

**Recovery of Fresh Water Resources from Desalination  
of Brine Produced During Oil and Gas Production  
Operations**

**Yearly Technical Report**

**A Global Petroleum Research Institute Report  
U.S. DOE DE-FC26-03NT15427**

**Performance Period  
January 1, 2006 – December 31, 2006**

**Principal Investigators**

**David B. Burnett, Director of Technology GPRI  
Mustafa Siddiqui, M.S. Petroleum Engineering**

**Harold Vance Department of Petroleum Engineering  
Texas A&M University  
3000 TAMU  
College Station, Texas 77843-3000**

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## ABSTRACT

# Recovery of Fresh Water Resources from Desalination of Brine Produced During Oil and Gas Production Operations

A Global Petroleum Research Institute Quarterly Report

U.S. DOE DE-FC26-03NT15427

Performance Period

January 1, 2006 – December 31, 2006

Management and disposal of produced water is one of the most important problems associated with oil and gas (O&G) production. O&G production operations generate large volumes of brine water along with the petroleum resource. Currently, produced water is treated as a waste and is not available for any beneficial purposes for the communities where oil and gas is produced. Produced water contains different contaminants that must be removed before it can be used for any beneficial surface applications. Arid areas like west Texas produce large amount of oil, but, at the same time, have a shortage of potable water.

### Major achievements of the project 4<sup>th</sup> Quarter

- Sponsored an industry workshop “*The Future of Desalination*” at the Texas A&M University Food Protein Research and Development Center- Separations Laboratory.
- Completed the manufacture of a portable desalination unit that includes micro filter pre-treatment membranes.
- Performed pilot plant studies on produced brines from Anadarko Petroleum Company gas fields in Washington and Grimes Counties Texas.
- Performed Field tests of the portable treatment unit at the Fife No. 3 Well in Washington County Texas.
- Published Technical Paper

The process design developed by the project has been licensed for commercial development by GeoPure Water Technologies LLC. GeoPure is manufacturing 40,000 gpd and 1 MM gpd units for field projects to be kicked off in 2007.

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**Quarterly Report**

**DOE Project Number:**

DE-FC26-03NT15427

**Project Goals**

Since its beginning, the goal of the advanced membrane technology project has been to develop improved RO (reverse osmosis) membrane filtration technology for treating waste water produced during oil and gas production operations. Our most efficient process design to date has been the use of microfiltration as pre-treatment followed by RO desalination. A field mobile test unit has been constructed and is being used to screen various candidate brines for application of desalination technology. The process design developed by the project has been licensed for commercial development by GeoPure Water Technologies LLC. GeoPure is manufacturing 40,000 gpd and 1 MM gpd units for field projects to be kicked off in 2007.

**Testing of Advanced Technology at A&M Membrane Pilot Plant**

Figure 1 shows the project sponsors viewing the RO unit which is used for field demonstrations of the **GPRI Designs™ Desalination Technology**. The unit has been equipped with variable frequency drive to reduce power requirements. In addition, a new type of low pressure RO membrane has been installed to boost recovery efficiency and reduce pressure required for desalination. The unit is in almost continual use at the A&M Pilot Plant to evaluate brine water cleanup from the field sites. Once results indicate a practical desalination process might be feasible in the field, the unit is moved to the well site and run to determine “on-site efficiency” and operating cost.



Figure 1 shows a demonstration of the **GPRI Designs™ Desalination Technology**.

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 than 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. 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 most 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 1 shows a comparison of the cost of pre-treatment with UF and for RO for different types of brine.

**Table 1 Comparison of Desalination Operating Costs.**

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 energy cost of operating the desalination facility represents roughly one-third of the total operating costs. Using one of the examples given in Table 1, 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.

**Figure 2:**

Below shows the desalination trailer at McFaddin Ranch in the summer of 2005. It had been taken to McFaddin to brief area landowners about the potential for brine desalination for agribusiness operations.



**ADDITIONAL INFORMATION SECTION**

- Appendix 1 provides an electronic copy of Dr. Maria Barrufet's SPE paper presented to the Annual Technical Conference in Dallas, Texas, October 8, 2005.
- Appendix 2 provides an electronic copy of David Burnett's presentation to the "Future of Desalination" Workshop in August, 2005.

# Recovery of Fresh Water Resources from Desalination of Brine Produced during Oil and Gas Production.



**David Burnett, GPRI  
Department of Petroleum  
Engineering, Texas A&M  
University**

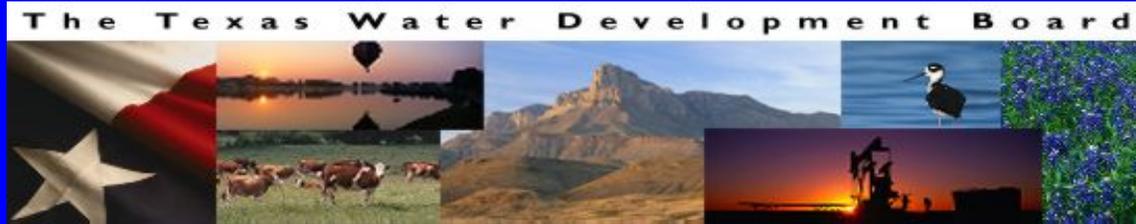
**Dr. C. Allan Jones, Director  
Dr. Bill Harris,  
Dr. Bill Fox,  
Texas Water Resources  
Institute, Texas A&M  
University**

**Dr. Gene Theodori  
Program in Rural Sociology &  
Community Services  
Texas A&M University**

# **A&M Water Resources: The State of Texas Program**

- **Rural Community Outreach**
  - “Drought proofing” projects
- **Critical Habitat/ Rangeland – Grassland Protection**
  - Remediation, restoration of rangelands & wetlands
- **Small Farm/ Ranching Operations**
  - High value use. Small volumes
  - Dispersed water sites
- **Oil and Gas Production Operations**
  - Oil Field Brine Desalination

# State of Texas Partners



**Texas Water  
Development  
Board\***



**Texas Commission on Environmental Quality**

**Texas Railroad Commission**



\*<http://www.twdb.state.tx.us/Desalination>

Texas A&M Desalination Programs, 2004

Slide No. 3

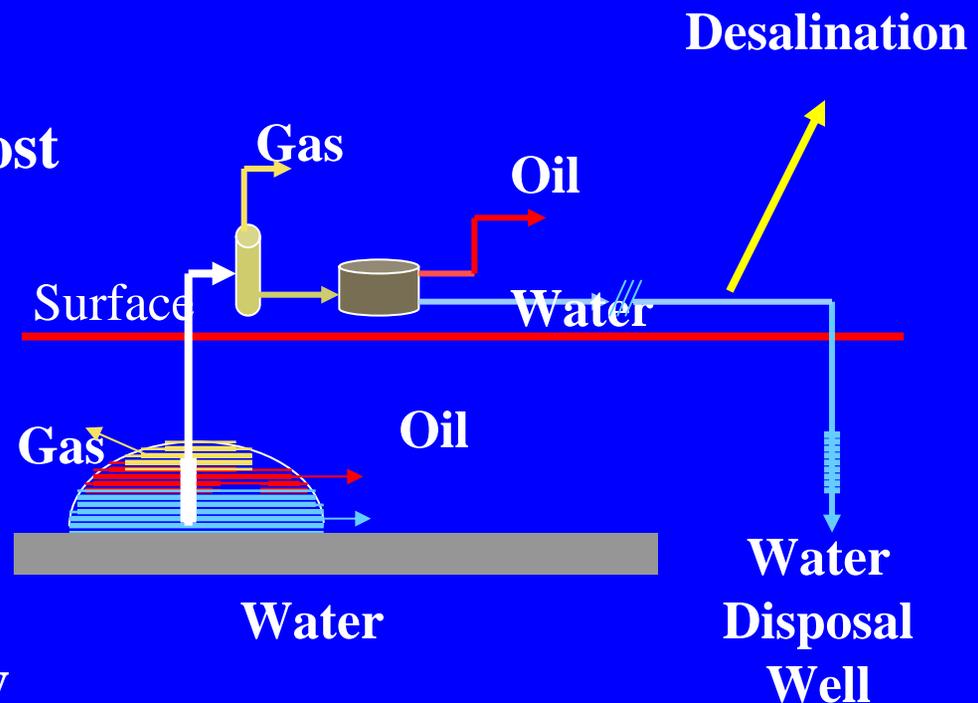
# The A&M Program: What We Do

## Saline Water Injection into Oil and Gas

### Zones

Brine disposal represents a significant fraction of the cost of operating a desalination facility.

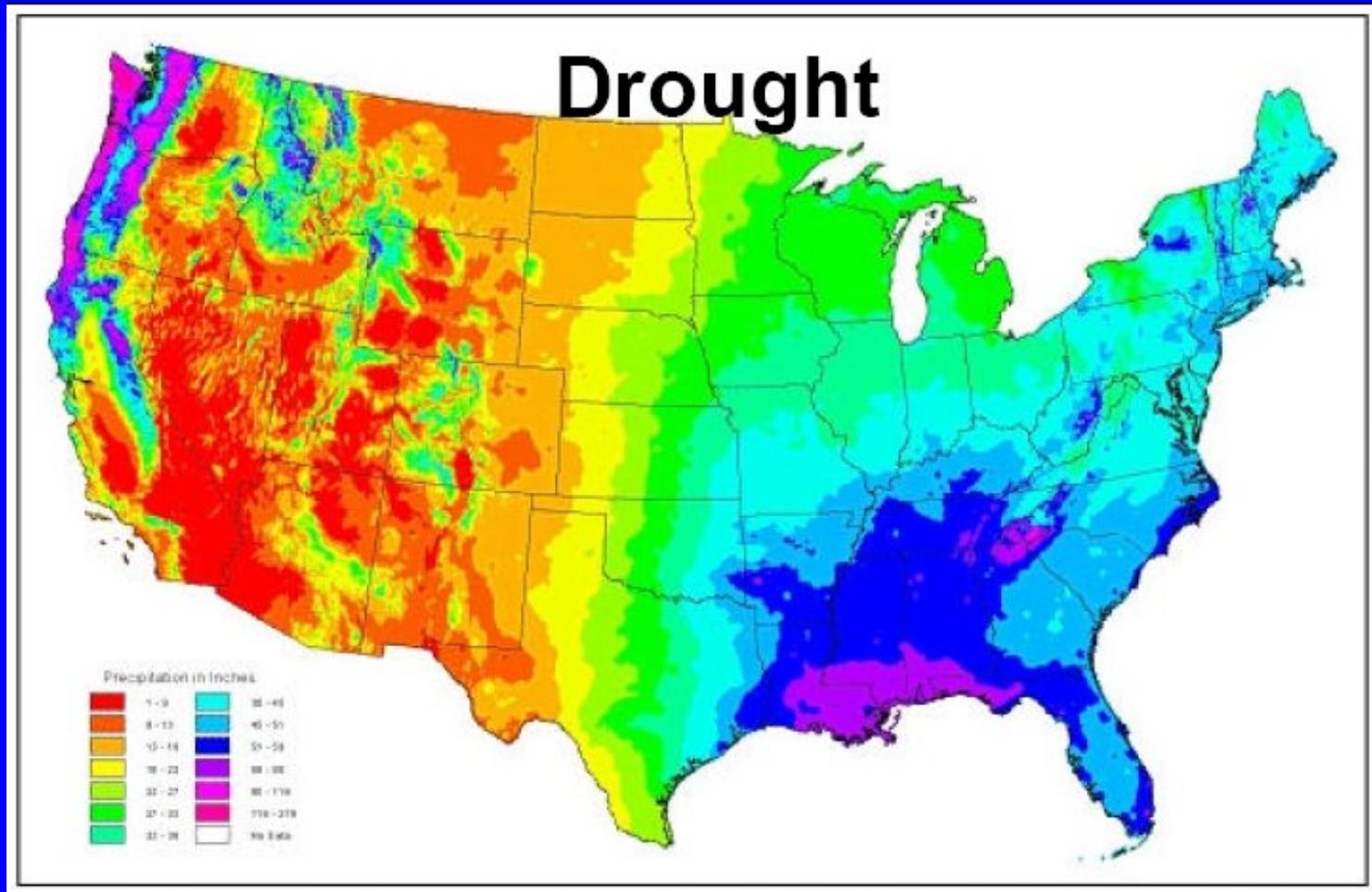
In the oil and gas industry, high salinity brines are routinely injected into formations for pressure maintenance and secondary recovery by water flooding.



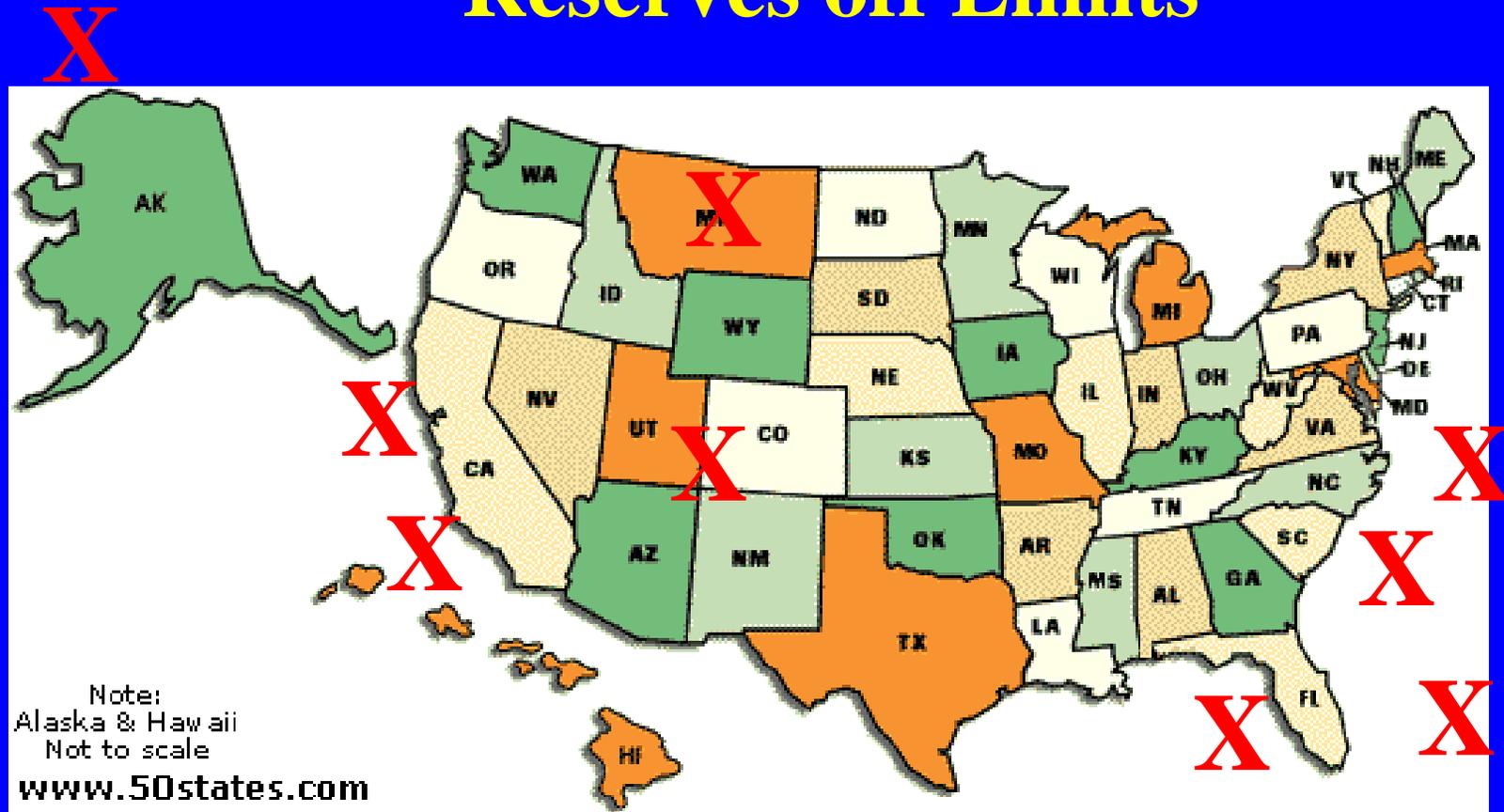
For more Info see:

<http://www.tamu.edu/>

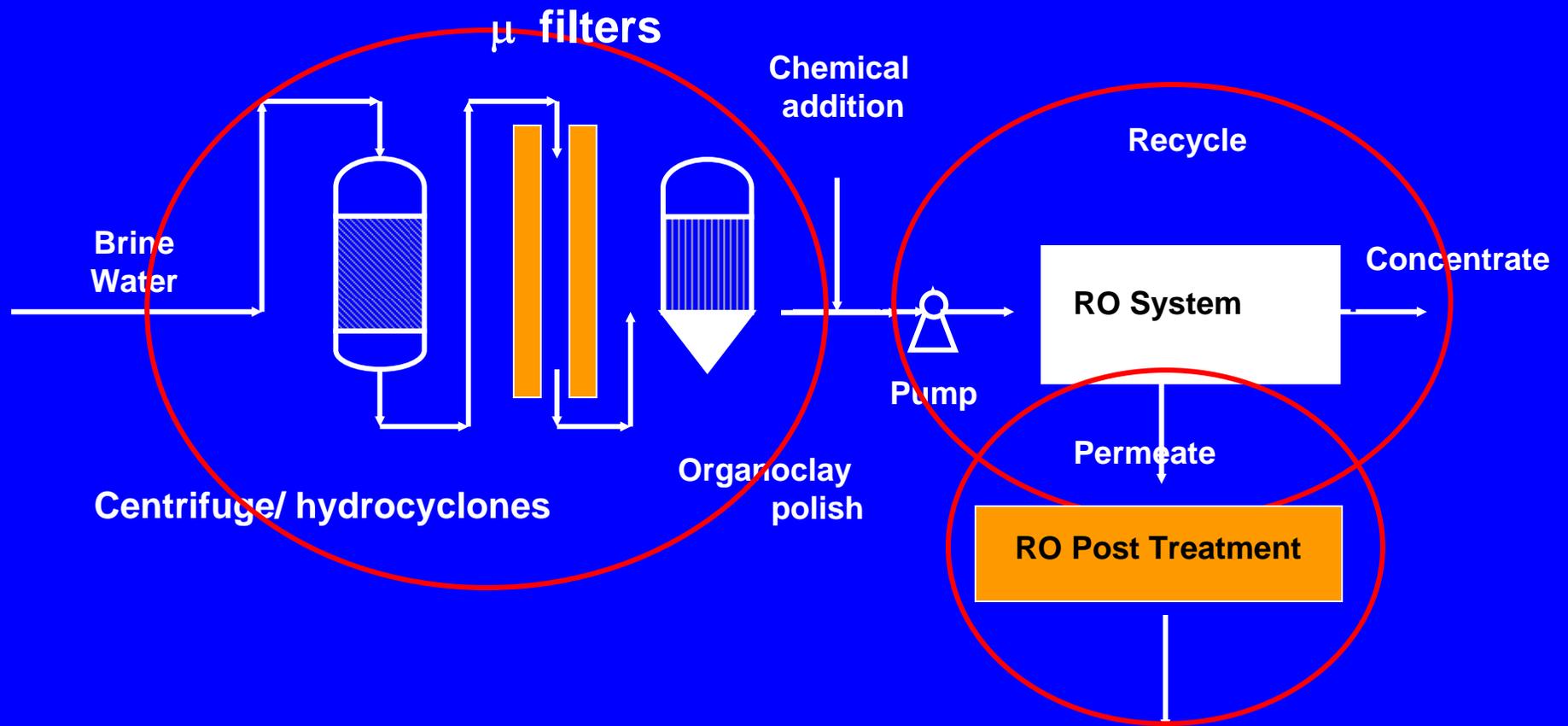
# Lack of Fresh Water Resources



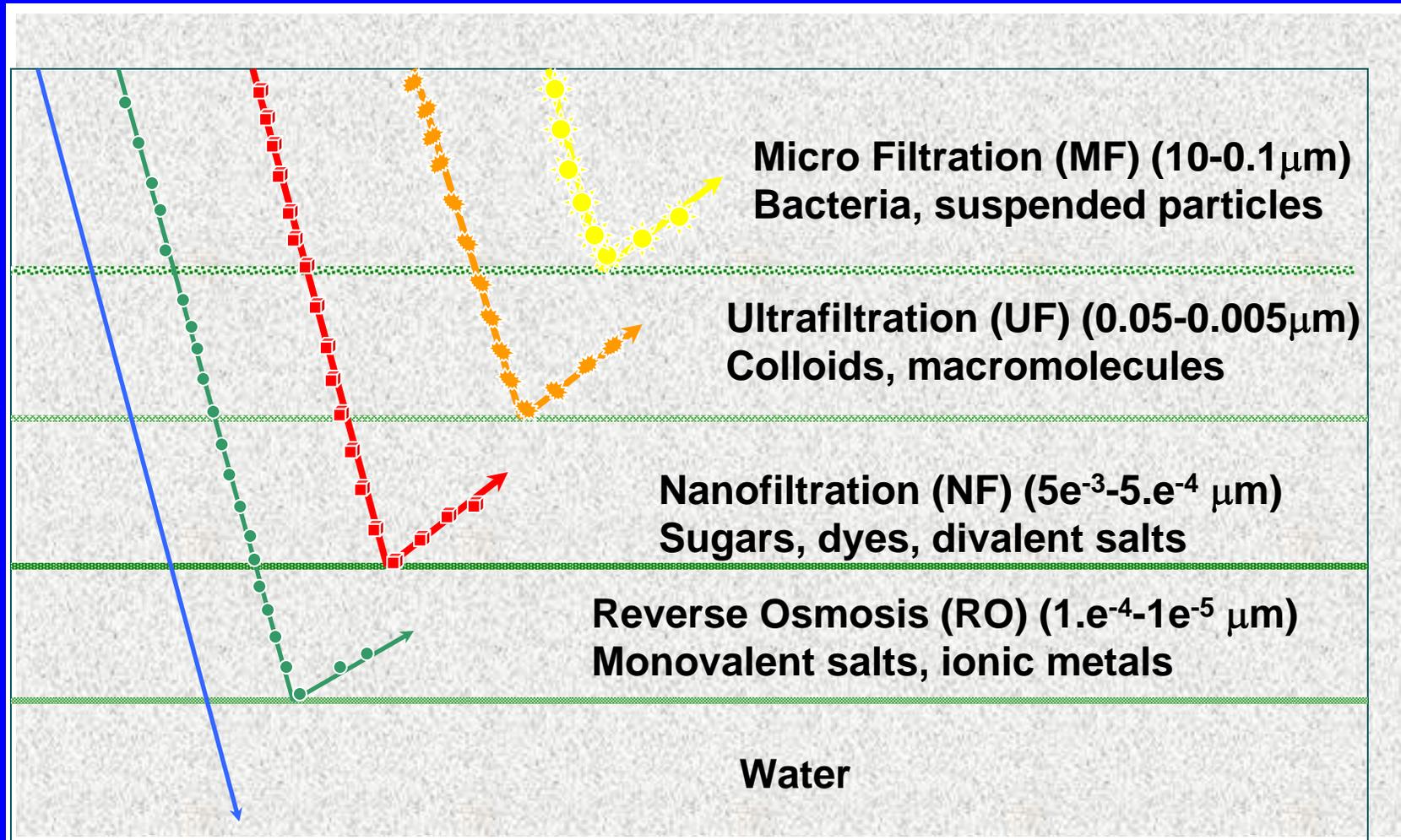
# Environmental Barriers Put Gas Reserves off Limits



## Brine Desalination Process



## Filtration and Reverse Osmosis: Definitions



# **Short Courses & Workshops**

**Original 15th Annual Practical Membrane & Separations  
Technology Short Course: Fundamentals, New Developments,  
Applications and Pilot Plant Demonstrations**

*Organized*

*by*

Separation Sciences Program  
Food Protein Research & Development Center  
Texas Engineering Experiment Station  
The Texas A&M University System  
College Station, TX 77843-2476  
**March 21-24, 2005**  
**College Station, TX**

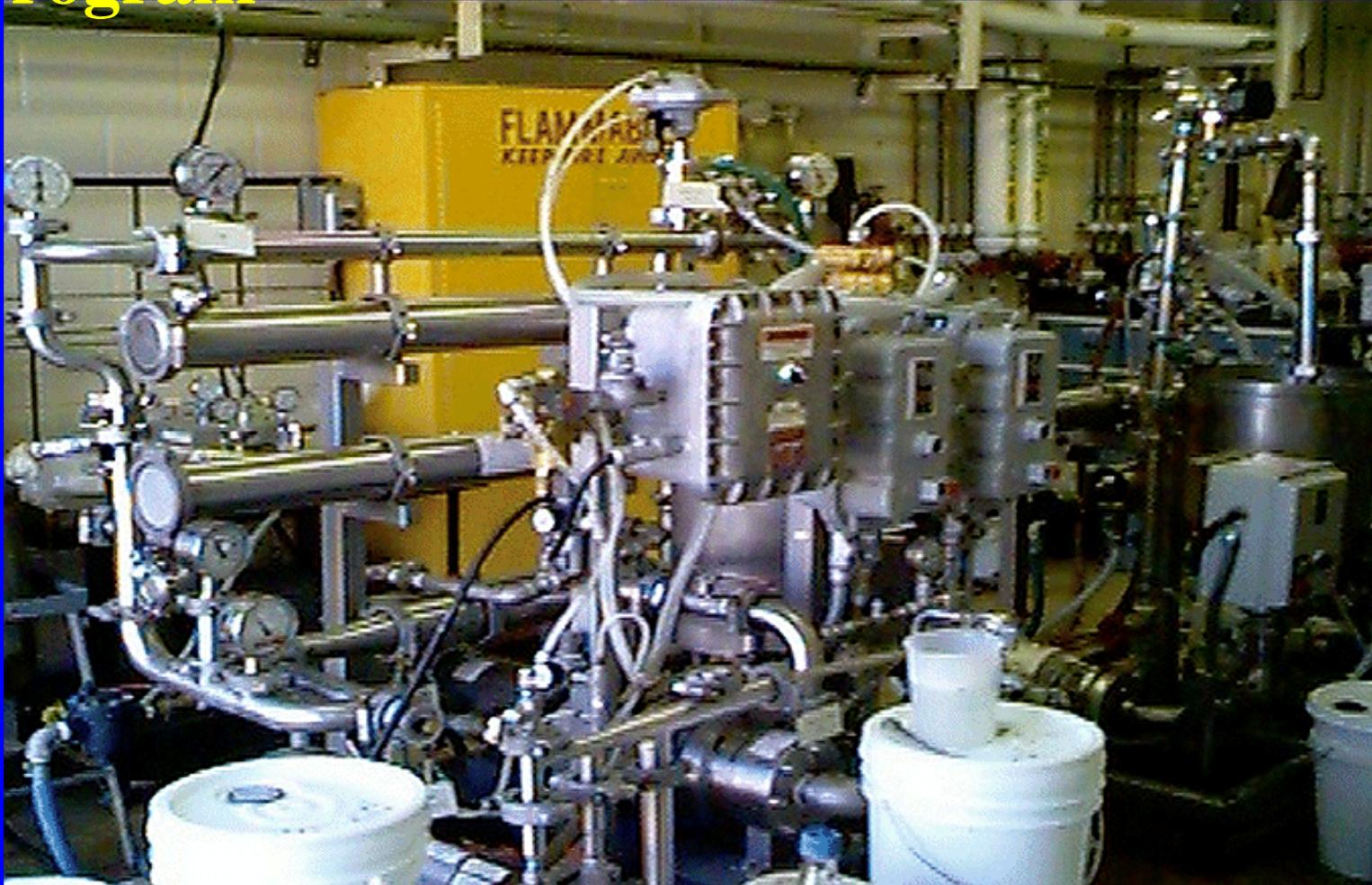
# Facilities: Separation Sciences Laboratory



# Facilities: Waste Water Treatment Program



# Facilities: Produced Water Treatment Program



# Koch Portable RO Unit



# Texas A&M Portable Desalination Rig



# Texas A&M Mobile Test Truck



For more Info see:

<http://foodprotein.tamu.edu/separations/equipmembrane.htm>

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# **Texas A&M Desalination: The “A” Team**

- **Texas A&M University System**
  - **Texas A&M Engineering (TEES)**
  - **A&M Ag Engineering**
  - **Texas Water Resource Institute (TWRI)**
  - **A&M Intl Agriculture Program**
  - **Global Petroleum Research Institute (GPRI)**
- **State and Federal Partners**
  - **Texas Railroad Commission (TRRC)**
  - **Texas Water Development Board**
  - **Texas Department of Agriculture**
  - **U.S. Department of Energy**
  - **U.S. Environmental Protection Council**
  - **U. S. Department of the Interior (BLM)**

# **Texas A&M Partners: How We Function**

- ***Identifying the problems, setting goals***
  - *Example: Roadmap of technology needs for cost effective oil field brine use*
- ***Creating and managing the programs***
  - *Example: TWDB Evaluation of Oil & Gas Industry Technology*
- ***Working to solve community needs***
  - *Example: Department of Rural Sociology Partnership with Howard Co. (Tx) Community College*

## **Premise:**

**Fresh water resources from desalination of wastewater including oil field brine.**

## **Advantages**

- Demand for fresh water is increasing its value.**
- Proximity of the water resource to the place of use.**
- Disposal of waste brine into depleted oil & gas zones.**

## **Disadvantages**

- Additional cost of demineralization of water.**
- The (probable) salinity of the produced brine.**
- Environmental compliance issues.**

# GPRI Field Operations at Burlington Resources

Burlington Resources performs water fracs in the Barnett Shale using water from the Trinity River.



Demonstration units are to be used to treat the frac water for re-use.

For more info see:

Texas A&M Desalination Programs, 2004  
[www.mcog.org/barnettfracs.html](http://www.mcog.org/barnettfracs.html)

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## **Task 2: Development in the Barnett Shale**

**Fresh Water from the Trinity River used for  
Fracturing Treatments**

<b>Devon Energy</b>	<b>~ 20 to 30/month</b>
<b>Burlington Resources</b>	<b>~ 20 /month</b>
<b>Other Operators</b>	<b>~ 30/month</b>

**Each Treatment is ~ 25,000 Bbls**

**Recovery Water Handling ~ 80,000,000 gal/m.**

# Texas A&M Portable Desalination Rig



# Texas A&M Portable Desalination Rig

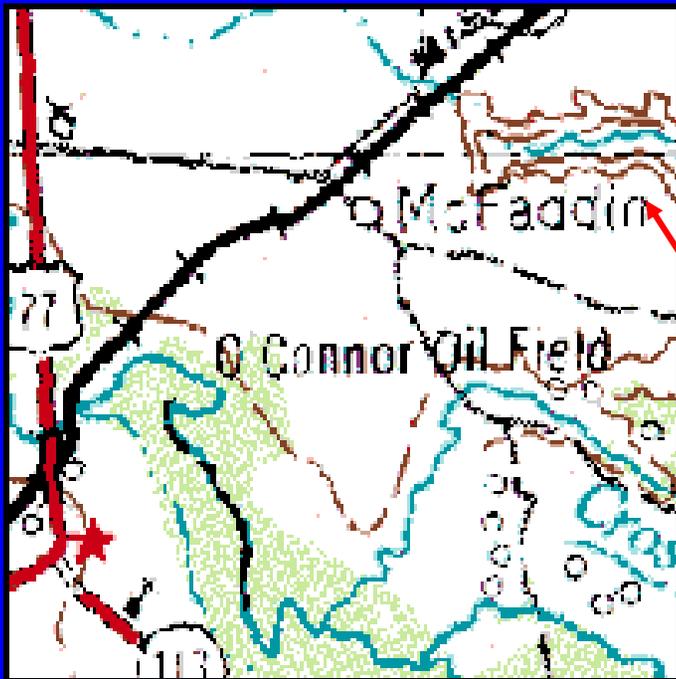


# Texas A&M Portable Desalination Rig



# Oil Field Brine Conversion:

## *Historic McFaddin Ranch & O'Connor Oil Field*

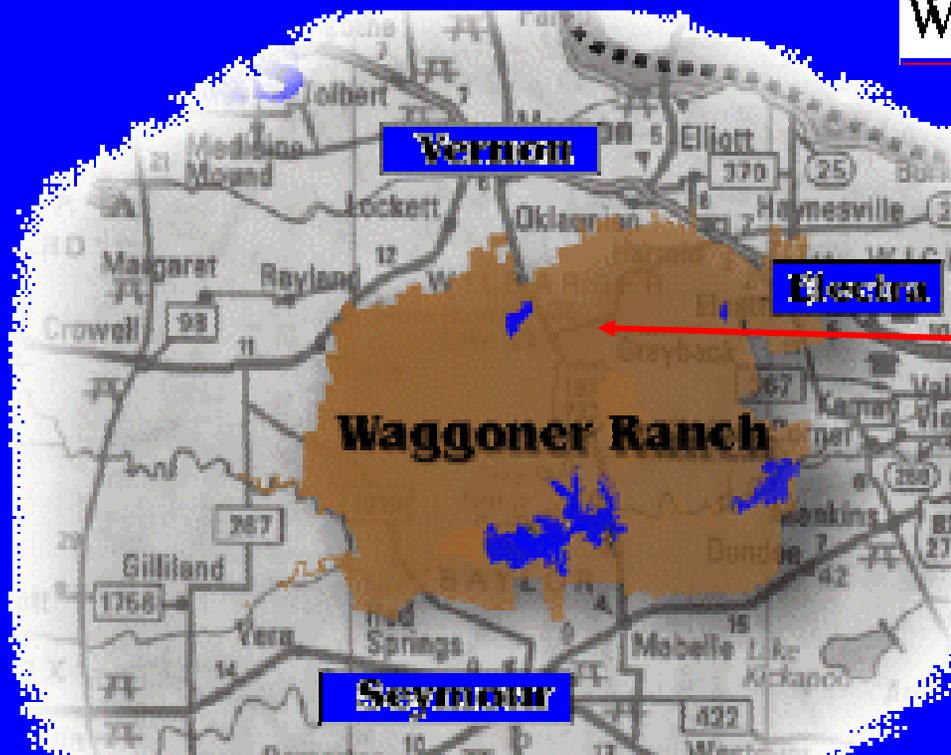


Test Site



# Fresh Water from Oil Field Brine for Livestock Watering

W.  WAGGONER ESTATE



Test Site

# **Texas A&M Programs in San Angelo Area**

**Evaluating Beneficial Use of Treated Produced Water in Arid and Semi-arid West Texas**

**Pilot Testing Water Treatment Technologies in Semi-Arid Regions: Addressing Non-Point Source Pollution through Water Treatment and Ecological Restoration**

**Low Power Water Purification Units for Remote Communities**

# Thank You to Our Supporting Agencies

## Texas A&M University Desalination Project

### Acknowledging

#### GPRI Sponsoring Companies

BP  
Burlington Recourses  
Key Energy  
Tarlton Mfg.  
Total

#### Contractors

Polymer Ventures  
Costner Industries Texas

#### Agencies

Texas Water Resources Institute  
Ground Water Protection Council  
Texas Railroad Commission



Stripper Well Consortium  
Texas Water Development  
U. S. Department of Energy



SPE 95647

## Modeling and Operation of Oil Removal and Desalting Oilfield Brines with Modular Units

Maria Barrufet and David Burnett, Petroleum Engineering Department, and Brett Mareth, Chemical Engineering Department, Texas A&M University

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### Abstract

Oilfield brine is the largest volume of waste generated by the oil and gas industry; typical produced brine volumes may easily exceed the oil production by 10 times with total dissolved solids ranging from 1,000 to over 250,000 ppm. Handling costs of produced brine may lead to the premature abandonment of many oil and gas wells. At the same time that oil and gas operators are trying to cope with excess produced water, many states are critically short of freshwater resources.

This paper describes and validates a process to treat this brine to meet the standards for irrigation-quality water. Components of the proposed brine-conversion plant include both microfiltration and a pretreatment system for the removal of solid particles and oil using sorption pellets made of a modified clay material, and reverse osmosis (RO) units with a variety of interchangeable semipermeable membranes for the removal of dissolved salts.

We collected experimental data for oil/water separation of controlled mixtures using packed columns with modified clay particles. The average oil loading capacity of these particles is better than activated carbon (over 60%) and our experimental results indicate that packed beds can remove over 90% of the oil.

We screened a variety of RO membranes and selected one to conduct a series of experiments with brines with salinity up to 40,000 ppm, transmembrane pressures up to 1,000 psia, and various rates. Our experiments indicate salt rejections of 95 to 99% depending upon the initial salt concentration, transmembrane pressure, and rate.

Based upon these experiments, we modeled and coupled these two processes. Our model can scale up a process to any desired throughput rate and concentration specifications. Simulation results indicate that at proper integration and

configuration of oil adsorption and RO units, depending upon initial total dissolved solids (TDS), up to 90% of the brine may be recovered as fresh water

### Introduction

The general approach for produced water treatment is de-oiling and demineralizing before disposal or use. The removal of oil and grease from produced water has been discussed in the literature by using downhole separators<sup>1</sup>; centrifuges<sup>2</sup>; air floaters, emulsifiers, and hydrocyclones<sup>3</sup>; membrane separators<sup>4</sup>; and adsorbents.<sup>5</sup> In comparison with the many oil-removal techniques, membrane technologies can be efficient, do not create additional waste product, but require large power, and membranes foul frequently and require periodic maintenance. Gravity-separation techniques lose oil-removal efficiency at lower oil concentrations. Oil adsorption is a cheaper and feasible technique although it requires disposal of the used adsorbent media. Produced oilfield brines typically contain oil ranging from 30 to 200 ppm, expressed as total organic carbon (TOC). For demineralization purposes, several methods such as microfiltration (MF), ultrafiltration (UF), ion exchange, and reverse osmosis (RO) are available.<sup>6,7,8</sup> Roberts<sup>6</sup> showed considerable reduction in demineralization cost with RO operation. Evans *et al.*<sup>9</sup> discussed several options for handling produced water including disposal, reinjection, and treatment. Disposal of produced water requires meeting stringent environmental regulations. Produced water reinjection requires skillful planning and treatment to meet the needed quality of reinjection water to avoid formation damage. Mackay *et al.*<sup>10</sup> described risk involved in reinjection. Wan *et al.*<sup>11</sup> showed that treatment of produced water before reinjection gives better performance. Alonzo *et al.*<sup>12</sup> assessed the produced-water treatment and disposal practices and addressed the research needs in this area. Hughes *et al.*,<sup>13</sup> Tao *et al.*<sup>14</sup> and Tsang *et al.*<sup>15</sup> discussed conversion of produced water into irrigation or drinking-quality water in their work. None of these works provides sufficient information on modeling the separation processes for application of produced-water treatments. Here we provide a dynamic model integrating oil adsorption and salt removal using a specific type of organoclay (OC) packed beds and RO units. We based our model upon our experimental characterization of the performance of the organoclay and the RO membrane selected and a rigorous material-balance computation.

**Oil Adsorption: Experimental and Modeling**

We tested a new adsorbent, organoclay-PS12385, for oil removal from produced water. The organoclay-PS12385, manufactured by Polymer Ventures, is a structurally modified clay that does not swell upon adsorption of oil.

Oil adsorption depends upon various parameters such as surface area of the adsorbent material, porosity of bed, residence time in the bed, feed concentration, and bed-packing techniques. The surface area can be increased by crushing the particle size, but too fine a powder may cause plugging and an excessive pressure drop. We used several combinations of oil concentration in the feed, column size, residence time, and OC particle-size distributions to evaluate the effects of these parameters on oil adsorption. The method used to estimate the oil adsorption capacity and the kinetics was the breakthrough curve. We used an upflow configuration with different residence times and plotted the outlet oil concentrations from the packed bed vs. time.

The analysis of oil in water from the effluent streams was conducted with a TD-500 an oil-in-water analyzer using UV fluorescence. The TD-500 oil-in-water meter uses an easy-to-use solvent-extraction procedure with high accuracy and repeatability. The standard procedure of solvent extraction is specified by EPA-1664A, better known as the FastHex method of analysis. The analyzer measures the samples in less than 4 minutes.

We conducted experiments with crude-oil/water and kerosene/water emulsions prepared gravimetrically. Obtaining a breakthrough curve for each experiment allowed us to provide an empirical adsorption model and an estimate of the loading capacity of the adsorbent expressed as weight of oil adsorbed per weight of adsorbent. The dimensionless oil adsorption, defined as the ratio of outlet over inlet grams of oil flowing through the column versus time is,

$$\frac{W_{ads}}{W_{in}} = \frac{K_{ads}}{(1 + bD(t/t_s))^{(1/b)}} \dots (1)$$

The adsorption coefficient  $K_{ads}$  depends on the contact time ( $EBCT$ ) defined in Eq. 4, on the clay loading capacity ( $\eta$ ), and on the initial oil concentration ( $C_{in}$ ).

$$K_{ads} = a \frac{\log(EBCT \times \eta)}{\log(C_{in})} + c \dots (2)$$

The stoichiometric time  $t_s$  (in Eq. 1) is obtained by assuming that the outlet concentration is identical to the inlet concentration, and is obtained from a first-order kinetics model as indicated in Eq. 3:

$$C_d = \frac{C_{out}}{C_{in}} = \exp \left[ k_w \left( \frac{C_{in} \times t}{\eta \rho_b} - \frac{A_{cs}L}{Q} \right) \right] \dots (3)$$

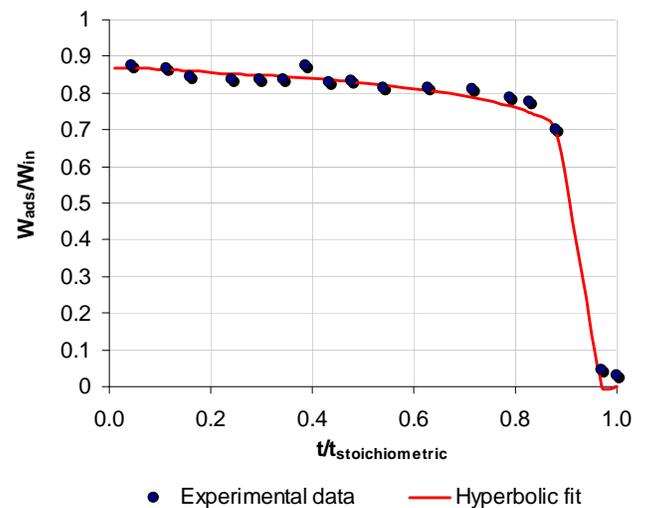
This model considers no axial dispersion.  $A_{cs}L$  represents the packed bed volume,  $Q$  is the flow rate through the column,  $\eta$  is the oil-loading capacity in grams or oil adsorbed per gram of OC, and  $\rho_b$  is the bulk density of the OC. The empty bed contact time ( $EBCT$ ) is the clay volume divided by the flow

rate. Another common indicator is the residence time ( $\tau$ ), which considers the pore volume ( $A_cL\phi$ ) rather than the column volume. These two properties relate as follows,

$$EBCT = \frac{A_cL}{Q} = \frac{\tau}{\phi} \dots (4)$$

The coefficients in Eqs. 1 to 3 were determined from least-squares fit using experimental oil adsorption data. Patel *et al.*<sup>16</sup> provide additional details of this model.

**Fig. 1** illustrates the match of our empirical model with experimental data for one experiment with a crude-oil/water emulsion



**Fig. 1—Oil adsorption data and empirical fit.**

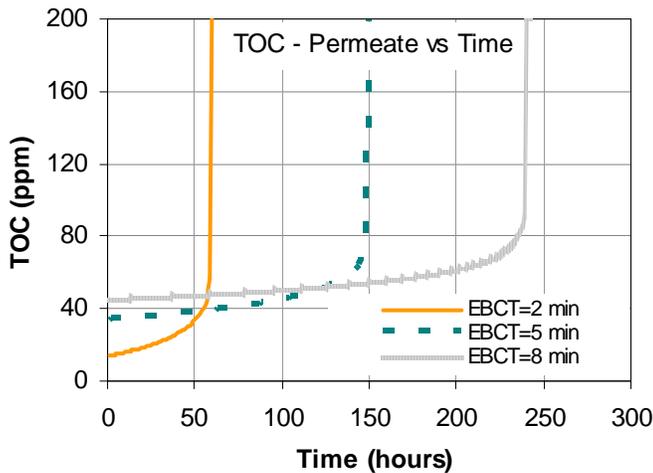
**Table 1** shows the physical properties of the clay material and the dimensions of the columns used throughout this manuscript.

**Fig. 2** shows the predicted breakthrough time for one packed column as a function of  $EBCT$  using the physical properties and operating parameters indicated in **Table 1**.

The inlet oil concentration is 200 ppm of total organic carbon ( $TOC$ ). Note that a shorter  $EBCT$  would imply faster operation and better adsorption kinetics; however, from an operational viewpoint, at shorter  $EBCT$ s we observed channeling as illustrated in **Fig. 3**. Therefore, our base design consists of two identical columns in series removing over 90% of the initial  $TOC$  and providing over 150 hours of operation before needing replacement. Our recommended  $EBCT$ s are 5 to 8 minutes. All the simulations in this paper use a conservative loading capacity of 50% and  $EBCT$  of 5 minutes.

**Table 1—Properties of proposed new adsorbent organoclay PS18385 for oil removal from produced water.**

Organo Clay Properties	
Bulk Density of Packed Bed [=] lbs/gal	5.84
Loading Capacity, gm oil/gm organoclay ( $\eta$ )	0.50
Porosity of packed bed	0.40
Average particle size, mm	1.60
Organoclay packed per column, lbs	38.12
Average residence time, min	2.00
Column Dimensions	
Length of Canister, inch	36.00
Length of Packed Bed, inch	30.00
Diameter of Packed Bed, inch	8.00
Length to Diameter Ratio	3.75
Volume of Canister, gal	6.52
Operating Conditions	
EBCT, min	5.00
Maximum Allowable Output TOC, ppm	20.00

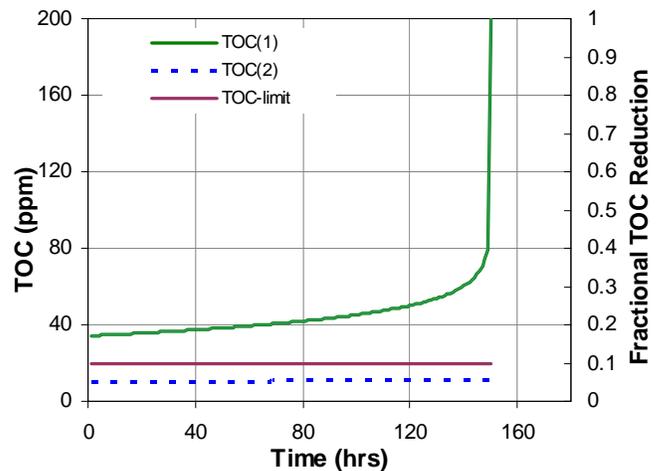


**Fig. 2—Faster breakthrough times correspond to shorter EBCT. Column has the dimensions indicated in Table 1.**



**Fig. 3—Oil adsorption experiments and different EBCT indicate plug flow in left column (EBCT = 5 minutes), and channeling in the other columns for lower EBCT.**

Fig. 4 shows the simulated adsorption of two columns in series with an initial oil concentration of 200 ppm.



**Fig. 4—Simulated performance of two OC columns in series operating at the specifications of Table 1.**

**Removal of Dissolved Solids: Experimental and Modeling**

We used reverse osmosis (RO) for the dissolved salts removal. Osmosis is the movement of solvent from a dilute solution into a concentrated solution through a semipermeable membrane such that the concentrations of solute on the two sides of the membrane will equalize. In reverse osmosis (RO), the water (solvent) flow reverses and water flows from the more-concentrated solution to the less-concentrated solution. This can happen only when the applied pressure exceeds the osmotic pressure of the concentrated solution. This pressure increases with solute concentration and temperature.

Most RO technologies use a process known as crossflow to allow the membrane to clean itself continually. Fig. 5 shows a sketch of the flow directions for the feed stream (F), the concentrate (C) or reject stream, and the permeate (P). The transport of pure water from feed side to permeate side depends on the transmembrane pressure across the RO unit, the feed flow rate and the membrane area.

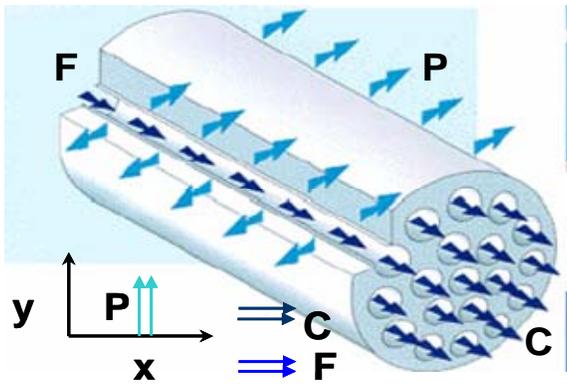


Fig. 5—Cross flow configuration of a spiral membrane. *F* (feed), *P* (permeate), and *C* (concentrate or reject).

Eqs. 5 to 7 define common terms in *RO* processes. Transmembrane pressure is the average pressure applied across the membrane minus the pressure on the permeate side,

$$TMP = \frac{P_i + P_o}{2} - P_p, \dots\dots\dots (5)$$

where  $P_i$  is the pressure at the feed inlet side,  $P_o$  is the pressure at the concentrate outlet side and  $P_p$  is the pressure at the permeate outlet side (psia).

Permeate recovery is defined as the volumetric fraction of feed flow rate recovered and is defined as,

$$P_r = \frac{Q_p}{Q_F} \dots\dots\dots (6)$$

and salt rejection is defined as

$$R = 1 - \frac{C_{perm}}{C_{feed}}, \dots\dots\dots (7)$$

where  $C_{perm}$  is the salt concentration in the permeate, and  $C_{feed}$  is the salt concentration in the feed; these are usually expressed in ppm or mg per liter.

We used a standard commercial 4×40 spiral membrane (4-in. diameter and 40-in. length) SWC-1-4040 from Osmonics for the experiments with water having total dissolved solids (*TDS*) up to 40,000 ppm. The membrane area was 70 ft<sup>2</sup>. Temperature affects the transmembrane pressure required across the *RO* membrane; as the temperature increases, the osmotic pressure increases, and a higher transmembrane pressure is needed to achieve the desired salt removal. However, as the temperature increases, the viscosity of water decreases and this offsets the demand on transmembrane pressure. We kept the temperature constant at 35°C in all our experiments

The feed was prepared gravimetrically using NaCl. Since the osmotic pressure of NaCl is higher than the pressure of other salts that may be present in the produced water at equal concentration, the experiments performed with NaCl determine the range of operating parameters conservatively.

A minimum flux, defined as the ratio of flow rate over membrane flow area, is required to avoid polarization and malfunctioning of the membrane. These are provided by the manufacturer, the lowest flux for our experiments was 0.086 GPM/ft<sup>2</sup> (which corresponded to 6 GPM for a membrane with a cross sectional area of 70 ft<sup>2</sup>).

The performance of an *RO* unit is analyzed from the permeate recoveries and salt rejections obtained. We conducted experiments at different transmembrane pressures, feed flow rates and salinities, and measured permeate and concentrate flow rates, permeate, and reject salt concentrations at regular time intervals.

*TDS* in each sample were determined by a conductivity meter. These measurements provided a definite tool for modeling transient *RO*-filtration performance.

Fig. 6 shows that the permeate recovery increases with transmembrane pressure and decreases with initial salt concentration. Additionally, higher feed rates do not increase the permeate recovery. Note that for pure water at 800 psia the permeate for a feed rate of 10 GPM is 0.15×10 = 1.5 GPM, while for a rate of 6 GPM, it is 0.3×6 = 1.8 GPM.

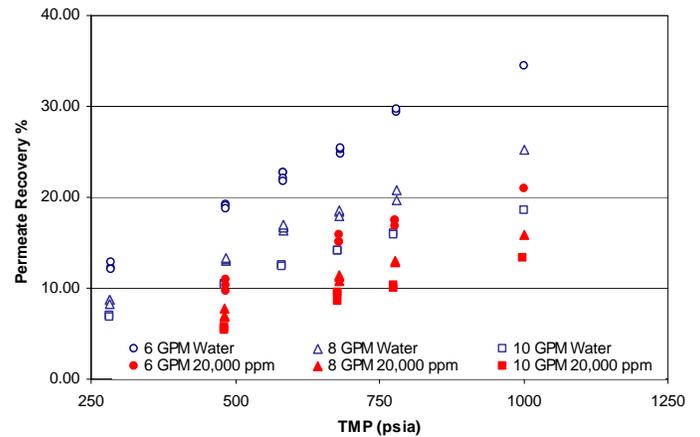


Fig. 6—Permeate recoveries increase as salt concentration decreases and *TMP* increases.

Fig. 7 indicates the effect of *TMP* and initial salt concentration upon salt rejection for different feed rates. As expected, a higher *TMP* provides higher salt rejections while a more concentrated solution exhibits lower rejections. For a fixed *TMP* rejections are slightly higher at lower flow rates.

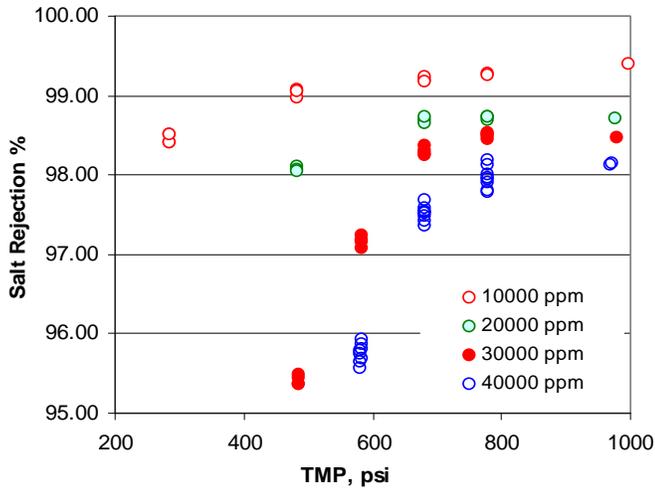


Fig. 7—Salt rejection improves with TMP

The combined effect of transmembrane pressure, feed rate, and salt concentration was analyzed in a systematic way; we collected over 500 data points that were the basis to model the permeate recovery and the salt rejection. The percent fraction of permeate and salt rejection are modeled from the following equations.

$$P = \left[ a_1 \left( \frac{TMP}{J_F} \right)^{a_2} + a_3 \left( \frac{TDS}{TMP} \right)^{a_4} + a_5 \left( \frac{TDS}{J_F} \right)^{a_6} \right] \dots \dots \dots (8)$$

$$R = \left[ b_1 \left( \frac{TMP}{J_F} \right)^{b_2} + b_3 \left( \frac{TDS}{TMP} \right)^{b_4} + b_5 \left( \frac{TDS}{J_F} \right)^{b_6} \right] \dots \dots \dots (9)$$

The coefficients for these equations, specific for the SWC-1-4040 membrane, are in **Table 2**.

Table 2—Coefficients for Eqs. 8 and 9

Permeate Flux (Gallons/Day/ft <sup>2</sup> )	Coefficients		
To obtain permeate flux multiply equation (8) by Feed Flux (gal/day/ft <sup>2</sup> ) times membrane area	a <sub>1</sub>	=	3.8444
	a <sub>2</sub>	=	1.0425
	a <sub>3</sub>	=	0.6099
	a <sub>4</sub>	=	-0.3133
	a <sub>5</sub>	=	-0.0271
	a <sub>6</sub>	=	1.0963
Salt Rejection %	Coefficients		
Salt rejection is expressed in %. Fluxes are expressed in gal/day/ft <sup>2</sup>	b <sub>1</sub>	=	99.9901
	b <sub>2</sub>	=	-0.0013
	b <sub>3</sub>	=	-0.0045
	b <sub>4</sub>	=	1.6575
	b <sub>5</sub>	=	9.357E-06
	b <sub>6</sub>	=	2.0710

**Figs. 8 and 9** show the experimental permeate-recovery data and salt-rejection levels compared with our predicted values using Eqs. 8 and 9. Error bars included in these figures indicate the experimental uncertainty based on three or more replicates.

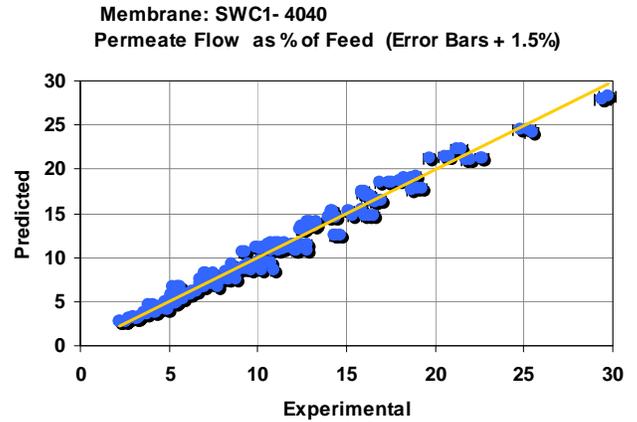


Fig. 8—Experimental and predicted permeate recoveries show a correlation better than 98%.

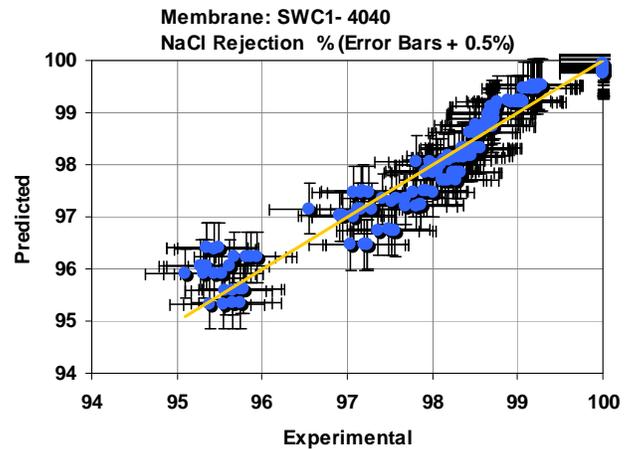


Fig. 9—Experimental and predicted permeate salt rejection show correlation within experimental uncertainty.

Eqs. 8 and 9 are limited to TDS concentrations up to 40,000 ppm, transmembrane pressure of 200 to 1,200 psi, and, feed flux ranges from 0.085 to 0.2 GPM/ft<sup>2</sup>. These correspond to flow rates of 6 to 14 GPM for a membrane surface area of 70 ft<sup>2</sup>.

**Simulations of Brine Processing**

Several options can be analyzed in terms of number and size of *OC* and *RO* units parallel, series, or combinations of both configurations. **Fig. 10** shows a sketch of two possible configurations. Brine feeds two packed-bed columns in series with *OC* material to remove the oil. The outlet stream from the *OC* columns goes to a holding tank that feeds the *RO* unit(s). The concentrate from the *RO* unit(s) is recycled back to the holding tank, so we have a continuously increasing feed composition to the *RO* units.

The number of units, configurations and sizing are static design variables, while dynamic variables include feed rates,

transmembrane pressures, and feed oil and salt concentrations. Once the configuration and sizes are defined, the best operating variables depend upon the feed stream concentrations. This turns to an optimization process that should include power requirements and capital expenses not yet built into our model. In this paper, we conducted a sensitivity analysis to the most important design variables using the modular designs sketched in Fig. 10.

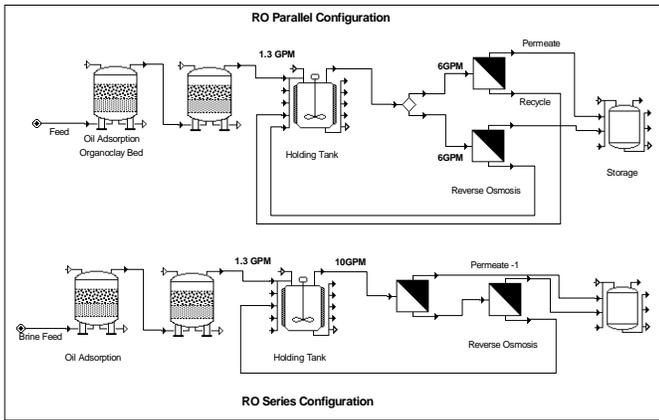


Fig. 10—Pilot size series and parallel configurations to process oilfield brines.

To reduce the dimensionality of the problem, the residence time and technical specifications of the *OC* canisters remained fixed as indicated in Table 1. The flow rate of de-oiled brine under these conditions is 1.3 GPM (*TOC* < 20 ppm). Considering a conservative loading capacity of 50%, oil breakthrough from the first column occurs after over 150 hours of operation, but the oil concentration from the second column is still below the maximum *TOC* allowed.

The base run for the series configuration has an initial brine concentration of 5,000 ppm *TDS*, with 200 ppm of *TOC*; the feed rate to the primary *RO* unit is 6 GPM, the surface area of the first *RO* membrane is 70 ft<sup>2</sup>, and the area of the second membrane is 35 ft<sup>2</sup>. Both *RO* units operate at a *TMP* of 800 psia, and the concentrate is fully recycled to a tank. The holding tank (*HT*) has a capacity of 300 gallons but operation begins with the tank filled to 200 gallons.

The base case for the parallel configuration is identical to the series configuration, except that both membranes have an area of 70 ft<sup>2</sup>. Note that the flow rate including the two parallel membranes is twice the rate of the configurations series. This may not seem a valid comparison since the total rate in the parallel configuration is twice the rate of the series configuration, and its total membrane area is about one-third higher. However, if we compare the performance of these two cases, the parallel setting does not offer a competitive advantage as indicated in Figs. 11 and 12. Fig. 11 shows that the batch time is longer for the series configuration, but not twice as long. The amount of permeate produced by the parallel configuration is higher, but not twice as much as one would be inclined to believe according to the rates and increased membrane area. Fig. 12 shows that the holding tank volume decreases with time and eventually cannot sustain the pumping rate; thus, the batch cycle terminates sooner in the parallel configuration.

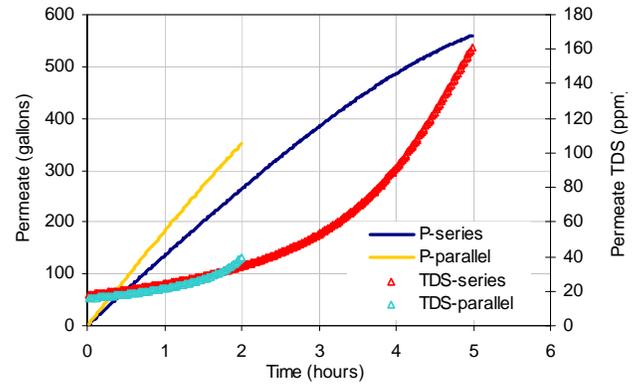


Fig. 11—Series configuration is more attractive in terms of permeate obtained, capital, and operational expenses.

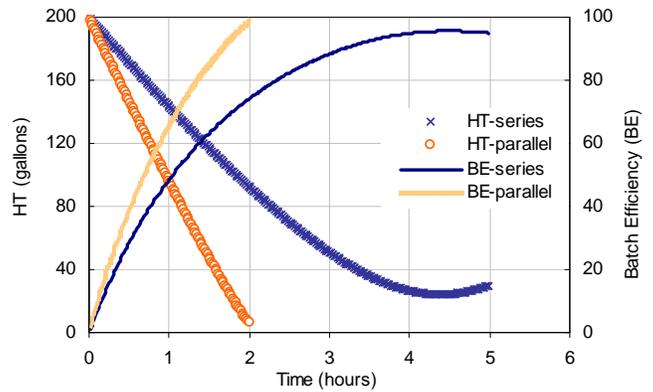


Fig. 12—Holding tank volume in parallel base configuration is unable to sustain permeate rate produced.

Parallel and series configurations exhibited similar efficiencies; however, lower pumping requirements are needed in the series configurations but produced permeates have slightly higher *TDS* than for a parallel configuration.<sup>19</sup> Based upon these results, all future simulations are for a series configuration.

The objective of recycling is to improve the permeate recovery or efficiency, which is defined as the total permeate produced per batch cycle divided by the volume processed as,

$$BE = \frac{\int_0^{t_b} Q_p \times dt}{Q_{OC} \times t_b + HV^i}, \dots \dots \dots (10)$$

where *t<sub>b</sub>* is the time of the batch cycle, *HV<sup>i</sup>* is the initial volume of the holding tank, *Q<sub>p</sub>* is the volumetric rate of permeate produced, and *Q<sub>oc</sub>* is the rate from the *OC* to the *HT*.

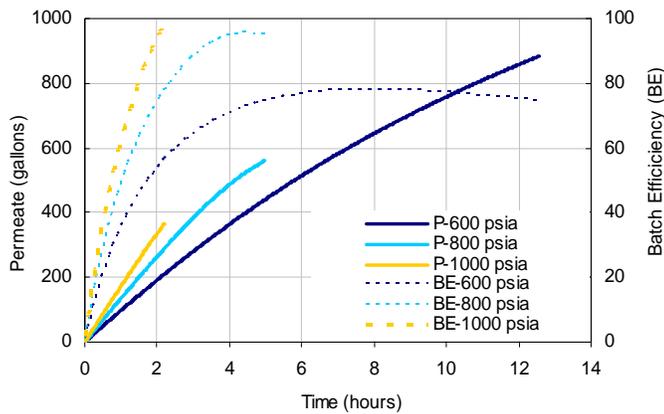
The batch cycle ends when any one of the following situations occurs

- The volume of fluid in the *HT* tank exceeds its capacity: the permeate fraction will decrease with time and will be lower than the *OC* feed stream to the tank. In this case the

output (permeate) is lower than the input (*OC* to *HT*) stream and the *HT* fills up.

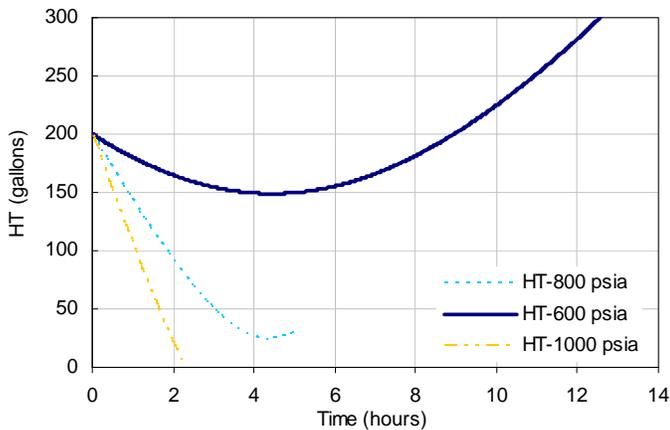
- The fluid volume of the tank becomes too small to sustain the pumping rate to the *RO* unit(s): This occurs when permeates exceed the *OC* feed stream to the holding tank.
- The salt concentration of the feed to the *RO*'s exceeds 40,000 ppm (which is beyond our experimental data).
- The permeate salt concentration exceeds 500 TDS, which is a reasonable target for irrigation-quality water.

**Fig. 13** shows more permeate production for higher transmembrane pressures; the rate is fixed at the base case of 6 GPM. Efficiency at higher pressures is high, but the size of the batch may be too small for manual operation. One way of making the batch cycles longer is to increase the size of the holding-tank volume. The size of the holding tank does not significantly affect the efficiency but only the length of the cycle.



**Fig. 13—Longer batch cycles at obtained at lower *TMP*.**

**Fig. 14** shows the variation of the holding tank volume with time. Two extremes are met: At 600 psia the batch ends because the tank overflows, while at 1,000 psia the cycle ends because the fluid volume in the tank becomes too small.



**Fig. 14—Extreme variations of holding tank volume with pressure meet the constraints set to terminate the batch cycle.**

Additionally we tested three different feed rates (6, 8, and 10 GPM), initial brine concentrations (5,000, 10,000, and 20,000 ppm), and holding-tank capacities. Initial tank volume and capacity are not the same since the tank fluid level may increase or decrease during operation. The volume-capacity pairs analyzed are 100 to 200 gallons, 200 to 300 gallons, and 300 to 400 gallons.

**Table 3** summarizes the output at the end of the batch time for all cases analyzed. The first column indicates the variable changed from the base case. The base case is in bold face. A comparison of the holding tank volume indicates that the larger the volume, the longer the batch time, although the incremental increase is not proportional. For most of the cases presented, the batch terminates because the feed concentration reaches 40,000 ppm.

**Table 3—Ultimate batch performance of *RO* units in series (*S*) and in parallel (*P*)**

<i>TMP</i> (psia)	<i>t<sub>b</sub></i> (hrs)	<i>P</i> (gallons)	<i>BE</i>	<i>HV</i> (gallons)	Tank TDS (ppm)	<i>P</i> TDS (ppm)
600	12.55	883.03	74.67	299.59	30685	299
800	4.98	560.52	94.97	29.66	39958	161
1000	2.22	367.22	98.30	6.34	22316	47
<b>Feed Rate (GPM)</b>						
6	4.98	560.52	94.97	29.66	39958	161
8	4.95	560.45	95.38	27.12	39987	172
10	4.92	559.48	95.65	25.47	39911	173
<b>HV Volume Capacity (gallons)</b>						
100,200	2.48	279.74	95.01	14.69	39914	160
200,300	4.98	560.52	94.97	29.66	39958	161
300,400	7.48	841.29	94.96	44.63	39973	161
<b>Feed TDS (ppm)</b>						
1000	2.93	422.72	98.38	6.95	5156	6
5000	4.98	560.52	94.97	29.66	39958	161
10000	4.85	469.62	81.01	110.12	39958	301
20000	2.42	200.26	51.45	188.96	39885	485
Series Base	4.98	560.52	94.97	29.66	39958	161
Parallel Base	2	350.42	98.27	6.17	20807	40

**Power Requirements and Preliminary Costs**

Power consumption is relatively independent of the feed salinity, but when we express the energy consumed per barrel

of permeate obtained, we can see large differences depending upon the salinity and TMP. Specific *RO* performance data was simulated using Dow Chemical Company's Reverse Osmosis System Analysis (ROSA) software.<sup>17</sup> ROSA output includes the specific energy (energy required per unit volume of freshwater produced), while specific costs were obtained by multiplying specific energy by electricity unit cost. Grid electricity unit cost was assumed to be 5¢/kWh, while the cost of electricity produced by diesel generators was estimated at about 18¢/kWh using guidelines given by Jimenez,<sup>18</sup> and assuming a diesel cost of \$2/gallon.

Fig. 15 shows the specific energy obtained using a membrane compatible with the membranes used in this project. Feed fluxes and *TMP*s were equivalent to the ones we used in our simulation, but we did not test this membrane.

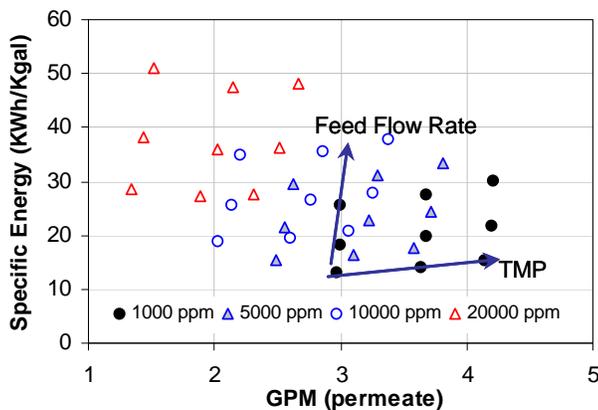


Fig. 15—Specific energy increases with salinity and flow rate.

Fig. 16 shows the estimated cost per barrel of permeate assuming grid electricity; this cost triples when using electricity produced from diesel generators.

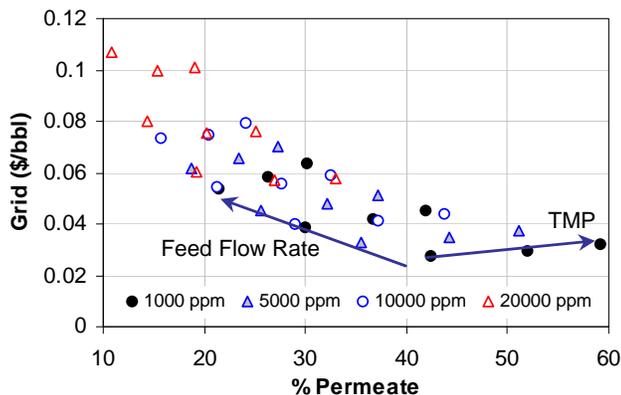


Fig. 16—Cost per barrel of permeate increases more with flow rates than with *TMP*.

Our modular design implies a varying feed concentration during the batch cycle, while ROSA software assumes a constant feed concentration; however, these estimates provide a guideline of the expected energy intensity and power costs from an *RO* desalination process.

The data show that substantially lower energy costs result when operating the *RO* units at lower feed fluxes, with a tradeoff of higher capital costs since more membrane area is then required to process a given quantity of brine. As for the effect of transmembrane pressure (*TMP*), energy efficiency for brackish feeds (1,000 to 10,000 mg/L) is best at the lowest *TMP* (600 psia), while higher-salinity feeds favor higher pressures.

## Conclusions and Recommendations

We conducted experiments and developed a model that can forecast the performances of oil and salt separation techniques from produced water. Based upon this model, Organoclay PS12385 can remove more than 90% *TOC* content of produced water, provided two column configurations in series. The *RO* membranes and process parameters selected can remove more than 95% *TDS* of produced water. A combination of continuous adsorption and batch *RO* units is an effective system for the treatment of produced water and it provides maximum permeate recoveries.

An important observation to be made is that while the total volume through the parallel units may be higher than for the series configuration, using two membranes in series with a lower surface area for the second membrane than for the primary membrane may achieve similar performances to a configuration in parallel at a lower capital cost.

Based upon these results we recommend:

1. Additional experimentation of organoclay adsorption with produced water of different salinity and type of oil contaminant to generalize the sorption kinetics.
2. Additional testing on different *RO* membranes at higher pressures.
3. Evaluation of power-consumption requirements and capital expenses for a varying feed concentration typical of the batch processes analyzed.
4. Design and evaluation of automation and control strategies.

## Nomenclature

$a_1$ to $a_6$	=	Constants for Eq. 8 defined in Table 2
$b_1$ to $b_6$	=	Constants for Eq. 9 defined in Table 2
<i>BE</i>	=	Batch efficiency (Eq. 10)
$C_-$	=	Concentration, ppm
<i>C</i>	=	Concentrate, or reject, GPM
<i>EBCT</i>	=	Empty bed contact time, min (Eq. 9)
<i>F</i>	=	Brine feed, GPM
<i>HV</i>	=	Holding tank, gallons
<i>J</i>	=	Flux, gallon/ft <sup>2</sup> /day
$K_{ads}$	=	Adsorption constant (Eq. 2)
$K_w$	=	Kinetic constant (Eq. 3)
<i>MF</i>	=	Microfiltration
<i>OC</i>	=	Organoclay
$p_r$	=	Permeate recovery
<i>P</i>	=	Permeate, GPM
<i>Q</i>	=	Flow rate, GPM
<i>TDS</i>	=	Total dissolved solids, ppm
<i>R</i>	=	Salt rejection % (Eq. 7)
<i>RO</i>	=	Reverse Osmosis
<i>TMP</i>	=	Transmembrane pressure, psia
<i>TOC</i>	=	Total organic carbon, ppm
$t_s$	=	Stoichiometric time (Eq. 3), hours
<i>UF</i>	=	Ultrafiltration

$W$  = Weight, grams

### Subscripts

$in, i$  = Input, initial

$o, out$  = Output

$ads$  = Adsorbed

$perm, P$  = Permeate

$feed, F$  = Feed

### Greek Letters

$\rho_b$  = Bulk density clay bed

$\phi$  = Porosity

$\tau$  = Residence time, min

$\eta$  = Oil loading capacity, (gm oil/ gm clay)

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### References

- 1 Veil, J.A., Langhus, B.G., and Belieu, S.: "Downhole Oil/Water Separators: An Emerging Produced Water Disposal Technology," paper SPE 52703 presented at the 1999 SPE/EPA Exploration and Production Environmental Conference, Austin, 28 February – 3 March.
- 2 Rye, S.E. and Marcussen, E.: "A New Method for Removal of Oil in Produced Water," paper SPE 26775 presented at the 1993 Offshore European Conference, Aberdeen, 7-10 September.
- 3 Meldrum, N.: "Hydroclones: A Solution to Produced-Water Treatment," *SPEPE* (November 1988).
- 4 Fernandez, L.G. *et al.*: "The Study of Oil/Water Separation in Emulsion by Membrane Technology," paper SPE 69554 presented at the 2001 SPE Latin American and Caribbean Petroleum Engineering Conference, Buenos Aires, 25-28 March.
- 5 Doyale, D.H. and Brown, A.B.: "Produced Water Treatment and Hydrocarbon Removal With Organoclay," paper SPE 63100 presented at the 2000 SPE Annual Technical Conference,, Dallas, 1-4 October.
- 6 Roberts, J.A.: "Reverse Osmosis System Reduces Demineralised Water Costs," paper SPE 27862 presented at the 1994 SPE Western Regional Meeting held in Long Beach, 23-25 March.
- 7 Kasper, D.R.: "Optimization of Reverse Osmosis Treatment of In Situ Wastewaters," paper SPE 9492 presented at the 55<sup>th</sup> Annual Fall Technical Conference and Exhibition , Dallas, Texas, September 21 – 24, 1980.
- 8 Siddiqui, M.A.: "Sustainable Development through Beneficial Use of Produced Water for the Oil and Gas Industry," thesis dissertation, Texas A&M University-College Station, December 2002
- 9 Evans, P., and Robinson, K. "Produced Water Management-Reservoir and Facilities Engineering Aspects," paper SPE 53254 presented at the 1999 SPE Middle East Oil Show held in Bahrain, 20-23 February.
- 10 Mackay, E.J., Collins, I.R., Jordan, M.M., and Feasey, N.: "PWRI: Scale Formation Risk Assessment and Management." paper SPE 80385 presented at the 2003 SPE 5<sup>th</sup> International Symposium on Oilfield Scale held in Aberdeen, 29-30 January.
- 11 Wan J., X *et al.*: "Reinjection of Finely Disposed Produced-water Reduces Formation Damage in Low Permeability Zones," paper SPE 82234 presented at the 2003 SPE European Formation Damage Conference,, The Hague, 13-14 May.
- 12 Alonzo, W. L., *et al.*: "Regional Assessment of Produced Water Treatment and Disposal Practices and Research Needs," paper SPE 29729 presented at the 1995 SPE/EPA Exploration & Production Environmental Conference held in Houston, 27-29 March.
- 13 Hughes, S.W., Sehsauvafu, S.A. and Slater, J.M.: "Produced Water Treatment Technologies: A Case Study," paper SPE 27131 presented at the Second International Conference of Health, Safety & Environment in Oil & Gas Exploration & Production held in Jakarta, Indonesia, 25 – 27 January, 1994.
- 14 Tao, F.T *et al.*: "Conversion of Oilfield Produced Water Into an Irrigation/Drinking Quality Water," paper SPE 26003 presented at the 1993 SPE/EPA Exploration & Production Environmental Conference,, San Antonio, 7-10 March.
- 15 Tsang, P.B., and Martin, C.J.: "Economic Evaluation of Treating Produced Water for Potable Use," paper SPE 86948 prepared to present at the 2004 SPE International Thermal Operations and Heavy Oil Symposium and Western Regional Meeting held in Bakersfield, 16-18 March.
- 16 Patel, C.V., Barrufet, M.A. and Petriciolet, A.B.: "Effective Resource Management of Produced Water in Oil and Gas Operations," paper presented at Canadian International Petroleum Conference held at Calgary, Canada in June 8-10, 2004.
- 17 ROSA, Version 6.0, FilmTec Corporation, 2004.
- 18 Jimenez and K. Olsen, "Renewable Energy for Rural Health Clinics," National Renewable Energy Laboratory, 1998
- 19 Barrufet M. A. and Burnett D. "A modular design and implementation of a brine conversion process: oil removal and desalting units" 11<sup>th</sup> IPEC Conference, Albuquerque New Mexico, October 11-13 (2004).