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Technology Status Assessment of Proposed Technologies for Treating Oil and Gas Produced Water Under Cooperative Agreement No. DE-NT0005681

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Current State of Technology

Summary of Existing Treatment Technologies

Produced water is a byproduct from oil or gas producing wells. Every year, about 14 to 18 billion barrels of produced water is generated from on-shore oil and gas production in the U.S. alone (Veil et al. 2004). The volume of produced water from oil and gas wells changes over time and the water:oil/gas ratio usually increases over the lifetime of a well.

Produced water generally contains free phase oil (droplets), suspended solids, and dissolved organics and inorganics (e.g., total petroleum hydrocarbons, BTEX, fatty acids, salts, sodium chloride, and metals). Some of these constituents are toxic, and improper disposal of produced water can result in soil, water, and air contamination.

Common disposal practices for produced water management include surface impoundment, use for dust suppression on roads, reuse for production processes, surface/subsurface irrigation, surface discharge, and subsurface injection. For example, in the gas industry, typically 60 to 90% of produced water is injected into the subsurface during well drilling, fracturing, or disposal (Hayes and Arthur 2004), while the rest is evaporated or land applied on-site, or transported and disposed of off-site.

Comprehensive treatments are usually needed to remove suspended solids, free oil, and volatile organics compounds (VOCs) before the produced water is discharged, injected, or consumed. For example, for underground injection, scaling from calcium carbonate and barium sulfate, excessive solids, corrosion and biomass need to be controlled to prevent plugging of subsurface formations. Conventional treatment technologies for oil removal include oil water separators, corrugated plate separators, centrifugation, hydrocyclone separation, and gas floatation with or without chemical addition. Corrugated plate separators, centrifugation, hydrocyclone separation and gas floatation are also widely used for solids separation with chemical enhanced treatment (Interstate Oil and Gas Compact Commission and ALL Consulting 2006). These technologies have been applied by the oil and gas industry with relatively low capital investment. Effluents from these treatments usually meet water quality requirements for surface impoundment and subsurface injection.

Other technologies that have been utilized to treat produced water include filtration, constructed wetlands, freeze and thaw separation, and ion exchange. These methods are usually limited to relatively low flow rates and can be influenced by the local climate. For example, filtration methods such as packed bed adsorption, which use activated carbon, organo clay and other sorbents, are usually limited by flow rate and pressure drop (<10 gpm and 10 psi pressure drop) through the bed.

Solvent extraction, sorbent adsorption and membrane separation are recently developed technologies for produced water treatment (Interstate Oil and Gas Compact Commission and ALL Consulting 2006). Due to high operation and maintenance (O&M) costs, the use of solvent extraction and sorbent adsorption are limited. Micro or ultra-filtration (MF or UF) membrane technologies can effectively remove dispersed and emulsified oil, as well as suspended solids from produced water, however, the conventional membranes used are susceptible to fouling by suspended solids and organics in the produced water. Cleaning of such fouling is difficult and costly.

Enhanced biological treatment technologies such as fluidized bed bioreactors and membrane bioreactors have been successfully used in refinery industries to eliminate organic compounds in process wastewater to meet effluent discharge limits (Hayes and Arthur 2004). However, biological treatment processes are susceptible to large flow fluctuations and variations in organic contents. Factors such as temperature and metals in the produced water may also limit the performance of biological treatment technologies.

Ceramic ultrafiltration is a newly emerging technique that can remove large organic molecules such as oil and grease, dissolved hydrocarbons, proteins, large colloidal particles, and some microorganisms. It can tolerate high variations in concentrations of suspended solids and oil and grease in the produced water. Ceramic UF can also be cleaned with chemicals that do not compromise membrane performance, which is critical for waste streams with variable quality or a high propensity for membrane fouling (Ashaghi et al. 2007).

Electrodialysis (ED) relies on cationic (positive) and anionic (negative) movements of ions that are induced by an electrical field generated by cathode and anode electrodes. In ED, ion selective membranes are placed between a pair of electrodes. A spacer sheet that permits feed water to flow along the face of the membrane is placed between each pair of membranes. Positively charged ions migrate toward the cathode and negatively charged ions migrate toward the anode. During migration the charged ions are rejected by similarly charged ion exchange membranes. As a result, water within the alternate compartment becomes concentrated, leaving desalinated water within the effluent compartment of the ED unit. The concentrate and desalinated water are continuously removed from the unit in a flow-through system. Pilot studies of electrodialysis of produced water (Miller et al. 1997) demonstrated that electrodialysis may be cost effective for reducing TDS when it is less than 10,000 mg/L, achieving an effluent TDS of < 2,500 mg/L. The process of electrodialysis reversal (EDR) operates on the same principle as ED except that the polarity of the electrodes is periodically reversed to push anions and cations back through the ion exchange membranes into the main channel to back flush and extend the life of the membranes.

Reverse osmosis (RO) technology has been successfully used for sea water desalination for more than 30 years. Bench and pilot studies using the RO process for produced water treatment have produced mixed results due to the high organic content of the produced water, scaling constituents, and fine particles present in the produced water that tend to foul RO membranes within a short time. Therefore, a well designed pretreatment process is critical for RO treatment of produced water. Cakmakci et al. (2008) concluded that a combination of sedimentation, oil-water separation, dissolved air floatation (DAF), and ceramic MF are among common pretreatment options. Bench and pilot scale packages including pretreatment and RO have been tested for treating oil produced water (Burnett and Siddiqui 2006). These packages include centrifugation, organo-clay adsorption, MF, and UF membrane separation followed by RO. The system showed >50% water recovery and the effluent was used for agricultural irrigation. The RO membrane used in those studies was of conventional spiral wound configuration, which contains spaces that tend to host biological growth and trigger membrane fouling, adversely affecting the system flow and performance (Siler 1993). Consequently, spiral wound membranes need extensive cleaning and regeneration maintenance restore and maintain high performance.

Recently, a new disk tube (DT) module membrane for RO separation was developed in Switzerland and Germany. Siler (1993) compared the DT module with a conventional spiral wound module in a controlled study and results indicate that the DT module achieved a 30% higher in flux than the spiral wound module. Furthermore, the DT module can be cleaned and restored with a single flush of 1% sodium hydroxide, while the spiral wound module needs two flushes of special chemicals, resulting in higher O&M costs.

This DT RO technology has been used to treat landfill leachate containing elevated TDS, organics and trace metals. The U.S. Environmental Protection Agency evaluated this technology in landfill leachate treatment applications and reported that "…the DT module technology was very effective in removing contaminants from the landfill leachate" (EPA 1998). The removal rate for total organic carbon (TOC), TDS, total metals, and VOCs were 97, 99, 99, and 90%, respectively. The water recovery rate from DT RO was 73% and membrane cleaning was easily achieved.

A DT RO system for landfill treatment was installed in Japan in 1999 and it maintained the expected performance during a 2.5-year test treating high salinity water containing highly-scaling ions (Ushikoshi et al. 2002). Additionally, a full scale DT RO was installed in China for treating landfill leachate and was determined to perform well (Liu et al. 2008).

Technologies to be Tested

This project will utilize two treatment trains to clean oil and gas produced water: (1) physiochemical pretreatment (DAF + organo-clay) followed by DT RO or (2) physiochemical pretreatment (DAF + organo-clay) followed by EDR to reduce organic and inorganic constituent loads in oil and gas produced water. The potential benefit of either treatment train will be the ability to process high volumes of poor quality water with limited membrane fouling, thus, reducing O&M costs of treating produced water using processes already established for other water treatment applications. Potential inadequacies of using RO and EDR technologies for treating produced water are the propensity for membrane fouling and the lack of robust data describing the performance of such treatment trains under demanding on site water quality and climactic conditions.

Development Strategies

Large volumes of produced water, lack of injection sites, and complicated regulatory permitting processes warrant the use of alternative produced water treatment technologies that can treat produced water and meet requirements for surface discharge or beneficial uses such as irrigation and livestock consumption. Although produced water from the oil and gas industry is similar to landfill leachate in terms of TDS and a high scaling potential, technologies such as DT RO and EDR have yet to be thoroughly evaluated for produced water treatment. Therefore, a determination of how these technologies perform in conjunction with pretreatment technologies for treatment of oil and gas produced water is necessary. The potential for high volume through put using these treatment systems make them attractive for produced water management if membrane fouling can be mitigated. This research project will address pretreatment options for limiting membrane fouling as well as optimal blends of treated and untreated water for irrigation.

Future

Successful applications of new technologies such as DT RO and EDR in produced water treatment will help the oil and gas industry reduce environmental impacts during production, realizing beneficial use of produced water in areas where the water supply is limited, such as in the western US. It will also sustain expanded exploration and production of oil and gas from existing operations. This project will provide insight on the logistics and economics of treating produced water with the aforementioned treatment trains as well as optimal blending ratios of treated water with untreated water for irrigation. Additionally, we expect the data obtained regarding optimal water blends to maintain high crop quality/yields as well as good soil permeability will be readily extrapolated to other water treatment methods currently in use such as ion exchange.

References

Ashaghi, K.S., M. Ebrahimi, and P. Czermak. 2007. Ceramic Ultra- and Nano-filtration Membranes for Oilfield Produced Water Treatment: A Mini Review. The Open Environmental Journal 1:1-8.

Burnett, D. and M. Siddiqui. 2006. Recovery of Fresh Water Resources from Desalination of Brine Produced During Oil and Gas Production Operations, Final Report. DOE Contract number: FC26-03NT15427.

Cakmakci, M., N. Kayaalp and I. Koyuncu. 2008. Desalination of Produced Water from Oil Production Fields by Membrane Process. Journal of Desalination 222:176-186.

EPA. 1998. Rochem Separation System, Inc. Disc Tube™ Module Technology-Innovative Technology Evaluation Report. EPA-504-R-96-507.

Hayes, T. and D. Arthur. 2004. Overview of Emerging Produced Water Treatment Technologies. Proceedings of the 11th Annual International Petroleum Environmental Conference, Albuquerque, NM October 12.

Interstate Oil and Gas Compact Commission and ALL Consulting. 2006. A Guide to Practical Management of Produced Water from Onshore Oil and Gas Operations in the United States. Report Prepared for U.S. DOE National Petroleum Technology Office.

Liu, Y., X. Li, B. Wang and S. Liu. 2008. Performance of Landfill Leachate Treatment System with Disc-tube Reverse Osmosis Units. Journal of Frontiers of Environmental Science & Engineering in China 2:24-31.

Miller, J., A. Lawrence, R. Hickey, and T. Hayes. 1997. Pilot Plant Treatment of Natural Gas Produced Water to Meet Beneficial Use Discharge Requirement. Society of Petroleum Engineering (SPE) 37903.

Siler, J. 1993. Novel Disk Modules for Membrane Separation Processes. DOE Contract number: AC09-89SR18035.

Ushikoshi, K., T. Kobayashi, K. Uematsu, A. Toji, D. Kojima and K. Matsumoto. 2002. Leachate Treatment by the Reverse Osmosis System. Journal of Desalination 150:121-129.

Veil, J., M. Puder, D. Elcock and R. Redweik. 2004. A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas and Coal Bed Methane. Prepared for DoE NETL Contract No. W-31-109-ENG-38.