

# **Advanced Membrane Filtration Technology for Cost Effective Recovery of Fresh Water from Oil & Gas Produced Brine**

## **Technical Progress Report**

For the period January through December 2004, (Revised June, 2006)

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**Revised Report Issued July 2006.**

**DOE Project Number: DE-FC26-03NT15427**

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## **Abstract**

Produced water is a major waste generated at the oil and natural gas wells in the state of Texas. This water could be a possible source of new fresh water to meet the growing demands of the state after treatment and purification. Treatment of brine generated in oil fields or produced water with an ultrafiltration membranes were the subject of this thesis. The characterization of ultrafiltration membranes for oil and suspended solids removal of produced water, coupled with the reverse osmosis (RO) desalination of brine were studied on lab size membrane testing equipment and a field size testing unit to test whether a viable membrane system could be used to treat produced water. Oil and suspended solids were evaluated using turbidity and oil in water measurements taken periodically. The research considered the effect of pressure and flow rate on membrane performance of produced water treatment of three commercially available membranes for oily water. The study also analyzed the flux through the membrane and any effect it had on membrane performance. The research showed that an ultrafiltration membrane provided turbidity removal of over 99% and oil removal of 78% for the produced water samples. The results indicated that the ultrafiltration membranes would be asset as one of the first steps in purifying the water. Further results on selected RO membranes showed that salt rejection of greater than 97% could be achieved with satisfactory flux and at reasonable operating cost.

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### INTRODUCTION

Oil and gas operations on leases that have been on production for extended time produce copious amounts of brine water along with the associated oil and gas. Produced water, (any water that is present in a reservoir with the hydrocarbon resource) is produced to the surface with the crude oil or natural gas. Not only in Texas, but world-wide, the oil and gas industry is experiencing increased volume of produced water handled in both onshore and offshore petroleum production operations. The resulting operational costs and environmental issues are a major concern, especially with the possibility of further reduction in the oil content allowed in the discharged water (offshore operations), as well as the fact that produced water contains a number of undesirable toxic components.

Figure 2 shows a slide from Shell Oil Company on that company's production of brine worldwide in the past decade [10]. On average, Shell's operating units re-inject 55% of produced water and discharge the remainder to the environment. Practically all of the produced water must be treated to remove harmful contaminants. Treatment and disposal costs for Shell are greater than \$400 million annually. According to Shell's Zara Khatib, disposal can cost from \$.50 to \$50 per 1,000 gallons of water handled [1].

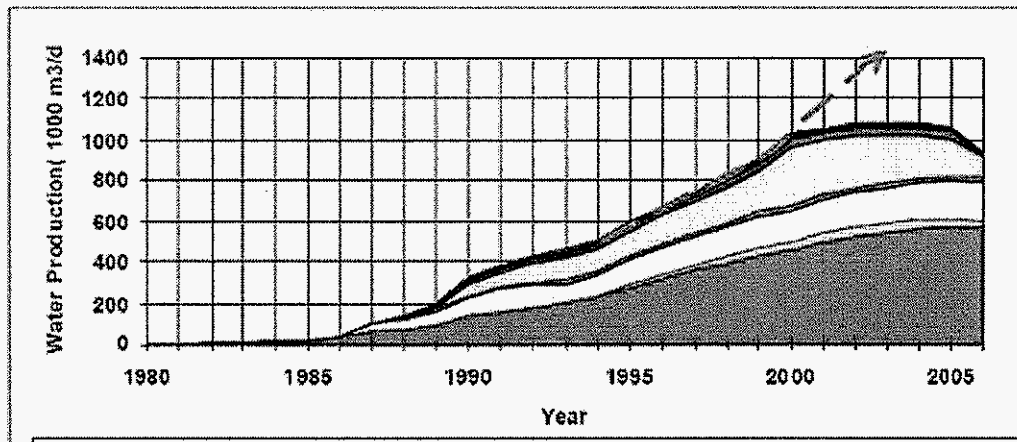


Figure 1. Oil field produced water volume trends

The chart shows each of the five major operating areas for Shell Oil. (1,000 m<sup>3</sup> = 6289 bbls). The trend increases in each of the areas until (assumed) new technology can intervene.

For the United States, the U.S. Department of Energy estimated more than 18 billion

barrels per year were generated from onshore wells in 2000, and similar volumes are generated today [2]. Offshore wells in the United States generate several hundred million barrels per year of produced water. Internationally, three barrels of water are produced for each barrel of oil. Production in the United States is more mature; the U.S average is about 7 barrels of water per barrel of oil. Closer to home, in Texas the Permian Basin averages more than 9 barrels of water per barrel of oil and represents more than 400 million gallons of water per day processed and re-injected [3]. New technology is needed to forestall these trends.

To speed up the adoption of technology, the industry has established a number of techniques for handling produced water in both mature fields and in new and planned developments [4, 5]. These practices take into consideration the nature of the water, technology limitations, both emission to the atmosphere and discharges into the sea, nature of the discharges, safety concerns and cost, as well as establishing any environmental gains in each case. The integrated oil company Shell uses a systematic empirical ranking and indicator tool applied to the different aspects of the alternative options considered. Most operators, big and small, handle produced water management in the same way. (Most often in Texas however, the option is brine injection back into the producing formation.)

Management of water issues is a major emphasis of the DOE's Oil and Gas Environmental Program administered by the National Energy Technology Laboratory's National Petroleum Technology Office [6]. Water issues include several concerns: injection water, produced water (including Coalbed Natural Gas-CBNG) and its effects on the environment, treatment of waste water, and the availability of water in arid lands. NETL currently has 26 projects grouped under Water Management Approaches and Analysis, Water Management Technologies, and Coalbed Methane and Produced Water. The shared goal of all of these projects is to ensure that water produced through oil and gas development does not adversely impact the environment and that it is put to beneficial uses where possible.

### **Managing Produced Water**

Oil and gas operators re-inject practically all their brine into leases to provide pressure maintenance\* and to sustain production. Mature leases gradually end up re-cycling water until the field reaches its economic limit. Many gas fields and smaller oil leases have produced water transported to commercial salt water disposal wells. Figure 3 shows gas well distributions in Texas. Production is found in practically every county.

To handle produced water, the O&G industry operates a large number of injection wells to re-inject the water to maintain production. All wells in Texas are regulated whether by the Texas Commission on Environmental Quality (TCEQ) or the Texas Railroad Commission (TRC) Records of where produced water is currently being disposed and practices in different regions of the state are kept by the TRC organized into oil, gas, and water production for each district in the state. That data has been combined with United States Geologic Survey (USGS) databases. The USGS database is extensive, compiled in

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\* Oil field terminology can be obtuse. The Society of Petroleum Engineers maintains a Glossary dedicated to the definition and interpretation of important oil field terms<sup>1</sup>.

the past 50 years on formation waters to characterize the type of brine that is being produced. Additionally costs of current methods of managing produced water have been obtained from operators and from companies that transport and dispose of brines in salt water disposal wells. Additional information on formation water and produced brine is also available from the West Texas Geological Society.

Texas producing fields are representative of most major, mature production areas in the U.S. because it has long been one of the top petroleum producing states in the nation. As fields have matured, more brine water is produced along with the petroleum resource. More brine water is being re-injected as well, to sustain production, prevent subsidence, and to dispose of excess produced brine. Texas has long been struggling with a lack of water resources and as the population of the state grows, more demand is being placed upon surface and ground water sources of fresh water. As these issues become more important, more attention is turning to recovery of fresh water from these brine byproducts of O&G activity.

Unfortunately, produced brine cannot be used without treatment to remove harmful substances. Untreated produced brine has contaminants that make it unpalatable for humans or livestock. Re-injection of the brine back into the formation from where it was produced has been the least expensive, hence preferred disposal method for brines. Other issues include:

- (1) Desalination of wastewater such as oil field brine can be expensive.
- (2) Oil and gas companies are not water providers.
- (3) Less expensive surface and ground water has provided adequate supplies of fresh water for communities, livestock and agriculture interests.

Most of these issues are the result of the characteristics of oil field brine. Large quantities of produced water are brought to the surface in Texas as a result of various natural resource extraction activities. The composition of this produced fluid is dependent on whether crude oil or natural gas is being produced and generally includes a mixture of either liquid or gaseous hydrocarbons, produced water, dissolved or suspended solids, produced solids such as sand or silt, and injected fluids and additives that may have been placed in the formation as a result of exploration and production activities.

Texas A&M initiated its study in 2001 to determine whether desalination of produced brine offers promise as a source of fresh water resources. A number of companies are also working to assess the economic and technological feasibility of desalting this product water to develop water of sufficient quality to meet certain local water supply needs and to allow consideration of disposal options other than well injection. At Texas A&M University, a team of scientists and engineers is working on this concept and is working to further the technology and put it into commercial practice.

Specific research needs are harder to prioritize. For the past five years A&M has worked to find technologies to employ in desalination and to outline ways to establish a value for the resource that is recovered by this treatment. The research has found that the technology is available to desalinate certain brines produced in petroleum operations. However, that technology needs to be improved, the value of fresh water and local water supply needs must be established, and the environmental and regulatory issues associated with beneficial use must be addressed.

## **EXECUTIVE SUMMARY**

### **Goals**

The goal of the project has been to develop improved RO (reverse osmosis) membrane filtration technology for treating waste water produced during oil and gas production operations.

### **Objectives**

The objectives include evaluation of a new pre-treatment technology using combinations of liquid-liquid centrifuges, organoclay absorbents, microfiltration, and the evaluation and modification of different oil resistant membrane materials and membrane types. We will also develop a dynamic model using variable feed flow, trans-membrane pressures, and recycling ratios to permit optimization of a process design. We plan to experimentally validate models and the equipment process trains.

### **Investigators**

Performing the work is a team from the Harold Vance Department of Petroleum Engineering. Dr. Maria Barrufet and her graduate assistants are designing the process models, while David Burnett and his associates are constructing the filtration train and testing its operation. Leading the pilot plant operation of the team is Mr. Carl Vavra.

### **Advancements in RO Process Design**

In 2004 Dr. Maria Barrufet's technical paper was accepted for presentation at the SPE Annual meeting in October 2004. The paper describes a model integrating pre-treatment with RO filtration. The model is based upon experiments conducted in both laboratory and field conditions. This model will be used to scale-up a process to any desired throughput rate and specifications. Simulation results indicate that that by proper integration and configuration of adsorption and RO units can provide up to 90% efficiency. An abstract of her paper is in Appendix 2. NOTE. The process design model is part of the GPRI Joint Venture and is confidential. Dr. Barrufet will work with anyone wishing to perform simulations using the model.

Dr. Barrufet visited the scientists at the research facility of Total Oil and Gas in Paris France in July to discuss A&M's process design model. Total (formerly TotalFinaElf) has both oil and gas production world wide and, like other operators, faces increasing costs to manage produced water. In Texas, Total has a lease in Star County that is in the proximity to Key Energy's salt water disposal facility. (Key Energy is also a sponsor of the A&M GPRI project.)

## EXPERIMENTAL

### Field Trials

In late 2004, the team completed the first “field trial” of the desalination unit on the A&M campus at the water treatment plant located at the Brayton Firefighter Training Center. Figure 1 shows the mobile desalination unit on site during preliminary testing. This unit has a capacity to deliver from 2,000 gpd to 5,000 gpd depending upon the salinity of the water to be treated.



**Figure 2 shows the GPRI desalination trailer during its trial run.**

The test was conducted at the water treatment plant on the A&M campus. Filter efficiency and filter cleanup can be readily measured for a number of agents, and oil/water systems with the mobile unit.

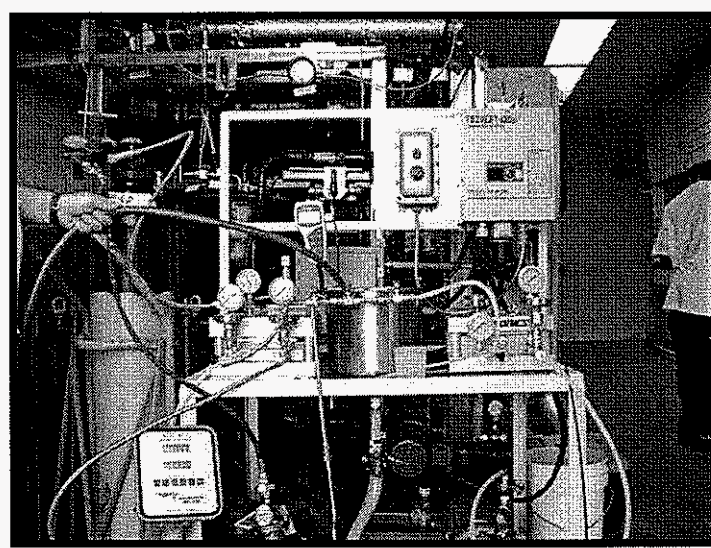
Preliminary tests showed promise. Oil content (residual diesel and combustion products) was reduced more than 90%. Data from the meters indicated that the electrical power required to perform the water conditioning (pre-treatment steps) was less than (\$.02 per barrel of fresh water (\$0.50 per 1,000 gallons)).

### Current Pilot Plant Trials

In the fall of 2004, tests were run on new membrane types, new backwashing procedures and new cleaning procedures were planned to extend operating time of the filters. A small scale flat sheet membrane test work station has been constructed to use in the pilot plant. The unit can be operated either at low or high pressures and can test membrane performance with less effort than with large scale systems. The unit is being used to evaluate the performance of new types of low pressure membrane. It will also be used to



evaluate new types of cleaning materials being developed in a separate DOE project.



**Figure 3. The small scale membrane test rig.**

The unit can test separation of fluids of five liters volume or greater. The system allows operations to 1,000 psi with flat membrane sheets. This unit is being used to test actual field produced water brought to the pilot plant from Key Energy's Grimes County disposal well.

## **RESULTS AND DISCUSSION**

The project will continue a three-year A&M program studying the beneficial re-use of produced water resources from oil and gas operations. We expect that new materials and procedures, when used to desalinate produced water, will reduce treatment costs by 50% or greater.

Testing using our prototype portable units has shown that membrane filtration technology can treat such brines and recover fresh water for beneficial use at a cost comparable to disposal. Now new technology has been developed that offers the potential to allow RO desalination to be employed for large-volume systems and to recover a greater fraction of fresh water from the produced brine.

The technology offers significant savings in produced water management costs to operators, while the resulting fresh water can be used for rangeland and habitat restoration, stream flow augmentation, or treatment of saline ground waters threatening fresh water aquifers.

## CONCLUSIONS

Once an optimal design for the unit has been determined the trailer will be taken to a field site operated by Key Energy Inc. (Key Energy operates salt water disposal wells (SWD) in Texas and surrounding areas). Once on site, the unit will be tested for cost effectiveness in a series of long term operations.

We are also working with the TRC (Texas Railroad Commission), the regulatory agency for the oil and gas industry in Texas, and with the TCEQ (Texas Commission on Environmental Quality), the agency responsible for clean water regulations in Texas.

## REFERENCES

1. Kathib, Z. and ver Beek, P. "*Water to Value- Produced Water Management for Sustainable Field Development for Mature and Green Fields*," paper SPE 73853 presented at the SPE International Conference on Health, Safety and the Environment in Exploration and Production, Kuala Lumpur, March 2002
2. U.S. Department of Energy "Eye on the Environment", Water Resources Issues, Spring, 2004.
3. Texas Railroad Commission Digital Information, Districts and Wells <http://www.rrc.state.tx.us/divisions/og/ogmap.html>
4. Barrufet, M.A. Morales, G. A. "Desalination of Produced Water Using Reverse Osmosis," Gas Research Institute, Gas TIPS, Summer 2002, Volume 8 Number 3 pages 13-17.
5. Georgie, W. J., Sell, D., and Baker, M.J. "*Establishing Best Practicable Environmental Option Practice for Produced Water Management in the Gas and Oil Production Facilities*" SPE 66545, presentation at the SPE/EPA/DOE Exploration and Production Environmental Conference, San Antonio, Texas, 26-28 February 2001.
6. U. S. Department of Energy National Energy Technology Laboratory, Fossil Energy, Drilling & Completion Research Projects, <http://www.fossil.energy.gov/fred/feprograms.jsp?prog=Gas/Oil+-+Drilling,+Completion+and+Stimulation>