Produced Water Treatment Using the Switchable Polarity Solvent Forward Osmosis (SPS FO) Desalination Process: Preliminary Engineering Design Basis

Daniel Wendt, Birendra Adhikari, Christopher Orme, and Aaron Wilson Idaho National Laboratory

Keywords

Desalination, co-produced water, oil and gas produced water, switchable polarity solvent, forward osmosis, geothermal energy

ABSTRACT

Switchable Polarity Solvent Forward Osmosis (SPS FO) is a semi-permeable membrane-based water treatment technology. The Idaho National Laboratory (INL) is currently advancing SPS FO technology such that a prototype unit can be designed and demonstrated for the purification of produced water from oil and gas production operations. The SPS FO prototype unit will use the thermal energy in the produced water as a source of process heat, thereby reducing the external process energy demands. Treatment of the produced water stream will reduce the volume of saline wastewater requiring disposal via injection, an activity that is correlated with undesirable seismic events, as well as generate a purified product water stream with potential beneficial uses. This paper summarizes experimental data that has been collected in support of the SPS FO scale-up effort, and describes how this data will be used in the sizing of SPS FO process equipment. An estimate of produced water treatment costs using the SPS FO process is also provided.

Introduction

Significant quantities of produced water are brought to the surface during oil and gas production operations. Produced water generally consists of naturally occurring brine present in the reservoir, but may also contain fracturing fluid or other injection fluids associated with oil and gas recovery operations (Engle, Cozzarelli, and Smith 2014). The quality of produced water is variable, ranging in salinity similar to that of drinking water to several times more saline than sea water. Various constituents can be contained in produced water from petroleum reservoirs, including dissolved salt, petroleum and other organic compounds, suspended solids, trace elements, bacteria, naturally occurring radioactive materials (NORM), and anything injected into the well (Clark and Veil 2009).

The majority of produced water from hydrocarbon resource development is disposed of by injection. Produced waters that aren't injected are treated and disposed of in the surface environment, beneficially utilized, or recycled for use in hydraulic fracturing or other oil and gas operations. Lower salinity and better quality produced waters, which are often treated in some way, have many uses, including for irrigation, water for livestock, ecosystem and habitat maintenance, and aquaculture (Engle, Cozzarelli, and Smith 2014).

Cost effective treatment of produced water streams from oil and gas operations can reduce the volume of fluid that otherwise requires disposal at a cost to the operator. Switchable Polarity Solvent Forward Osmosis (SPS FO) technology, which could be used for treating produced water streams and reducing overall disposal costs, is currently being developed at the Idaho National Laboratory.

SPS FO Technology

Switchable Polarity Solvent Forward Osmosis (SPS FO) is a semi-permeable membrane-based water treatment technology. In forward osmosis, a draw solution with high osmotic pressure (a measure of chemical potential) is used to extract water from a feed water stream with comparably low osmotic pressure.

The SPS class of solvents is capable of switching between an aprotic non-ionic form, to a water-soluble ionic liquid/solute through the introduction and removal of CO_2 (Equation 1).

$$NR_{3(org)} + CO_{2(g)} + H_2O \rightleftharpoons HNR_{3(aq)} + HCO_{3(aq)}$$
 (1)

The ionic form can act as a draw solute in an FO process and then be separated from the product water through the application of heat, which drives off carbon dioxide and generates the water-immiscible aprotic tertiary amine. SPS is an example of a growing number of switchable thermolytic and thermal sensitive solutes (Boo, Khalil, and Elimelech 2015, Cai et al. 2013, Kim et al. 2014, Li and Wang 2013, McCutcheon, McGinnis, and Elimelech 2005, Miller and Evans 2006, Ou et al. 2013, Zhao et al. 2013, Zhao et al. 2014).

SPS FO Water Treatment Process Description

The SPS FO water purification process has five primary process components: An FO membrane unit; a CO_2 degasser; a mechanical liquid separator (gravity separation unit), a low pressure filtration unit, and a gas contactor. The connectivity of these process components is illustrated in Figure 1.

The produced water feed stream is optionally filtered to remove any particulates before entering the FO membrane unit, where contaminants in the feed water stream are removed as the water passes through the semipermeable membrane and into the aqueous draw solution. The dilute draw solution flows to a degasser where addition of heat initiates chemical decomposition of the bicarbonate ions in the aqueous solution, resulting in the generation of gaseous CO₂ and the changing of the SPS polarity from hydrophilic to hydrophobic.

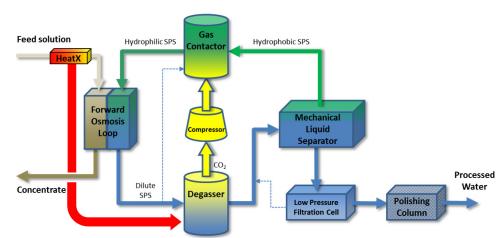


Figure 1. SPS FO process schematic.

The CO_2 is removed from the degasser for subsequent reuse in the process, while the hydrophobic SPS reaction products will partition to an organic phase that can be gravity separated from the immiscible aqueous phase containing the water extracted from the feed stream. The product water is separated from the low concentration of SPS that remains soluble in the aqueous phase using a low pressure nanofiltration (NF) and reverse osmosis (RO) polishing step. The organic-phase SPS exiting the gravity separator and CO_2 exiting the degasser are sent to a gas contactor where the concentrated aqueous-phase draw solution is regenerated for reuse in the membrane unit.

System Testing and Design Analyses

DOE is currently funding a project to design a prototype unit for field testing the treatment of oil & gas produced water using SPS FO technology. SPS FO technology was developed in recent years (Stone et al. 2013) and desalination of produced water from oil & gas operations will be the first industrial demonstration of the technology (Wendt, Mines, et al. 2015). In order to design a prototype unit for field testing, experimental testing and process modeling activities have been performed.

The goals of modeling the SPS FO process include the development of process flow diagrams and mass and energy balances for characterizing process energy use and product throughput rates. Process component sub-models that satisfactorily represent the reactive and transport phenomena occurring within each of the major process components will allow for successful equipment design and the evaluation of equipment costs. Following model development and validation

against experimental data, the model will be utilized for process scale-up activities, predicting off-design performance, and optimizing system performance measures including, but not limited to, throughput rates, process energy consumption, and/or system costs.

Prior to the development of a process model, considerable experimental testing and evaluation of candidate equipment configurations was necessary to ensure that the operational requirements of each process component could be met (verification that target product compositions could be met), and to determine the operating conditions necessary to achieve the required performance specifications.

Due to the novel nature of SPS FO technology, a baseline process design did not previously exist and the majority of the equipment selection and performance characterization had to be performed by the project team. Additionally, much of the 1-cyclohexyl piperidine (CHP) physical property and reaction kinetic data necessary to perform design calculations for each process component is unavailable in the open literature and/or in process modeling software property databanks such as Aspen Properties. Therefore, the collection and analysis of experimental data to characterize these properties was required.

The key parameters for sizing/costing each of the major process components, and the experimental data collected in order to evaluate these parameters, are described below.

Forward Osmosis Unit

The FO unit operating requirements include continuous operation with low membrane fouling. All components of the FO membrane must be chemically compatible with the range of feed and draw stream compositions that could be encountered during process operation. The semi-permeable FO membrane must operate with high rejection of the chemical constituents in the feed stream and low reverse solute flux. The Porifera FO MEM-0513 membranes have demonstrated the ability to achieve these general requirements in the laboratory testing performed by the INL research group.

The FO unit will operate in a countercurrent flow configuration in which the concentrated draw solution is used to extract water from the most concentrated feed stream. This configuration will include three sequential stages, each with specified feed and draw solution concentrations. Each stage is designed to operate with an average flux that is correlated to the osmotic pressure differential of the associated feed and draw streams. Each stage will include a specified number of membrane modules operating in a parallel configuration to provide the area necessary to achieve the required water recovery. The lower concentration stages will require greater membrane area since greater permeate flux is required to alter the concentrations of the dilute feed and draw solutions in these stages. The feed and draw solutions will pass through each stage once without recirculation of either stream within any stage.

The FO membranes are housed in modules with a defined membrane area. The process size may be scaled by adjusting the number of membrane modules that comprise each of the three stages. This approach will allow near linear scaling of the size and cost of the process with minimal impact on FO unit operating conditions or overall performance. The primary design parameters for the FO unit include the number of stages and the membrane area per stage. Once the number of stages has been determined, the feed and draw stream inlet and outlet concentrations can be determined and the average flux requirements per stage can be calculated. From this information the total membrane area can be determined. This approach assumes that the fluid velocity within each membrane module is maintained at the manufacturer's specified level; if the fluid velocity is altered the effect of the modified operating conditions on membrane flux must be evaluated through use of the appropriate mass transfer correlations.

Osmotic pressure π may be approximated though the following equation:

$$\pi = C_{ov}RT \tag{1}$$

where C_{aw} is the activity-based concentration, R is the universal gas constant, and T is the absolute temperature. For most systems, the activity-based concentration C_{aw} may be approximated using osmolality $(Osm/kg = i \cdot \rho \cdot C_{mol/kg})$ where i is the van't Hoff index, ρ is the solution density, and $C_{mol/kg}$ is the concentration in units of molality (mol/kg) such that the osmotic pressure π can be approximated as (Wilson and Stewart 2013):

$$\pi \cong i\rho C_{mol/kg}RT \tag{2}$$

The solvent flux through a semi-permeable membrane is computed using the following idealized equation:

$$J_W = A(\Delta P - \Delta \pi) \tag{3}$$

where J_W is the membrane water flux, A is the membrane permeability coefficient, ΔP is the hydraulic pressure differential across the membrane and $\Delta \pi$ is the osmotic pressure differential across the membrane (Singh 2015). In practice, the flux will vary as a result of concentration polarization and membrane fouling. The following expression accounts for the effects of external concentration polarization on the active layer and internal concentration polarization on the porous

support layer assuming the support layer is in contact with the draw solution as is the case when operating in FO mode (Cath et al. 2013):

$$J_{W} = A \left[\pi_{D,b} exp \left(\frac{-J_{W}}{k_{D,eff}} \right) - \pi_{F,b} exp \left(\frac{J_{W}}{k_{F}} \right) \right]$$

$$\tag{4}$$

where $\pi_{D,b}$ and $\pi_{F,b}$ are the bulk osmotic pressure of the draw and feed solutions, respectively, k_F is the mass transfer coefficient on the feed side of the membrane, and $k_{D,eff}$ is the effective mass transfer coefficient for internal concentration polarization occurring on the draw side of the membrane within the porous support layer defined as:

$$k_{D,eff} = \frac{D_S \phi}{\tau \delta} = \frac{D_S \phi}{\tau t} \tag{5}$$

where D_S is the diffusivity of the solute, δ is the thickness of the boundary layer (assumed equal to the support layer thickness), and ϕ , τ , and t are the porosity, tortuosity, and thickness of the membrane support layer, respectively (Cath et al. 2013). Additional description of the effects of concentration polarization and fouling may be found in Cardew and Le (1998), Lee, Kim, and Hong (2014), McCutcheon and Elimelech (2006), McCutcheon and Elimelech (2007), and Yun et al. (2013)

While the above equations will be used to evaluate process performance over varying operating conditions, the current analysis evaluates the design point performance of the SPS FO process based on experimental data obtained in the laboratory. In the current analysis, the produced water feed stream is assumed to have an osmotic pressure of approximately 26 bar, which is equivalent to that of a 0.5 mol/kg or 28,400 ppm NaCl solution. Recovery of 50% of the water in the feed stream is specified in each of the three FO stages, for a total recovery of 87.5%, which results in a concentrated feed stream with a composition of 4.0 mol/kg. The draw solution is specified as a 5.5 mol/kg CHP-H₂CO₃ solution that is diluted to 0.5 mol/kg at the outlet of the final FO stage. Experimentally determined average FO membrane flux data obtained from INL testing of various feed streams are presented in Figure 2. Using this experimental data, the flux in the concentrated, intermediate, and dilute stages of the process are specified as 3.5, 5.2, and 4.1 L m⁻² hr⁻¹, respectively.

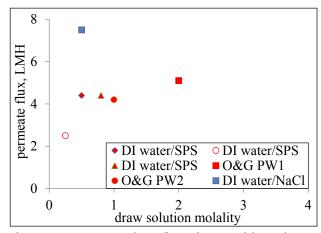


Figure 2. Average FO membrane flux as function of draw solution concentration tested for various feed stream compositions.

Degasser

The degasser operating requirements include driving the bicarbonate decomposition reactions to reduce the \sim 10 wt% CHP-H₂CO₃ dilute draw stream solution concentration to \sim 1.5 wt%. The target operating conditions for the treat-

ment of oil & gas produced waters are a temperature of 80°C and an absolute pressure greater than 0.25 bar. Process economics favor minimization of the residence time within the degasser and continuous operation at pressures near ambient (for minimization of compressor energy consumption).

The degasser design configuration (Figure 3) will include a series of tanks with internal spray nozzles. The nozzles increase the mass transfer area available to enhance the transport of CO₂ from the aqueous to the vapor phase. Heat exchangers upstream of the nozzles increase the fluid tem-

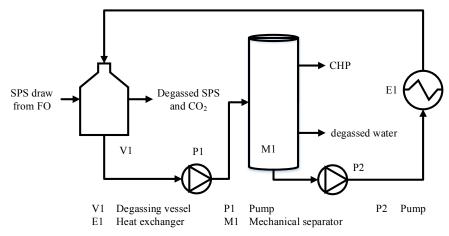


Figure 3. Integrated degasser – mechanical separator configuration.

perature to the level necessary to drive the bicarbonate decomposition reaction. The immiscible liquid phase products resulting from the bicarbonate decomposition reaction occurring in the degasser are continuously separated in a mechanical separator positioned at the degasser outlet.

Applicable design parameters include the number of stages, residence time (volume) per stage, flow rate per nozzle (pressure-dependent), heat exchanger configuration (including whether recuperation can be used for heat recovery) and heat transfer area. The selection of these design parameters will ultimately be based on the chemical reaction kinetics and mass transfer coefficients at the selected operating conditions. In the current, non-optimized process design and economic analysis, the reaction time is determined from experimentally determined kinetic data while the vessel and nozzle configurations are based on the mass transfer performance observed during experimental tests. The industrial-scale process equipment selection will most likely provide enhanced mass transport relative to the experimental configuration and the process design

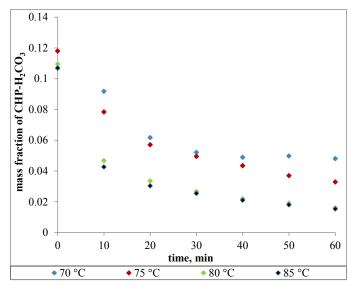


Figure 4. Aqueous phase CHP-H₂CO₃ composition as functions of temperature and time.

parameters and cost estimates will therefore need to be revisited accordingly.

A subset of the degasser experimental data collected is included in Figure 4. A kinetic expression for the 1-cyclohexyl piperidinium bicarbonate (CHP-H₂CO₃) decomposition reaction

$$CHPH^{+}(aq) + HCO_{3}^{-}(aq) \rightleftharpoons CHP(org) + CO_{2}(g) + H_{2}O$$

$$\tag{6}$$

was determined from this degasser experimental data. The rate of CHP-H₂CO₃ decomposition was determined to follow a first order rate law of the form:

$$rate = k_{eff} \left[CHP - H_2CO_3 \right] \tag{7}$$

The kinetic factor k_{eff} is of the form:

$$k_{eff} = ke^{-\left(\frac{E}{RT}\right)} \tag{8}$$

with the values of the experimentally determined parameters as follows:

$$k = 1.05 \times 10^8$$

 $E = 64.8 \text{ kJ/mol}$

The ideal CSTR design equation can then be used to estimate the outlet concentration from each stage of the degasser:

$$V = \frac{v_0 C_{A0} - v C_A}{-r_A} \tag{9}$$

where V is the reactor volume, v is the volumetric flow rate, C_A is the concentration of component A (moles/volume), v is the rate of formation of component A per unit volume, and subscript v indicates the initial value of the referenced parameter.

The process cost estimates in the current analysis are based on a degasser configuration that includes three stages with a cumulative residence time of 1 hour. A degasser operating temperature of 80°C was selected. The mechanical separator flow rate is specified as 10% of the degasser internal circulation flow rate.

Mechanical Separator (Decanter)

The decanter operating requirements include the continuous, single-pass gravity separation of the organic and aqueous phases. The design specification for the aqueous phase bulk outlet composition is a CHP-H₂CO₃ concentration less than 1.5 wt%. The selected configuration for the decanter is a vertical vessel with multiple liquid inlet and outlet ports (Figure 3). The exit ports are located near the top and bottom of the decanter to remove the bulk organic and aqueous fluid phases. The inlet port is positioned at a height between that of the two exit ports.

The primary design parameter is the cross sectional area of the vessel, which determines the bulk fluid velocity of the continuous phase. Plug flow (velocity is independent of radial position) is assumed when evaluating the continuous phase velocity. The decanter vessel is sized on the basis that the continuous (aqueous) phase velocity must be less than the settling velocity of the droplets in the dispersed (organic) phase (Sinnott and Towler 2009). The velocity of the continuous phase is calculated using the area of the interface:

$$u_c = \frac{L_c}{A_i} < u_d \tag{10}$$

where u_d is the settling velocity of the dispersed phase droplets, u_c is the velocity of the continuous phase, L_c is the continuous phase volumetric flow rate, and A_i is the interface area (Sinnott and Towler 2009). Stokes' law is used to determine the settling velocity of the dispersed phase droplets:

$$u_d = \frac{d_d^2 g(\rho_d - \rho_c)}{18\mu_c} \tag{11}$$

where d_d is the droplet diameter, ρ_c is the density of the continuous phase, ρ_d is the density of the dispersed phase, μ_c is the viscosity of the continuous phase, and g is the gravitational acceleration constant (Sinnott and Towler 2009).

Gas Contactor

The gas contactor operational requirements include the continuous production of ~ 50 wt% CHP-H₂CO₃ solution. The gas contactor feed streams include organic, aqueous, and vapor phase bulk compositions, so the apparatus must provide mixing sufficient to thoroughly contact the various fluid phases in order for the 1-cyclohexyl piperdinium bicarbonate formation reaction to proceed.

The gas contactor configuration includes a gas diffusion membrane unit with gas and liquid phases fed to the respective sides of the membrane. CO_2 flows into the gas side of the membrane unit, where it passes through the semi-permeable membrane before diffusing into the CHP (organic) and H_2O (aqueous) mixture on the liquid side of the membrane. The membrane provides a well-defined mass transfer area to enhance the rate of diffusion of the vapor phase reactants into the liquid phase reactants. Use of a membrane also provides excellent ability to independently control the vapor and liquid phase flow rates without the slugging or flooding that can occur at extreme L/G ratios associated with conventional columns.

Relevant gas contactor design parameters include the mass transfer area, number of stages, and residence time (volume) of the equipment. The selection of these design parameters is based on the chemical reaction kinetics and mass transfer coefficients at the selected operating conditions.

A kinetic expression for the cyclohexyl piperidinium bicarbonate formation reaction

$$CHP(org) + CO_{2}(g) + H_{2}O \rightleftharpoons CHPH^{+}(aq) + HCO_{3}^{-}(aq)$$

$$(12)$$

was determined from gas contactor experimental data presented in Figure 5. The rate of CHP-H₂CO₃ formation was determined to follow a second order rate law of the form:

$$rate = k_{eff} \lceil CO_2 \rceil \lceil CHP \rceil \tag{13}$$

where $[CO_2]$ is the mass fraction basis concentration of CO_2 dissolved in the aqueous solution as determined from Henry's law correlations. The kinetic factor k_{eff} is of the form:

$$k_{eff} = k \left(\frac{T}{T_0}\right)^n e^{-\left(\frac{E}{R}\right)\left[\frac{1}{T} - \frac{1}{T_0}\right]}$$
(14)

with the values of the experimentally determined parameters as follows:

$$k = 0.255$$

 $n = 1$
 $E = 50 \text{ kJ/mol}$
 $T_0 = 283 \text{ K}$

In the current study the gas contactor sizing was based on the experimentally determined reaction kinetic expression with a residence time of 54 minutes. It was assumed that the mass transfer rates in the scaled-up system will match

or exceed those observed experimentally. A gas contactor operating temperature of 28°C with gas and liquid feed stream pressures of 20 and 40 psig, respectively, was selected as the design basis for the economic analysis.

Low Pressure Nanofiltration / Reverse Osmosis

The low pressure polishing filtration process operations are required to provide >98% rejection from a 1-4 wt%

CHP-H₂CO₃ solution at <20 bar of hydraulic driving force. The filtration modules must be constructed of materials that are compatible with the CHP and CHP-H₂CO₃ present in the coarse water product stream exiting the decanter. Relevant design parameters include the recovery, membrane area, filtration module flow path/configuration/ stages, and operating conditions (especially feed and permeate pressures). The selection of these design parameters is based on the membrane permeance and rejection, which are functions of feed stream composition.

The membrane permeance is the flux per unit of applied trans-membrane pressure, while the recovery and

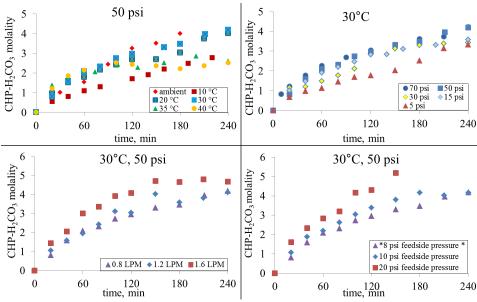
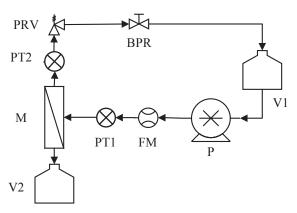


Figure 5. Experimental gas contacting results for various feed and liquid size temperatures and pressures.

rejection are defined by the following equations:

$$Recovery(\%) = \left(\frac{F_p}{F_f}\right) \times 100 \tag{15}$$

$$Rejection(\%) = \left(\frac{C_f - C_p}{C_f}\right) \times 100 \tag{16}$$



BPR Back pressure regulator P Pump

PT2 Pressure transducer 2

FM Flow meter PRV Pressure relief valve V1 Feed vessel M Membrane

PT1 Pressure transducer1

V2 Permeate vessel

Figure 6. Schematic of coupon-testing experimental apparatus.

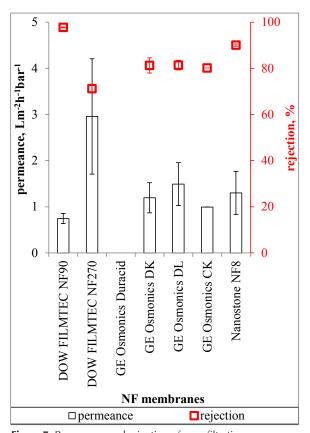


Figure 7. Permeance and rejection of nanofiltration coupons tested using 2 wt% CHP- H_2CO_3 feed stream.

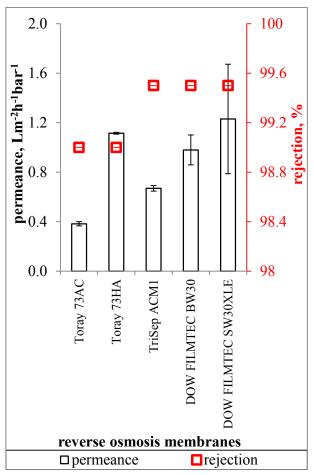


Figure 8. Permeance and rejection of reverse osmosis coupons tested using 1 wt% CHP-H₂CO₃ feed stream.

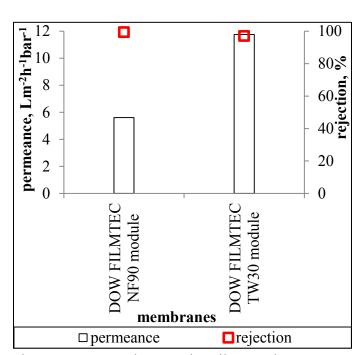


Figure 10. Permeance and rejection of nanofiltration and reverse osmosis modules tested using 1.5 wt% CHP- $\rm H_2CO_3$ feed stream.

where F is flow rate, C is the concentration, and subscripts f and p designate the feed and product streams, respectively (Singh 2015). Recovery is influenced by operating pressure and membrane area.

Coupon testing of various nanofiltration and reverse osmosis membranes was performed to determine the permeability and rejection of each membrane to CHP-H₂CO₃ feed streams. A schematic of the testing apparatus is depicted in Figure 6 and the test results are summarized in Figure 7 and Figure 8. The DOW Filmtec NF90 nanofiltration membrane and the DOW Filmtec TW30 reverse osmosis membrane achieved the greatest rejection of CHP-H₂CO₃ solution.

The proposed SPS FO polishing filtration operations will include a two-stage configuration with DOW Filmtec NF90 and DOW Filmtec TW30 membranes operated in series. A single pump will be used to pressurize the nanofiltration unit feed stream, with the nanofiltration permeate stream pressure maintained at a level sufficient to provide hydraulic driving force for the reverse osmosis unit. This configuration is depicted in Figure 9. A CHP-H₂CO₃ rejection of 99.98% from a 1.5 wt% feed solution has been experimentally achieved from this configuration, resulting in single-digit ppm level product stream concentrations. Experimentally observed permeance and rejection of the nanofiltration and reverse osmosis units at the design feed stream concentration of 1.5 wt% CHP-H₂CO₃ are presented in Figure 10. Table 1 summarizes the design operating parameters for the NF and RO units operating in series.

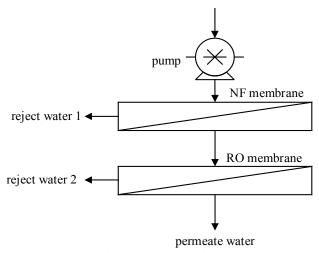


Figure 9. Schematic of proposed polishing filtration operations.

Table 1. Summary of polishing nanofiltration and reverse osmosis membrane performance with CHP-H₂CO₃ feed stream.

	NF: DOW Filmtec NF90	RO: DOW Filmtec TW30
Rejection (%)	99	98
Recovery (%)	90	95
Permeance (L m ⁻² hr ⁻¹ bar ⁻¹)	5.5	12
ΔP (bar)	10	1.7

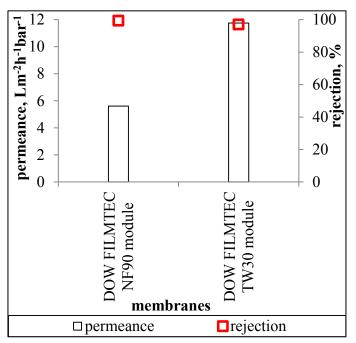


Figure 11. Permeance and rejection of DOW Filmtec NF90 membrane as function of feed stream CHP-H₂CO₃ concentration.

Table 2. Estimated equipment costs for 20 m³/hr SPS FO process.

component	sizing parameter	value	equip- ment cost	total installed cost	source
feed stream cooler	heat transfer area	65 m^2	\$22,700	\$105,600	a
feed stream pump	flow rate	23 m³/hr	\$900	\$2,100	b
FO Unit (3 stages)	membrane area	4,700 m ²	\$117,600	\$270,400	С
degasser (3 stages)					
preheater	heat transfer area	318 m^2	\$52,900	\$182,100	a
vessel	volume	31 m^3	\$101,700	\$402,700	a
heat exchanger	heat transfer area	10 m^2	\$10,200	\$70,500	a
spray nozzles	flow rate	467 m ³ /hr	\$21,400	\$49,200	b
circ pump	flow rate	467 m ³ /hr	\$39,200	\$90,300	b
decanter (3 stages)					
vessel	volume	9.0 m ³	\$39,300	\$90,400	b
circ pump	flow rate	47 m³/hr	\$5,400	\$12,500	b
gas contactor					
membrane	membrane area	1,206 m ²	\$24,100	\$55,500	С
pump	flow rate	4.8 m ³ /hr	\$900	\$2100	b
heat exchanger	heat transfer area	33 m^2	\$18,300	\$87,300	a
NF polishing filter	membrane area	383 m ²	\$7,700	\$17,600	С
RO polishing filter	membrane area	833 m ²	\$16,700	\$38,300	С
pumps					
SPS circulation	flow rate	24 m³/hr	\$900	\$2,100	b
NF/RO feed	flow rate	23 m³/hr	\$8,300	\$40,500	a
HTF pump	flow rate	50 m ³ /hr	\$1,800	\$4,200	b
gas compressor	flow rate	900 m ³ /hr	\$193,300	\$263,700	a
compr exh cooler	heat transfer area	23 m ²	\$15,900	\$84,600	a

Sources:

- (a) Aspen Process Economic Analyzer
- (b) vendor pricing listed or quoted as of June 2016
- (c) assumed membrane cost of \$20/m² for gas diffusion, NF, and low-pressure RO membranes (Pabby, Rizvi, and Sastre 2015); 5 year cost target of \$25/m² for Porifera FO membranes (Desormeaux 2015).

Lab testing has demonstrated the permeance and rejection performance of the Filmtec NF90 membrane as a function of feed stream concentration, with the results summarized in Figure 11 indicating that reasonable performance is maintained at conditions that deviate considerably from design. Additionally, this testing demonstrated the materials compatibility of this membrane at feed stream concentrations of up to 11 wt% CHP-H₂CO₃.

Economic Analysis

Results from the system testing and analysis described in the previous section were used to size and cost the individual SPS FO process components. These equipment costs were then used as the basis to estimate the overall project costs and treatment cost per unit volume of desalinated produced water. This analysis uses a 20 m³/hr (3,000 bbl/day) throughput rate as the basis for the SPS FO process costs. The feed stream was specified as a 0.5 mol/kg NaCl solution (28,400 ppm TDS) with 87.5% recovery of the feed water. The desalinated product water is evaluated as a water treatment cost rather than a profit source, such that taxes and depreciation are not applicable

in the economic evaluation.

This economic evaluation is a revision of an initial analysis performed in 2015 (Wendt, Orme, et al. 2015). The current analysis includes use of a second-generation draw solution (1-cyclohexyl piperidine) instead of the first-generation draw solvent (N,N-dimethyl cyclohexyl amine) evaluated in the previous analysis. The current analysis is therefore based on data that either differs from, or was unavailable in the initial economic analysis. This data includes CHP physical property data and reaction kinetics, and the equipment configurations in the current evaluation are therefore significantly more detailed than in the initial evaluation. Additionally, experimental data regarding the polishing filtration steps was not available for the initial economic evaluation; the cost and performance of the polishing filtration steps is an additional CAPEX line item in this evaluation.

While the current design and cost estimates are based on component performance that has been validated in the laboratory, it is anticipated that an industrial scale process would utilize process equipment with improved and/or optimized operational performance, which would ultimately result in improved process economics relative to those presented in this analysis. This analysis is therefore considered a preliminary design and cost estimate, with further improvements in performance and cost expected to result from additional process optimization efforts.

Total Fixed Capital Costs

Total fixed capital costs include direct capital costs and indirect capital costs. Direct capital costs include inside battery limits (ISBL) and outside battery limits (OSBL) cost contributions. ISBL costs include equipment and associated

components that act upon the primary feed stream of the process, while OSBL costs include utilities, common facilities, and other equipment not included in the ISBL definition and may include systems that support several process units. The ISBL capital costs include the equipment costs for the major process components, which are summarized in Table 2.

For process components in Table 2 where the equipment costs were obtained from vendor pricing/quotes or assumed costs, an installation factor of 2.3 was used to estimate the total installed cost. This factor was obtained by summing the installation factors for the installation categories identified in Table 3. The installation factors are

Value used in cur-Value suggested by

Table 3. Factors for estimation of fluid-based process fixed capital costs.

Category	rent study (modular process assumed)	Sinnott and Towler (2009)	
Equipment erection	0.1	0.3	
Piping	0.5	0.8	
Instrumentation and control	0.3	0.3	
Electrical	0.2	0.2	
Civil	0.1	0.3	
Structures and buildings	0.1	0.2	
Lagging and paint	0.0	0.1	
Installation Factor	2.3	3.2	

lower than those recommended for a fluid-based chemical process by Sinnott and Towler (2009) due to the relatively small scale process considered and the assumption that the process will be installed as a modular unit, which will result in decreased installation costs. The installation factors suggested by Sinnott and Towler for a fluid-based chemical process are included in Table 3 for reference.

The OSBL costs are calculated as a percentage of the ISBL costs. Sinnott and Towler (2009) recommend the OSBL costs be estimated as 30% of the ISBL costs. However, many of the OSBL items identified by Sinnott and Towler are either accounted for as ISBL costs, or are expected to be available to the SPS FO process installation due to the installation of the process at an oil & gas production site. Therefore, the OSBL costs for the current analysis are evaluated as 20% of the ISBL capital costs. Table 4 provides a listing of the OSBL costs that are intended to be included in the 20% estimate in the current analysis, as well as a summary of the OSBL costs that are not required or should already be in place for the produced water treatment application.

Indirect capital costs include design & engineering and contingency costs. It is assumed that a standard design for the SPS FO process for oil & gas produced water treatment will be developed for deployment at multiple sites. The use of a standard, or module-based, design will reduce the design & engineering costs for installation number N (with $N\gg 1$) in such a deployment scenario. It is likely that the majority of engineering costs may be associated with feed water pretreatment, which will be an applicationspecific cost depending on the feed water composition and existing oil & gas production site infrastructure. Design & engineering costs in the current analysis are estimated as 10% of ISBL +

Table 4. OSBL costs included and excluded from economic evaluation. Adapted from Sinnott and Towler

(2009).		
Item	Description	Notes
OSBL capital cost	ts required for SPS FO process installation	
Water	water demineralization, waste water treat- ment, site drainage and sewers	
Piping	pipe bridges, feed and product pipelines	
Transport	tanker farms, loading facilities	
Analytical	laboratories, analytical equipment, offices, central control room	
Utility: Cooling	cooling towers, circulation pumps, cooling water mains, cooling water treatment	
OSBL capital cost	ts NOT required for SPS FO process installation	
Utility: Electric	electric main substations, transformers, switchgear, power lines, etc.	assumption of use of existing infrastructure at production site and purchase of electrical power
Utility: Power	power generation plants, turbine engines, standby generators	assumption of use of existing infrastruc- ture at production site and purchase of electrical power
Utility: Steam	boilers, steam mains, condensate lines, BFW treatment plant, supply pumps	thermal energy to be provided by feed stream
Utility: Air	air separation plants	N/A
Maintenance	workshops and maintenance facilities	existing production site infrastructure
Emergency Services	emergency services, fire-fighting equipment, fire hydrants, medical facilities, etc.	existing production site infrastructure
Security	site security, fencing, gatehouses, landscaping	existing production site infrastructure

OSBL costs, which is on the lower end of the range recommended by Sinnott and Towler (2009) for the reasons listed above. Contingency costs to cover changes in commodity pricing, currency fluctuations, and problems/ issues associated with the overall project schedule are estimated as 10% of the ISBL + OSBL costs.

Table 5. Estimated fixed capital investment for 20 m³/hr SPS FO process.

Cost Item	Value (\$K)	Basis
ISBL Plant Cost	\$1,871	Sum of total installed equipment costs
OSBL Plant Cost	\$374	20% of ISBL cost
Engineering	\$225	10% of ISBL + OSBL cost
Contingency	\$225	10% of ISBL + OSBL cost
Fixed Capital Investment	\$2,695	Total of above

Working Capital

The SPS FO process does not require inventory of raw materials, products or by-products; working capital costs will therefore only include SPS, CO₂, and spare parts inventory requirements. In the current analysis, working capital costs are estimated as 5% of the ISBL + OSBL costs.

Operating Costs

Fixed and variable operating costs are included in the estimation of the water treatment cost. It was assumed that the process would operate with an availability factor of 95%. A breakdown of the included and excluded operating costs, as well as a description of the calculation basis for each cost item, is included in Table 6.

Table 6. Operating costs for oil & gas produced water treatment using SPS FO process.

Cost Item	Annual Cost	Notes
Fixed Operating Costs		
Operating labor	\$57,600	estimated as 20% of one shift position at \$60K/yr per operator (4.8 operators/shift position)
Supervision	\$14,400	25% of operating labor
Direct salary overhead	\$28,800	40% of operating labor + supervision
Maintenance	\$56,100	3% of ISBL investment
Property taxes & insurance	\$18,700	1% of ISBL fixed capital
Excluded items	N/A	rent, general plant overhead, allocated environmental charges, license fees and royalty payments
Variable Operating Costs		
Utilities	\$104,000	electricity at \$0.08/kWh
Membrane Replacement	\$28,300	assumed 5 year membrane life
Waste Disposal	N/A	Process-related waste disposal costs not applicable in industrial process where no activated carbon disposal (from polishing purification operations) is required. Concentrated feed water disposal cost discussed separately in text.
Shipping	N/A	feed and product water stream transport (site and application specific)
Excluded items	N/A	raw materials (no raw materials consumed by SPS FO process)

Project Financing

The SPS FO process water treatment costs were estimated using the annualized capital charge method described by Sinnott and Towler (2009). The annual capital charge ratio (ACCR) for this estimate was specified as 0.094 based on the following assumed values:

interest rate on debt: 7%project debt fraction: 100%

project life: 20 years

The specified ACCR value was then used to estimate the annual capital charge (ACC) as the product of total capital costs (fixed capital investment + working capital) and ACCR. The total annualized cost (TAC) was then computed as the sum of the total operating costs and the ACC. The

Table 7. Estimated total annualized costs for 20 m³/hr SPS FO process.

Cost Item	Annual Cost (\$K)	Notes
Annual Capital Charge	\$265	Total capital costs include fixed capital investment and working capital
Fixed Operating Costs	\$176	Additional detail provided in Table 6
Variable Operating Costs	\$132	Additional detail provided in Table 6
Total Annualized Costs	\$573	Total of above

estimated total annualized cost for a 20 m³/hr (3,000 bbl/day) SPS FO water desalination process are presented in Table 7. The total annualized cost divided by the annual water product volume yields an estimated oil & gas produced water treatment cost of 0.55 USD/bbl (3.44 USD/m³). Puder and Veil (2006) indicate that disposal costs for produced waters can vary from 0.30 to 105 USD/bbl (1.88 to 660 USD/m³) depending on disposal method, which may include injection, evaporation, and burial. Injection is the most common means of disposal, with costs ranging from 0.30 USD/bbl (1.88 USD/m³) to as high as 10.00 USD/bbl (62.90 USD/m³); generally the injection costs are under 1.00 USD/bbl (6.29 USD/m³).

If injection disposal of the produced water feed stream concentrate exiting the SPS FO process is added to the water treatment cost, the net produced water processing cost for each unit volume of produced water from an oil & gas production site would be 0.60 USD/bbl (3.80 USD/m3), which is considerably less than the typical reported cost of 1.00 USD/bbl (6.29 USD/m3) for injection disposal of the full produced water volume. Site specific additional cost items such as pretreatment, etc. would require this estimate to be revised accordingly. As previously noted, the SPS FO process costs in the current analysis are based on observed experimental system component performance. A full-scale, optimized system utilizing industrial process equipment is expected to operate with enhanced performance that would result in further reductions in the estimated cost per unit of treated water.

Conclusion

This paper summarizes experimental testing and process cost estimation activities that have been completed in support of SPS FO process scale up for oil & gas produced water treatment. The preliminary design is based on a product water throughput rate of 20 m³/hr (3,000 bbl/day).

- The FO unit will include three stages each having different feed and draw stream concentrations. This analysis is based on a produced water feed stream having an osmotic pressure of 26 bar, which is equivalent to that of a 0.5 mol/kg or 28,400 ppm NaCl solution, and a concentrated draw solution with a concentration of 5.5 mol/kg or ~55 wt% CHP-H₂CO₃.
- The degasser utilizes heat from the produced water to drive the bicarbonate decomposition reaction. Mass transfer
 enhancement in the degasser occurs via the use of spray nozzles, but alternative means of mass transfer enhancement are currently being investigated.
- The mechanical separator utilizes a vertical vessel for separation of the continuous aqueous phase and the dispersed organic phase. Only a fraction of the fluid flow rate recirculating within the degasser must be processed to achieve continuous liquid-liquid separation within the mechanical separator.
- The gas contactor utilizes a gas diffusion membrane to introduce carbon dioxide into the liquid reactant stream. A continuous, non-recirculating membrane unit configuration is considered in the economic analysis.
- The polishing filtration operations include a nanofiltration and low-pressure reverse osmosis unit operated in series with a single pump providing the required hydraulic pressure. A CHP-H₂CO₃ rejection of 99.98% from a 1.5 wt% feed solution has been experimentally observed for this configuration, resulting in single-digit ppm level product stream concentrations.

An economic analysis of the process estimates that the produced water treatment cost associated with the SPS FO process will be 0.55 USD/bbl (3.44 USD/m³) for the current, non-optimized system. The net produced water processing cost for each unit volume of produced water from an oil & gas production site (including injection disposal of the concentrated feed water) is estimated as 0.60 USD/bbl (3.80 USD/m³). This value is considerably less than 1.00 USD/bbl (6.29 USD/m³), which previous studies have suggested is a typical cost for injection disposal of the full produced water volume. Process equipment selection and sizing in this study were based on lab-scale testing. Optimization of the equipment selection and process design is expected to further improve performance and decreased cost for larger scale operations.

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