to achieve the application concentration; the dilution factor for this solute would be 8.5. Therefore, the required dilution water is likely the controlling factor that determines the applicability of this process compared to membrane area.
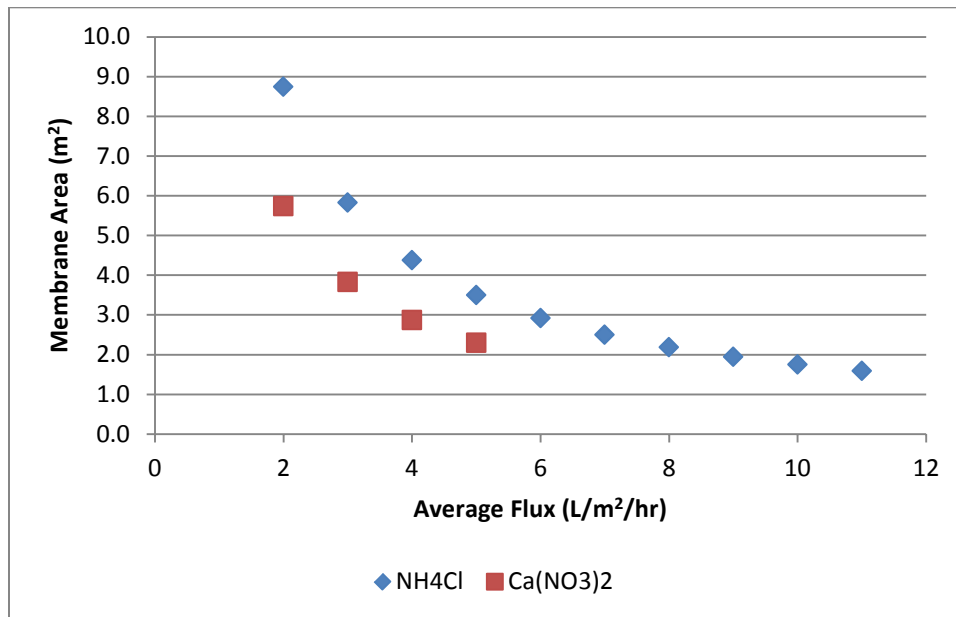
Figure 4.—FO membrane area as a function of average flux to dilute feed solution with 2.74 atm osmotic pressure by either NH_4Cl or $Ca(NO_3)_2$ for 1 acre case study application.

Another way to evaluate the potential of fertigation is to evaluate the relative amount of brackish groundwater that FO can contribute relative to other sources of irrigation water. The more brackish groundwater that can be utilized via FO treatment decreases the water usage from other sources. Ultimately, the potential utilization of brackish groundwater depends on the feed water osmotic pressure and draw solute, which dictates the required dilution necessary prior to application. For NH_4Cl with low TDS brackish groundwater, FO treated water has a potential to accommodate 16% of the irrigation water volume (figure 6). As the feed osmotic pressure increases, the potential rapidly decreases to less than 4%. For a solute with the lowest extraction capacity ($Ca(NO_3)_2$), the maximum utilization of FO treated water is only 10%. Given the low potential to utilize brackish groundwater through FO (4-10%), selecting FO would have to be justified considering process economics and operational ease of use relative to other treatment alternatives.
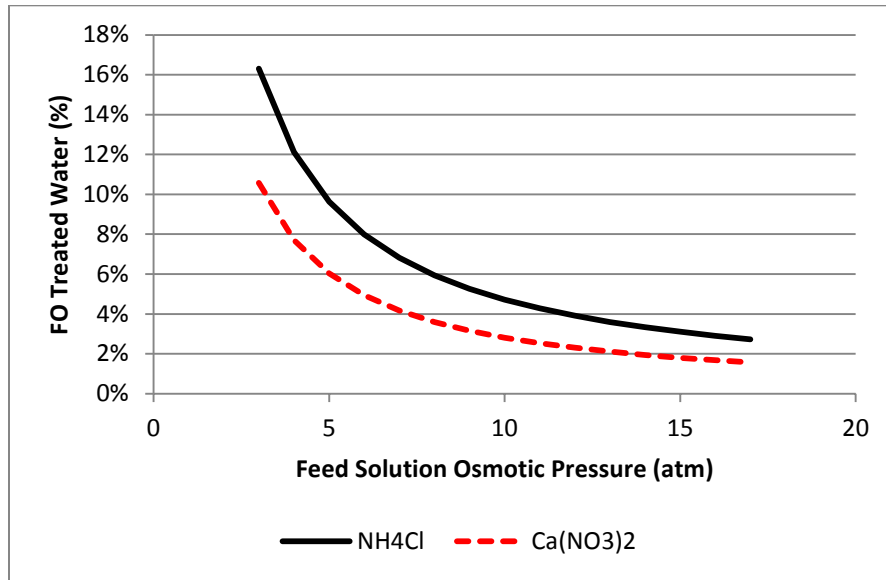
Figure 5.—Fraction of fertigation water that can be sourced from brackish groundwater as a function of feed osmotic pressure. Calculations based on data from [Phuntsho et al., 2012b].

To maximize the potential for FO, NF pre-treatment of the feed water and NF post-treatment of the diluted draw solution have both been suggested [Phuntsho et al., 2013a]. NF pre-treatment lowers the osmotic pressure of the brackish groundwater increasing extraction capacity. NF post-treatment reduces the concentration in the diluted draw solution and reduces dilution needs. For low TDS brackish groundwaters, NF treatment has the potential to increase the utilization of FO treated water for the fertigation case study (figure 7), but this potential greatly diminishes when the brackish groundwater osmotic pressure exceeds 10 atm. Therefore, this technology is not likely to be feasible with solutions such as seawater (osmotic pressure = 27 atm). Blending fertilizers have also been suggested as a method to increase draw solution osmotic pressure, but decrease the required dilution due to a lower concentration of individual nutrients at equilibrium [Phuntsho et al., 2012a]. Use of NF as post-treatment with blended fertilizers would introduce additional operational considerations as the system would have to take into account differences in selectivity across the nanofiltration membrane between ions and the desired nutrient balance of the permeate. Pressure-assisted FO would increase extraction capacity but would have to be justified in the context of alternative treatment methods [Sahebi et al., 2015].
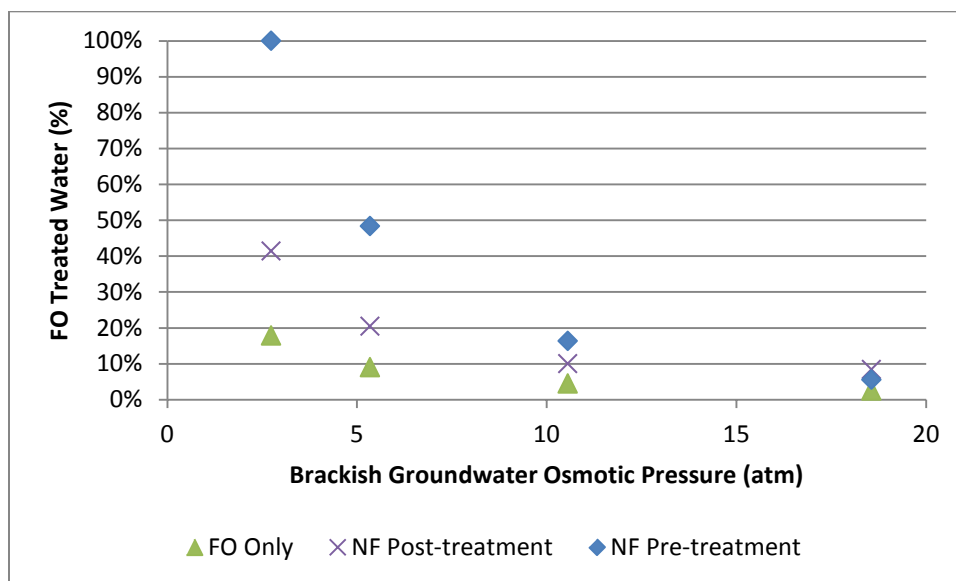
Figure 6.—Effect of NF treatment to utilize brackish groundwater as a function of feed solution osmotic pressure. Calculations based on data from Ref [Phuntsho et al., 2012b]. NF process was operated at 15 bar (2.7 and 5.3 atm BGW) and 20 bar (10.6 and 18.6 atm BGW).

The promising aspects of fertigation are that it presents an FO application where concentration and recovery of the draw solute is not a primary concern. The disadvantage, however, is that the draw solute concentrations needed for practical fluxes generate a diluted draw solution that is still too concentrated for direct application to crops. The dependence of extraction capacity (and diluted draw solution concentration) on feed solution osmotic pressure limit the potential feed sources where this technology may be viable. From a practical standpoint, the feed solution likely has to have an osmotic pressure less than 5 atm and be pre-treated with an NF process, if the FS salts have divalent cations, for any substantial gains from implementing an FO process to be realized. Therefore, the practical application of FO for fertigation has to be justified in the context of other available BGW desalination technologies (e.g., direct NF treatment) in order to be a viable technology.

4.2   Emergency Water Supply

Forward osmosis has been commercialized by Hydration Technology Innovations (HTI) as a treatment technology for providing a potable electrolyte drink during emergency situations. In this application, the draw solution is an edible electrolyte that is placed on the inside of a bladder constructed with FO membrane material. In some models, the whole bladder can be submerged in untreated water at which point water begins to permeate the membrane and fill the bladder. In other designs, the FO membrane is contained in a secondary bladder that can be filled with untreated water to allow for water treatment away from a water source. Some units are single use while others can have re-fillable electrolytes for continual use over extended periods of time. Specifications for commercially available products are summarized in table 3.

Table 3.—Commercially available FO water treatment units from HTI, LLC.

Model	Treated Water Capacity	Operation	Use	Production rate
SeaPack Crew	500 mL	Submersible	Single	500 mL in 10 hours at 20°C
HydroPack	355-500 mL	Submersible	Single	355 mL in 10-12 hours
Expedition	3 L	Fillable Bladder	30-90 day life	0.8 L/hr
LifePack	1.8 L	Fillable Bladder	5 day life	3 L/day for 3 days
HydroWell	20 L	Fillable Bladder	90 day life	Up to 30 L/day
XPack	1.6 L	Fillable Bladder	10 day life – 32 L total production	1.6 L / day
SeaPack	500 mL	Fillable Bladder	Eight uses within 10 days	500 mL in 5 hours

These systems are ideal for providing potable water to individuals in the immediate aftermath of a natural disaster. The units are easier to transport than bottled water. HTI claims that 1 lb of their XPack product is the equivalent of transporting 15 lbs of bottled water. The lower weight decreases transportation costs and time. These kits are likely easier to use in the immediate aftermath of a catastrophic event. They require no power source or use of chemicals (e.g., chlorine). Minimal training is required to use these products. The small units are also amenable to be distributed among communities in sparsely populated areas. An added benefit of these units compared to chemical disinfection is that they also provide a barrier against heavy metal contamination and produces a product with nutritional value [Butler et al., 2013].

Several FO units that treat non-potable freshwater have been developed to provide emergency potable water supply. The largest commercially available unit can only produce 32 L of dilute sports drink from non-potable freshwater over a period of 10 days. This technology would probably be inefficient to supply water over a long period of time for larger communities. An economic analysis of the HydroWell product found that the minimum cost is $0.23/L without having the benefit of an economy of scale, which is significantly greater than other technologies [Butler et al., 2013]. For example, other freshwater treatment alternatives, where the primary objective is protection against microbial contaminants (e.g., chlorination), cost between $0.0005/L [Butler et al., 2013] and $0.0008/L [Lantagne and Clasen, 2009]. Hand-powered membrane filters can remove microbial contaminants. Microfilters (e.g., MSR® SweetWater), which do not provide a barrier against viruses, cost about $100 and produce 1 L/min with a cartridge life of about 750 L. With the economy of scale associated with these filters, the cost per liter of water is more economical than the Hydrowell once 434 L are produced. A new product (MSR® Guardian, available 2016) is a hand-powered unit that also provides protection against viruses and will offer comparable virus protection to the HydroWell, at a cost of $349 and a capacity of 10,000+ liters. Beyond economic cost, the Hydrowell does not produce non-saline water that can be used for other beneficial purposes (e.g., cooking), which must be taken into consideration when selecting an appropriate technology. The best application of FO for emergency water supply is to address immediate potable water needs where freshwater is unavailable until equipment, such as membranes or chemical treatment processes that are more cost effective, can be mobilized to deliver emergency water.

In emergency relief cases where desalination is also required, the SeaPack and SeaPack Crew FO units can produce edible syrup from seawater. These units can only produce 500 mL over 5 to 10 hours, depending on the model. Depending on the vendor, the cost of syrup product is greater than $20/L. hand-powered desalination units are available but require a significant capital investment. Commercially available hand-powered units from Katadyn®, suitable for short-term relief during emergency situations, cost $2400. With the economy of scale, the hand-powered unit would be cheaper than FO once the hand-powered unit produces 23 L of water. Contrary to the FO unit that produces a concentrated high-sugar solution, the membrane units produce non-saline water that can be used for cooking and other beneficial uses. Due to the high osmotic pressure of seawater, hand-powered membrane units are recommended to meet emergency water needs.

4.3   High Salinity Wastes

Forward osmosis has been proposed as a viable treatment option for highly saline waters, such as RO brine or industrial wastewater (e.g., produced water from natural gas extraction, landfill leachate, anaerobic digesters, brines containing hazardous waste etc.). In many of these applications, the overarching objectives are to increase water recovery and minimize waste principally due to associated disposal costs. For RO brine applications, increased brine volume can increase transportation and disposal costs. For produced water, reducing waste volume decreases disposal volume for deep well injections. In any application, the feasibility of applying FO depends not only on the waste concentration in the FS but also on the subsequent use, treatment or disposal of the DS.

The nature of the FO process stipulates that water from a highly saline waste is transferred to an even more saline draw solution. Holistic analysis of the process is necessary to evaluate the feasibility of applying FO. Simply achieving a high recovery of the FS water in the DS does not justify the use of FO if the DS is difficult to manage. Recovering water from the DS may be just as difficult (or energy intensive) as treating the primary waste stream directly. Energy efficiency cannot be the primary motivator for applying FO if reverse osmosis is used to recover water from the draw solution. Through the arguments outlined by Shaffer et al (2015) and McGovern and Lienhard (2014), a two stage FO-RO process cannot be more energy efficient than directly applying RO directly. In the case of a highly saline waste stream, the concentrated DS may have an osmotic pressure that requires RO operating pressures that exceed most membrane element capabilities. Many membrane elements have maximum operating pressures around 70 atm, and NaCl draw solutions in concentrations greater than 85 g/L (1.5 M) will have osmotic pressures that are too high for RO water recovery [Phuntsho et al., 2014a]. Draw solution concentrations used in brine concentration applications are often greater than 1 M NaCl [Coday et al., 2014; Hickenbottom et al., 2013; Martinetti et al., 2009]. In these cases, alternate draw solutions, recovery methods or direct beneficial reuses of the draw solution are necessary.

An example of an alternate DS that allows for water recovery from high salinity brines is the use of a thermolytic draw solute that dissociates into gases upon heating. An NH_3/CO_2 draw solution

has been proposed as an energy efficient DS for concentrating highly saline feed streams [McCutcheon et al., 2005; McGinnis et al., 2013]. The advantages of this DS are that high osmotic pressures can be achieved, and water recovery is more energy efficient than distillation processes. The draw solutes are stripped out of solution using heat, which requires less thermal energy than distilling the solvent (water) as an alternative water recovery method [McGinnis et al., 2013].

The justification for using FO for treating highly saline solution usually lies in the selectivity of FO membrane to exclude divalent scalants (e.g., Ca^{2+}, Mg^{2+}, SO_4^{2-}) and its low potential for irreversible organic fouling [Coday et al., 2014]. In the case of RO brines, FO excludes divalent salts allowing a secondary RO process to operate at higher recoveries to improve water recovery. For example, Martinetti et al (2009) achieved over 95% total water recovery by treating RO brines with a high scaling risk from $CaSO_4$ and SiO_2. Without FO treatment, the two source waters investigated would have operated at 70% or 89% water recovery. FO effectively concentrated the brine, selectively retaining the divalent ions so that an additional RO recovery step using the DS could operate at 70-90% recovery. Given the high osmotic pressures needed in a draw solution compared to RO concentrate, the RO process will be energy intensive but the added energy cost may be justified depending on water value. Similar to the selective rejection of divalent ions by FO membranes, pre-treatment of highly saline solutions by FO may be justified if the FS has a high propensity for organic fouling and alternative treatment methods for organic removal are not practical (e.g. large coagulant doses required, hydrophilic character of organic matter, high alkalinity, etc.). For organic rich waters, such as produced water, FO membranes have shown good rejection of organic and inorganic constituents [Hickenbottom et al., 2013; McGinnis et al., 2013] and nearly full flux recovery after cleaning [Hickenbottom et al., 2013].

Identifying an application for direct use of the diluted DS is an alternate approach for treating highly saline waters using FO. Using the diluted DS directly eliminates the need for additional processes to recover water from the DS. For example, in the case of produced water, the diluted DS may be used as the base solution for another hydraulic fracturing process. The FO treatment effectively removes potential scalants and other constituents that prevent crosslinking of the hydraulic fracturing fluid [Lord et al., 2013]. One study demonstrated successful reuse of electrocoagulated produced water with a final TDS of 270,000 mg/L in hydraulic fracturing operations [Lebas et al., 2013]. Hickenbottom et al (2013) used FO to recover 80% of water from pretreated produced water yielding a DS with 50-70 g/L NaCl and good rejection of other inorganic and organic compounds from the wastewater. This diluted DS could potentially be reused without further treatment.

4.4 Wastewater Treatment and Trace Organic Contaminant Rejection

FO for water recovery from wastewater has been investigated from two different approaches. In the first approach, the primary objective is to use a two-step, closed loop process to recover all water that permeates across the FO membrane to the draw solution. This process is termed

'direct desalination' of wastewater herein. An alternative operational approach exists were the primary objective is not to recover water from wastewater but simply to decrease the energy requirement of another existing water treatment process by reducing the osmotic pressure of a feed stream (i.e., RO). This process will be referred to as 'indirect desalination.'

Direct desalination by FO has been proposed to recover water from wastewater as it has a lower propensity to foul irreversibly compared to pressure-driven processes [Cath et al., 2010]. FO has been applied for the direct treatment of wastewater (either treated or untreated) to recover water [Valladares Linares et al., 2014]. The disadvantage of FO compared to other treatment processes (e.g., membrane filtration, advanced oxidation processes) is the low flux. Reported fluxes for FO processes where wastewater acts as a feed solution range from 0.8 to 10 L/m^2/hr when using inorganic salts as draw solutes [Valladares Linares et al., 2014]. One study integrating FO with a membrane bioreactor recovered 50% of water from wastewater at fluxes between 0.8-2.9 L/m^2/hr [Qin and He, 2014]. All reported tests were bench-scale tests operating in batch mode over the course of several hours with flux decreasing to the lower end of the reported range over time. Larger-scale, longer duration tests are required for process validation. Direct desalination of wastewater requires a second step to recover water from the diluted DS. From an energy consumption perspective, if RO is used in a two-step, closed-loop desalination process to recover water from wastewater, it cannot be more energetically favorable than direct RO filtration of the wastewater effluent as the osmotic pressure of the RO brine drives the separation energetics [McGovern and Lienhard, 2014; Shaffer et al., 2015].

Therefore, the motivation for applying a closed-loop FO/RO process for wastewater recovery must be driven by other operational considerations, such as membrane scaling or organic fouling. Sources of foulants when wastewater acts as the FS include effluent organic matter, microorganisms and inorganic scalants [Lutchmiah et al., 2014]. The lower operating pressures during FO minimize the cake formation on the membrane surface, and fouling can be minimized by maintaining sufficient cross flow velocities. Studies have shown good recovery of membrane flux after cleaning [Cath et al., 2010], but irreversible fouling from biopolymers is still possible [Lutchmiah et al., 2014]. Another potential benefit of implementing FO as a pre-treatment for pressure-driven membrane processes is the selective separation of divalent ions that are potential scalants. As water is recovered from the wastewater, the concentration of scalants (i.e., calcium, barium, sulfate) is lower thus lowering the scaling potential of downstream RO processes.

Indirect desalination by FO is a potential application where water recovery from wastewater can be energetically favorable, because a hybrid process couples FO with a feed source where a closed-loop design is not necessary. Wastewater (or another impaired water source) is used to dilute a water source already treated by RO (e.g., seawater). Wastewater effluent or another impaired water source acts as the FS and seawater as a DS [Cath et al., 2010; Lutchmiah et al., 2014; Valladares Linares et al., 2014]. The premise is that the seawater draw solution can be diluted prior to RO membrane separation processes. Compared to treatment of undiluted seawater, this dilution step decreases the required RO operating pressure for an equivalent recovery of water (or increases the water recovery for an equivalent operating pressure). This process can be considered more energetically favorable, because the basis for comparison is different. In a closed-loop FO/RO process to recover water from wastewater, the FO/RO process

20

is compared to direct RO separation of the wastewater. In this scenario, the energy requirement for recovering water from osmotically diluted seawater will always be lower than direct desalination of seawater. Full recovery and recycle of the draw solution is not necessary. FO plays an important role in the dilution step by acting as a barrier, because seawater cannot be directly diluted by wastewater effluent. The FO membrane provides a barrier to selectively retain fouling effluent organic matter, pathogenic organisms and trace organic contaminants. Pilot scale tests of this application using synthetic seawater (35 g/L NaCl) have demonstrated fluxes across FO membranes around 7.2 L/m^2/hr [Cath et al., 2010]. The same study presented an economic analysis that concluded that it would be economically favorable to recover up to 63% of water from wastewater by adding FO membranes to osmotically dilute seawater [Cath et al., 2010].

An added benefit of applying FO (or RO) for water reuse is an additional barrier to minimize trace organic contaminants (TrOCs) in potable water. Since wastewater treatment plants are not optimized to remove TrOCs (e.g., pharmaceuticals, personal care products, pesticides and fire retardants), several studies have explore the use of FO to desalinate wastewater and their ability to reject TrOCs for water reuse applications to provide advanced TrOC treatment. A comprehensive review on the topic was recently published by Coday et al (2014). Two approaches have been taken aimed at either gaining a fundamental or practical understanding of TrOC rejection.

To elucidate the rejection mechanisms of TrOCs, several studies have been performed in controlled conditions where TrOCs are added to either DI water [Alturki et al., 2013] or a synthetic feed solution with NaCl and carbonate buffer [Xie et al., 2014]. While these studies are not representative of true wastewater conditions with other organic constituents and fouling potential, they do allow for a fundamental investigation into the mechanisms by which TrOCs are rejected through FO. Other studies have taken a more applied approach using wastewater (secondary or tertiary treated) or wastewater impaired streams to measure TrOC rejection in scenarios with fouling potential [Cath et al., 2010; Hancock et al., 2011].

TrOC rejection depends largely on the compound charge and size. Charged species are better rejected due to the slightly negative charge on cellulose acetate FO membranes and resulting electrostatic interactions [Alturki et al., 2013; Hancock et al., 2011; Holloway et al., 2014a; Xie et al., 2014]. Size exclusion affects rejection of ionic contaminants as rejection increases with molecular weight [Alturki et al., 2013]. Most studies found rejections of greater than 80% for ionic TrOCs [Coday et al., 2014; Hancock et al., 2011; Holloway et al., 2014a; Xie et al., 2014]. High rejection of negatively charged species is attributed to electrostatic interactions, and rejection of positively charged TrOCs is attributed to the large hydrated radii of the solutes [Holloway et al., 2014a]. Size exclusion does appear to also affect the rejection of charged solutes with rejection increasing with increasing molecular weight [Xie et al., 2014]. Rejection of nonionic contaminants is lower (30-90%) [Hancock et al., 2011; Xie et al., 2014] than charged species and depends on the hydrophobicity and molecular weight of the TrOC. Rejection increases with increasing molecular weight for nonionic TrOCs [Alturki et al., 2013; Hancock et al., 2011; Xie et al., 2014]. Rejection of hydrophilic nonionic TrOCs is higher than hydrophobic

compounds, because CTA membranes are hydrophilic [Coday et al., 2014; Holloway et al., 2014a].

In wastewater treatment using FO, the fouling layer that develops on the FO membrane affects TrOC rejection [Coday et al., 2014; Hancock et al., 2011; Holloway et al., 2014b. Organic fouling on the active FO membrane layer can alter the surface chemistry, primarily the surface charge, and alter rejection. The carboxylic and hydroxyl function groups in natural organic matter can lead to an increasingly negative surface charge [Coday et al., 2014]. Fouling can have a temporal effect on TrOC flux. Initially, hydrophobic TrOCs can sorb to the organic fouling layer, leading to an apparent increase in rejection. At higher sorbed concentrations, the diffusive driving force increases causing an apparent decrease in rejection [Coday et al., 2014; Holloway et al., 2014a]. Hydrophilic nonionic TrOCs, Bisphenol A and DEET, have had the lowest reported rejections across studies utilizing DI water and secondary treated wastewater [Hancock et al., 2011; Xie et al., 2014], but higher rejections were observed for systems with activated sludge likely due to an accumulation of a fouling layer that affects transport properties [Holloway et al., 2014a]. These results demonstrate the need to run FO systems long enough to see a representative rejection of TrOCs.

FO membrane material and orientation affects TrOC rejection. Comparing FO membrane material, TFC membranes exhibited higher TrOC rejection than CTA membranes [Jin et al., 2012; Xie et al., 2014]. A study by Xie et al (2014) found that even though the pore size of TFC membranes (0.42 nm) is slightly larger than CTA membranes (0.37 nm), differences in surface chemistry affect the effective pore size [Xie et al., 2014]. TFC membranes are hydrated, which decreases the effective pore size and increases rejection. For the FO and PRO orientations, rejection is higher in the FO orientation. When the system is oriented in PRO mode, rejection is lower for all classes of TrOCs (i.e., charged and nonionic). The porous support layer in PRO mode is in contact with the TrOC-containing feed solution. Water flux leads to an accumulation of TrOCs in the support layer and internal concentration polarization [Alturki et al., 2013].

Lastly, draw solution concentration affects TrOC rejection. Reverse solute flux of the draw solution increases with increasing concentration [Alturki et al., 2013], which affects charged and nonionic TrOCs differently. For ionic TrOCs, the increased reverse salt flux from the draw solution increases the ionic strength at the membrane interface. Increased ionic strength compresses the diffuse double layer around the solute and reduces the electrostatic interactions between the solute and membrane, decreasing rejection. For nonionic TrOCs, rejection increases with increasing reverse solute flux due to a suspected decrease in forward diffusion. The effect of DS concentration on TrOC rejection is most apparent for small molecular weight compounds in PRO mode [Alturki et al., 2013].

The importance of TrOC rejection by FO membranes depends on the intended application and solute recovery process. For water reuse applications to reclaim wastewater, a secondary process is needed to produce a water stream that is usable for potable or non-potable applications. Hybrid processes with FO and reverse osmosis is commonly employed to re-concentrate and recycle the draw solution [Cath et al., 2010; Holloway et al., 2014a]. In such systems, it is the net rejection of the multi-barrier system that determines possible exposure to TrOCs in reclaimed water, and

RO membranes have high rejections [Cath et al., 2010; Holloway et al., 2014a]. The overall rejection of TrOCs in FO-RO hybrid systems is greater than 99% for most TrOCs [Hancock et al., 2011]. If other draw solutes are used (e.g., ammonium-carbonate thermolytic solutes, magnetic nanoparticles) without a second treatment barrier, FO membranes would be the primary barrier for TrOCs elevating the importance of their rejection.

4.5   Conventional Desalination Pre-treatment

A final application where FO has been proposed is to desalinate water that has a high scaling potential by using a two-step approach. Hybrid FO-NF processes have been proposed where seawater or brackish groundwater (BGW) is the FS with a synthetic DS (e.g., $MgCl_2$, $CaCl_2$, $MgSO_4$, Na_2SO_4 and $C_6H_{12}O_6$). This configuration is slightly different from the approach presented in Section 5.3 where FO is applied to recover water from the concentrated RO brine. In this case, FO is applied directly to the saline water source prior to RO treatment. By pre-treating a saline water source, such as seawater, there is the potential to increase overall water recovery of the entire process. The driving force behind this application is not energy conservation but the potential for high water recovery free of scalants via nanofiltration. By implementing a low-flux, non-pressure driven separation process, potential scalants can be concentrated in FS prior to a pressure-driven NF process to recover water from the diluted draw solution. Divalent draw solutes are typically used due to high rejections by NF membranes. Two studies have evaluated the desalination of seawater [Tan and Ng, 2010] and BGW [Zhao et al., 2012] using divalent draw solutes.

FO applicability depends on the water value and the price of draw solute and draw solute recovery cost, but implementing FO to pre-treat a feed stream is not likely to be practical. Significant FO membrane area will be needed to meet the necessary process flow rate to pre-treat the feed to an RO system. Compared to the FO configuration treating the RO brine (Section 4.3), this increased membrane area is a significant disadvantage of this proposed application. Another important consideration is the effects of reverse solute flux. Loss of draw solute presents an important operating cost. Using divalent draw solutes also have a potential to be transported across the FO membrane and exceed saturation once combined with the seawater or BGW leading to scaling on the active layer. Implementing FO is likely better suited for process streams with lower throughput where the lower fluxes of CA membranes do not result in unfeasible membrane area requirements.

5.   Conclusions

FO has been proposed for a wide range of water treatment applications as a passive separation process driven by chemical potential differences. In recent years, a primary research focus has been focused on understanding and modeling the transport phenomena. Membrane material research has focused on maximizing flux by minimizing internal concentration polarization and fouling effects. Substantial research efforts have also been placed on identifying novel draw solutes to decrease the energy requirements of recovery methods.

Potential applications range from desalination of seawater, recovery of water from wastewater, fertigation, emergency water supply and treatment of high salinity brines. The rationales behind FO treatment of each application vary. The direct use of the diluted draw solution is promising for fertigation FO, but significant dilution prior to agricultural application likely limits the practicality of implementing FO without a low salinity water source for dilution or another treatment process. FO is a potential treatment alternative for highly saline brines for minimizing volume and recovering water. This technology may have a niche, because pressure-driven processes are not feasible as salinity increases. Identifying uses for the diluted draw solution, however, remains imperative. Ideally, brine waste minimization would be highly favorable if there was a direct use for the diluted draw solution or draw solute recovery did not include membrane processes. If the original brine is hazardous, concentrating the hazardous material prior to shipping or disposal may yield large cost benefits despite treatment needs of the diluted DS. For desalination and water reuse applications, a benefit from FO is water transferred from a feed solution with a high scaling or fouling potential to a solution with a low potential so that membrane processes can operate at higher recoveries.

Based on the comprehensive literature review, it is evident that there is a substantial body of knowledge with process fundamental and proof-of-concept studies. For FO to move from bench-scale to the full-scale applications, more focus on identifying specific niches where FO makes both economic and practical sense compared to more conventional treatment processes is required. Table 4 summarizes the current state of each FO application, the prospects for future development and likelihood for future use. Forward osmosis is generally most viable in the following scenarios: 1) highly fouling and scaling brines where increased water recovery is required and other high throughput treatment technologies are not feasible, 2) highly saline solutions where other methods of water recovery become operationally unsuitable, 3) applications where multiple barriers are required for water recovery, 4) situations where the draw solution can be directly used for beneficial purposes, and 5) dilution of a high salinity feed stream with a low salinity waste stream.

Table 4.—Summary and outlook of potential FO applications

Application	Maturity of Technology	Potential for Improvement	Likelihood of Use Compared to Other Technologies	
			Now	At full maturity
Fertigation	Bench scale tests only	**Low** • Draw solutes with the greatest extraction capacity are also most susceptible to reverse salt flux – where fertilizer is lost to the FS • Acceptable nutrient concentrations for crop application require significant dilution by another fresh water source, most likely requiring another treatment process	**Low** • Studies beyond bench scale have not been conducted • FO cannot be a stand-alone process - additional NF treatment process required to obtain dilution water	**Low** • Rationale for adding additional treatment step for incremental energy reductions compared to NF not established
Emergency Water Supply	Commercially available	**Low** • Process fundamentals are well established. • No further development areas have been identified.	**Moderate** • Products currently available • Offer a lightweight option for water treatment (either freshwater or saline) and protect against organic and inorganic contaminants • Significantly more expensive than alternatives	**Low** • Commercial manufacturing improvements and market competition needed to decrease product cost, but technology will likely remain significantly more expensive than alternatives • No fresh water production; only a 'sports drink' is end product • Novelty decrease
Highly Saline Wastes	Bench and pilot scale tests	**High** • Proof-of-concept established for applying FO to select brine streams. Additional applications will likely be identified. • Additional pilot scale studies needed • Critical technical and economic comparison to other treatment alternatives needed	**Moderate** • Some private companies currently implementing FO based treatment • Potential applications identified but closed-loop designs needed to evaluate waste minimization and water recovery relative to other technologies	**High** • Process design improvements will likely yield modular systems for specific applications

Application	Maturity of Technology	Potential for Improvement	Likelihood of Use Compared to Other Technologies	
			Now	At full maturity
Direct Wastewater Treatment	Bench Scale tests	**Moderate** • Benefits of applying FO to minimize fouling identified but critical analysis (both technical and economical) is needed	**Low** • Technology not demonstrated at larger scale • Benefits of potential water recovery relative to increased operational complexity not established • Economic analysis relative to other technologies needed	**Moderate** • Low FO membrane flux and high membrane area needed to compete with other water reuse technologies likely to be limiting factor for implementing technology
Osmotic dilution of saline water using impaired water	Bench and pilot scale	**Moderate** • Long-term pilot scale testing needed in parallel with other best available treatment options including economic assessment	**Moderate** • Economic gains from any dilution of RO feed water beneficial as full closed-loop recovery of draw solution not required	**Moderate** • Increased operational complexity must be justified relative to higher energy requirements without osmotic dilution but potential exists • For seawater applications combined with wastewater outfalls, rapid developments in direct potable reuse make this a more likely technology in the near future compared to seawater desalination and FO
Conventional Desalination Pre-treatment	Bench Scale	**Moderate** • Technoeconomic analysis comparing FO pretreatment to other pretreatment options (e.g., NF) needed	**Low** • Given low membrane flux, FO treatment of RO brine likely more economical than treatment of RO feed	**Low** • Given low membrane flux, FO treatment of RO brine likely more economical than treatment of RO feed

References

Achilli, A., Cath, T.Y., Childress, A.E., 2010. Selection of inorganic-based draw solutions for forward osmosis applications. J. Memb. Sci. 364, 233–241. doi:10.1016/j.memsci.2010.08.010

Alturki, A.A., McDonald, J. a., Khan, S.J., Price, W.E., Nghiem, L.D., Elimelech, M., 2013. Removal of trace organic contaminants by the forward osmosis process. Sep. Purif. Technol. 103, 258–266. doi:10.1016/j.seppur.2012.10.036

Arena, J., Chwatko, M., Robillard, H., McCutcheon, J., 2015. pH Sensitivity of Ion Exchange through a Thin Film Composite Membrane in Forward Osmosis. Environ. Sci. Technol. Lett. 177–182. doi:10.1021/acs.estlett.5b00138

Butler, E., Silva, A., Horton, K., Rom, Z., Chwatko, M., Havasov, A., McCutcheon, J.R., 2013. Point of use water treatment with forward osmosis for emergency relief. Desalination 312, 23–30. doi:10.1016/j.desal.2012.12.013

Cai, Y., Shen, W., Wei, J., Chong, T.H., Wang, R., Krantz, W.B., Fane, A.G., Hu, X., 2015. Energy-efficient desalination by forward osmosis using responsive ionic liquid draw solutes. Environ. Sci. Water Res. Technol. 1, 341–347. doi:10.1039/C4EW00073K

Cath, T.Y., Childress, A.E., Elimelech, M., 2006. Forward osmosis: Principles, applications, and recent developments. J. Memb. Sci. 281, 70–87. doi:10.1016/j.memsci.2006.05.048

Cath, T.Y., Hancock, N.T., Lundin, C.D., Hoppe-Jones, C., Drewes, J.E., 2010. A multi-barrier osmotic dilution process for simultaneous desalination and purification of impaired water. J. Memb. Sci. 362, 417–426.

Coday, B.D., Xu, P., Beaudry, E.G., Herron, J., Lampi, K., Hancock, N.T., Cath, T.Y., 2014. The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams. Desalination 333, 23–35. doi:10.1016/j.desal.2013.11.014

Coday, B.D., Yaffe, B.G.M., Xu, P., Cath, T.Y., 2014. Rejection of trace organic compounds by forward osmosis membranes: a literature review. Environ. Sci. Technol. 48, 3612–24. doi:10.1021/es4038676

Emadzadeh, D., Lau, W.J., Matsuura, T., Hilal, N., Ismail, a. F., 2014. The potential of thin film nanocomposite membrane in reducing organic fouling in forward osmosis process. Desalination 348, 82–88. doi:10.1016/j.desal.2014.06.008

Ge, Q., Ling, M., Chung, T.S., 2013. Draw solutions for forward osmosis processes: Developments, challenges, and prospects for the future. J. Memb. Sci. 442, 225–237. doi:10.1016/j.memsci.2013.03.046

Gray, G.T., Elimelech, M., McCutcheon, J.R., 2006. Internal concentration polarization in Forward Osmosis: role of membrane orientation. Desalination 197, 1–8.

Hancock, N.T., Xu, P., Heil, D.M., Bellona, C., Cath, T.Y., 2011. Comprehensive bench- and pilot-scale investigation of trace organic compounds rejection by forward osmosis. Environ. Sci. Technol. 45, 8483–8490. doi:10.1021/es201654k

Hickenbottom, K.L., Hancock, N.T., Hutchings, N.R., Appleton, E.W., Beaudry, E.G., Xu, P., Cath, T.Y., 2013. Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations. Desalination 312, 60–66. doi:10.1016/j.desal.2012.05.037

Holloway, R.W., Regnery, J., Nghiem, L.D., Cath, T.Y., 2014a. Removal of Trace Organic Chemicals and Performance of a Novel Hybrid Ultrafiltration-Osmotic Membrane Bioreactor. Environ. Sci. Technol. 48, 10859–10868.

Holloway, R.W., Regnery, J., Nghiem, L.D., Cath, T.Y., 2014b. Removal of Trace Organic Chemicals and Performance of a Novel Hybrid Ultra fi ltration-Osmotic Membrane Bioreactor.

Holloway, R.W., Wait, A.S., Fernandes da Silva, A., Herron, J., Schutter, M.D., Lampi, K., Cath, T.Y., 2014. Long-term pilot scale investigation of novel hybrid ultrafiltration-osmotic membrane bioreactors, Desalination. Elsevier B.V. doi:10.1016/j.desal.2014.05.040

Hoover, L. a, Phillip, W. a, Tiraferri, A., Yip, N.Y., Elimelech, M., 2011. Forward with Osmosis : Emerging Applications for Greater Sustainability. Environ. Sci. Technol. 9824–9830.

Imas, P., 1999. Recent Techniques in Fertigation of Horticultural Crops in Israel, in: Recent Trends in Nutrition Management in Horticultural Crops. International Potash Institute, Dapoli, Maharashtra, India.

Jin, X., Shan, J., Wang, C., Wei, J., Tang, C.Y., 2012. Rejection of pharmaceuticals by forward osmosis membranes. J. Hazard. Mater. 227-228, 55–61. doi:10.1016/j.jhazmat.2012.04.077

Lantagne, D.S., Clasen, T.F., 2009. Point of Use Water Treatment in Emergency Response 1–94.

Lau, W.J., Gray, S., Matsuura, T., Emadzadeh, D., Chen, J.P., Ismail, A.F., 2015. A review on polyamide thin film nanocomposite (TFN) membranes: History, applications, challenges and approaches. Water Res. 80, 306–324.

Lebas, R., Lord, P., Luna, D., Shahan, T., 2013. Development and Use of High-TDS Recycled Produced Water for Crosslinked-Gel-Based Hydraulic Fracturing. SPE 163824, SPE Hydraul. Fract. Technol. Conf. 1–9. doi:10.2118/163824-MS

Lee, K.L., Baker, R.W., Lonsdale, H.K., 1981. Membranes for power generation by pressure-retarded osmosis. J. Memb. Sci. 8, 141–171. doi:10.1016/S0376-7388(00)82088-8

Li, D., Wang, H., 2013. Smart draw agents for emerging forward osmosis application. J. Mater. Chem. A 1, 14049–14060. doi:10.1039/c3ta12559a

Loeb, S., Titelman, L., Korngold, E., Freiman, J., 1997. Effect of porous support fabric on osmosis through a Loeb-Sourirajan type asymmetric membrane. J. Memb. Sci. 129, 243–249. doi:10.1016/S0376-7388(96)00354-7

Lord, P.D., Lebas, R., Trial, F., 2013. Treatment Enables High-TDS Water Use as Base Fluid for Hydraulic Fracturing. J. Pet. Technol. 30–33.

Lotfi, F., Phuntsho, S., Majeed, T., Kim, K., Han, D.S., Abdel-Wahab, A., Shon, H.K., 2015. Thin film composite hollow fibre forward osmosis membrane module for the desalination of brackish groundwater for fertigation. Desalination 364, 108–118. doi:10.1016/j.desal.2015.01.042

Lu, X., Boo, C., Elimelech, M., 2014. Bidirectional Diffusion of Ammonium and Sodium Cations in Forward Osmosis: Role of Membrane Active Layer Surface Chemistry and Charge. Environ. Sci. Technol. 48, 14369–14376.

Luo, H., Wang, Q., Zhang, T.C., Tao, T., Zhou, A., Chen, L., Bie, X., 2014. A review on the recovery methods of draw solutes in forward osmosis. J. Water Process Eng. 4, 212–223. doi:10.1016/j.jwpe.2014.10.006

Lutchmiah, K., Verliefde, a R.D., Roest, K., Rietveld, L.C., Cornelissen, E.R.,

2014. Forward osmosis for application in wastewater treatment: a review. Water Res. 58, 179–97. doi:10.1016/j.watres.2014.03.045

Martinetti, C.R., Childress, A.E., Cath, T.Y., 2009. High recovery of concentrated RO brines using forward osmosis and membrane distillation. J. Memb. Sci. 331, 31–39. doi:10.1016/j.memsci.2009.01.003

McCutcheon, J.R., Elimelech, M., 2006. Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis. J. Memb. Sci. 284, 237–247. doi:10.1016/j.memsci.2006.07.049

McCutcheon, J.R., McGinnis, R.L., Elimelech, M., 2005. A novel ammonia-carbon dioxide forward (direct) osmosis desalination process. Desalination 174, 1–11. doi:10.1016/j.desal.2004.11.002

McGinnis, R.L., Hancock, N.T., Nowosielski-Slepowron, M.S., McGurgan, G.D., 2013. Pilot demonstration of the NH3/CO2 forward osmosis desalination process on high salinity brines. Desalination 312, 67–74. doi:10.1016/j.desal.2012.11.032

McGovern, R.K., Lienhard V, J.H., 2014. On the potential of forward osmosis to energetically outperform reverse osmosis desalination. J. Memb. Sci. 469, 245–250. doi:10.1016/j.memsci.2014.05.061

Phillip, W. a., Yong, J.S., Elimelech, M., 2010. Reverse draw solute permeation in forward osmosis: Modeling and experiments. Environ. Sci. Technol. 44, 5170–5176. doi:10.1021/es100901n

Phuntsho, S., Hong, S., Elimelech, M., Shon, H.K., 2014a. Osmotic equilibrium in the forward osmosis process: Modelling, experiments and implications for process performance. J. Memb. Sci. 453, 240–252. doi:10.1016/j.memsci.2013.11.009

Phuntsho, S., Hong, S., Elimelech, M., Shon, H.K., 2013a. Forward osmosis desalination of brackish groundwater: Meeting water quality requirements for fertigation by integrating nanofiltration. J. Memb. Sci. 436, 1–15. doi:10.1016/j.memsci.2013.02.022

Phuntsho, S., Lotfi, F., Hong, S., Shaffer, D.L., Elimelech, M., Shon, H.K., 2014b. Membrane scaling and flux decline during fertiliser-drawn forward osmosis desalination of brackish groundwater. Water Res. 57, 172–182. doi:10.1016/j.watres.2014.03.034

Phuntsho, S., Sahebi, S., Majeed, T., Lotfi, F., Kim, J.E., Shon, H.K., 2013b. Assessing the major factors affecting the performances of forward osmosis and its implications on the desalination process. Chem. Eng. J. 231, 484–496. doi:10.1016/j.cej.2013.07.058

Phuntsho, S., Shon, H.K., Hong, S., Lee, S., Vigneswaran, S., 2011. A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: Evaluating the performance of fertilizer draw solutions. J. Memb. Sci. 375, 172–181. doi:10.1016/j.memsci.2011.03.038

Phuntsho, S., Shon, H.K., Majeed, T., El Saliby, I., Vigneswaran, S., Kandasamy, J., Hong, S., Lee, S., 2012a. Blended fertilizers as draw solutions for fertilizer-drawn forward osmosis desalination. Environ. Sci. Technol. 46, 4567–4575. doi:10.1021/es300002w

Phuntsho, S., Vigneswaran, S., Kandasamy, J., Hong, S., Lee, S., Shon, H.K., 2012b. Influence of temperature and temperature difference in the performance of forward osmosis desalination process. J. Memb. Sci. 415-416, 734–744. doi:10.1016/j.memsci.2012.05.065

Qasim, M., Darwish, N.A., Sarp, S., Hilal, N., 2015. Water desalination by forward (direct) osmosis phenomenon: A comprehensive review. Desalination 374, 47–69. doi:10.1016/j.desal.2015.07.016

Qi, S., Li, Y., Zhao, Y., Li, W., Tang, C.Y., 2015. Highly efficient forward osmosis based on porous membranes - applications and implications. Environ. Sci. Technol. 4690–4695. doi:10.1021/es504164w

Qin, M., He, Z., 2014. Self-Supplied Ammonium Bicarbonate Draw Solute for Achieving Wastewater Treatment and Recovery in a Microbial Electrolysis Cell- Forward Osmosis-Coupled System. Environ. Sci. Technol. Lett. 1, 437–411.

Razmjou, A., Liu, Q., Simon, G.P., Wang, H., 2013. Bifunctional polymer hydrogel layers as forward osmosis draw agents for continuous production of fresh water using solar energy. Environ. Sci. Technol. 47, 13160–13166. doi:10.1021/es403266y

Ren, J., McCutcheon, J.R., 2015. Polyacrylonitrile supported thin film composite hollow fiber membranes for forward osmosis. Desalination 372, 67–74.

Sahebi, S., Phuntsho, S., Eun Kim, J., Hong, S., Kyong Shon, H., 2015. Pressure assisted fertiliser drawn osmosis process to enhance final dilution of the

fertiliser draw solution beyond osmotic equilibrium. J. Memb. Sci. 481, 63–72. doi:10.1016/j.memsci.2015.01.055

Setiawan, L., Wang, R., Li, K., Fane, A.G., 2011. Fabrication of novel poly(amide-imide) forward osmosis hollow fiber membranes with a positively charged nanofiltration-like selective layer. J. Memb. Sci. 369, 196–205. doi:10.1016/j.memsci.2010.11.067

Shaffer, D.L., Werber, J.R., Jaramillo, H., Lin, S., Elimelech, M., 2015. Forward osmosis : Where are we now ? Desalination 356, 271–284. doi:10.1016/j.desal.2014.10.031

Sukitpaneenit, P., Chung, T.S., 2012. High performance thin-film composite forward osmosis hollow fiber membranes with macrovoid-free and highly porous structure for sustainable water production. Environ. Sci. Technol. 46, 7358–7365. doi:10.1021/es301559z

Tan, C.H., Ng, H.Y., 2010. A novel hybrid forward osmosis - nanofiltration (FO-NF) process for seawater desalination: Draw solution selection and system configuration. Desalin. Water Treat. 13, 356–361. doi:10.5004/dwt.2010.1733

Tang, C.Y., She, Q., Lay, W.C.L., Wang, R., Fane, A.G., 2010. Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration. J. Memb. Sci. 354, 123–133. doi:10.1016/j.memsci.2010.02.059

Tian, M., Wang, Y., Wang, R., 2015. Synthesis and characterization of novel high-performance thin film nanocomposite (TFN) FO membranes with nanofibrous substrate reinforced by functionalized carbon nanotubes. Desalination 370, 79–86.

Valladares Linares, R., Li, Z., Sarp, S., Bucs, S.S., Amy, G.L., Vrouwenvelder, J.S., 2014. Forward osmosis niches in seawater desalination and wastewater reuse. Water Res. 6, 122–139.

Wang, H., Wei, J., Simon, G.P., 2014. Response to Osmotic pressure versus swelling pressure: Comment on "bifunctional polymer hydrogel layers as forward osmosis draw agents for continuous production of fresh water using solar energy." Environ. Sci. Technol. 48, 4214–4215. doi:10.1021/es5011016

Wang, W., Zhang, Y., Esparra-Alvarado, M., Wang, X., Yang, H., Xie, Y., 2014.

Effects of pH and temperature on forward osmosis membrane flux using rainwater as the makeup for cooling water dilution. Desalination 351, 70–76. doi:10.1016/j.desal.2014.07.025

Xie, M., Nghiem, L.D., Price, W.E., Elimelech, M., 2014. Relating rejection of trace organic contaminants to membrane properties in forward osmosis: Measurements, modelling and implications. Water Res. 49, 265–274. doi:10.1016/j.watres.2013.11.031

Yang, Q., Wang, K.Y., Chung, T.S., 2009. Dual-layer hollow fibers with enhanced flux as novel forward osmosis membranes for water production. Environ. Sci. Technol. 43, 2800–2805. doi:10.1021/es803360t

Zhao, S., 2014. Osmotic Pressure versus Swelling Pressure: Comment on "Bifunctional Polymer Hydrogel Layers As Forward Osmosis Draw Agents for Continuous Production of Fresh Water Using Solar Energy." Environ. Sci. Technol. 48, 4212–4213.

Zhao, S., Zou, L., Mulcahy, D., 2012. Brackish water desalination by a hybrid forward osmosis-nanofiltration system using divalent draw solute. Desalination 284, 175–181. doi:10.1016/j.desal.2011.08.053

Zirehpour, A., Rahimpour, A., Seyedpour, F., Jahanshahi, M., 2015. Developing new CTA/CA-based membrane containing hydrophilic nanoparticles to enhance the forward osmosis desalination. Desalination 371, 46–57. doi:10.1016/j.desal.2015.05.026

Zotarelli, L., Dukes, M.D., Liu, G.D., Simonne, E.H., Agehara, S., 2015. Principles and Practices of Irrigation Management for Vegetables, in: 2015 Vegetable Production Handbook for Florida. pp. 11–18.