Forward osmosis: Novel desalination of produced water and fracturing flowback

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Treatment and reuse of oil and gas (O&G) production wastewater in a cost-effective and environmentally sound manner is critical to sustainable industrial development and for meeting stringent regulations. High salinity, free and emulsified hydrocarbons, silts and clays released from producing formations, and process additives common in O&G drilling wastewater render many conventional treatment technologies ineffective. Forward osmosis (FO) has been established as a promising solution for treatment and desalination of complex industrial streams and especially O&G exploration and production wastewaters. FO has achieved up to 85% water recovery from O&G wastewaters and can concentrate feed streams salinities to greater than 150,000 ppm. The process can operate as a stand-alone technology with minimal pretreatment or be coupled with other advanced processes such as reverse osmosis or distillation. FO minimizes O&G wastewater disposal and produces clean water for intrabasin reuse. Recent developments in membrane fabrication, system configurations, and draw solutions are briefly reviewed.

Keywords: *desalination, forward osmosis, fracturing flowback, membranes, osmotic dilution, produced water, wastewater treatment*

The oil and gas (O&G) industry is rapidly expanding the exploration and development of unconventional O&G resources, including shale gas, coal bed methane, and tight sands (Weijermars, 2013; Xingang et al, 2013; Aguilera & Ripple, 2012; Chang et al, 2012; Lin & Wang, 2012). With recent improvements in horizontal drilling and hydraulic fracturing, unconventional gas is projected to account for nearly 90% of the natural gas produced in the United States by 2035 (Rahm & Riha, 2012; Rahm, 2011). As production increases and new formations become economically viable, water demands for well development and the volume of wastewater generated during exploration and production will increase substantially.

Drilling muds, hydraulic fracturing flowback, and produced waters are the main streams that need treatment. More than 1 mil gal of freshwater is commonly used during drilling of a single well, producing borehole waste contaminated with dissolved solids, drilling additives, and inorganic and organic compounds leached from the formation (Hickenbottom et al, 2013; Hutchings et al, 2010; Xu et al, 2008). After drilling, these fluids receive minimal treatment and are commonly trucked offsite for deep well injection—deep enough to minimize the potential for intrusion and contamination of groundwater resources. Yet in many cases and especially when drilling for shale gas, the largest stream that can be treated and reused is the return flow from hydraulic fracturing. More than 4 mil gal of water-based slurry are commonly used for high-pressure fracturing of one well (McIlvaine & James, 2010; Horn & Newfield Exploration Mid-Continent, 2009), ultimately increasing the recovery of oil and gas from formations previously considered economically unfavorable.

After fracturing, the fracturing fluid is recovered over several weeks, generating a waste stream of water, proppant, and chemical additives (Rahm & Riha, 2012). Depending on the formation, the flowback wastewater may be highly saline, containing elevated concentrations of total dissolved solids (TDS) that may range from 10,000 to 200,000 mg/L. Fracturing flowback also receives minimal treatment before it is commonly deep well–injected (Rahm & Riha, 2012). Wastewater treatment is possible, and the reclaimed water can supplement or replace freshwater resources necessary for gas exploration; however, highly saline waste streams (Shaffer et al, 2013) and some hydraulic fracturing chemical additives are difficult to treat with conventional wastewater treatment processes.

After hydraulic fracturing, and depending on the type of O&G resource, water is produced from the formation with the oil or gas throughout the productive lifetime of the well. Produced water can represent 70–90% of the total wastewater generated during the lifetime of a well; the remaining 10–30% is the drilling mud and fracturing flowback water (Cakmakce et al, 2008). The quantity of water produced is highly dependent on well location, and its quality is just as variable. These streams typically contain a wide range of TDS concentrations equal to those in fracturing flowback, free and emulsified hydrocarbons, and silt and clay leached from the formation (Ebrahimi et al, 2009; Xu et al, 2008). Depending on the quality of the produced water, a range of technologies can be used for its treatment; however, the complexity and total cost of treatment scales with its salinity and ultimate use (Hickenbottom et al, 2013).

As the development of unconventional O&G continues, properly managing water resources while minimizing the volumes of exploration and production waste will become increasingly important. Several O&G basins in the United States are in urgent need of more water resources (Xu et al, 2008), providing an excellent opportunity for beneficial reuse of reclaimed water and reducing the use of limited freshwater supplies.

TREATMENT OF O&G EXPLORATION AND PRODUCTION WASTEWATER

Conventional physical, biological, and chemical treatment processes have been investigated for treatment of O&G exploration and production waste streams; however, high TDS concentration, capital cost, chemical demand, installation footprint, residuals (brines and solids) management, and limited removal of trace organic compounds are barriers to successfully implementing many technologies (Shaffer et al, 2013). Distillation and membrane desalination processes have demonstrated the ability to adequately treat these complex streams; yet more effective pretreatment and improvements to these technologies are sought before they are commercially developed and more widely implemented (Hancock et al, 2013a; Hickenbottom et al, 2013; Hutchings et al, 2010; Ebrahimi et al, 2009; Fakhru'l-Razi et al, 2009; Cakmakce et al, 2008).

Common desalination processes. *Membrane separation.* Traditional membrane separation technologies include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). These membrane technologies are commonly driven by hydraulic pressure and rely on diffusive- or convective-based mass transfer phenomena and unique membrane properties to separate dissolved and suspended constituents from aqueous solutions. Although MF and UF sieve suspended particles and macromolecules, NF and RO can effectively reject monovalent and divalent ions and trace organic compounds (Fakhru'l-Razi et al, 2009).

Membrane processes, and especially NF and RO, can reject a broad range of contaminants and dissolved solids in impaired feedwaters; however, hydraulically driven membrane processes are highly susceptible to inorganic scaling and to particulate, biological, and organic fouling (Sutzkover-Gutman & Hasson, 2010). Foulant layers can be tightly compacted and difficult to clean, leading to decreased water permeability, increased head loss, excessive chemical consumption for cleaning, and ultimately irreversible fouling and membrane failure. Additionally, polymeric membranes can be sensitive to feed stream chemical and oil contaminants, which can compromise membrane performance and surface-layer chemistry. Hydraulically driven membrane processes must also overcome the osmotic pressure of the feed stream, limiting the ability to concentrate streams to not much more than 70,000 mg/L TDS.

Distillation. Multi-effect distillation, multistage flash, and mechanical vapor compression distillation are common commercial thermal desalination technologies (Van der Bruggen & Vandecasteele, 2002). In distillation, a feed stream is heated and may also be placed under partial vacuum to increase its vapor pressure and generate water vapors that can be condensed and recovered as high-quality water. This vapor extraction process can be repeated several times to enhance evaporation and further concentrate the feed stream. The process can minimize physical and chemical pretreatment and the amount of deoiling equipment needed for treatment of O&G wastewater, thus minimizing capital costs and secondary chemical waste sludge (Fakhru'l-Razi et al, 2009). Furthermore, distillation is not influenced by the high osmotic pressure of feed streams and therefore can be used to treat saline and hypersaline water. Yet corrosion and scaling can occur and incur high operating and maintenance costs in distillation (Van der Bruggen & Vandecasteele, 2002). In addition, energy demand is a limiting factor responsible for more than 95% of the total operating and maintenance costs of distillation (Fakhru'l-Razi et al, 2009).

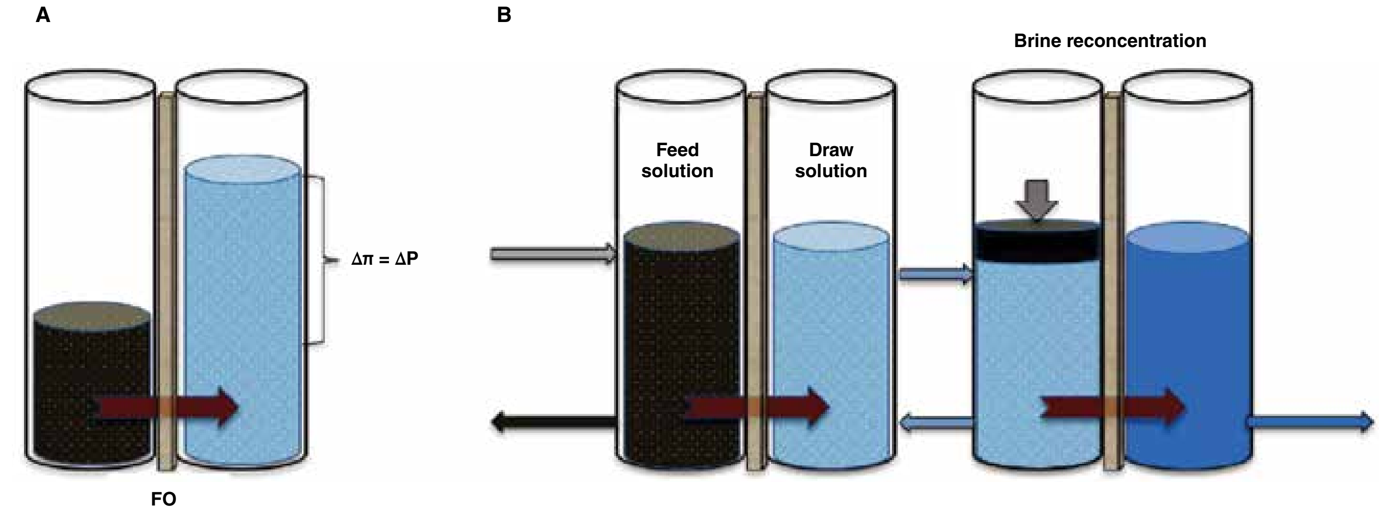
Desalination pretreatment. Distillation systems, and especially pressure-driven membranes processes, must be protected with appropriate pretreatment processes. NF and RO membranes are highly susceptible to scaling, fouling, extreme pH, oil and grease, insoluble liquids, and microorganisms (Sutzkover-Gutman & Hasson, 2010; Fakhru'l-Razi et al, 2009; Prihasto et al, 2009). Common pretreatment strategies may include one or a combination of technologies, including coagulation/flocculation/sedimentation, pH control, softening, filtration (granular/MF/UF), dissolved air floatation, advanced oxidation, and disinfection (Sutzkover-Gutman & Hasson, 2010; Fakhru'l-Razi et al, 2009; Prihasto et al, 2009). Other traditional and emerging processes, including biological processes, are possible.

Appropriately designed pretreatment will promote system/membrane longevity and minimize capital, operating, and maintenance costs associated with chemical cleaning (Kim et al, 2011). Yet some of the streams—and specifically fracturing flowback water—pose unique challenges to conventional and existing advanced treatment technologies. The fast expansion of the O&G industry also necessitates the development of more modular, onsite water treatment systems. Novel technologies that use different driving forces, minimize pretreatment requirements, and can separate a broad range of contaminants are needed for both the O&G industry and other waste treatment industries. Forward osmosis (FO) might be one of these technologies.

Engineered osmosis: FO. Engineered osmosis, and specifically FO, is an emerging desalination and water treatment technique that can provide robust and versatile treatment, reject contaminants found in O&G waste streams, and avoid the shortcomings of pressure-driven membrane processes. FO can be used as a standalone desalination process or as an advanced pretreatment process for RO.

Fundamentals of FO. In osmosis (Figure 1, part A), a synthetic, dense polymeric membrane separates an impaired feed stream and a concentrated draw solution. The difference in osmotic pressure ($\Delta\pi$) across the membrane facilitates diffusion of water through the membrane from the low-osmotic-pressure feed to the high-osmotic-pressure draw solution. Simultaneously all suspended constituents and nearly all dissolved mono- and multivalent ions are rejected (Cath et al, 2006; Salter, 2006). When used

FIGURE 1 The fundamental operation of FO



Δπ—difference in osmotic pressure, ΔP—difference in hydraulic pressure, FO—forward osmosis,

In FO, a synthetic polymeric membrane separates a feed stream and a concentrated draw solution, and the osmotic pressure difference across the membrane facilitates diffusion of water through the membrane (A). The FO process can be coupled with a brine reconcentration system (e.g., reverse osmosis) (B), sustainably producing high-quality product water while concentrating and reducing the volume of the feed stream.

as advanced pretreatment, the FO process is completed in two steps: (1) recovery of water from a feed stream and dilution of the draw solution and (2) production of high-quality product water using RO or distillation while reconcentrating the draw solution for reuse in the osmosis process (Figure 1, part B; Ge et al, 2013; Hancock et al, 2013a; Chung et al, 2012a; Shaffer et al, 2012; Zhao et al, 2012; Cath et al, 2010). However, FO is also attractive as a stand-alone process; several industrial applications, including in the O&G industry, are able to use the dilute draw solution, eliminating the need for the reconcentration step.

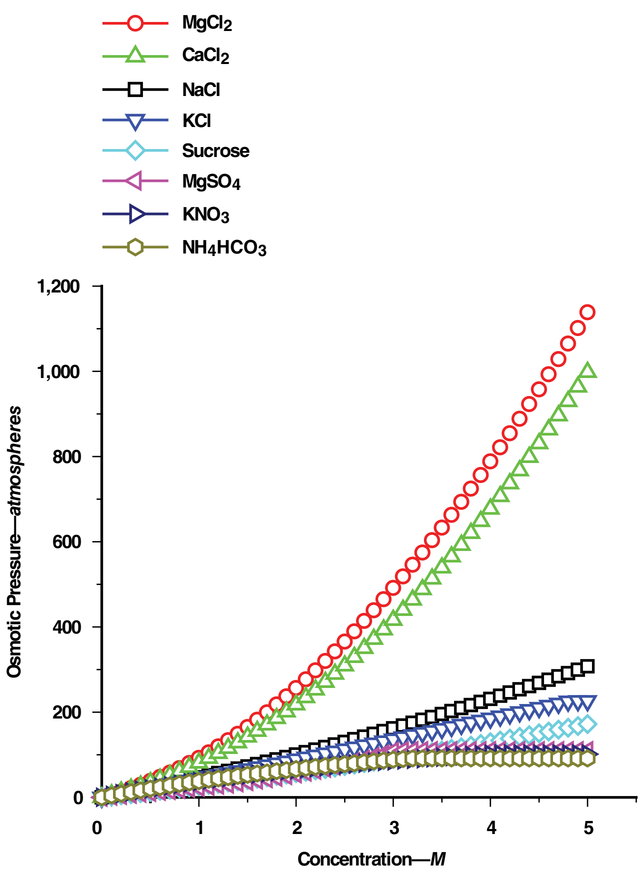
In addition to high solute and suspended solids rejection, FO is less susceptible to membrane fouling compared with pressure-driven membrane processes (e.g., NF, RO), mainly because of minimal compaction of foulant layers on the membrane. Fouling on FO membranes can be more easily removed with osmotic backwashing (Hoover et al, 2011; Sagiv et al, 2008; Avraham et al, 2006; Sagiv & Semiat, 2005; Spiegler & Macleish, 1981) or scouring via increased flow rate and turbulence-enhancing spacers at the feed–membrane interface (Hickenbottom et al, 2013). FO can also be used to treat highly saline feed streams when coupled with an adequate draw solution because it does not require hydraulic pressures to overcome high osmotic pressures.

Draw solutions. Efficient and sustainable FO operations are highly dependent on the selection and use of an efficient and suitable draw solution. Draw solution solutes should be highly soluble to avoid precipitation or scaling during RO or distillation reconcentration. They must also be industrially compatible, nontoxic, readily available, and inexpensive to be used in commercial FO systems (Bowden et al, 2012; Chung et al, 2012b; Ge et al, 2012; Zhao et al, 2012; Phuntsho et al, 2011; Achilli et al, 2010; Yen et al, 2010; Cath et al, 2006; McCutcheon et al, 2005). A review of promising draw solutions was recently published (Klaysom et al, 2013), and the osmotic pressures of potential inorganic draw solutions as a function of their molar concentration are shown in Figure 2 (Cath et al, 2006).

FO membranes. Unlike RO membranes, FO membranes have unique physical and chemical properties that enable efficient diffusion of water through their polymer structure. These include a very thin active layer cast on top of a highly porous support layer having low tortuosity and minimal thickness. Several manufacturers have developed and are already commercializing suitable FO membranes (Klaysom et al, 2013). The main commercially available membranes are the cellulose triacetate (CTA) and polyamide thin-film composite (TFC) membranes manufactured by company A[1] (HTI, 2013) and the TFC membrane from company B[2] (Oasys, 2013).

Other companies and many research institutes and universities are in the process of developing new FO and pressure-retarded osmosis membranes (Amini et al, 2013; Klaysom et al, 2013; Li et al, 2013; Nguyen et al, 2013; Fang et al, 2012; Han et al, 2012; Li et al, 2012; Qiu et al, 2012; Tiraferri et al, 2012; Wang et al, 2012; Yong et al, 2012; Song et al, 2011; Wang et al, 2010; Yen et al, 2010; Zhang et al, 2010). For example, Wang (2012) investigated the production of thin-film composite FO hollow fibers with an ultrathin active layer. This active layer, very similar to an RO-selective layer, can be produced on the inside or outside wall of the hollow fiber. Experimental conclusions suggest the ability to easily tailor this process and a membrane-active layer to meet specified requirements. Such membranes could further increase the packing density of membranes in a

FIGURE 2 Osmotic pressure of select draw solution solutes



Adapted from Cath et al, 2006

$CaCl_2$—calcium chloride, KCl—potassium chloride, KNO_3—potassium nitrate, $MgCl_2$—magnesium chloride, $MgSO_4$—magnesium sulfate, NaCl—sodium chloride, NH_4HCO_3—ammonium bicarbonate

Water diffusion through forward osmosis membranes is driven by the osmotic difference between the concentrated draw solution and impaired feed stream and requires negligible hydraulic pressure to operate. Osmotic pressure as a function of draw-solution concentration can be significantly different for potential draw solutions.

smaller footprint and avoid hydraulic shortcomings of membrane spiral-wound modules as they become fouled. Qiu et al (2012) produced a positively charged flat-sheet membrane using polyamide-imide substrate with a polyelectrolyte posttreatment. This produced an asymmetric, microporous membrane with an active layer similar to that of an NF membrane. Unfortunately, membranes for O&G wastewater treatment should be negatively charged, which will decrease the affinity of negatively charged organic molecules to adhere to the membrane surface. Qiu et al (2010) built on this same research, developing a polyamide-imide membrane with a less positively charged active layer to help mitigate the attraction of negatively charged organic molecules. In general, both casting techniques and membrane substrate selection have allowed polymer scientists to produce better FO membranes that are more precisely tailored for specific applications and different feed water compositions.

FO DESALINATION OF O&G WASTEWATER

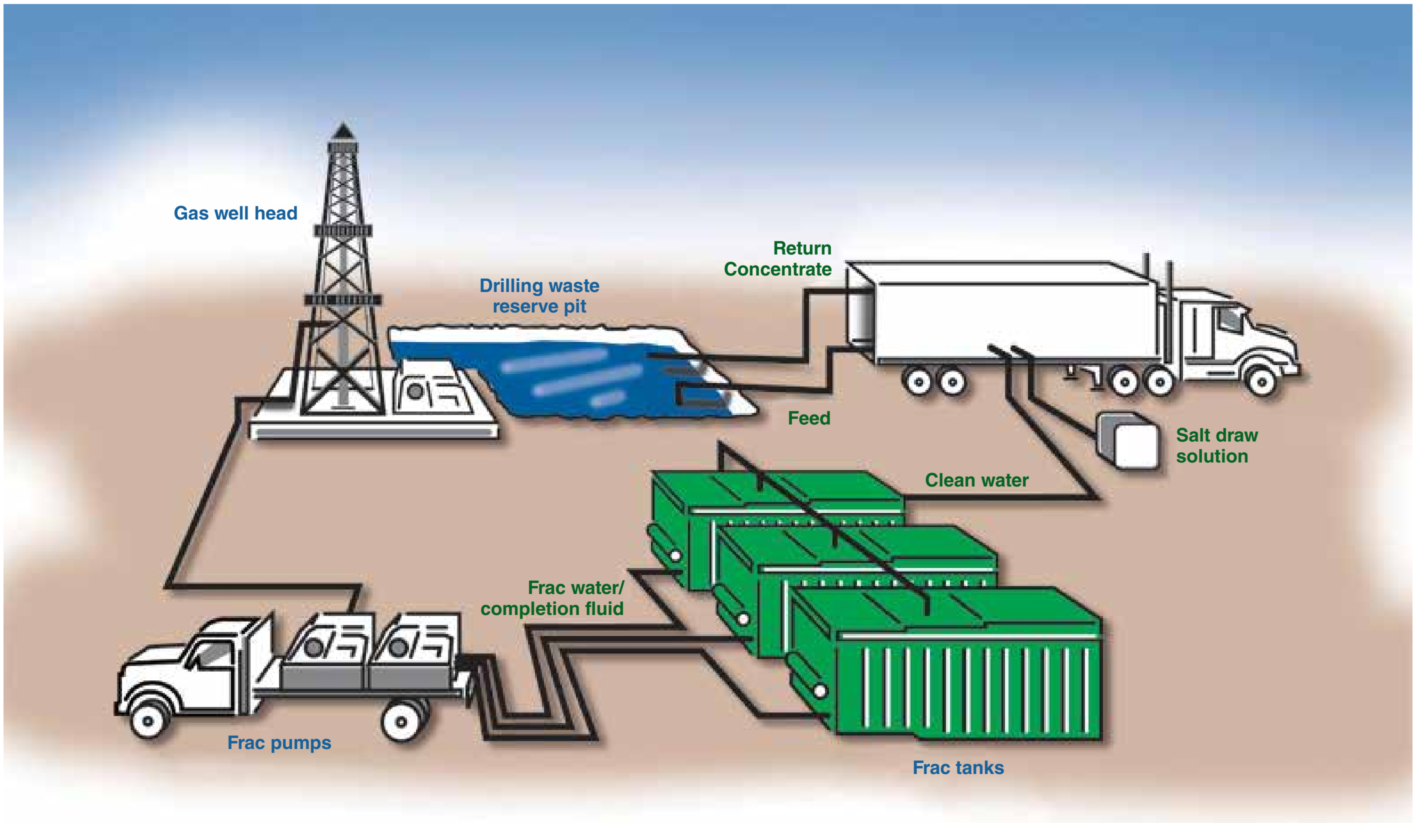
In recent years, FO has been demonstrated as a promising technology for treatment of difficult and complex liquid streams. Successful processes include desalination of seawater and brackish water, concentration of landfill leachates, treatment of domestic wastewater (including in osmotic membrane bioreactor configurations), and processing of liquid foodstuffs (Chung et al, 2012b; Zhao et al, 2012; Cath et al, 2006). Here we summarize specific applications in which FO was successfully tested for treatment and reuse of O&G industrial waste streams.

FO process A[3]. Hutchings et al (2010) were the first to investigate the performance of FO for treatment of O&G waste streams for beneficial, intrabasin reuse using the concept of FO process A. FO process A is a mobile and scalable FO treatment process operated at the well site, thus limiting water and wastewater trucking (resulting in a reduced carbon footprint) and providing a local, reusable water source. Operational success was measured by the system's ability to minimize freshwater demand through reuse, prevent secondary waste generation, reduce O&G wastewater volumes for deep well injection, and use readily available chemical energy to generate an osmotic pressure driving force.

Since 2010, two models of FO process A have been manufactured and pilot-tested by companies A and C[4]. The first generation of FO process A (Figure 3) used up to 280 vertically oriented, 8-in.-diameter × 40-in.-long spiral-wound FO membrane elements to treat streamflows of up to 170 gpm. The system operated in an osmotic dilution mode, in which a 260,000-mg/L sodium chloride (NaCl) draw solution was recirculated inside the membrane envelope while raw drilling wastewater (approximately 25,000 mg/L TDS) was flowing by gravity on the active side of the membrane. The highly concentrated NaCl draw solution was diluted to less than 70,000 mg/L NaCl while achieving greater than 70% water recovery, concentrating the exploration and production wastewater by more than 3.5 times. Test results (Webb & Riley, 2010) showed that this system was able to reclaim more than 125,000 gal of O&G wastewater using less than 20 gal of diesel fuel for fluid pumping, eliminating the need for pretreatment of the feed stream. This same volume would have required more than 25 truckloads for disposal at an offsite deep well injection facility. FO treatment systems could ultimately save nearly 1 mil gal of water per well developed (approximately 150 saved truckloads) and account for up to 12% of the saline completion fluid needed for hydraulic fracturing of a single well (Hutchings et al, 2010).

However, in a recent study (Hickenbottom et al, 2013), results suggested that FO treatment using the first generation of FO process A could be optimized. Using a custom-made FO membrane test cell with a CTA membrane and a 260,000 mg/L NaCl draw solution, osmotic dilution experiments were performed during which at least 75% of the water in O&G drilling waste was recovered. Results from the study agreed with previous findings that FO can concentrate O&G drilling waste streams by up to three times; however, the study demonstrated that increased

FIGURE 3 Company A's first generation of FO process A



Adapted with permission from HTI, 2013.

FO—forward osmosis

The first generation of FO process A operated under osmotic dilution using vertically oriented spiral-wound FO elements. The membrane elements were grouped into several pods and installed on a trailer that was operated at oil and gas drilling locations in the field.

feed-stream velocities can decrease membrane fouling and concentration polarization (McCutcheon & Elimelech, 2006a) and minimize feed-channel clogging, all of which promote higher and sustainable water flux. Also, minimal irreversible fouling was observed after implementing osmotic backwashing of the FO membranes (Hoover et al, 2011; Sagiv et al, 2008; Avraham et al, 2006; Sagiv & Semiat, 2005; Spiegler & Macleish, 1981). In osmotic backwashing, the draw solution was replaced with freshwater having an osmotic pressure lower than that of the concentrated O&G waste stream. This induced the permeation of water in the opposite direction across the membrane, thus promoting the release of foulants from the membrane surface. Additionally, high rejection of inorganic and organic constituents during pilot-testing was confirmed by the bench-scale study.

As a result of previous experimental work and pilot-testing, system performance was optimized, and the second generation of FO process A was developed in 2012 (see the photograph on page E60). The second-generation FO system uses 24 horizontally oriented, 8-in.-diameter × 40-in.-long spiral-wound FO membrane elements housed in pressure vessels. The system operates under forced-feed flow through the membrane elements (~40–60-psi hydraulic transmembrane pressure) and simultaneously fed with an NaCl draw solution generated by an RO system.

Preliminary pilot-testing was conducted in which 60,000 mg/L NaCl draw solution was diluted to approximately 45,000 mg/L after a once-through pass in the FO system. The diluted draw solution was then reconcentrated by the RO system, simultaneously producing a high-quality permeate stream. During week-long testing, the system recovered 85% of O&G wastewater (6.8 mS/cm; Figure 4, part A) while concentrating it by five times (32.5 mS/cm) and producing highly purified water for reuse (Figure 4, part B). The system treated raw produced water (no prior pretreatment) without membrane cleaning and experienced a mere 18% flux decline (Figure 4, part C). Flux decline was attributed mainly to loss in an osmotic-pressure driving force that resulted from increased osmotic pressure of the concentrated feed. Unlike the first generation of FO process A, in which the diluted draw solution was suitable for use as hydraulic fracturing fluid in future exploration and well development, the second generation of FO process A produces a high-quality RO permeate suitable for a range of reuse applications. However, the operation of the second-generation FO process A requires higher

Company A's second generation of forward osmosis process A operates under constant influent draw solution concentration using a reverse osmosis membrane reconcentration system. The 8-in. spiral-wound forward osmosis elements are housed in membrane pressure vessels.

pressure pumping and more energy; at this time, the system is limited to approximately 70,000 mg/L NaCl draw solution if RO reconcentration is used.

FO process B[5]. Company B has developed an FO process B (Figure 5) using a patented ammonia/carbon dioxide draw solution and targeting treatment of high-salinity feed steams and O&G wastewater. The system consists of three components: pretreatment, FO process B platform, and product water/brine polishing. Raw feed water is first pretreated using chemical oxidizer, caustic soda, and soda ash to precipitate low-solubility minerals and generate organic flocs. The precipitated solids pumped through a filter press to dewater the sludge and the clarified supernatant is filtered through a greensand filter for additional iron and particulate removal, and ultimately is polished using a cartridge filter. Pretreated feed water is pumped into the FO process B platform and concentrated to between 150,000 and 250,000 mg/L TDS, depending on subsystem operating conditions (Hancock et al, 2013a).

The patented draw solution is a mixture of ammonium bicarbonate and ammonium hydroxide dissolved in water. The resulting solution is highly soluble and produces a high-osmotic-pressure-driving force suitable for treating O&G waste streams up to 200,000 mg/L TDS. At the final stage of treatment, the diluted draw-solution is heated to evaporate the thermolytic draw solution solutes, which requires less energy than would be required to overcome the enthalpy of vaporization for water (McGinnis et al, 2013). The ammonia and carbon dioxide gases are then condensed, and a reconcentrated draw solution is generated for reuse in the FO system. Product water is stripped of dissolved ammonia and carbon dioxide and then polished using low-pressure RO (additional ammonia recovery), exiting the system as a purified water stream. During piloting of FO process B (see the rendering to the right), the system retained more than 99.75% of its nitrogen-containing species during 100 h of operation (Hancock et al, 2013a), an indication of sustainable long-term osmotic driving force.

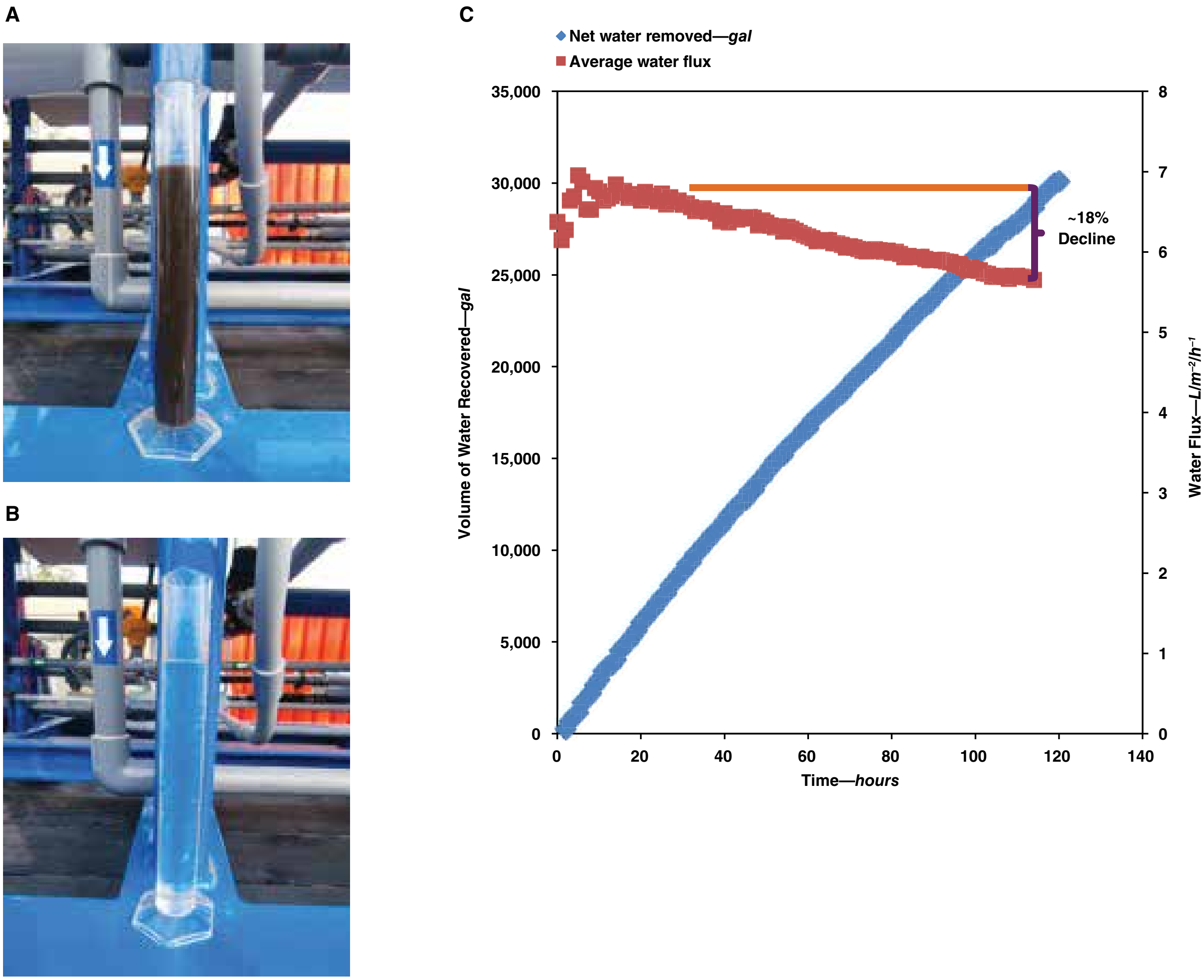
In two case studies, FO process B provided water treatment and waste volume minimization of fracturing flowback water and produced water from the Marcellus Shale and Permian Basin. During the Marcellus Shale trail, approximately 60,000 gal of produced water were treated during 800 h of operation. Average daily steady-state water flux was between 2 and 3 L/m^2/h (1.2–1.8 gfd), depending on system operating conditions (i.e., draw solution and feed temperature, draw solution concentration, and solution flow rates); system water recovery averaged 64%.

During system operations in the Permian Basin, approximately 40,000 gal of produced water were treated during 400 h of operation. The average feed salinity of FO process B in the Permian Basin was 103,000 mg/L and contained a high concentration of total organic carbon, boron, and heavy metals. Although TDS and hardness were relatively constant, organic and heavy metal concentrations varied substantially between wastewater batches. The average TDS concentration of product water from FO process B in the Permian Basin trial was 737 mg/L, and the concentrated brine concentration averaged 241,000 mg/L TDS. System water flux averaged 3 L/m^2/h (~1.8 gfd), and average system recovery was 60% (Hancock et al, 2013a). The higher water flux and percent recovery, despite the higher salinity of the feed stream compared with the Marcellus Shale pilot-testing, were attributed to improvements in company B's membrane, membrane elements, and other subsystem refinements.

Looking to the future. Using FO has shown many advantages in the treatment of O&G exploration and production wastewater. These include low hydraulic pressure operation, minimal pretreatment, reduced fouling propensity compared with pressure-driven processes (RO), and substantial rejection of known contaminants found in produced water, fracturing flowback, and drilling muds. Although pilot-testing and bench scale–testing

Rendering of company B's forward osmosis process B (adapted from Hancock et al, 2013a and 2013b).

FIGURE 4 Company A's second generation of FO process A



FO—forward osmosis

The second generation of FO process A targeted raw produced water in the Haynesville Shale basin (A). The system recovered > 30,000 gal of water (B) and the FO membranes experienced a mere 18% flux decline over the entire testing period (C).

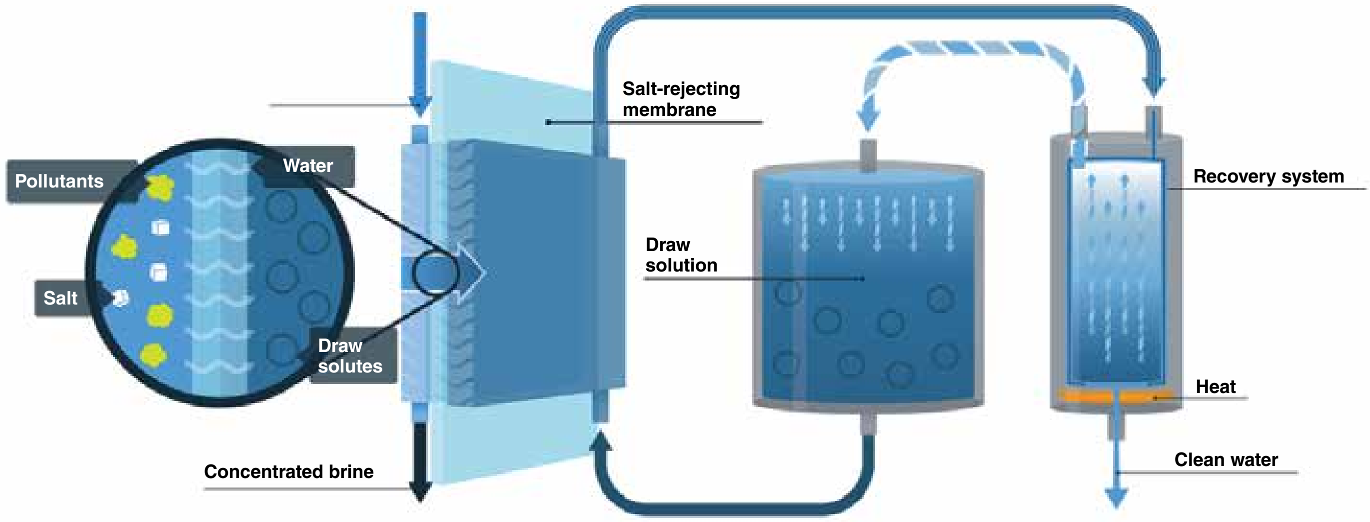
studies have provided promising results, there is still a need to better understand the nature and mechanisms of fouling and their effects on FO process efficiency when treating O&G saline exploration and production wastewater. Treatment of these wastewaters is challenging, mainly because of variations in feed water quality over time and because the results from most FO studies are only for shorter durations. Feed water composition changes from well to well and between basins; therefore, more investigations are required to broaden the application of FO to waste streams of different complexities and to basins other than the Haynesville, Marcellus, and Permian.

TECHNOLOGICAL PROGRESS

Despite the successful demonstration of FO in the laboratory and in the field, additional improvements are still needed. Previous reviews of the technology (Klaysom et al, 2013; Zhao et al, 2012; Cath et al, 2006) indicated that there are several shortcomings of FO that need to be addressed through future research and development.

New FO membranes. First-generation FO membranes were produced by company A using various blends of cellulose acetate polymer. These robust membranes are still under development and are used in FO process A; however, studies and recent field

FIGURE 5 Schematic of FO process B manufactured by company B



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FO—forward osmosis

The FO treatment system operates under constant influent draw solution concentration using a thermolytic reconcentration system. Several pretreatment technologies are used before FO membrane treatment to reduce oil emulsions and elevated hardness concentrations in oil and gas wastewaters.

tests have shown that although these membranes are robust, their water permeability needs improvement and they can operate only in a narrow pH range of 4 to 7 (Qiu et al, 2012; Yen et al, 2010). Recently developed TFC FO membranes by companies A and B were tested and compared (Coday et al, 2013). The TFC membranes exhibited better water flux than did the CTA membranes; however, the reverse salt flux of the TFC membranes was higher and more affected by the transmembrane pressure common in the latest O&G FO treatment membrane modules. Rejection of organic molecules was comparable between the TFC and CTA membranes, with both exhibiting organic rejection of approximately 96%. The study demonstrated that new membrane materials and structure, coupled with operating conditions, might influence the preferential reverse diffusion and rejection of charged ions.

For O&G wastewater treatment, membrane manufacturers are challenged with balancing several requirements, including high membrane robustness, high support-layer porosity, and high solute rejection while minimizing the thickness and tortuosity of the membrane and porous support layer. Looking to the future, Wang et al (2012) suggest that the most effective FO membranes must have a very thin active layer supported by a thin support whose structure is highly porous to minimize internal concentration polarization. The membrane surface should be hydrophilic, which may help minimize O&G foulant deposition on the membrane surface and increase water permeability when treating viscous fracturing flowback fluids. Furthermore, the membrane chemistry must withstand large pH ranges to provide the most effective envelope of treatment capabilities, including maintenance with various aggressive chemicals.

New membrane configurations. Several different membrane configurations (e.g., plate-and-frame, spiral wound, hollow fiber, tubular) have been developed and investigated to provide the best overall rejection, water flux, and operating efficiency given certain feed water composition and characteristics. For O&G wastewater treatment, one challenge is the need to improve process hydraulics to avoid clogging the flow channels in the membrane elements. Dissolved and suspended constituents in drilling and fracturing flowback wastewater and produced water are major membrane foulants; when concentrated, they can clog the membrane elements. Although typical FO membranes are highly hydrophilic and thus reduce the fouling propensity of the membrane, precipitation of solids in the feed channels may retard the performance of the process. Novel membrane feed spacers, new membrane configurations (such as capillary membranes), and adjusting pretreatment processes will enable more efficient use of FO in the O&G industry.

New draw solutions. There are more than 500 inorganic compounds that can be potentially used as draw solutions; 14 were chosen and investigated in a recent study by Achilli et al (2010). Other investigations have studied the applicability of dissolved gases or even nanoparticles as suitable draw solutions in tailored FO applications (Hancock et al, 2013a; Bowden et al, 2012; Ge et al, 2012; Phuntsho et al, 2011; Achilli et al, 2010; Yen et al, 2010; McCutcheon et al, 2005). Organic solutes such as ethanol, glucose, and fructose can also be used as osmotic draw solutions

TABLE 1 Overview of draw solutes/solutions used in FO investigations and their recovery methods

Year	Draw solute/solution	Recovery method	Research group
1964	NH_3 and CO_2	Heating	Neff, 1964
1965	Volatile solutes (e.g., SO_2)	Heating or air stripping	Batchelder, 1965
1965	Mixture of water and another gas (SO_2) or liquid (aliphatic alcohols)	Distillation	Glew, 1965
1970	Organic acids and inorganic salts	Temperature variation/chemical reaction	Neff, 1964
1972	Al_2SO_4	Precipitation by doping $Ca(OH)_2$	Frank, 1972
1975	Glucose	None	Kravath & Davis, 1975
1976	Nutrient solution	None	Kessler & Moody, 1976
1989	Fructose	None	Stache, 1989
1992	Sugar	RO	Yaeli, 1992
1997	$MgCl_2$	None	Loeb et al, 1997
2002	KNO_3 and SO_2	SO_2 is recycled through standard means	McGinnis, 2002
2005–07	NH_3 and CO_2 (NH_4HCO_3)	Moderate heating (~60°C)	McGinnis & Elimelech, 2007; McCutcheon et al, 2006b; McCutcheon et al, 2005; Loeb et al, 1997
2007	Magnetic nanoparticles	Captured by a canister separator	Adham et al, 2007
2007	Dendrimers	Adjusting pH or UF	Adham et al, 2007
2007	Albumin	Denatured and solidified by heating	Adham et al, 2007
2008	Salt, ethanol	Pervaporation	McCormick et al, 2008
2010	2-Methylimidazole–based solutes	FO-MD	Yen et al, 2010
2010–11	Magnetic nanoparticles	Recycled by a magnetic field	Ge et al, 2010; Ling et al, 2010
2011	Stimuli-responsive polymer hydrogels	Deswelling the polymer hydrogels	Li et al, 2011
2011	Fertilizers	Unnecessary	Ling & Chung, 2011; Liu, 2007
2011	Hydrophilic nanoparticles	UF	Ling & Chung, 2011
2011	Fatty acid-polyethylene glycol	Thermal method	Iyer, 2011
2012	Sucrose	NF	Su et al, 2012
2012	Thermo-sensitive solute (derivatives of Acyl-TAEA)	None	Noh et al, 2012
2012	Urea, ethylene glycol, and glucose	None	Yong et al, 2012
2012	Polyglycol copolymers	NF	Carmignani et al, 2012
2012	Hexavalent phosphazene solutes	None	Stone et al, 2013b
2012	Organic ionic salts [e.g., $Mg(CH_3COO)_2$]	RO	Bowden et al, 2012
2012	Polyelectrolytes	UF	Ge et al, 2012

Adapted from Ge et al, 2013; Zhao et al, 2012

Al_2SO_4—aluminum sulfate, $Ca(OH)_2$—calcium hydroxide, CO_2—carbon dioxide, FO—forward osmosis, KNO_3—postassium nitrate, MD—membrane distillation, $Mg(CH_3COO)_2$—magnesium acetate, $MgCl_2$—magnesium chloride, NF—nanofiltration, NH_3—ammonia, NH_4HCO_3—ammonium bicarbonate, RO—reverse osmosis, SO_2—sulfur dioxide, UF—ultrafiltration

and be tailored to obtain the desired physiochemical properties; however, simple organic draw solutions typically yield low osmotic pressure and water flux (Klaysom et al, 2013). Recently, more complex organic draw solutions have been investigated, including 2-methylimidazole–based compounds (Yen et al, 2010) and switchable polarity solvents (Stone et al, 2013a) that generate high osmotic pressures that yield comparable or higher water flux than traditional inorganic solutes. Organic draw solutions might be advantageous because they may be biodegradable and are well rejected by reconcentration technologies such as RO; however, these draw solutions are still experimental and require further research and development. A summary of FO draw solutions is shown in Table 1. Because of the highly saline nature of O&G-produced water, innovative draw solutions with high osmotic pressure are required.

CONCLUSIONS

FO is a promising technology that may enable exploration companies to use an effective desalination treatment technique and promote beneficial water reuse. Currently there are two commercial systems with distinctly different approaches to implementing the technology; however, it is unclear which approach is most suitable, leaving significant room for more research. Regardless, FO has shown great versatility by successfully treating a wide range of feed stream salinities and producing a wide range of product water quality—from diluted saline solution to RO permeate suitable for potable and nonpotable reuse.

More important, sustainable FO desalination is a step in the right direction toward the crucial goal of addressing the water use and wastewater generation by an industry under heavy public and political scrutiny. The studies discussed in this article are short-term and treated only a limited volume of water compared with the billions of gallons consumed and produced per year in the United States; however, the studies demonstrate that novel FO technology should be more closely investigated, both for effective wastewater management and for promoting internal water reuse in the O&G industry.

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FOOTNOTES

[1]Hydration Technology Innovations, Albany, Ore.
[2]Oasys Water, Boston, Mass.
[3]Green Machine, Hydration Technology Innovations, Albany, Ore.
[4]Emerald Surf Sciences (previously Bear Creek Services), Shreveport, La.
[5]Membrane Brine Concentrator, Oasys Water, Boston, Mass.

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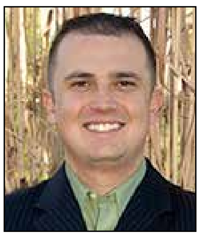

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