Technology Status Assessment

Introduction

This report provides a summary of state-of-the-art treatment technologies proposed in the study entitled "An Integrated Framework for Treatment and Management of Produced Water". Currently there are a number of technologies that have been used or tested for treatment of produced water. Produced water can be classified based on the dominant salt present in solution.

Water with higher concentrations of sodium bicarbonate is frequently treated with the continuous ion-exchange (IX) process (i.e., the Higgins Loop) [1]. The Higgins Loop can achieve 97-99 percent water recovery and the concentrated brine is deep injected or transported offsite for disposal in deep injection wells [2, 3]. The limitations of ion-exchange processes include the excessive use of acids for resin regeneration in remote areas; concentrate hauling; disposal through deep well injection; and low cost-effectiveness for small volumes of produced.

For coal bed methane (CBM) and gas shale produced water characterized by high sodium chloride concentrations, reverse osmosis (RO) treatment has been applied, but typically only at the pilot scale [1]. While both RO and electrodialysis (ED) are effective desalination technologies, they require rigorous pre-treatment. The complexity of pre-treatment processes, large volumes of waste generated, sensitivity of membranes to impurities, and rather low tolerance to system upsets (e.g., well water quality changes, temperature variations, filter plugging) has hindered widespread application of membrane processes for treatment of produced water.

Alongside membrane technologies, thermal distillation processes can be used for very high salinity produced water types leading to zero-liquid discharge. The energy consumption of thermal technologies, however, is high.

Evidently, a single process cannot achieve an ultimate treatment goal for complex and variable water compositions and volumes, particularly if high water quality and recovery are desired. In order to take advantage of process synergies, to achieve higher recoveries, and to save cost, various potential technologies will be tested during this research and employed in hybrid configurations. Modular treatment strategies comprised of pre-treatment, desalination, post-treatment, and brine management and disposal will be verified in the laboratory. Combined treatment processes that are efficient and appropriate for treatment of produced water and brines from CBM or gas shale will be tested in the laboratory, and subsequently validated during field trials.

Evaluation Criteria

Potential pre-treatment, treatment, and post-treatment technologies will be evaluated in this study for their separation efficiency (rejection and recovery), robustness, and O&M cost in treatment of produced water. Special considerations will be given to variability of water chemistries and range of total dissolved solids (TDS) concentration. Given the conditions under which produced water is generated, development of a treatment strategy requires special design and construction considerations. Therefore, the evaluation criteria to assess the potential technologies in treating different types of produced water will consider: (i) separation efficiency (rejection and recovery); (ii) product water quality and variability; (iii) maturity of the process; (iv) energy demand; (v) life cycle costs including capital and O&M cost; (vi) infrastructure considerations, including footprint, modularity, and durability; and (vii) operational and maintenance considerations, including chemical uses and handling, system robustness, ease of operation, flexibility, and scalability.
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### Proposed Technologies

Currently, IX, ED, electrodialysis reversal (EDR), RO, and nanofiltration (NF) represent the most broadly employed desalination technologies for treatment of produced water. In comparison to existing desalination technologies, we will investigate the viability of emerging technologies and hybrid systems for treatment of produced water. These will address the challenges related to treatment of produced water, including high scaling and fouling propensity, low water recovery, and large volumes of waste streams generated. Processes that will be tested on the bench- and pilot-scale include:

- Polymeric membranes (RO/NF/UF/MF)
- Ceramic membranes (MF/UF)
- Membrane distillation
- Forward osmosis
- Capacitive deionization
- Cationic selective electrodialysis
- Temperature-resistant NF membranes
- Novel electrodialization
- And combination of the above (high-recovery hybrid systems)

### Polymeric membranes

Polymeric membranes, including microfiltration (MF), ultrafiltration (UF), NF and RO, have been used widely in treatment of municipal and industrial water and wastewater as well as for desalination of brackish water and seawater. MF and UF membranes are used to separate suspended solids, microorganisms, and large molecular weight organic substances such as humic acids from water. NF membranes are often used as softening process to remove divalent ions, or to selectively reject low molecular weight organic compounds such as pesticides, color, and taste compounds from water. RO membranes can achieve high removal of almost all ions and organics.

Depending on raw water quality, polymeric membranes may require pre-treatment as minimal as cartridge filtration or as complex as individual or combination of coagulation/flocculation (or air-floatation), chemical precipitation, media filtration, ion exchange, and final cartridge filtration. Because certain produced waters may contain emulsified oil, dissolved hydrocarbons, or polymers added to hydraulic fracturing (frac) water, it is challenging to use conventional polymeric membrane processes for desalination without suitable and effective pretreatment. Polymeric membranes are very susceptible to fouling by oil and grease or organic polymers. Furthermore, high silica, hardness and other sparingly soluble salts in produced water can cause severe membrane scaling in high-pressure membrane applications. Frequent chemical cleaning is required in order to maintain the effectiveness and integrity of these polymeric membranes; this generates waste streams that must be handled and often limit the overall water recovery of the treatment process. Being a widely used desalination technology, polymeric membranes will be tested for treatment of produced water with proper and improved pretreatment. Result will be used as benchmark for evaluating other emerging technologies.

### Ceramic membrane pretreatment

Ceramic materials are being used in manufacturing of MF and UF membranes that can remove organic matter from produced water. Ceramic membranes are monolithic structures made from oxides, nitrides, or carbides of aluminum, titanium, or zirconium [4]. Typically, a tubular configuration is used with an inside-out flow path; water flows in the membrane channels and permeates through the support structure to the shell side of the module.
Ceramic membranes have extremely high thermal, chemical, and mechanical stability. These characteristics have significant implications for maintenance of membrane processes deployed in harsh environmental conditions. For example, ceramic membranes can be cleaned using steam and/or high and low pH chemicals. Ceramic membranes are also resistant to oxidants, such as ozone and chlorine, which usually degrade polymeric membranes [9]. All of these benefits lead to a significantly longer operational life for ceramic membranes as compared to polymeric membranes. Ceramic membranes are also capable of achieving flux rates between 100 gfd and 300 gfd; 3 to 10 times higher than polymeric membranes.

Ceramic membranes have capital cost that is approximately ten times higher than that of polymeric membranes. However, because of the many advantages to ceramic membrane, the overall lifecycle cost may be lower for ceramic membranes as compared to polymeric membranes.

For this project, we will evaluate ceramic membranes as pretreatment to subsequent desalination processes. Based on previous studies that used ceramic membranes to treat wastewater, bilge water, and surface water, the following key parameters have been identified for further study [5-8]: (i) flow regime characterization within the module for flux enhancement; (ii) optimization of inline coagulation, cleaning strategies, and operational performance based on water quality; (iii) fouling potential reduction; and (iv) lifecycle cost assessments for comparison to polymeric membranes.

**Membrane distillation (MD)**

The MD process is a new separation method that can utilize low-grade heat sources to facilitate evaporative mass transport through a hydrophobic microporous membrane [10]. Mass transfer is achieved evaporation of a volatile solute or solvent, such as water. The driving force for mass transfer in MD is vapor pressure differential across the microporous membrane. If waste heat is available, MD is capable of producing ultra-pure water at a fraction of the cost of conventionally distillation processes. Furthermore, if hot produced water is to be treated, MD can facilitate simultaneous water cooling before downstream processes and water production. Yet, MD is vulnerable to fouling, which may also cause pore flooding, and feed water typically requires pretreatment. Recent studies [11] have demonstrated that more than 98% water recovery could be achieved when combining RO and MD for treatment of brackish water concentrates. Currently, there are no commercial operations of this technology existing. The technical feasibility, product water quality, and economic justification of MD in treatment of produced water will be investigated and demonstrated in this study.

**Forward Osmosis (FO)**

FO is an emerging membrane contactor process that has recently been the subject of numerous scientific inquiries and is gaining wider recognition for its ability to efficiently treat highly impaired water [12]. Mass transfer in FO is diffusion based and is similar to that of pressure driven membrane processes such as RO and NF. Yet, the driving force for mass transfer in FO due to osmotic pressure difference and not hydraulic pressure such as in RO and NF. FO takes advantage of osmotic pressure differentials between an osmotic agent (draw solution) and a feed solution to transport water across a thin, semi-permeable membrane from a feed solution into a draw solution. The draw solution stream has a very specific chemical makeup and therefore it is easier to treat with downstream processes.

Recent investigations of FO for water treatment have revealed that it is useful for desalination either as a standalone process [13] or in tandem with RO to concentrate the reject brine and improve recovery up to 98% [11]. Overall, these studies serve to promote FO as an effective pretreatment for source waters that contain high levels of suspended materials,
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organics, and/or sparingly soluble salts.

FO has distinct advantages over other processes. It is less prone to membrane fouling from dissolved solutes and particulate matter because hydraulic pressure is not applied to the membrane, and therefore foulants are not compacted onto the membrane. FO is also less susceptible to solution chemistries that may affect membrane hydrophobicity. FO membranes are therefore easier to clean and maintain than RO and NF membranes. Additionally, FO has the advantage of not requiring high hydrostatic pressures, which results in minimal energy expenditures.

One key limitation of the FO process is that the draw solution requires constant reconcentration in order to maintain process efficiency. Another issue is that currently available FO membranes are not perfectly selective and will allow for some diffusion of dissolved solids through the membrane. Dissolved solids that pass through the membrane may prove problematic for downstream processes.

**Capacitive deionization**

Capacitive deionization (CDI) is an electrosorption process that removes ionic species from aqueous solutions in an electrical field. When water passes between matching pairs of carbon aerogel electrodes, ionic species are held at the charged electrode surfaces and are temporarily removed from the solution. After the electrodes become saturated with salts or impurities, the electrodes are regenerated by electrical discharge or chemical solutions; allowing the captured salt ions to be released into a relatively small, concentrated purge stream.

This electrochemical process exhibits several advantages, such as a simple, modular, plate-and-frame construction, performing at ambient conditions and low voltages (e.g., 1.0-1.3 volt). The CDI requires minimum pretreatment, and can selectively recover valuable constituents from water.

Given the limited adsorption capacity of carbon aerogel electrodes, the required number of modules increased with increasing feed water TDS level. The current CDI technology is not cost competitive compared to RO at high TDS range (>3,000 mg/L) [14, 15]. However, the advantages of CDI justify its testing and evaluating its viability for treatment of produced water.

**Cationic selective electrodialysis (ED)**

ED uses electrical potential as a driving force to remove ions through ion-selective membranes between opposing electrodes. Polarity is periodically reversed in electrodialysis reversal (EDR) to mitigate scaling. EDR has the potential to operate at very high water recoveries. ED and EDR are being used in brackish water desalination and wastewater reclamation. EDR was demonstrated for desalting 5,000-mg/L TDS groundwater at 94% water recovery [16]. EDR has also been applied to reclaim 8,000-mg/L TDS RO concentrate to achieve RO-EDR recoveries of up to 96% [17].

RO is often preferable over ED and EDR, based on the high rejection of both ionizable and non-ionizable components, and also from an energy usage perspective. However, for produced water with high silica, hardness, and silt density index (SDI), ED/EDR may offer an advantage over RO through its ability to achieve high water recoveries without incurring scaling [18].

By using new ion selective membranes and combination of different functionalized ion exchange membranes, ED treatment can be tailored to produce the desired water quality such as low sodium adsorption ratio (SAR). Monovalent selective membranes with high sodium permeation and low divalent permeation are commercially available. Argonne National Lab’s preliminary results with monovalent selective membranes indicate that ED is a promising technology for treatment of produced water [19]. This technology however needs to be
demonstrated through laboratory and pilot-scale testing in the field and in parallel to RO membranes. Depending on the input and target water quality, electrodeionization (EDI) could prove valuable. In EDI, the process chamber is filled with commercial ion exchange resin [20].

**High stability NF membrane**

Eltron Water’s patent pending high stability nanofiltration (NF) membrane technology, Duraflux™, will be evaluated for produced water treatment in this project. Significant reduction in treatment costs, energy consumption, and associated CO₂ emissions are anticipated using this NF technology in place of conventional membrane products. Exceptional thermal and oxidative stability of Eltron’s unique NF membranes will allow filtration of produced water with little or no pre-filter cooling while superior water flux will reduce pumping costs and energy demand. Benefits of this NF technology compared to commercial state-of-the-art NF products include 30-150% greater water flux, 10-20 times greater chlorine/oxidizer stability, higher thermal stability (up to 140°C), and high tolerance to repeated pressure cycling. This technology requires additional testing to determine its extended performance under conditions specific to produced water, particularly at elevated geothermal temperatures. While Eltron's NF technology is not yet in commercial production, its manufacture is amenable to conventional membrane fabrication process line infrastructure.

**Novel electrodeionization (EDI)**

Eltron’s unique electrodeionization technology will be evaluated for treatment of produced water treatment in this project. Based on results from laboratory trials, Eltron’s treatment technology has the potential to reduce the cost of salt removal from produced water by approximately 60-70% compared to conventional ion exchange deionization while eliminating the use of mineral acids for resin regeneration. Additionally, a low-volume, high purity caustic product with commercial value will be produced as the byproduct rather than a waste stream. Key features of Eltron’s electrodeionization system that distinguishes it from commercial electrodialysis include in-situ management of membrane scaling, lower operating power, no hydrogen emissions, and a potentially useful byproduct. This technology requires evaluation of two operating configurations and verification of long-term performance under conditions specific to produced water; particularly for CBM production and SAR adjustment. Eltron’s electrodeionization platform is a unique electrolytic reactor with many patent-pending features. It has been recently scaled up for industrial use in other applications unrelated to produced water.

**High-recovery hybrid system**

High-recovery hybrid systems will be tested in the study. They will comprise of several treatment trains such as ultraviolet disinfection, ceramic UF membrane, intermediate chemical precipitation followed by RO, MD or FO or ED, to achieve high recovery. Hybrid systems provide the advantages of high water quality, minimal concentrate volume, and reduced disposal costs. It is flexible and can be adapted for treatment of different quality produced water. By using the combination of commercialized technologies, hybrid systems can provide a solution to produced water treatment and management in the near future.

The proposed hybrid systems need to be demonstrated technically and economically. The operating parameters in treating different types of produced water need to be optimized and evaluated based on water quality and variability, recovery, and economic criteria.
References


