

SPE 115952

Is Reverse Osmosis Effective for Produced Water Purification? Viability and Economic Analysis

Shanker Muraleedaaran, SPE, Xinhua Li, SPE, Liangxiong Li, SPE, and Robert Lee, SPE, Petroleum Recovery Research Center, New Mexico Institute of Mining and Technology

Copyright 2009, Society of Petroleum Engineers

This paper was prepared for presentation at the 2009 SPE Western Regional Meeting held in San Jose, California, USA, 24-26 March 2009.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

Abstract

The ultimate goal of produced water management is to remove dissolved components and use the desalinated water for beneficial uses that can effectively alleviate environmental impact and water shortage. Presently, many of the efforts have been focused on membrane technologies including reverse osmosis and electrodialysis. Unfortunately, no large scale implication of produced water desalination by membranes has been reported. The main obstacle against the deployment of desalination technologies for produced water purification has always been the complicated chemical composition and associated high operating cost. Membrane technologies are generally believed to be energy efficient due to single-phase operation comparing to thermal-based desalinations. However, the presence of dissolved organics and scale deposition on membrane surfaces require sophisticated pretreatment and frequent membrane replacement, adding to the water treatment costs.

Reverse osmosis membranes including polymeric membranes and molecular sieve zeolite membranes were investigated for ion removal from produced water by a cross-flow RO process. Considerable flux decline with elapsed operation time was observed from 11.5 to 6.8 L/m².h at a transmembrane pressure of 3.5 Mpa. Pretreatments including nanofiltration and adsorption by active carbon were studied for their influence on the RO performance and impact on the overall desalination cost. Both polymeric membranes and molecular sieve zeolite membranes have been tested for actual produced water from oilfield and coalbed methane site. The study has revealed that (1) most of permeation tests lasted less than 3 months due to serious fouling and drastic flux decline (>30%), (2) scale precipitation and organic sorption are the major fouling mechanisms of membranes, (2) multistage pretreatment is crucial to extend membrane lifetime, and (3) nanofiltration is the only effective process tested that can extend the life of a RO membrane to over 6 months. But periodic chemical cleaning, typically twice a week, is necessary to maintain the desired water flux. The economical efficiency of these processes was discussed from the aspects of produced water chemistry, energy consumption, and water treatment capacity. Considering small to mid-sized water treatment capacity (50 m³/day), the cost of produced water desalination by RO membranes is around \$3.7/m³ including nanofiltration pretreatment. Pretreatment and membrane replacement are the major factors that increases the operation cost and limits the economic efficiency of membrane technology for produced water desalination.

INTRODUCTION

Produced water is the formation water produced along with hydrocarbons during oil and gas production: emboding the primary waste stream of oil, natural gas and coalbed methane production. It is very saline, sometimes nearly six times as salty as seawater, and contains dissolved hydrocarbons and organic matter as well. For the purpose of disposal or beneficial reuse, separation technologies need to be deployed for treating the produced water to an appropriate quality for meeting the purposes of disposal and industry uses. Produced water is conventionally treated by removing the suspensions and floating oil. More than 90% of this purified produced water is then injected into oil zones for enhanced oil recovery/enhanced coalbed methane (EOR/ECBM) or into specially designated reinjection horizons for disposal, which are deemed to be geologically isolated for protection of ground water system^[1,2]. Methods for removing suspended solid and oils include gravity separation, hydrocycloning,

centrifuging, gas floatation, and filtration^[3]. Suspended particles with particle size of 5.0 μ m or above can be removed with these conventional processes^[4]. As petroleum companies and regulatory agencies initiate more stringent regulations for water disposal and reinjection, removal of suspensions with large particles will be not sufficient for meeting the requirements. Advanced technologies must be developed to remove both fine particles and dissolved components, particularly dissolved salt and hydrocarbons. For example, the European Standard for effluents from onshore petroleum activities requires that the total hydrocarbons in effluent is less than 5 mg/l and suspended solids is less than 10 mg/l^[5]. More stringent water quality is also regulated by petroleum companies for produced water reinjection into low-permeability formations for enhanced oil recovery (EOR) by water flooding. To avoid or minimize damages to the injectivity, the Daging oilfield has established water guality criteria for EOR: less than 5.0 mg/l total hydrocarbons, less than 1.0 mg/l suspended solids, and less than 1.0 μm medium particle size distribution for suspensions^[6]. Apparently, the conventional purification processes (i.e., sedimentation and floatation) cannot attain such high standards of water quality. In addition, surface disposal and beneficial uses such as irrigation and tower cooling require removal of dissolved components, which has a major impact on the receiving environment, due to toxicity and corrosion problems^[7]. Membrane filtration processes, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, have the potential to generate high quality water by removing suspensions and dissolved components. Zaidi^[8] reviewed micro/ultrafiltration membranes for removal of oil and suspended solids to obtain sufficiently high quality of water for reinjection or surface disposal. He suggested that membrane technology is the best available technology for treating oilfield brine. He also pointed out that no single technology can purify produced water to desirable quality and integrated process is very necessary. A few field tests have indicated that polymeric membranes are problematic for application in produced water purification, due to fouling and membrane degradation^[9].Thus, multistage pretreatment of water and periodic chemical cleaning of the membranes are recommended^[10]. More recently, produced water desalination with inorganic membranes, i.e., ceramic microfiltration membranes and zeolite membranes have been reported and laboratory testing of these membranes have shown promising results in cleaning produced water^[11, 12].

Even with the rapid advancement in desalination technologies, large application of produced water desalination has not been reported due to complexity of produced water chemistry and economic inefficiency. Firstly, the amount of water at each particular site is limited; by well production and by available storage capacity and distribution pipelines at the site. The desalination technology used must be efficient for application in small or medium-scale water treatment scenarios. Secondly, formation and production history will have a dramatic influence on produced water quality and how the purification technology can be deployed. Technologies for produced water purification must be insensitive to the variability in water chemistry. Finally, any sophisticated pretreatments should be minimized because they are generally energy-intensive.

This article studied the characteristic of produced water from different formations and dicussed subsequent impact of such quality variation on selection of treatment technology and desalination performance. Reverse osmosis membranes including polymeric and ceramic membranes have been tested for produced water desalination. Specifically, membrane materials, pretreatment deployment, membrane fouling and regeneration have been studied for their influence on the efficacy of produced water purification as well as economic efficiency.

CHARACTERISTICS OF PRODUCED WATER

A unique characteristic of produced water comparing to other wastewater resources is the large variation in water chemistry. Produced water chemistry varies considerably from the type of formation (i.e., oilfield, coalbed methane), depth, and production history. Even in case of produced water from the same formation, a large variation in composition can be seen as shown in Figure 1. These water samples were obtained from the same formation and closely located sites at the San Juan basin. The chemistry of produced water from Howell D353 was further monitored over time: variations of total dissolved solid (TDS) and trace metal ions are shown in Figure 2. Large variations of both total dissolved solids (TDS) from 2000 to 6500 mg/L and trace metal ion concentration was observed.

WATER QUALITY AND BENEFICIAL USES

It should be noted that produced water from gasfield and CBM operations have relatively lower TDS but higher level of hydrocarbons. Further investigation of gasfield produced water indicated that benzene is the major contributor of the organic load; the remaining organic loads come from polar fatty acid and phenols. In some areas, production chemicals, such as corrosion and scale inhibitors and emulsion breakers, will also affect the organic components in produced water. These factors all play a crucial role in the selection of appropriate technologies for produced water treatment. The produced water treatment technologies targeting removal of different elements is summarized in Figure 3.

Water quality and quantity are the two most important factors that dictate the technologies to be deployed. The end use of the purified produced water also plays important roles on technology deployment and water quality

criteria, as well as acceptable water treatment cost. Generally, the energy consumption and operating costs for treatment are directly related to the ultimate water quality: operation cost will increase with increased requirement of water quality. For example, both onshore and offshore disposals need to meet increasingly stringent standards that are generally regulated by the U.S. Environmental Protection Agency (EPA) under the Clean Water Act (CWA)^[5]. Onshore disposal of produced water will only be allowed for agriculture and wildlife propagation, for which the maximum daily effluent limitation for oil and grease is 35 mg/l and total dissolved solids (TDS) is less than 2000 mg/l^[13, 14]. Deep well injection for disposal or enhanced oil recovery is the most common option for produced water cleaned by current treatment methods. The water must be injected into an isolated formation to avoid potential contamination on groundwater or surface water systems. Industry operators usually have their own standards for suspensions and solid contents in treated produced water, because these can cause formation harm injectivity^[15]. Table 1 summarizes the potential uses of produced water and the water quality requirements for different uses.

PROCESS DESIGN OF PRODUCED WATER DEMINERALIZATION BY REVERSE OSMOSIS MEMBRANES

Produced water desalination by reverse osmosis membrane is the most studied process for volume reduction. In a RO separation process, feed water flows across a membrane surface. Under hydraulic pressure, water molecules permeate through the membrane while particles, dispersed oil, or even ions and organic molecules are rejected by the mechanism of size exclusion or competitive diffusion. The permeate will be collected as purified water for beneficial uses and the small volume of concentrate with high concentration of salt and organics are disposed off by conventional methods such as deep-well injection or evaporation. Figure 4 schematically shows diagram of a typical crossflow RO membrane unit with ultrafiltration pretreatment.

The primary issue for membrane technology of produced water desalination is membrane fouling. As suggested in Table 1, produced water contains both organics (dissolved and suspended) and high concentration of multivalent ion species that adhere to membrane surface and/or pore entrance. As a result, membrane performance can be seriously deteriorated, i.e., reduced water flux and declined rejection efficiency. As a consequence of fouling, increasing transmembrane pressure or periodic chemical cleaning for membrane regeneration is needed to achieve the designed water flux, resulting increase in energy costs and membrane replacement. In addition, experiments have indicated that most of membrane fouling are irriversible and flux loses can not be compensated by increasing operating pressure. Table 2 lists the recent studies of produced water desalination by RO membranes with different pretreatments.

Water flux of both polymeric membranes and inorganic ceramic membranes decline quickly as microfiltration pretreatment by 0.45µm filter is deployed. The stabilized water permeation of RO membranes ranges from 0.30 to 0.51 L/m².h.bar. Strategies to minimize the impact of fouling and to extend the operating lifetime of a membrane system include: (1) deploying appropriate pretreatment to remove fine suspensions (colloid fouling), organics, and multivalent ion species (scalling), and (2) membrane regeneration by mechanical washing or chemical cleaning.

Colloid fouling

Suspensions in produced water contain clay particles, fine coal powder, and oil droplets. A typical coalbed methane (CBM) produced water obtained from Farmington of New Mexico was studied by dynamic light scattering particle analysis (DLS, Microtrac 3000). The water was settled for 24 hours for large particle separation. Figure 5 gives the particle size distribution of fine coal powder and clay in the CBM produced water. Most of the fine coal powder in CBM produced water have a particle size in the range of 1.6–6.5µm, which suggested that gravity sedimentation and filtration (pore size of 5µm) can not remove the colloid effectively from produced water.

Organic fouling

Produced water contains high concentration of dissolved organics and floating oil. A typical produced water has a total organic carbon (TOC) ranging from a few hundred part per million to as high as 4200 mg/L and floating oil of 50–400 mg/L. The organic materials constitute a wide range of compounds including fatty acids (C2-C5), phenols, aromatic hydrocarbons, and aliphatic components^[9]. The presence of organics in produced water is determined by the type of reservoir (oil/gas/CBM) and environmental conditions. Therefore, solubility-sensitive factors, including temperature and pH, all affect the concentration and type of dissolved hydrocarbons^[14]. Usually, CBM produced water contains higher amounts of low molecular weight aromatic hydrocarbons such as BTEX than are found in oilfield produced water^[2], and thus has more impact on receiving environments. Other factors including type of oil, artificial lift technique and age of production, also show considerable influence on the characteristics of produced water. Table 3 compares dissolved organic components in produced water from different sources.

The organic material in produced water can adhere strongly on the surface of RO membranes and cause severe decline in flux. Organic fouling on membrane surfaces is the biggest hurdle of deployment of membrane technologies in produced water desalination. Many factors including surface charge, membrane material selection, and surface morphology play crucial role on organic adsorption and subsequent fouling. For example, most of

polyamide membranes have a strong negative charge and strongly repels ionic foulant, i.e., fatty acid. Also, hydrophilic membranes with smooth surfaces were reported to be more foulant resistant than hydrophobic and rough membranes^[17]. As a result of organic fouling, water flux drops drastically and operation pressure increases corespondingly. It was reported that quite amount of dissolved organics (>60%) in produced water have average molecular weight smaller than 50,000 Dalton and have >15% of small molecules with molecular weight less than 3,500^[10]. Nanofiltration based membrane technologies provide a well-defined pore structure that can be tailored to meet this specific separation requirement.

Scaling

Produced water from oil and gas production has a complex solution composition, which varies over the life of a well. The dissolved salts contain different cations and anions in varying concentrations. The primary cations from dissolved salts include Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Sr^{2+} and Fe^{2+} ; the anions are mainly F⁻, Cl^- , SO_4^{2-} , CO_3^{2-} and HCO_3^- . Produced water from CBM is considerably different from that in oil and gasfields due to the difference in formation, coal type and depth^[20].

Specific concentrations of dissolved salts in oilfield and CBM produced water vary considerably with the geographical location and history of the well^[19]. Table 4 gives chemical compositions of produced water from different formations. For comparison, the chemical composition of typical seawater is also listed. Scaling occurs whenever the ionic salt concentration exceeds the equilibrium solubility by the mechanism of homogeneous and heterogeneous crystallization. Figures 6 and 7 display surface images of scanning electron microscopy (SEM) of a polymeric and a zeolite membrane before and after testing produced water for two weeks. San Juan CBM produced water with chemical composition listed on Table 1 was deployed for this permeation test. Drastic flux decline was observed as scale deposition progress on the membrane surface. Over 30% flux decline was observed after two weeks permeation. After washing and drying, the surface foulant was further investigated by surface scanning electron microscopy with x-ray microanalysis (SEM/EDS) which revealed that the scaling on the membrane surface is mainly attributed to the precipitation of cacium carbonate, silica, and SrCO₃, as shown in Figure 8.

Apparently, scale deposition is directly related to the chemical composition of produced water. To minimize the scale fouling, different techniques have been tested including adding additives, pH control, and pretreatment for multivalent ion removal^[10, 22].

pH adjustment Organic solubility in produced water generally increases with increase of pH. Thus, increasing solution pH to 10–11 can reduce organic fouling on the membrane surface. Unfortunately, produced water also contains significant amount of $SO_4^{2^2}$ and $CO_3^{2^2}$ in which high pH enhances the deposition of scale on the membrane surface. Appropriate pH should be determined according to the chemical composition of produced water and the dominant fouling mechanism.

Antifouling additives The experimental test has indicated that additives are essential for fouling control even sophisticated pretreatment was deployed, i.e., nanofiltration. Antiscalants (3 mg/L), Alkaline solution (20 mg/L NaOH), sodium ehtylenediaminetetraacetate (20 mg/L EDTA) were generally used as antiscalants for fouling control.

Pretreatment for multivalent ion removal A typical characteristic of a nanofiltration membrane is its low rejection on monovalent ions, but maintaining high rejection of multivalent ion species and high water flux compared to RO membranes. Most of nanofiltration membranes are made of polyamide based thin film composites (TFC) with relatively high surface charge. Over 90% multivalent ions, specifically Ca²⁺, Mg²⁺, and SO₄²⁻, will be separated by NF pretreatment.

Membrane regeneration by mechanical and chemical methods

Severe scale precipitation and organic adsorption on membrane surface was observed on both organic reverse osmosis membranes and inorganic zeolite membranes during long-term RO desalination test on produced water. Periodic cleaning must be conducted to restore membrane performance when the flux drops below the expected permeate flow rate (i.e., 10–15% of original water flux). Mechanical washing and chemical cleaning can be deployed for membrane regeneration. Mechanical cleaning includes back flushing, air spurge, and automatic sponge ball cleaning while chemical cleaning includes adding chemical agents, such as alkalis, acids, metal chelating agents, surfactants, oxidation agents and enzymes, for removing the foulants from membrane surface by chemical reaction with foulant and modification of membrane surface. Figure 9 gives the SEM images of a fouled RO membrane that was treated by different methods for regeneration.

As revealed by Figure 9, acid cleaning is effective for removal of precipitated carbonate salts, such as CaCO₃, while back flush and alkaline solvent cleaning show limited effect on the salt removal. It was observed that the

membrane treated by alkaline ultrasonic cleaning shows clear crystal morphology, indicating the surface removal of adsorped organic foulant. Acid cleaning is more efficient than back flush and alkaline solvent cleaning which is controversial to the study by Xu and coworkers^[17]. Considering no antiscalent was used in this experiment, it is reasonable to derive that scale fouling dominates the mechanism. The water flux was recovered to different extents according to the type of chemicals used. However, all the regeneration experiments show similar trend on recovered water flux: the water flux drops more quickly after repeated regeneration. We attributed this permeation behavior to non-dissolvable salt in acid solution, i.e., SrSO₄, which increases the surface roughness and the concentration polarization at pore entrance after fouling and regeneration.

Oxidizing agents were found to be effective to break the organic foulant. A zeolite membrane fouled by toluene was treated by $15\% H_2O_2$ solution for 10 min, over 95% water flux and ion rejection was recovered^[12]. Unfortunately, polyamide membranes cannot be treated by the oxidising agents due to permanent detrimental effects of the strong oxidant on the pore structure of the membrane.

Frequency of chemical cleaning could range from a few hours to months depending on produced water quality and efficiency of pretreatment. A general standard for membrane regeneration includes decline in water flux by 10% or feed pressure increase by 10%^[23].

MANGEMENT OPTIONS AND COST ANALYSIS OF PRODUCED WATER PURIFICATION AT OILFIELD

Even with numerous experiments and practices for produced water purification, no cost-effective technologies have been reported for dissolved component removal due to the complexity of water chemistry and variability in water volume. As a result, majority of produced water (>90%) is currently managed through a three-step process: (1) lifting produced water to the surface, (2) transportation to the disposal site, and (3) deep well injection or evaporation. The average disposal cost for produced water in New Mexico is ~2.5\$/bbl, with a major part of this cost attributed to its transportation^[2]. Figure 10 gives a typical produced water disposal site at San Juan basin. The economic burden posed by produced water disposal can mean uneconomical production from otherwise viable wells, particularly marginal wells, forcing producers to abandon these operations.

Many efforts for produced water purification and beneficial uses have attracted widely interest from industry. Recent approach in practice of produced water purification includes purifying produced water to substantial quality and uses the purified water for either agriculture or industry, such as tower cooling, agriculture watering, and feedstock. Deployment of advanced technologies for removing salts and dissolvable organics is generally required for attaining surface water discharge standards or reuse criteria. Because water quality and quantity are generally considered the most important parameters dictating desalination technology to be deployed, two options were proposed for produced water purification, as shown in Figure 11.

Option 1 is to transportate produced fluid to a disposal site and to clean the produced water at the disposal site. Advantages of this option include relatively stable feed water quality, reliable and medium to large scale water supply with capacity ranging from 500 to 2000 bbl/day.

For many small oil/gas producers, purification of the produced water at the wellhead for on-site treatment and disposal is the primary option to reduce management costs and benefit the local ecosystem. Due to the shortage of storage capacity and limitations of distribution technologies, current treatment by transporation and disposal has highly weakened economic efficiency of marginal well operation. Option 2 is to purify produced water at the wellhead. The purified water can be disposed of directly for landscape restoration or well stimulation application. Comparing this to option 1, water purification at the wellhead needs to be robust to feed water quality and insensitive to water treatment capacity.

Factors affecting cost of produced water desalination

For a typical produced water treatment plant, the produced water will be pretreated first by filtrating or centrifuging for particulate removal. A high pressure pump will then be deployed to drive water molecules to pass through a semipermeable membrane and produce clean water. Several factors including quantity of produced water and plant capacity are believed to be curcial for unit production costs.

Quality of feedwater Produced water shows a wide range of TDS and organic contents, thus feed water quality is a crucial factor affecting process design and economic efficiency. Formation and production history will have a dramatic influence on produced water quality as well as how the purification technology can be deployed.

Pretreatment Produced water desalination cost comprises two parts: pretreatment and desalination operation. Appropriate pretreatment is crucial to improve the membrane performance and reduce the chemical uses. Due to the high fouling nature of suspended colloids and dissolved organics in produced water, NF/UF is the only effective process that can extend the lifetime of a RO membrane to six months. Potential combination for produced water pretreatment includes:

- Ultra/nano filtration,
- Gravity separation and nanofiltration,
- Microfiltration (0.45 μm) and nanofiltration,
- Membrane bioreactor (MBR) and nanofiltration.

It is suggested that UF or NF must be deployed as a pretreatment option for extending the lifetime of a membrane. As a result, the investment cost will increase significantly. The most recent study indicates that pretreatment cost of produced water ranges from 0.2–0.7 US\$/m³ depending on produced water quality and unit cost of electricity^[22, 24].

Water treatment capacity Water treatment capacity is determined by reliable water supply, i.e., well production, storage capacity, and transportation. These factors are also the crucial factors for the initial capital investment and operation cost. Small plants have small capital investment, but generally is less economically efficient compared to large scale desalination plants. Produced water desalination typically requires treatment capacity in a small or medium-scale water treatment scenario: 30-200 bbl/day for individual wells and 500-2,000 bbl/day for disposal sites.

Transportation The proximity of the water desalination plant to the water source is crucial for reducing water treatment costs. If the water treatment plant can be at the wellhead in which long-distance water transportation is not necessary, pipe installation or truck-related transportation cost could be substantially reduced. Recent efforts are to develop a desalination technology that can be deployed at the wellhead, thus drastically reducing transportation cost as well as overall capital cost.

Desalination implementation cost and economic analysis

Major elements of economic calculation include: (1) direct capital cost; (2) indirect capital cost; and (3) annual operating cost. The direct capital cost includes purchase of equipment, land use, building construction, and membrane unit. Indirect costs includes insurance, construction overhead and owner's costs. The operating costs include electricity, labor, membrane replacement, maintainence and amortization charges. Figure 12 gives the major elements of a RO cost evaluation described by Ettouney^[25].

Table 5 shows the percent cost of various factors for desalination of produced water compared to seawater and brackish water. The seawater and brackish water data were obtained from Younos's report^[26]. By comparing the percent distribution of cost factors, pretreatment and RO membrane replacement are the major factors affecting the total cost of water purification. The difference of produced water desalination compared to commercial seawater and brackish water desalination include:

- Produced water requires a much more complicated pretreatment. So far, the only effective pretreatment that can significantly reduce RO membrane fouling is nanofiltration. All other pretreatment combinations, including Microfiltration by using filters with pore size of 0.45 µm, active carbon adsorption, and Multimedia gravity filter + air floating, show limited effect on fouling removal.
- 2) With the best practice in pretreatment by nanofiltration, the average lifetime of RO membrane for produced water is about half of seawater desalination. The membrane replacement cost play crucial role on the economic efficiency of produced water desalination by RO membranes.

Since storage capacity and transportation infrastructure are limiting factors, a typical produced water purification plant requires a desalination capacity of 2000 bbl/day or less. Cost of reverse osmosis incurred for treatment of produced water with and without transportation was obtained from the excel spread sheet of Desalination Economic Evaluation Program (DEEP) developed by the International Atomic Energy Agency. The reverse osmosis operation cost is estimated based on the assumptions: (1) transportation option using pipeline, (2) appropriate pretreatment have been implemented. Figure 13 gives the water cost estimated for produced water with transport by pipeline and water treatment cost without transportation.

For a medium-scale produced water treatment scenario (50 m³/day for individual wells and 300 m³/day for disposal site), produced water desalination cost is estimated to be 3.08\$/m³, approximately 60% of the cost is attributed to transporation. Since membrane lifetime for produced water desalination is generally less than six months^[18], the membrane replacement cost and chemical dosing cost (for membrane regeneration or scale removal) will be much higher than this estimate.

CONCLUSIONS

Produced water desalination by reverse osmosis process has been investigated from the aspects of material screening, process design, and economic evaluation. A number of conclusions can be drawn from this study and a few produced water desalination practices:

- (1) Produced water chemistry varies considerably over the operation time and formation. For an individual coalbed methane production well, the TDS varies from 25,000 to 65,000 mg/l when monitored between a 6 month period.
- (2) Scale deposition and organic adsorption are the major fouling mechanisms for RO membranes when deployed for produced water desalination. Drastic flux decline (>30%) was observed for both polymeric reverse osmosis membranes and molecular sieve zeolite membranes after two weeks permeation. Average water permeation of reverse osmosis membrane for produced water desalination ranges from 0.30–0.51 L/m².h.bar.
- (3) Among the tested pretreatments, nanofiltration and ultrafiltration is the only effective process that can reduce RO membrane fouling and extend membrane operation lifetime. The additional cost of replacing UF or NF membranes weighs much on the overall desalination cost.
- (4) Pretreatment and membrane replacement are the two crucial factors that impact the water treatment cost compared to commercial seawater and brackish water desalination. Lack of effective pretreatment that can remove both fine colloids and soluble organics and noval membranes that are tolerant to produced water environments has limited successful implementation of membrane technology in produced water desalination. The cost of produced water desalination by membrane technology is estimated to be above \$3.7/m³ including transportation, which is well above the average disposal cost of deep well injection and/or evaporation.
- (5) To date, no technology has been reported cost-effective for produced water desalination. The major obstacles for integrating RO membrane technology to oilfield brine treatment include sophisticated pretreatment, i.e., nanofiltration, frequent membrane replacement, and large chemical dosinig for scale removal or flocculant precipitation.

ACKNOWLEDGEMENTS

This research was sponsored by the Research Partnership to Secure Energy for America (RPSEA) (grant # 07123-05) and Southwest Carbon Sequestration Partnership (Grant DE-FC26-05NT42591).

REFERENCES

- 1. Hayes, T., and Arthur, D. (2004) Overview of emerging produced water treatment technologies. The 11th Annual International Petroleum Environmental Conference, Albuquerque, NM, October 12-15.
- Veil, J.A., Puder, M.G., Elcock, D., and Redweik, R.J. (2004) A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane. ANL Report under DOE (NETL) Contract W-31-109-Eng-38.
- 3. Ciarapica, FE., Giacchetta, G. (2003) The Treatment of Produced Water in Offshore Rigs : Comparison between Traditional Installations and Innovative Systems. *The Fifth International Membrane Science & Technology Conference*, University of New South Wales, Sydney, Australia.
- 4. Frankiewicz, T. (2001) Understanding the Fundamentals of Water Treatment, the Dirty Dozen 12 Common Causes of Poor Water Quality. Presented at the 11th Produced Water Seminar, Houston, TX, Jan. 17.
- 5. Ashaghi, K.S., Ebrahimi, M., and Czermak, P. (2007) Ceramic ultra- and nanofiltration membranes for oilfield produced water treatment: a mini review. *The Open Environmental J.*, 1: 1.
- 6. Liu, H. (2008) Personal communication with He Liu, Vice Chief Engineer of Daqing Oilfield Limited Company.
- 7. Ray, J.P., and Engelhart, F.R. (2002) Produced Water ; Plenum Press : New York.
- 8. Zaidi, A., Simms, K., Kok, S., and Nelson, R., (1992) Recent advances in the application of membrane technology for the removal of oil and suspended solids from produced waters. In : Produced Water, Ed. by J.P. Ray and F.R. Engelhart ; Plenum Press, New York.
- 9. Santos, S.M., and Wiesner, M.R. (1997) Ultrafiltration of water generated in oil and gas production. *Water Env. Research*, 69: 1120.
- 10. Visvanathan, C., Svenstrup, P., and Arlyamethee, P. (2000) Volume Reduction of Produced Water Generated from Natural Gas Production Process Using Membrane Technology. *Water Sci. Technol.*, 41: 117.
- 11. Li, L.X., Dong, J., and Lee, R. (2004) Preparation of alumina-supported mesoporous bentonite membranes for reverse osmosis desalination of aqueous solutions. *J. Colloid and Int. Sci.*, 273:.540.

- N. Liu, L. Li, B. McPherson, and R. Lee, "Removal of Organics from Produced Water by Reverse Osmosis Using MFI-type Zeolite Membranes," J. Membr. Sci. 325, 357-361, 2008.
- 13. EPA/625/R-04/108. (2004) Guideline for Water Reuse. US Environmental Protection Agency.
- McFarlane, J.; Bostick, D.T., and Luo, H. (2002) Characterization and modeling of produced water. Presented at the 2002 Ground Water Protection Council Produced Water Conference, Colorado Springs, CO, Oct. 16–17.
- Abou-Sayed, A.S., Zaki, K. S. Wang, G., Sarfare, M.D., and Harris, M.H. (2007) Produced water management strategy and water injection best practices: design, performance, and monitoring. SPE Production & Operations, 22: 59.
- 16. Rowe, D.R., and Abdel-Magid, I.M. (1995) Handbook of Wastewater Reclamation and Reuse. CRC Lewis Publishers, Tokyo.
- Xu, P, J.E. Drewes, "viability of Nanofiltration and Ultra-low Pressure Reverse Osmosis Membranes for Multi-Beneficial Use of Methane Produced Water," Separation and Purification Technology, 52 (2006), 67-76.
- 18. Visvanathan, C., Svenstrup, P., and Arlyamethee, P. (2000) Volume reduction of produced water generated from natural gas production process using membrane technology. *Water Sci. Technol.*, 41: 117.
- 19. Hansen, B.R., and Davies, S.R.H. (1994) Review of potential technologies for the removal of dissolved components from produced water. *Trans IChemE*, 72: 176.
- Jackson, L., and Myers, J. (2002) Alternative Use of Produced Water in Aquaculture and Hydroponic Systems at Naval Petroleum Reserve No. 3. Presented at the 2002 Ground Water Protection Council Produced Water Conference, Colorado Springs, CO, Oct. 16–17.
- 21. Al-Anezi, K., and Hilal, N. (2007) Scale formation in desalination plants: effect of carbon dioxide solubility. *Desalination*, 204: 385.
- 22. Xu, P, J.E. Drewes, D. Heil, 2008, Beneficial Use of Co-Produced Water through Membrane Treatment : Technical-Economic Assessment, Desalination, 225, 139-155.
- 23. Al-amoudi, A., and Lovitt, R.W., "Fouling Strategies and the Cleaning System of NF Membranes and Factors affecting Cleaning Efficiency," J. Membr. Sci. 303 (2007), 4-28.
- 24. Scholz, W., and M. Lucas, (2003) Techno-economic evaluation of membrane filtration for the recovery and re-use of tanning chemicals, Water Research, 37, 1859-1867.
- 25. Ettouney, H.M., El-Dessouky, H.T., Faibish, R.S., and Gowin, P.J., Evaluating the Economics of Desalination, Chemical Engineering Progress, Dec. 2002, 32-38.
- Younos, T. The Economics of Desalination, J. Contemporary Water Research & Education, 132, 2005, 39-45.

	Water quality requirement			
damage and Uses	Suspensions	Dissolved component	Main concerns Environmental impact	
offshore disposal	Solid <10 mg/l Oil<5 mg/l	No limitation		
Reinjection	Oil<5 mg/l Solid<1 mg/L D<1 μm	No limitation	Formation damage	
Irrigation ^[16]	Oil & grease < 35 mg/l	TDS: 500-2000 mg/l	Salinity, trace elements (boron), chlorine residue, and nutrients	
Cooling water ^[13]	N/A	TDS<2700	Corrosion, biological growths, and scaling	
Chemical process ^[13]	N/A	TDS<1000	Low turbidity, suspended solids, and silica	

Table 1. Produced Water Disposal and Water Quality

Note: D=median particle size.

Table 2. Performance of produced water desalination by RO membranes

	Pretreatment	RO Membrane	Membrane lifetime	Stablized water permeability (L/m².h.bar)	References
1	0.3 mg/L antiscalants+ 0.45μm microfiltration	TFC-HR, Koch	80 hrs	0.375	[17]
2	Multimedia gravity filter +nanofiltration by MWCO=200 membrane	BW 30-4040, FilmTech	Regeneration every two weeks	0.510	[18]
3	Multimedia gravity filter +nanofiltration by hollow fiber filter with MWCO=8000–50,000	BW 30-4040, FilmTech	Failled due to drastic flux decline	N/A	[18]
4	Multimedia gravity filter + 20μm microfiltration+ 1.0μm microfiltration	RO, FilmTech	Significant flux decline in hours	N/A	[18]
5	Microfiltration by 0.45µm membranes	Zeolite	2 months	0.304	This work
6	Activated carbon+microfiltration by 0.45μm membranes	Zeolite	2 months	0.344	This work

	Components	Typical concentration, mg/l		
		Oil field	Gas field	CBM
Aliphatic				
•	Aliphatic, C_2 - C_5	1	1	
	Aliphatics, $>C_5$	5	10	
Aromatic	•			
	BTX	8	25	120
	Naphthalenes	1.5	1.5	3
Polar compounds				
	Phenols	5	5	
Fatty acids				
	C_2-C_5	300	150	
	>C ₅			

Table 3. Organic Content of Produced Water from Different Formations^[19]

BTX: benzene, toluene, and xylene.

Table 4. Characteristics of Produced Wa	ter Compared wi	ith Seawater	
Component	San Juan Basin (CBM), mg/L	Permian Basin (Oilfield), mg/L	Typical Seawater, mg/L ^[21]
Bicarbonate (HCO_3^-)	5870.3	1538.1	107
Hydrogen sulfide (${m H}_2 S$)	65	22.5	N/A
Chloride (Cl^-)	2389.5	130636	19352.9
Sulfate (SO_4^{2-})	24.1	4594.1	2412.4
Sodium (Na^+)	4169.3	80421.2	10783.8
Potassium (K^+)	35	398.6	399.1
Magnesium ($Mg^{^{2+}}$)	19	894.1	1283.7
Calcium (Ca^{2+})	11	4395.5	412.1
Strontium (Sr^{2+})	6.3	88.9	7.9
Iron (Fe^{2+})	0.65	65.3	15.5
Total Dissolved Solids (TDS)	12590.2	223054.3	34774.4

Table 5. Percent distribution of cost factors

	Produced Water (%)	Seawater (%)	Brackish water (%)
Pretreatment	36	17	10
RO membrane replacement	12	6	7
Fixed costs	20	27	54
Electric power and	32	50	20
maintanence			



Figure 1. Produced water samples from nearby offset wells at San Juan basin.

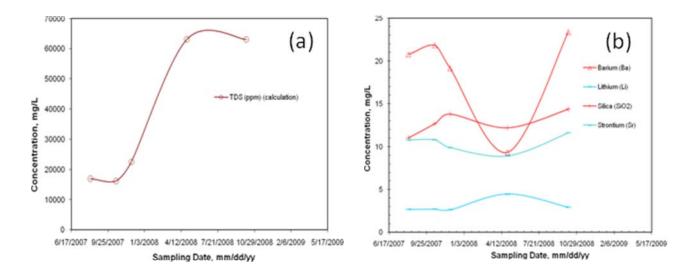


Figure 2. Variation of water chemistry with lifetime of operation (a) TDS, (b) trace metal ions.

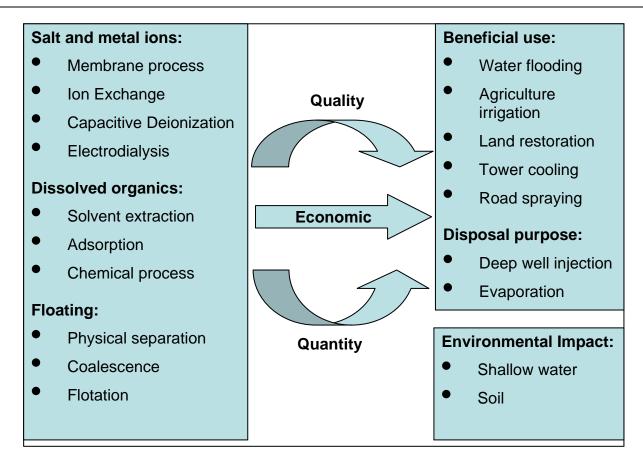


Figure 3. Strategies of produced water purification and beneficial uses.

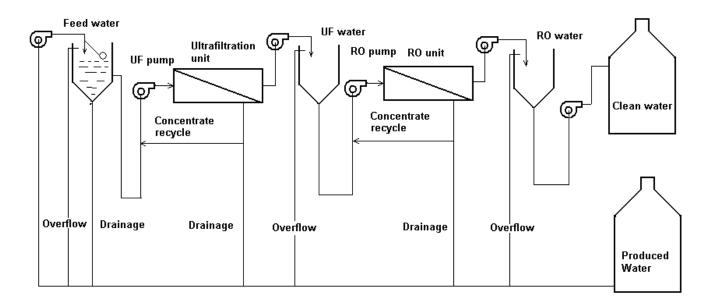


Figure 4. Schematic digram of crossflow RO membrane with ultrafiltration pretreatment.

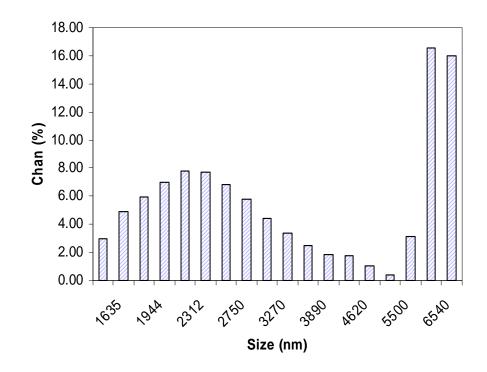


Figure 5. Particle size distribution of suspensions in produced water.

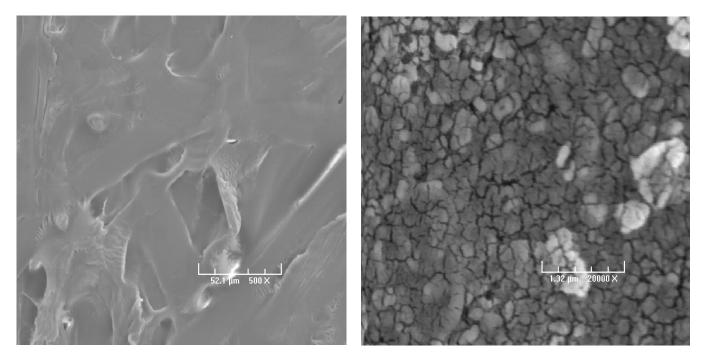


Figure 6. SEM images of scale formation on polymer membrane surface.

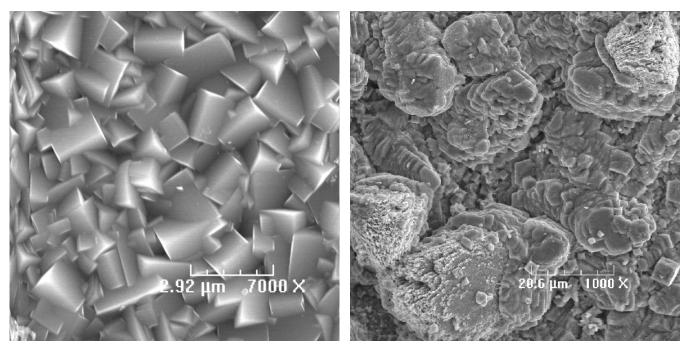


Figure 7. Surface SEM image of zeolite membrane with foulant.

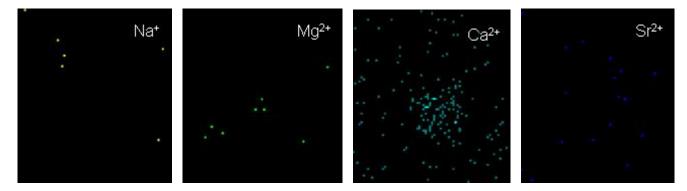
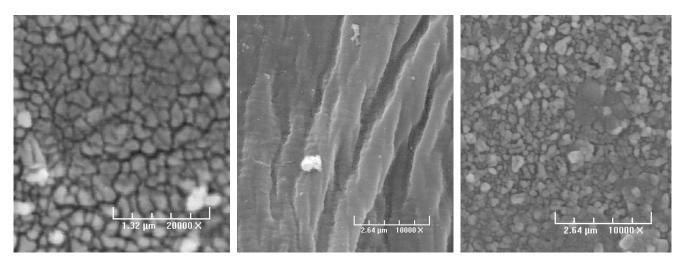


Figure 8. Element (Na, Mg, Ca and Sr) mapping on exterior surface after washing with DI water.



(a) back flush

(b) 0.1M HCI cleaning

(c) Alkaline solvent ultrasonic cleaning





Figure 10. A produced water disposal site at San Juan basin.

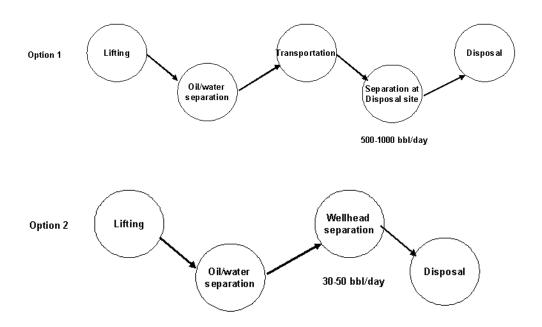


Figure 11. Options for produced water management for beneficial uses.

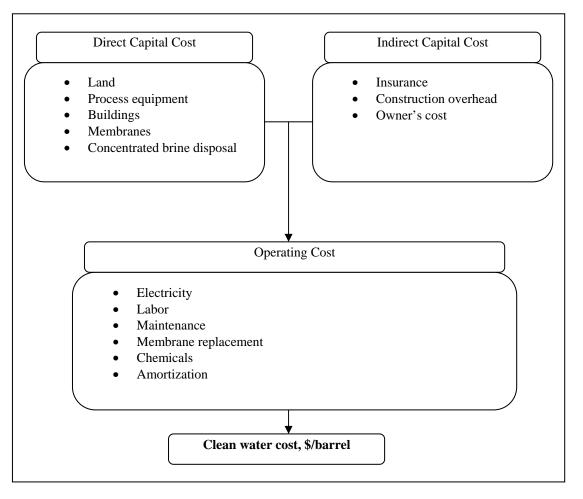


Figure 12. Elements used for cost analysis of RO desalination.

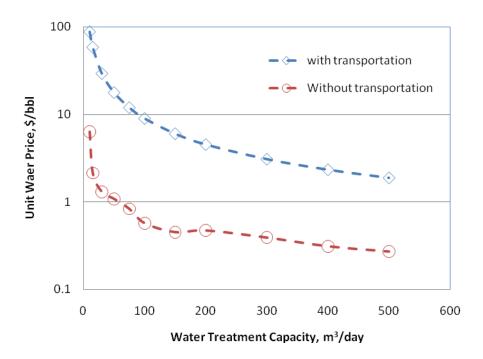


Figure 13. Unit water cost of standard RO process if appropriate pretreatment is deployed.