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

Technical Progress Report

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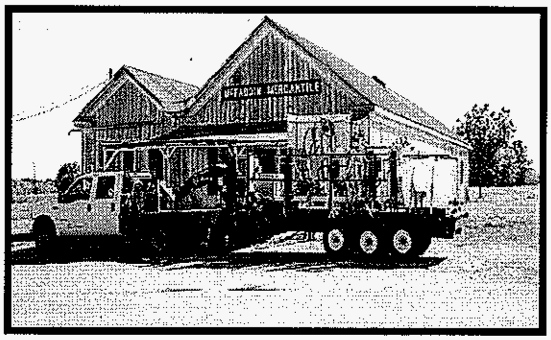

ABSTRACT

This study is developing a comprehensive study of what is involved in the desalination of oil field produced brine and the technical developments and regulatory changes needed to make the concept a commercial reality. It was originally based on "conventional" produced water treatment and reviewed (1) the basics of produced water management, (2) the potential for desalination of produced brine in order to make the resource more useful and available in areas of limited fresh water availability, and (3) the potential beneficial uses of produced water for other than oil production operations. Since we have begun however, a new area of interest has appeared that of brine water treatment at the well site. Details are discussed in this technical progress report.

One way to reduce the impact of O&G operations is to treat produced brine by desalination. The main body of the report contains information showing where oil field brine is produced, its composition, and the volume available for treatment and desalination. This collection of information all relates to what the oil and gas industry refers to as "produced water management". It is a critical issue for the industry as produced water accounts for more than 80% of all the byproducts produced in oil and gas exploration and production. The expense of handling unwanted waste fluids draws scarce capital away for the development of new petroleum resources, decreases the economic lifetimes of existing oil and gas reservoirs, and makes environmental compliance more expensive to achieve.

More than 200 million barrels of produced water are generated worldwide each day; this adds up to more than 75 billion barrels per year. For the United States, the American Petroleum Institute estimated about 18 billion barrels per year were generated from onshore wells in 1995, and similar volumes are generated today. Offshore wells in the United States generate several hundred million barrels of produced water per year. 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 produces 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.

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INTRODUCTION

Background Information

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.

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. 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. 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. 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

Produced Water Volumes and Composition

The volume of produced water from oil and gas wells in Texas (conventional production) is increasing yearly as fields mature and oil production decreases. A majority of the fields in Texas that are still producing petroleum exhibit slowly increasing gas-water ratios or water-oil ratios. This means that the total liquid production tends to stay constant while the oil or gas volume gradually decreases. The implication for those considering the use of brine for a field is that there is little likelihood of water production ceasing, only that the field and the wells comprising the field may no longer be economical to operate. Only then is the well shut in and abandoned.

With high prices for petroleum, economic recovery of oil and gas allows O&G operators to keep wells on production for longer and longer times. The most recent well abandonment statistics from the TRC show that fewer that 3% of the wells in Texas were abandoned in 2005. Out of 227,796 wells, 6,688 were abandoned and their permits ended. Figure 1 shows how broadly distributed the gas wells in Texas are.

Figure 2 shows the statewide distribution of produced brine. Distribution of produced water is shown for three categories of brine. Approximately 1/3 of the sites represent brines with salinity less than 10,000 ppm tds. This is brackish water and can be treated for only slightly more expense than brackish ground water resources in Texas. The advantage of this is that the cost of producing this water is zero (paid for by the oil and gas production). The degree of difficulty in treating this brackish water is discussed in the following section.

Brackish Water Produced in Texas Oil and Gas Wells

Many of the producing fields in Texas discharge water having less than 10,000 ppm tds (total dissolved solids). Figure 2 shows the state divided into Water Planning Districts. Each district has a number of producing wells that discharge brackish water (<10,000 ppm tds), saline water (10,000 to 50,000 ppm tds), and hyper-saline water (>50,000 ppm tds). The locations of the fields are shown with salinity represented by a different color.. The entries on the map do not contain all of the information listed in the U.S.G.S. data base. There is not a 1:1 correspondence of the map to the tabular list as many of the locations do not have latitude and longitude position locations. For more detailed information, the USGS database should be referenced. The best source for this information for those planning studies of desalination of produced water should refer to the records of each county being considered.

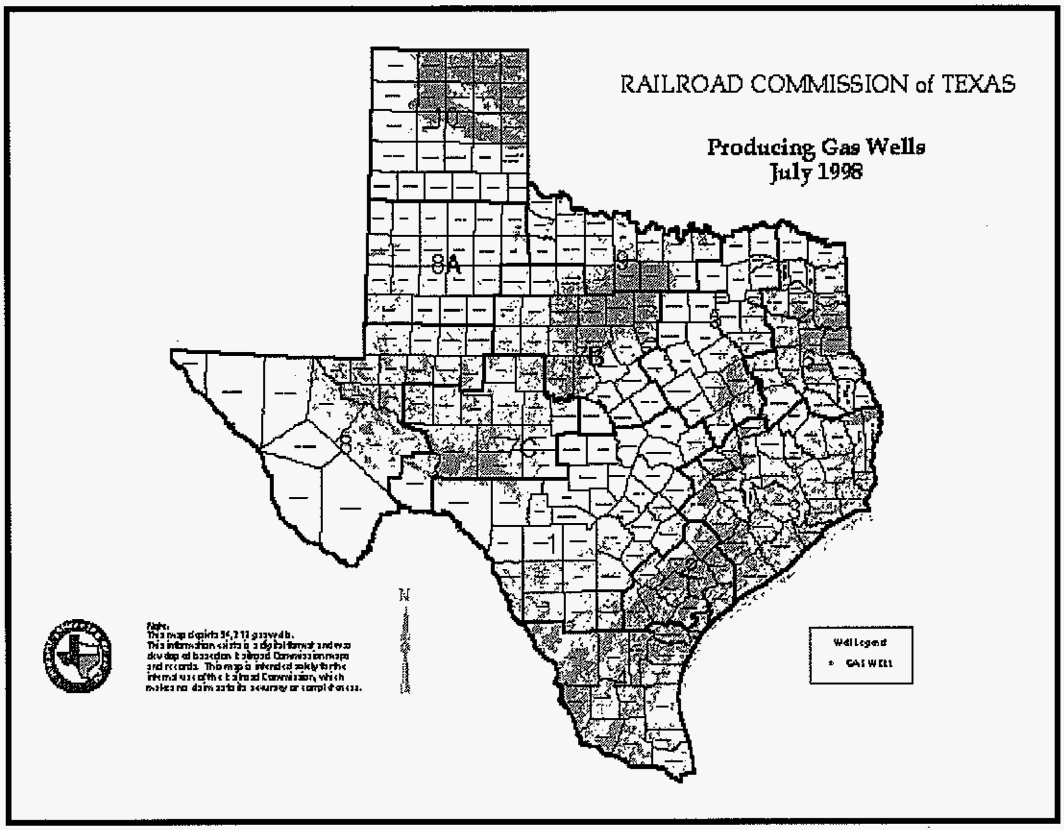

Figure 1. Location of active gas wells in Texas.

There are approximately 300,000 oil and gas wells, 2/3 of these wells are on production. The majority of these wells produce water that is usually re-injected to maintain pressure and production [13].

Desalination of oil field brackish brine may be less expensive because of the disposal options available to the water treatment operator.

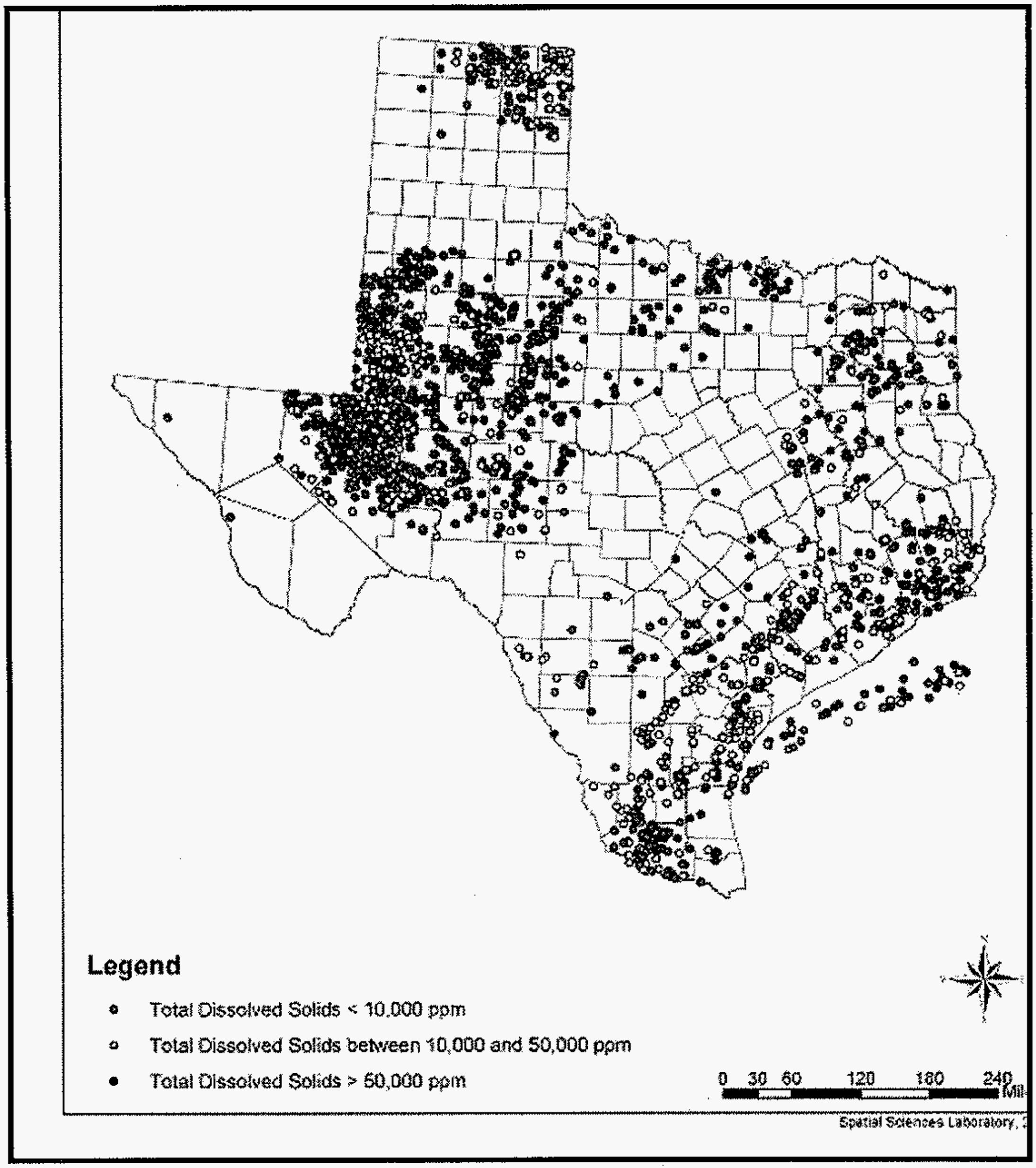

Figure 2. Distribution of produced water sites in Texas.

Approximately 1/3 of the sites represent brines with salinity less than 10,000 ppm tds and can be classified as "brackish water". Detailed maps of wells producing brackish water in each Water Resource Planning District are available from the A&M desalination group.

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.

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 of Project

The overriding goal is to develop improved RO (reverse osmosis) membrane filtration technology for treating waste water produced during oil and gas production operations. A specific goal is to identify technology that can reduce the cost of membrane filtration.

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 are also developing a dynamic model using variable feed flow, trans-membrane pressures, and recycling ratios to permit optimization of a process design. Studies have experimentally validated 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.

Program funds have provided a graduate assistanceship and the education of one Masters Student, Mr. Scott Beech who will graduate in August 2006.

Experience has shown that membranes can be effective pre-treatment techniques and RO membranes can provide desalination at less cost than the cost of brine disposal. Testing has also shown that desalinating brackish oil field brine is more expensive that desalination of BGW but concentrate disposal will be less expensive. Newer desalination technology is also continuing its advance in the field of industrial, food, and pharmaceutical industries.

The A&M Mobile Desalination Unit was constructed to test both pre-treatment by membranes and RO desalination at field sites. Different types of membranes are tested and RO salt rejection efficiency can be determined directly. It is equipped to run either single stage or multi-stage membrane treatments and can be configured either for parallel or series membrane flows. The unit is shown in Figure 3 in Washington County, Texas in 2006.

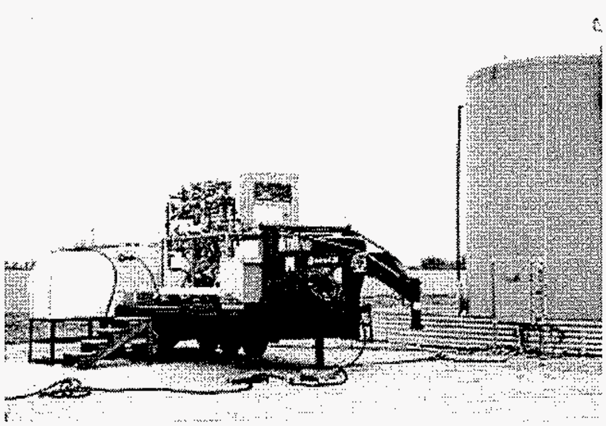

Figure 10. The A&M Mobile Desalination Unit.

The unit is shown at a well site in Washington County, Texas in early 2006. The unit took brine from the fiberglass storage tank (shown on the right of the picture) performed pre-treatment by micro-filtration, then de-salination by RO. Fresh water was directed to the tank to the left rear of the unit.

In addition to testing the capability of different types of membranes, the unit has power transformers to utilize oil field power and an electrical meter to measure power consumption, one of the highest cost factors in desalination. The cost of desalination is directly related to the power used to pump brine past the filters. As salinity increases, power consumption rises. Data from four different field sites are given for comparison, collected on four types of saline feed brines. Table 4 shows this comparison of electrical power costs.

Table 1 Representative power costs of desalination of oil field brine.

Salinity of Feed Brine, tds (ppm)	Power Costs Kw Hr per 1,000 gal. Permeate			
	Pre-treatment	RO desalination	Operating Cost, $ per 1,000 gal.	Operating Cost, $ per bbl
Contaminated Surface water ~1,500 tds.	$.65	$1.25	$1.90	$0.08
Gas well produced brine ~ 3,600 tds.	$2.50	**$2.00**	**$4.50**	$0.19
Oil well produced brine ~50,000 tds	$2.20	**$6.00**	**$8.20**	$0.34
Gas well produced brine ~ 35,000 tds	$2.00 (est.)	**$4.20 (est.)**	**$6.20 (est.)**	$0.26

The information in the Table should be used for estimates only. The prime performance monitor should be salt rejection efficiency, then operating cost. Two types of pre-treatment micro-filters were used. In addition, a new low pressure RO filter was employed in the oil well test. Salt rejection efficiency of the low pressure membrane was lower than the filter used earlier.

The energy cost of operating the desalination facility represents roughly one-third of the total operating costs. Using one of the examples given in Table 4, for desalination on-site of brackish produced water from a gas well, the total operating costs would be less than $10 per 1,000 gallons of fresh water produced ($.42 per bbl). For comparison, the operator of the well pays approximately $1.50 per barrel to truck the water to a commercial salt water disposal well. For this example, the field data indicate that a dedicated desalination unit on the site could reduce the water hauling volume by 50% and the total water hauling costs by almost 20%. For this example, the land owner was offered the fresh water for no cost. Under some circumstances, the fresh water represents income to the operator.

EXPERIMENTAL

Field 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 was constructed to use in the pilot plant. The unit operates either at low or high pressures and tests 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.

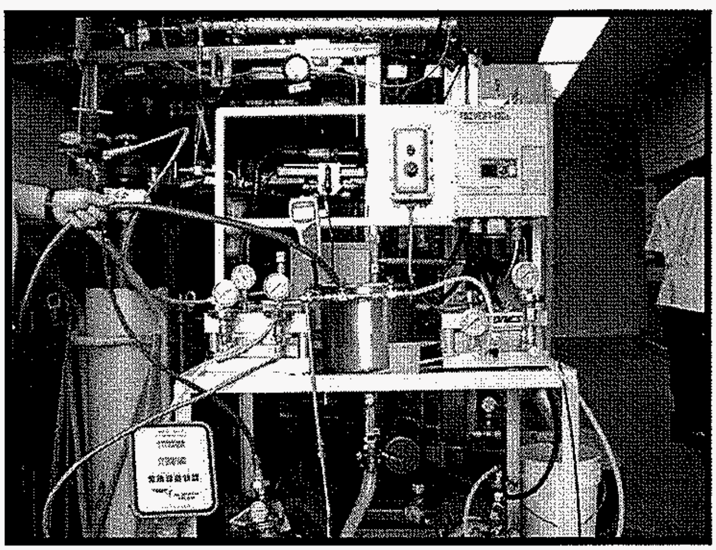

Figure 3. The small scale membrane test rig.

This 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.

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.

Efficiency of Desalination Unit

Desalination Efficiency

RO membranes are chosen on the basis of salt rejection, longevity, and efficient transmembrane pressure (TMP). The membrane being used for the majority of the testing program has performed well over a range of salinities and overall brine compositions. Table 1 shows the results of a one-pass throughput using membrane "DM".

Table 2. Salt Rejection Efficiency

Analyte	Raw Feed	RO filter permeate	Reduction
Alkalinity, Total as CaCO3	188	34	82%
Bicarbonate as HCO3	230	41	81%
Carbonate as CO3	< 1.2	1	n/d
Hydroxide as OH	< 1	1	n/d
Conductivity	33000	2270	93%
Magnesium	73	1	99%
Silicon	78	2	97%
Calcium	1055	23	98%
Potassium	124	5	96%
Sodium	11570	416	96%
Boron	87	34	61%
Silica	1664	4	99%
pH	6.1	7	
Solids, Total Dissolved TDS/180 C	38300	1291	97%

The example shown in the Table reveals that permeate from the RO treatment of a saline produced water will likely meet NPDES standards for potable use.

Operating Cost and Power Usage

The two major cost components of oil field brine desalination are (1) removal of suspended solids (pre-treatment) and (2) removal of dissolved solids (desalination). Desalination costs of saline brines are similar to conventional seawater desalination. Estimated costs for several seawater desalination facilities along the California coast range from $2.25 to $3.70 per 1,000 gallons ($711 to $1171 per acre-foot), a substantial decrease from the 1993 cost estimates of $3.17 to $12.70 per 1,000 gallons ($1000 to $4000 per acre-foot). During the same period, the cost of water from other sources in California has steadily increased. In 1991, the Metropolitan Water District of Southern California ("MWD") paid approximately $27 per acre-foot for water delivered from the Colorado River and $195 per acre-foot for water from the California Water Project. Now, MWD pays an average of $460 per acre-foot for delivered water.

In Texas, the three proposed desalination facilities on the Gulf Coast have cost estimates ranging from $3.58 to $4.23 per 1,000 gallons ($1,000 to $1,300 per acre-foot). These cost estimates include a "transference" cost representing the cost to deliver raw water to the RO facility and to deliver fresh water to existing municipal water lines. The estimates also include amortization of the facility (~25 years) and operation and maintenance costs.

The economic justification for desalination of oil field brine is entirely different than the cited examples. O&G production savings would come from the deferred cost of disposal of the excess brine from operating facilities. Enhanced oil recovery processes also require water that must have relatively low salinity. Rather than utilize fresh water from ground water sources, the industry has tried desalination of produced water extensively. One large-scale program to desalinate brackish produced water was in Crockett County Texas. Marathon Oil Company constructed and operated a facility producing 714,000 gallons per day (17,000 barrels per day) to supply feed water for steam flooding operations. The cost of the water treatment (no infrastructure costs) was reportedly less than $2.50 per 1,000 gallons. The steam flood was projected to boost oil production in the Yates Field by more than 100,000 barrels of oil. The facility was deactivated when more advanced oil recovery technology was developed.

More recently, pilot tests of a produced water treatment by membrane technology was performed in the Burgan Field, Kuwait to test the removal of dispersed oil. Over a five-month period the unit operated at an oil rejection efficiency of 83% to 89%.

Experience has shown that membranes can be effective pre-treatment techniques and RO membranes can provide desalination at less cost than the cost of brine disposal. Testing has also shown that desalinating brackish oil field brine is more expensive that desalination of BGW but concentrate disposal will be less expensive. Newer desalination technology is also continuing its advance in the field of industrial, food, and pharmaceutical industries.

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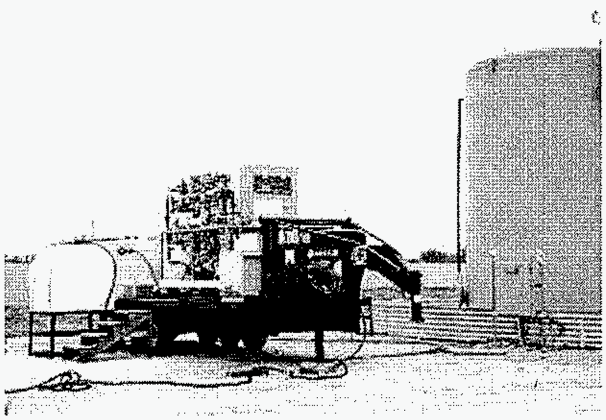

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RESULTS AND DISCUSSION

In addition to testing the capability of different types of membranes, the unit has power transformers to utilize oil field power and an electrical meter to measure power consumption, one of the highest cost factors in desalination. The cost of desalination is directly related to the power used to pump brine past the filters. As salinity increases, power consumption rises. Data from four different field sites are given for comparison, collected on four types of saline feed brines. Table 2 shows this comparison of electrical power costs.

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Desalination Workshops

TWRI and GPRI are teaming with the Food Protein R&D Science Center to propose establishment of an industrial waste water membrane treatment and desalination center. The center will allow industrial separation sciences programs to be separated from the food science research center, provide research capability on new membrane techniques, and allow outreach teaching opportunities.

The Membrane Technology Workshop was conducted by the Food Protein Science Center in March. Attendance was up 50% with 37 people in attendance. Those interested in attending this four day course next year can find more information and register at

http://foodprotein.tamu.edu/separations/scupcoming.htm .

Regulatory Relief

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. The barriers to adoption of desalination of waste water, brackish ground water and oil field produced brine include political issues, community perception issues, and technical issues. The Governor and the TWDB have provided leadership for the State in developing desalination programs in Texas. However, lack of public funding, environmental, and regulatory issues related to desalination of produced water (and other inland saline waters) inhibit technology advancement of this resource. Public perception and acceptance of the advantages of RO desalination is unclear. Cost reduction advancements in technology are slowed by a lack of a clear "path to market" of new products and processes. Supplemental state government funding for demonstration projects (both sea water desalination and inland BGW desalination) is lacking. With these issues affecting the market for commercial development, it is clear that a more concerted effort is needed to develop new water resources from desalination, address conveyance issues associated with water transfer, and be prepared to meet the demand for the new resource if it were to be made available. Some selected issues are discussed below.

The Texas Commission on Environmental Quality has been working with other state agencies to streamline regulations for the permitting process for disposal in deep-underground injection wells of brine produced by desalination operations. Applicants for permits to dispose of brine from desalination in injection wells must meet the current requirements for disposing of hazardous waste in Class I injection wells, including brine from desalination if it is classified as a waste material from "either industrial or municipal facilities". Since injection wells have been used for disposal of salt water associated with oil and gas operations for almost a century, (as Class 2 wells), it is hoped that new cooperative efforts in desalination will allow deep injection wells into oil and gas fields for brine byproduct use in enhanced oil recovery operations. Recent private meetings between TCEQ and the TRC may have removed the roadblock.

CONCLUSIONS

Local issues that communities would identify as barriers include the perception that desalinated produced water is not pure enough for consumption by humans or livestock and that there might be environmental drawbacks to its use for plants, range, and habitat sustainability. It is suggested however, that advanced technology and an improved regulatory climate will increase the likelihood of adoption of PWDS by water use groups in the state.

Schedule for 2006 Activity

Ultrafiltration Membranes

The program calls for a research project to evaluate the treatment of brine generated in oil fields (produced water) with ultrafiltration membranes. The characterization of various ultrafiltration membranes for oil and suspended solids removal from produced water will be studied to test whether they could be a possible pretreatment method. The research will be designed to measure the effect of pressure and flow rate on membrane performance of produced water treatment of three commercially available membranes for oily water. Oil and suspended solids removal are to be measured by using turbidity and oil in water measurements taken periodically.

Hollow Fiber Microfilter Membranes

One of the new pre-treatment techniques scheduled for evaluation will be capillary hollow fiber membranes. Capillary (hollow) fiber elements are comprised entirely of the filtration medium itself (no backing material as in the other configurations that all utilize sheet membrane), although most fibers have a "skin" of the medium on one or both surfaces.

The fiber outside diameters range from about 1 to 2 mm, with IDs in the 0.5 to 1.8mm range. The flow path can be either outside-in or inside-out (lumen feed); however, for all wastewater applications, the outside-in flow is favored, to minimize fouling.

Capillary fiber membrane elements only apply to microfiltration (MF) and ultrafiltration (UF) applications (one company, Norit X- Flow, introduced a nanofiltration element, but has subsequently withdrawn it from the market). A problem in definition must be addressed in discussing MF and UF. Many membrologists use pore size to define these processes, with MF pore sizes ranging from 0.1 to 1.0 micrometers (microns), and UF membranes possessing MWCO characteristics ranging from about 1,000 to 1,000,000. Other experts prefer to define these processes based on their function: MF removes suspended solids only, while UF removes dissolved organic solute based on molecular weight. MWCO is Molecular Weight Cutoff (expressed in Daltons), and is the smallest molecular weight of an organic compound retained by a specific UF membrane. It is extremely difficult to relate pore size in microns (μ) to MWCO in Daltons. A major problem is that organic molecules vary significantly in shape and size, not always in direct proportion to molecular weight. Although there are a number of charts and tables available which relate molecular weight to pore size, there is little agreement among them.

REFERENCES