Produced Water Treatment Using Switchable Polarity Solvent Forward Osmosis (SPS FO) Technology

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Keywords

Produced water, co-produced water, switchable polarity solvent, forward osmosis, water treatment

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 [1]. 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 [2].

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 [1].

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.

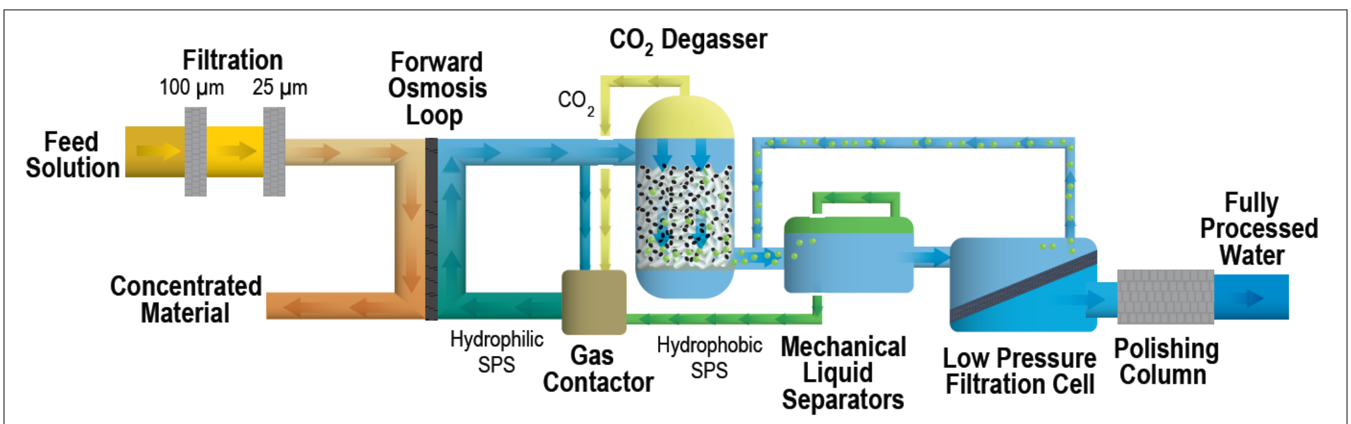

Figure 1. SPS FO process schematic.

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).

$$NR_{3(org)} + CO_{2(g)} + H_2O \rightleftharpoons HNR_3{}^{+}{}_{(aq)} + HCO_3{}^{-}{}_{(aq)} \quad (1)$$

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 [3-11].

SPS FO Water Treatment Process Description

The SPS FO water purification process has four primary process components: An FO membrane unit; a CO_2 degasser; a mechanical liquid separator (gravity separation 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 semi-permeable 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 CO_2 and the changing of the SPS polarity from hydrophilic to hydrophobic.

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 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.

SPS FO Process Advantages

Forward osmosis differs from reverse osmosis technology in that instead of a hydraulic pressure differential, an osmotic pressure differential is used to initiate the flux of water across the membrane surface. Forward osmosis has advantages in being able to treat feed water streams with higher concentrations of impurities while simultaneously extracting a greater fraction of the water from the feed stream. As a result of the water flux being driven by concentration differences rather than hydraulic pressure differences, forward osmosis is also characterized by reduced membrane fouling relative to reverse osmosis.

SPS FO is also an energy efficient water treatment technology. The CO_2 degasser is the only SPS FO process operation that requires thermal energy input. The chemical reaction by which CO_2 is removed from the SPS draw solution occurs in the range of 60-80°C. The heat input required to drive this reaction represents the single largest process energy demand. A produced water feed stream with a temperature at or above the specified temperature range could therefore potentially be used to provide the heat input required to meet the process thermal energy demands. Other SPS FO process energy demands include electrical power for fluid pumping as well as for operating air-cooler fans used to provide process cooling. In the event the produced water feed stream is supplied at a temperature of ~120°C or greater, a configuration in which an Organic Rankine Cycle (ORC) for electrical power generation and the SPS FO process were installed in series could be utilized such that all SPS FO process energy demands could be met without use of external energy sources. A complete analysis of the SPS FO process energy requirements and estimate of anticipated treatment costs is included in [12].

Use of SPS FO Technology for Reducing Produced Water Disposal Costs

Previous analysis estimated SPS FO treated water product costs to be in the range of \$1.65/m^3 to \$2.59/m^3 depending on feed water supply temperature and degasser operating temperature [12].

Throughout the U.S., there is considerable variability in the cost to dispose of produced waters. In a 2006 Argonne National Laboratory report, Puder and Veil report that disposal costs for produced waters can vary from \$0.30/bbl to \$105/

bbl (\$1.88/m^3 to \$660/m^3) depending on disposal method, which may include injection, evaporation, and other methods. Injection is the most common means of disposal, with costs ranging from \$0.30/bbl (\$1.88/m^3) to as high as \$10.00/bbl (\$62.90 /m^3); generally the injection costs are under \$1.00/bbl (\$6.29/m^3) [13].

Costs for medium scale seawater reverse osmosis (SWRO) desalination plants are reported to be approximately \$1/m^3 of product water, depending primarily on electricity price [14]. However, RO is limited to treating ~50% of a feed water stream with salinity similar to that of seawater (~35,000 ppm). At feed water stream concentrations greater than 35,000 ppm, the RO recovery factor decreases to levels below 50%. Consequently, the volume of concentrated brine discharge from RO water treatment processes is relatively large.

An analysis of total costs for the treatment and disposal of produced water from oil and gas operations with various processing schemes was performed. The produced water is assumed to have a TDS concentration similar to that of seawater (~35,000 ppm). If no treatment of the produced water from oil and gas operations was performed and the entire volume of produced water was injected back into a subsurface formation, the total disposal costs are assumed to be \$6/m^3, which is consistent with values reported in the open literature [13]. If RO were employed to treat 50% of the produced water volume at a cost of \$1/m^3 (parameters that are representative of typical SWRO cost and performance) and the concentrated discharge from the RO process was disposed of via injection, the total produced water treatment and disposal costs would be approximately \$3.50/m^3. Finally, if SPS FO were utilized to treat 90% of the produced water volume at a cost of \$1.65/m^3 to \$2.59/m^3 and the concentrated discharge from the SPS FO process was disposed of via injection, total produced water treatment and disposal costs could be further decreased to approximately \$2/m^3 to \$3/m^3. Therefore, use of SPS FO technology for produced water treatment could result in lower total disposal costs than scenarios that involve either complete injection or RO treatment with concentrated brine injection. When combined with the potential revenues from the sale of the product water, it is possible that the economic feasibility associated with use of SPS FO technology could be further enhanced. A graphical illustration of the impact of water treatment fraction on total produced water disposal cost is provided in Figure 2.

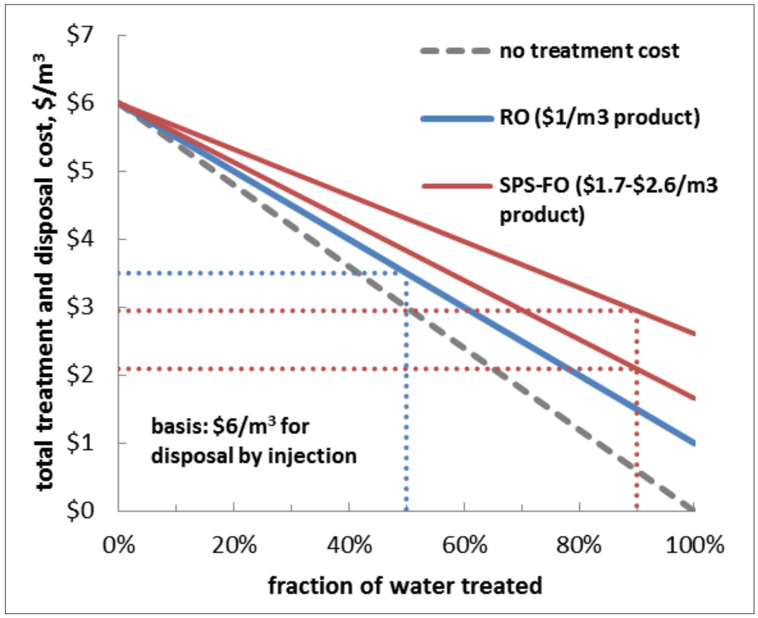

Figure 2. Impact of water treatment on disposal cost (feed water salinity similar to seawater).

Status of SPS FO Process Development

Bench scale testing of the SPS FO process equipment is currently being performed at the Idaho National Laboratory. A non-chemically aggressive SPS solvent (1cyclohexylpiperidine) has been identified, and FO membrane testing demonstrating consistent flux over various feed and draw stream concentrations has been completed as illustrated in Figure 3. Additionally, the degassing performance of 1cyclohexylpiperidine has been tested with significant rate improvements demonstrated relative to initial proof-of-concept testing (performed using N,Ndimethylcyclohexylamine first generation SPS solvent) as illustrated in Figure 4. Further, gas contactor equipment with flexible and robust operating characteristics, including the ability to operate with continuous vapor and liquid feed stream flows, has been tested. As a result of the mass transfer performance observed during gas contactor testing, degasser testing using a related

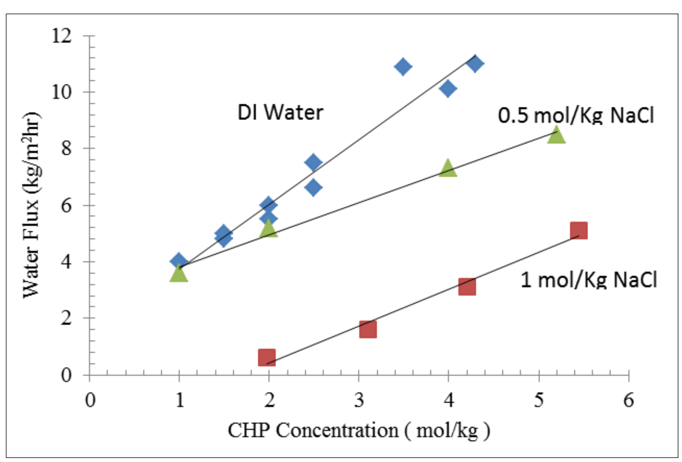

Figure 3. FO membrane water flux as function of CHP draw solution concentration.

technology is scheduled. Results from the bench scale testing will be used to refine existing SPS FO process and economic models and provide information needed to design and fabricate a prototype unit, with the goal of deploying and field testing that unit in 2017.

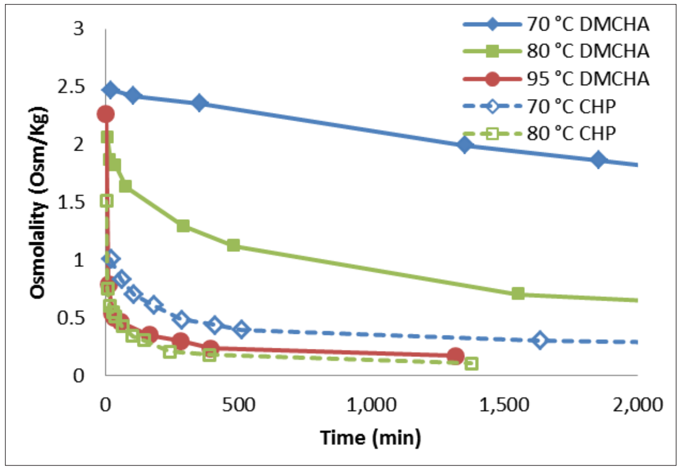

Figure 4. Comparison of 1st generation (DMCHA) and 2nd generation (CHP) SPS degassing performance at various temperatures.

Conclusion

Process and economic modeling suggest that the SPS FO water treatment process can economically treat approximately 90% of a produced water feed stream with salinity similar to that of seawater. If the produced water feed stream is supplied at a temperature of ~100°C, SPS FO process thermal energy requirements could be met entirely through use of heat provided by the feed stream. If the produced water feed stream is supplied at a temperature in excess of ~120°C, SPS FO process electrical and thermal energy requirements could potentially be met using energy in the feed stream.

Though the SPS FO process is likely to have higher costs per unit of product water than RO, it has an advantage in that it can recover a larger fraction of the feed stream over a wider range of salinity. The corresponding reductions in total disposal costs could make SPS FO technology appealing for treatment of produced water from oil and gas operations. Bench scale testing currently being performed at the Idaho National Laboratory is advancing SPS FO technology with the goal of field testing a prototype system in coming years.

Acknowledgement

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