Novel Cleanup Agents Designed Exclusively for Oil Field Membrane Filtration Systems

Low Cost Field Demonstrations of Cleanup Agents in Controlled Experimental Environments

A Global Petroleum Research Institute Report
U.S. DOE DE-FC26-04NT15543

February 2008

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ABSTRACT

The goal of our project is to develop innovative processes and novel cleaning agents for water treatment facilities designed to remove fouling materials and restore micro-filter and reverse osmosis (RO) membrane performance. This project is part of Texas A&M University’s **comprehensive study of the treatment and reuse of oilfield brine for beneficial purposes.**

Before waste water can be used for any beneficial purpose, it must be processed to remove contaminants, including oily wastes such as residual petroleum hydrocarbons. An effective way of removing petroleum from brines is the use of membrane filters to separate oily waste from the brine. Texas A&M and its partners have developed highly efficient membrane treatment and RO desalination for waste water including oil field produced water. We have also developed novel and new cleaning agents for membrane filters utilizing environmentally friendly materials so that the water from the treatment process will meet U.S. EPA drinking water standards.

Prototype micellar cleaning agents perform better and use less clean water than alternate systems. While not yet optimized, the new system restores essentially complete membrane flux and separation efficiency after cleaning. Significantly the amount of desalinated water that is required to clean the membranes is reduced by more than 75%.

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ACRONYMS

API	American Petroleum Institute
BGW	Brackish Ground Water
CBM	Coal bed methane
E&P	Exploration and production
EPA	Environmental Protection Agency
Kpa	kilopascal
Lpm	Liters per minute
MEDRC	Middle East Desalination Research Center
MWCO	Molecular weight cutoff
NTU	Nephelometric Turbidity Unit
O&G	Oil and gas
PPM	Parts per million
PSI	Pounds per square inch
PWDS	Produced water desalination
R&D	Research and development
TDS	Total dissolved solids
TMP	Trans-membrane pressure
TRC	Texas Railroad Commission
TSS	Total suspended solids
U.S.	United States

Executive Summary

Environmental Sustainability in O&G Operations

The search for energy to meet present demands and future forecasts is becoming more intense and more diversified than ever, but despite this diversification of sources to meet the energy demand globally, fossil energy remains the prime energy source today and in the foreseeable future. An increasingly important issue in the problem of meeting future energy needs is the critical need to protect the environment. Increasing energy demand goes hand-in-hand with an increasing awareness of environmental issues such as global warming, especially as they pertain to E&P operations. Emphasis is increasingly placed on reducing the impact of E&P operations on the environment to minimal levels. Produced water represents a very large percentage of the waste streams generated from O&G operations. Management of wastes generated from E&P operations represents a significant cost to those in the industry, costs of treatment. Disposal of produced waters could range from about $0.01 to more than $5 per barrel of produced water, amounting to a global industry cost of $50 billion per year. Disposal costs and the cost for procuring resources such as water for hydraulic fracturing are likely to continue to rise. , It is necessary that there be cost effective technological solutions that reduce the volume of the waste being disposed.

Membrane Technology in Produced Water Management

The prospects of using membranes in the treatment of drilling wastes has been the subject of several studies. Texas A&M has extensive experience with the use of membranes for the desalination of the produced water. Presently research is extending the investigation to include drilling wastes and other E&P waste streams such as hydraulic fracturing flowback water. Produced water, with its wide range of chemical and physical characteristics, can cause operational problems, such as. fouling of or loss of flux through the membrane surface, poor rejection characteristics, and membrane failure due to chemical reactions with the membranes. Fouling is a major operational factor that requires periodic cleaning [1-8]. Produced water and oily water can cause severe fouling problems on most membranes. Membranes can be fouled by four groups of materials: minerals, organics, particles and colloids, and microbiological growth. Any of these four types of membrane fouling, or a combination of types, could occur during produced water treatment.

Improving Performance of Membrane Treatment of Produced Water

Membrane filtration has been utilized in various industries for the treatment of water and wastewater. These membrane systems are design to treat a specific known water source and to remove the desired contaminants to meet environment regulations or to meet desired water quality for industrial use. These contaminants can have a wide range of characteristics that will allow them to be separated through membrane technology.

Membrane filtration and desalination of produced water has shown promise for converting a waste fluid to a usable resource[1]. In early field projects, however, the filters

[1] Early references to RO membrane filtration of oil field brine.

used in microfiltration, ultrafiltration, nanofiltration, and RO water treatment processes often did not perform as well as desired. One of the primary causes of the sub-optimal performance was fouling of the membranes. The projects described in this report are designed to increase efficiency of the treatment system by minimizing the fouling and to efficiently clean the membranes after fouling.

To efficiently clean membranes, the type of fouling should be known. This factor heavily influences the type and amount of cleaning that needs to be performed to get the fouling layers removed. Our research has examined the feasibility of using a micoemulsion[2] with different levels of oil and water solubility characteristics for membrane cleaning of produced water-fouled ultrafiltration membranes. The research tested the performance of microemulsion solutions used at ambient condition. These were shown to provide better performance than the standard cleaning procedures. The research evaluates the use of the micelle solution on polyvinyl difluoride ultrafiltration membranes from various manufacturers used in produced water treatment. It also determines whether physical conditions such as cleaning time, flow rates, and rinse times affect the cleaning performance to optimize the micellar cleaning solution for these ultrafiltration membranes.

Development of New Type of Cleaning Agents

As explained earlier, produced water can cause all four types of membrane fouling but typically will cause fouling by mineral and oil deposits. The mineral and oil deposits on the membrane are the primary concern because they will occur from every produced water source and will require a different cleaning approach than biological fouling. Particulate fouling will also typically occur but can be cleaned using physical cleaning or high flow rates to strip the layers from the membrane surface. Surface active agents were used in this study to form a micelle cleaning solution for cleaning of produced water-fouled ultrafiltration membranes. These surface active agents formed micelles that react with the mineral and oil droplets to form larger particles that are then removed by the high flow rate. This study tested the feasibility of using such a micelle solution to clean the membrane fouling that will occur during operation.

Performance of New Cleaning Agents

In the first series of cleaning experiments, the differences between the micelle micro emulsion solutions were tested. Each test was conducted on the same membrane under the identical cleaning parameters of flow rates and time.

Experiments were conducted using the best two micelle solutions from the first test series and performing three sets of flow experiments. In the first set, only flow rate of the cleaning solution was changed within the set. In the second set, flow rate and membrane were both changed. In the third set flow rate, cleaning formula, and membrane were changed with all other cleaning parameters kept the same as the first test series. Those experiments tested the effects of shear stress on cleaning solution effectiveness. This series of tests also considered whether the different formulas had different or

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[2] Microemulsions are defined as a stabilized emulsion in which droplets of one liquid phase is dispersed within the other phase. The droplets are extremely small (<100 nm), and are thermodynamically stable.

corresponding effect on cleaning performance and flow rate effect and whether the different membranes showed similar performance trends.

The results of the cleaning flow rate tests for formula 50406B and 50928A are summarized in Table 1 based on linear regression flux curves and averaged ratios as done previously. Table 1 also shows the effect of different membrane types on the micelle solution performance.

Table 1 Cleaning flow rate effect on performance results

Experiment Test	10	11	12	13	14	15	16	17	18
Micelle formula	50928 A	50928 A	50928 A	50928 A	50928 A	50928 A	50406 B	50406 B	50406 B
Cleaning flow Rate (gpm)	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
Membrane	JW	JW	JW	5k	5k	5k	5k	5k	5k
Clean flux/ Used flux	1.26	1.64	1.72	1.13	1.00	1.00	1.10	1.33	0.92
Clean flux/ New flux	0.63	0.59	0.70	0.30	0.46	0.28	0.34	0.39	0.35
Used flux/ New flux	0.50	0.36	0.41	0.27	0.46	0.28	0.32	0.30	0.38
New flux/used flux	2	2.8	2.4	3.7	2.2	3.6	3.1	3.3	2.6
Cleaning Effectiveness (%)	20.6	38.9	41.7	11.3	0.0	-0.4	7.8	24.1	-9.1

The results from the first series of tests showed the best results with highest cleaning effectiveness percentage and cleaned to uncleaned flux (new flux/used flux) ratios of as high as 3.7. In 1994, Lindau and Jonsson [2] reported acid and basic cleaning of oily water membranes cleaned to uncleaned flux ratio of 1.3 and 1.4, respectively. The data indicate that the performance of the micelle solutions were significantly better than the performance of the traditional acid or basic cleaning of oily water fouled membranes.

Micelle formulas 50406B, 50928A, and 50928C chemically reacted to the produced water-fouled membrane. They achieved better cleaning effectiveness by dissolving the oil particulates on the surface of the fouled membrane into the micelle solution. The results also indicate the micelle solution can be optimized to obtain the desired oil and water properties to enhance the performance of the solution.

An additional study objective was to determine the operational parameters effect on the performance of the micellar solution. The study consisted of sets of similar experiments to show if any of the parameters changed the micelle effectiveness. The parameters were the membrane type or size, cleaning flow rate, cleaning duration, rinse flow rate, and rinse duration. The studies showed that for the micelle solution the effectiveness of cleaning was not affected by cleaning duration or the rinse flow rate. The study demonstrated that the cleaning flow rate improved performance but is limited by membrane type or MWCO. The results also indicate that increasing the duration of the rinse before and after cleaning improved the overall effectiveness of the micelle solution cleaning of the produced water fouled membranes. The study also indicated that the micelle solution would also be effective on nanofiltration and RO membranes.

The micelle solution was effective on all membranes tested. The micelle solution showed better performance on higher molecular weight cutoff (MWCO) ultrafiltration membranes. The micelle solutions worked best on the membranes with an approximately 30,000 MWCO. The data showed that micelle solution generally behaved the same for each membrane type. The only effect that was indicated by the different membranes was the limit on cleaning flow rate for the tighter membranes tested.

The results indicate a micelle solution for oily water fouled ultrafiltration membranes is a feasible method to effectively clean the membranes and that the micelle solution can be customized to perform better on the fouled membranes according to oil and water solubility. The micelle solution cleaning parameters that should be used to optimize cleaning cycle performance are the cleaning flow rate determined by the MWCO and rinse duration. The micelle solution formulation had the most effect on performance with the cleaning flow rate and water rinse duration showing significant improvement on the base level of cleaning effectiveness of the solution.

The cleaning temperature data showed that a micelle solution can be formulated to operate at ambient conditions and to eliminate the requirement of a heat source for an onsite membrane unit. With optimization, a micelle cleaning solution can provide a very cost-effective solution to cleaning oily wate- fouled membranes at ambient temperature.

A final objective was to test the chemical cleaning process in field applications. Cleaning agents were tested on both ultrafiltration (UF) and RO membranes under a number of field conditions. Several of the cleaning tests were performed at the pilot plant after testing and return of the membranes from the field. A summary of the results is shown in Table 19. Excellent results were achieved

INTRODUCTION: MANAGING WASTE BRINE IN O&G OPERATIONS

Background

Energy availability is increasingly becoming one of the world's most pressing problems. The search for energy to meet present demands and future forecasts is becoming more intense and more diversified than ever. Despite this diversification of sources to meet the energy demand globally, fossil energy remains the prime energy source today and in the foreseeable future. Exploration and production activities regarding oil and gas have increased dramatically in the past five years with crude oil barrel prices hovering near a $100 dollars per barrel compared to about $12-$13 per barrel a decade ago. The United States, the largest energy consumer in the world, faces increased competition for global energy markets as oil rich nations are using more energy and cutting exports (9) due to increasing needs in their nations and are shrinking available exports. Likewise, developing nations in Asia and Africa have dramatically increased their demands for oil and gas supplies in recent years.

Increased global energy demand is leading to increased exploration & production (E&P) activities worldwide. Statistics from the American Petroleum Institute (API) show that there are about 1,801 active rotary rigs in the US as of November 2007 compared to a 2006 average of 1,649 (10). There is also a recognizable growth in increased stimulation techniques for existing oil wells to maximize yield as there continues to be further development and knowledge of stimulation techniques in the oil industry. Increased demand for energy and rising energy prices have renewed interest in unconventional oil resources-- a term for oil resources that are generally more challenging to extract than conventional oil. Examples are tar-sands, heavy-oil and oil-shale. Unconventional oil production requires more resources in the extraction of the oil and generally has more impact to the environment than conventional oil resource extraction. As demand grows in the United States and globally it is predicted that unconventional oil resources will increasingly become important in meeting future energy needs.

Another important issue in the problem of meeting future energy needs is the critical need to protect the environment. In addition to increasing energy demand is the increasing awareness of environmental issues such as global warming, especially as they pertain to E&P operations. The last decade has witnessed increasing environmental regulation imposed by federal, state, and local authorities on the industry, with increasing environmental awareness and activism. It is expected that these regulations will become increasingly stringent. Emphasis is placed on reducing the impact of E&P operations on the environment to minimal levels. Issues such as resource conservation, waste minimization (or waste reduction), recycling, and reuse are becoming topical issues as they are prominent in policy consideration in determining where exploration activities can be conducted on U.S. land., Often environmental concerns are the major determinants to future drilling concessions by the government.

Produced Water: A Problem for E&P

Produced brine represents a very large percentage of all the waste streams generated from O&G operations. Produced water is defined by the U.S. Environmental Protection Agency (EPA) as "Water brought up from hydrocarbon-bearing strata during the extraction of oil and gas, and can include formation water, injection water and any chemicals added downhole or during oil-water separation process" (4). Another useful parameter for describing produced water volume is the water-to-oil ratio. This ratio ranges from less than 1 in new wells to more than 100, depending on the maturity of the field (11). The average U.S. water-to-oil ratio is estimated to be about 7 barrels of produced water for 1 barrel of oil produced (114).

Approximately 18 billion barrels of produced water was produced onshore in the United States in 1995.These figures exclude the additionally large volumes of produced water generated in US offshore operations. From disposal statistics available 71% of produced water is used injected for enhanced oil recovery (EOR) and pressure maintenance in the reservoir, 21% is injected into disposal wells, while 3% is discharged and 2% re-used..

Unconventional natural gas is fast becoming a viable source of energy to meet increasing demands. Production of oil from unconventional sources requires large water resources in some cases and generates large amount of produced water in some other cases during their exploitation. Coal bed methane (CBM) is an unconventional natural gas source, in which methane is adsorbed to crystalline surfaces of coal due to hydrostatic pressure of overlying water in the coal beds (6).To strip the methane off the coal, the water needs to be pumped out. Unlike conventional oil fields where more and more produced water is generated as the field matures, the reverse is the case with CBM produced waters. Natural gas production in a gas shale such as the Barnett shale in Texas, requires technology such as hydraulic fracturing to make gas production economical. Hydraulic fracturing involves pumping water and some suitable proppant at high pressure to create and propagate a fracture in the surrounding rock formation downhole. These fracturing operations consume large volumes of freshwater to make up the fracture fluid. They also generate large volumes of fracture flowback water in some cases.

Management of wastes generated from E&P operations represent a significant cost to those in the industry. Costs of treatment and disposal of produced waters range from about $0.01 to more than $5 per barrel of produced water amounting to a global industry cost of $50 billion per year. Most of the disposal and treatment costs rely on disposal methods such as injection and do not in any way recover the produced water for reuse or recycle. Apart from the disposal costs, costs associated with acquiring fresh water resources are increasing. Operations such as hydraulic fracturing are straining municipal water supplies. Using the Permian Basin as an example, about 390 million gallons (9.3 million barrels) of water per day go into reinjection disposal, and less than 1% of this is recycled. Such prodigious use of scarce freshwater sources is bound to have socio-political implications as developing in the state of Texas (20).

There is a gap in the market place and on the technology shelf for cost-effective solutions to achieve better waste management emphasizing principles such as recycle, re-use and waste minimization. As shown, the leading waste disposal technology is injection into disposal wells. This technology takes no cognizance of recycle and or re-use.From an environmental standpoint, reinjection is not a sustainable technology as the water being disposed could be a possible source of potable or irrigation water. Although there are alternative source of energy, there are no alternative sources of freshwater. Therefore, the possibility of using produced water as a source of fresh water or recycling to use in drilling operations is becoming more attractive.

Disposal costs and the cost for procuring resources such as water for hydraulic fracturing are likely to continue to rise. It is necessary that there are cost-effective technological solutions that would significantly reduce the volume of the waste disposed, optimally reuse the resource, and also create a possible source of freshwater for various uses.

There are various technologies aimed at dealing with the various types of E&P wastes. Produced water composition varies considerably with the geographical region where it is produced and the formation characteristics from which it comes. Generally it contain dispersed oil, suspended solids, a variety of dissolved substances such as aromatics, heavy metals, dissolved hydrocarbons, salts, defoaming agents, and other production chemicals. Examples of technologies aimed at produced water management, separation, and/or treatment, include injection and reinjection, downhole separation (this involves the separation of the produced water from the oil down hole and injecting the produced water underground), and use of oil-water separation devices such as hydrocyclones, centrifuges, and gravity settlers before discharge. These technologies are not exhaustive of the range of treatment or management options in the treatment of these wastes. A wider range of examples can be found at the Produced Water Management Information System website (web.evs.anl.gov/pwmis).

Texas A&M University has had extensive experience with the use of membranes for the desalination of the produced water. Presently research is extending the investigation to include drilling wastes and associated drilling wastes such as frac flowback water. Development of membrane processes for separation of these wastes have been historically plagued by issues relating to membrane fouling, thereby producing relatively low permeate production. With recent advances in the membrane materials, configuration, and increased knowledge of operating parameters, the feasibility of using membranes in the E&P waste management is steadily rising. Membrane separation techniques help in recycling and reusing produced water, thereby providing a water management tool compatible with sustainable goals. As effluent standards become increasingly stringent, traditional separation techniques would not be feasible to use both technologically and economically, membranes such as UF membranes are showing that these lower effluent limits are easily attainable. Increased understanding of operation parameters in membrane technology is creating greater flexibility in designing systems that can deal effectively with the dominant issue of membrane fouling. At present the cost associated with waste management and disposal is helping to make the use of membranes more cost-effective and attractive.

Produced water discharge is covered by the Clean Water Act . It is treated as a non-hazardous waste from oil and gas production and is exempt from the hazardous waste provision of the Resource Conservation and Recovery Act (RCRA). Although discharge of produced water to surface streams and rivers is generally prohibited, in some limited cases in the western portions of the United States, clean produced water can be discharged as long as it is used for agricultural or wildlife purposes. EPA's regulations require that the produced water contain no more than 35 mg/l of oil and grease.

Currently, most onshore produced water is disposed into injection wells as waste or for pressure maintenance of the reservoir. These disposal wells are tightly monitored and controlled to prevent groundwater contamination. These restrictions on injection wells were developed by the EPA as part of the Underground Injection Control (UIC) program to prevent pollution of underground sources of drinking water.

Produced water has different characteristics. It contains different constituents which include oil and grease, organics, salt and other dissolved solids, suspended solids, and various trace metals. Their characteristics differ depending on the particular location of the well. These brines are typically saline with total dissolved solids (TDS) concentrations ranging from 100 ppm to over 300,000 ppm. Produced water also typically contains between fifty to a thousand parts per million total oil and grease along with low concentration of minor and trace metals [14].

Produced Water Treatment Technologies

Produced water treatment and purification is accomplished through a variety of chemical and physical separation techniques. Since produced water widely varies from source to source or locations, a single treatment method or procedure is not economically feasible for the variety of sources. Depending on the exact characteristic of the particular source of produced water different technology is appropriate. Hydrocyclones, centrifuges, membrane filtration, and activated carbon or filters are all techniques that have been used to perform produced water treatment [21-23]. A primary concern when treating produced water is the removal of the dissolved and suspended oil and grease. For onshore applications, another concern is salt removal. The common techniques currently used to for desalination are thermal distillation or RO [20]. New techniques for desalination of produced water are being reviewed including membrane pervaporation [23] and electrodialysis [24].

Membrane filtration has been proven effective in treating oily water in other industries like municipal wastewater, engine rooms, and industrial wastewater [25, 26, 27]. The concern with use of membrane technology is the reliability of the system and maintaining the permeate flow rate for economical treatment. Since the first membrane system was developed with cellulose acetate, the industry has developed a wide range of materials and techniques to improve the efficiency of the membranes. Most membranes available for use are thin film polyamide membranes on a polysulfone support [26]. Novel clay membranes have been tested for produced water treatment but with high TDS [28].

Produced water with its wide range of characteristics causes operational problems, including fouling of the membrane surface or loss of flux through the membrane surface, poor rejection characteristics, and membrane failure due to chemical reactions with the membranes. The major operational concern is the fouling of the membranes. Produced water and oily water can cause severe fouling problems on most membranes. Membranes can be fouled by four groups of materials: minerals, organics, particles and colloids, and microbiological growth. Any of these four types of membrane fouling, or a combination of types, could occur during produced water treatment.

Important parameters when cleaning membranes are the type of fouling, cleaning agent, pH, concentration, temperature, and time. The typical cleaning agents for membrane cleaning are bases, acids, enzymes, surface active agents, sequestering agents, detergents, and disinfectants. Each type of cleaning agent has benefits and drawbacks for use with produced water. For example, an acid cleaning of an oily wastewater UF membrane resulted in an appreciable increase of permeate flux but became time dependent, while an alkaline solution provided a lower flux with time independence [2]. Studies have been performed examining the effect of chemical and physical aspects of cleaning organic fouled membranes [6], enzymatic cleaning [7], and biological cleaning [3, 8].

Produced water is subject to all four categories of membrane fouling and should be pretreated to minimize the fouling of the membranes. The pretreatment should include steps to reduce the suspended particles, oil and grease, mineral deposit, and biofilm formation. For efficient operation, the pretreatment should reduce the fouling of the membranes without creating other fouling concerns. In actual operation, membrane fouling will not be completely avoidable. Fouling of membranes is a typical consequence of the separation process itself [5].

The Need to Improve Water Treatment Facility Efficiency

If produced water is to be used for beneficial purposes, it must meet exacting environmental standards. Since the oil content of produced water causes problems with traditional waste removal processes including desalination, other treatment steps must be used before commercial operations become possible. Membrane filtration and desalination of oil field brine has shown promise for converting a waste fluid to a usable resource[3]. In early field projects however, some of the filters used in microfiltration, UF, nanofiltration, and RO water treatment processes exhibited poor performance.

Contaminants Limit Produced Water Use for Beneficial Purposes

Oil field produced water contains many materials that limit its use in applications other than reservoir pressure maintenance or waterflooding. Dissolved salts prevent all but the freshest water from being used in agricultural, industrial, or municipal applications. Organic chemical components of the residual oil content make the brines unusable for other surface applications, as well. Even reinjection of produced water often requires some treatment in order to prevent well plugging. Industry has well-established water treatment practices for use in reservoir applications, but no proven way to make produced water a cost effective choice for use in either agricultural, industrial, or community applications.

Water Purification: An Alternative to Disposal of Produced Water

For practically any contemplated beneficial use, residual hydrocarbons, contaminants, suspended solids, and dissolved salts must be removed from produced water. The

[3] Early references to RO membrane filtration of oil field brine.

accepted method for treatment is filtration of the brine as either a stand-alone process or as a step in an overall water purification process. In the past, the cost of this type of treatment has prevented the establishment of any commercially successful projects. After several years of effort, Texas A&M University researchers have developed a portable water treatment and RO desalination system for produced water. In many cases, the cost of such treatment is less than the transportation costs of taking water to offsite disposal wells. Now, for the first time in the petroleum industry, water treatment and RO desalination offer a way to reduce disposed water volumes and disposal water handling costs. And since the need for new fresh water resources is becoming critical in many areas of the US, the value of this "new water" is increasing.

New Technology Will Reduce Costs and Allow More Widespread Use

Produced water management: a Texas example. Independent operators in the United States face ever increasing produced water management costs because of increasing oil-to-water ratios, increased production expenses, and more stringent environmental regulations. In Texas, more than three-fourths of the state's counties have oil production so the problem is widespread. Figure 1 shows a map of produced water sites in West Texas in the heart of the Permian Basin. The green sites (about 1/3 of the produced water) are considered brackish water, and can be treated at a cost comparable to desalination of ground water. The yellow sites (about 1/3) represent brines from 10,000 to 50,000 TDS, and can be treated if costs can be reduced.

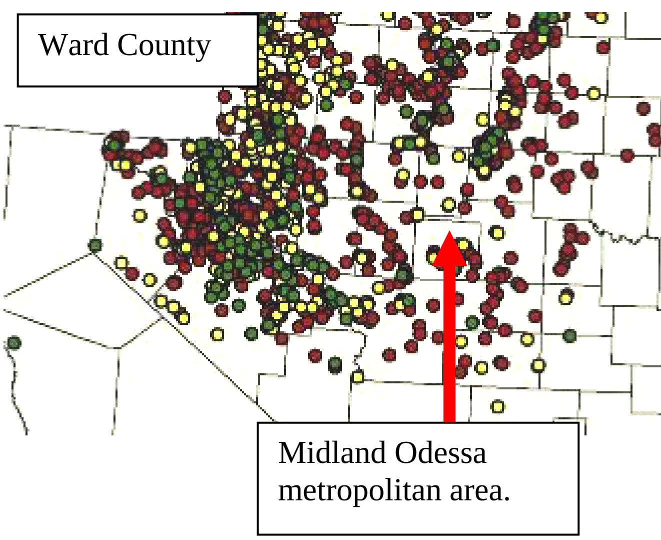

Figure 1 Texas produced water sites near the Pecos River

This area is south of the New Mexico border. Produced water is classified into three categories. The green sites (~1/3) are brackish water (less than 10,000 ppm) and could be used for beneficial purposes after treatment. One-third of the sites has salinity (TDS) from 10,000 to 50,000 ppm, and is the focus of this project.
A state-wide map in color can be found at
http://www.gpri.org/produced

Texas Railroad Commission (TRC) records and published studies [15] show that more than 14 million barrels of water (575 million gallons) are produced every day in Texas. A study conducted for the Texas Water Development Board [20] shows more than half of this water could be desalinated and made available for use for beneficial purposes. Fresh water can then be used in a beneficial manner, providing environmental benefits and community benefits, and the oil producers save money.

Another Texas example is in the Barnett Shale development in North Texas. This is the “hottest” play in Texas with more than 60 companies drilling wells. Recently the TRC limited disposal well surface injection pressure to prevent zone over pressuring. Disposal of produced brine from fracturing, once $1.30 per bbl, has doubled as salt water disposal wells charge more for deeper injection. Estimates are that well completions could drop more than 20% as companies cut back drilling programs because of the added expense of water hauling.

ADVANCED MEMBRANE TECHNOLOGY TO DESALINATE OIL FIELD BRINE

Waste Water Treatment & RO: Feasible but Expensive

Desalination refers to the process of removing salts from brackish water or salt water to produce potable water. It is primarily considered a technique to produce drinking water, but desalination technology has also been used to produce water for various industrial and agricultural processes. Simply put, desalination technology separates salt water into two separate streams: desalted water with a minimal concentration of dissolved salts and minerals, and a liquid containing the residual dissolved solids, referred to as the brine concentrate. For every 100 gallons of seawater, desalination can produce between 15 and 50 gallons of potable water [30]. Depending on the type of technology used, recovery rates are even higher for brackish water. Because of this economic advantage, brackish water desalination will be the most common option in areas away from the Gulf Coast of Texas. While the average salinity of produced water in Texas from conventional oil and gas production is roughly twice as great as seawater; many fields produce significant amounts of brine that can be categorized as brackish. With respect to unconventional O&G production, recent studies by the EPA on brine produced from coal bed methane, identified RO the method of greatest promise.

Desalination of highly saline brines is possible by several technologies. The two most common methods used today are thermal distillation and membrane desalination. Thermal distillation uses a very simple and natural process to separate out solids, salt water is heated to produce water vapor that is in turn condensed to form fresh water. Some of the more specific desalination technologies that depend on heat to produce water vapor include multi-stage flash distillation, multiple-effect distillation, and vapor compression. Approximately half of the desalination facilities in the world use some form of thermal distillation.

Membrane technology is the other major method used to desalinate salt water. Like thermal technology, membrane desalination is based on a simple concept; salt water is forced across a membrane, producing potable water on one side of the membrane, and leaving behind concentrated briny water on the other side. The two most common types of membrane desalination used today are electrodialysis and RO. Electrodialysis is a voltage-driven process that uses an electrical current to draw salts and other solids through a membrane, leaving pure water behind. With electrodialysis, ions travel through the electrically charged membrane, which differs from RO, where water molecules are forced through the membrane. Electrodialysis is not suited for the removal of dissolved organic constituents and microorganisms, which represents a serious drawback. Instead of using an electrical current, RO membrane desalination uses high pressure to pump salt water through a semi-permeable membrane, which acts as a microscopic strainer, filtering out salts, minerals, contaminants, viruses, bacteria, pesticides, and other materials.

The Middle East Desalination Research Center's (MEDRC) Research Advisory Council is conducting research on both thermal and membrane desalination technologies. Ongoing research is being funded and new research is being considered to bring these technologies closer to commercialization in this area of the world where population growth and lack of fresh water resources is even more common than in the U.S. [4]

The research focus in the Middle East is upon potable water systems for increased urban populations. Regardless, the advantage of oil field brine produced water desalination (PWDS) (by whatever technology) for providing fresh water resources is that the reverse osmosis concentrated brine can be reinjected into petroleum formations and so utilize Class II injection wells.

Development of Advanced Designs for RO Desalination of Produced Water

The technology most adaptable to PWDS is RO membrane technology. RO lends itself to scalable systems and is a commercial process. The chief difference for RO design in the oilfield is the care that must be taken with pretreatment. The feasibility of the concept has been proven by our work program established in 1999 in the Department of Petroleum Engineering.

RO desalination technology has been chosen by Texas as a preferred option of providing fresh water supplies for the Gulf Coast. Costs fo r providing water resources have been presented by three different agencies. The Texas Water Development Board is investigating the potential for similar RO desalination, this time from brackish aquifer sources (BGW) in West Texas, where water supplies are critically low. At present however, no cost estimate for BGW desalination have been reported.

Pretreatment of Oil Field Brine

The oil industry refers to water pretreatment as "water conditioning" and routinely performs this process as a necessary step to water reinjection. Since several billion gallons of water per day are reinjected, the practice of water pretreatment is well established. A waterflood engineer faces the same concerns facing those who are designing membrane treatment systems. Issues such as scale removal, biofilm suppression, and solids control must be handled in a cost-effective manner, otherwise the injection well plugs, necessitating a costly workover.

Comparing the cost of desalinating brackish oil field brine with the costs of desalinating BGW shows that pretreatment of the oil field brine will be more expensive, but

[4] MEDRC website (http://www.medrc.org)

concentrate disposal will be less expensive. Newer desalination technology is also expected to reduce these costs. Pretreatment to accommodate saline oil field brine desalination is critical. The characteristics of the materials, particularly oily water, make pretreatment mandatory. Several methods of oil and solids removal have been tested at the A&M facility.

Powered centrifuges are routinely used in offshore oil production operations to remove oil and solids from water before it is discharged into sea. Siddiqui [31] tested the use of a centrifuge to reduce oil concentration from the produced water as a pretreatment for desalination but found the power requirement to be too high. Hydrocyclone separators have been developed for more efficient oil/brine separation. Effective hydrocyclones impart more than 100 g centrifugal force at maximum efficient flow rate. Systems are best for fluids with significant density difference. Hydrocyclones work best over a narrow flow range but have proven to be effective in high pressure and medium pressure oil systems. This technology is now considered to be the most reliable for offshore applications in meeting the required level of oil for discharge. Hydrocyclones have limitations in low-pressure systems. The efficiency of oil removal with a hydrocyclone unit becomes less due to the fact that there is not enough pressure in the system to drive the water. Consequently, the water has to be pumped and as a result the produced water becomes more difficult to clean. Small oil droplets and the use of different chemicals, makes the hydrocyclone option not very effective in a number of gas condensate systems. Also, small density difference between the oil and water phase solid particles present in the feed reduced the efficiency of hydrocyclones.

Doyle [32] studied the use of organoclay for the removal of dispersed oil from water by adsorption and performed limited field tests with this technology. For onshore operation, evaporation of water using large surface area exposure of water in ponds is another option. Boysen et al. [33] looked into the commercial feasibility of using a freeze thaw evaporation process to treat produced water. This approach may cause environmental impacts relevant to the atmosphere as well as life around the ponds.

Removal of Dissolved Oil from Produced Water: The technology for removing soluble components from produced water is used for offshore platforms, but it has been used onshore only with a certain degree of success. The technology for removing soluble components can be based on extraction, precipitation, oxidation process, or by pervaporation systems. All these technologies require relatively large facilities to handle the large volume of produced water offshore. Most of these technologies involve the use of other chemicals and solvents, use of additional power as well as producing a concentrated waste stream. Activated carbon has been used in the chemical industry for a long time for the removal of dissolved organics from waste streams. Some of the new technologies that are available today for the removal of dissolved hydrocarbon components from the produced water are the "MPPE" system from Veolia Water Technologies and Solutions (http://www.mpp-systems.eu/), "Pertraction" technology (http://www.tno.nl/content.cfm?context=markten&content=case&laag1=190&item_id=267&Taal=2)) and surfactant modified zeolite microfiltration.

Table 2 contains data from a test of pretreatment of an oily water stream with heavy biological contamination using both oil absorbent and a new type of membrane microfilter. This data was collected at Texas A&M University using a specially designed portable unit that monitors power usage as a function of treatment type, water quality, and treatment time. Test results found that contaminants could be removed for less than $1.00 per 1,000 gallons of raw water processed (power cost only). Power cost is typically the largest expense in membrane plant operations thus measurement of this cost under field conditions should provide more accurate estimation of a full size facility's cost.

Table 2 Pretreatment Costs: Removing Contaminants from Waste Water

Type of Pretreatment	Kw Used	Fresh Water Produced	Power per 1,000 gal	Cost* per 1,000 gal
oil + biofilm removal	2.80	199.4	14.04	$0.98
oil removal	0.94	99.4	9.46	$0.66
* = Power cost @ $.07 per Kwh				

Disposal of Materials Removed from Brine during Desalination

Any form of desalination treatment will include some means of handling byproducts and waste removed during the purification process. In addition to brine concentrate, a desalination project may generate solid waste in the form of sand, silt and other debris found in the brine that must be filtered out before it is desalinated by the RO membranes. The amount of solid waste generated by a large-scale desalination facility is considerable. At the Tampa facility, the pretreatment process produces approximately 14 wet tons a day of organic material, suspended solids and metals found in the source water. However, it is also possible to handle slurries produced from the pretreatment process with the brine discharge directed to reinjection into the oil field. Otherwise, if pretreatment of raw water creates solid waste, then disposal must be addressed and quantities could be significant.

Since historically one of the major impacts of desalination has been the problem of the disposal of the salts ("concentrate") and other materials removed from the source water, one of the advantages of oil field brine desalination processes is that these materials can be re-introduced back into the petroleum reservoir where it originated. This brine contains concentrated dissolved salts and other materials. However, in the oil and gas industry, high salinity brines are routinely injected into formations for pressure maintenance and secondary recovery by water flooding. Since water from desalination operations may be injected into these oil and gas containing formations, the estimated cost savings can be as much as 30% of the cost of operating the desalination unit. This represents a significant cost savings for RO technology that offsets any added pretreatment needed for the oil field brine. Fresh water available is therefore available to communities in need of this valuable resource. This opportunity for the disposal of salts and other materials from water treatment processes is being considered for a number of industries [16, 20].

To illustrate the potential for disposal of brine in an oil field, the Spraberry Trend in West Texas was selected for a hypothetical brine disposal project. Spraberry reservoirs originally contained 10 billion bbls of oil in place (more than 2,000,000 M^3). Less than 10% of this oil has been recovered [34]. The reservoirs are between 5,000 and 8,000 ft. in depth and extend over portions of Borden, Dawson, Glasscock, Martin, Midland, Reagan, Sterling, Tom Green, and Upton counties**.** (More than 230,000 people live in this area including the cities of Midland, Odessa, and San Angelo.) There are more than 10,000 wells in the Spraberry reservoirs many of them operating in fields which are being waterflooded. A significant number of the injection wells in the Spraberry reservoirs take water on a vacuum (no surface injection pressure). Area rainfall ranges from less than 10” to 18” a year. All three of the major cities in this area are currently under restricted use of municipal water by households and represent potential markets for desalination facilities. There are also several waterways in the area considered “impaired”. Figure 3 shows the Colorado River Headwaters watershed (No 12080002, EPA). There are numerous oil leases producing brackish brine water in this watershed and an extensive infrastructure of pipelines used to carry oil and gas to gathering facilities and pipeline connections.

Another factor favoring alternate sources of potable water in West Texas is that many communities already have infrastructure developed for recycling waste water from municipal water treatment facilities. An example is Andrews, Texas. This city recycled 100% of its discharge from municipal water treatment into landscape irrigation for public parks, golf course and sports fields. Communities like Andrews have the resources to incorporate an additional source of water into their distribution systems if such a source became available [35].

Desalination of oil field brine has another advantage that being a means of disposing of the brine concentrate. Brine reinjection into producing formations serves as an example of alternate waste brine disposal for desalination. Byproducts from desalination, regardless of the technique employed, contain concentrated dissolved salts and other materials.

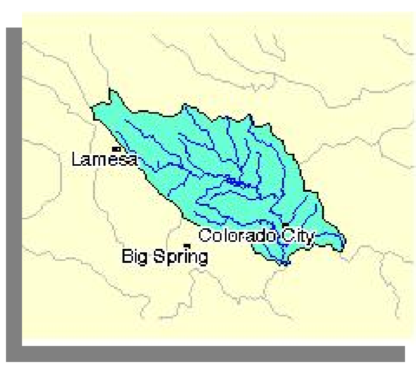

Figure 3 shows an impaired watershed in the Colorado River Basin of Texas. One of the proposed uses of fresh water produced from the Spraberry Trend is stream augmentation to reduce chlorides.

Disposing of this brine concentrate for traditional desalination processes can represent a significant fraction of the cost of operating the unit to recover fresh water. Since in the oil and gas industry, high salinity brines are routinely injected into formations for pressure maintenance and secondary recovery by water flooding, water from desalination operations could be injected into these oil and gas containing formations, the estimated cost savings are significant.

RO Desalination in the Field

Table 3 shows the cost of RO membrane treatment of produced brine from data collected on a prototype unit during our research program [31]. The field brine was an actual sample taken from a Grimes County, TX salt water disposal well (11,000 ppm total dissolved solids (TDS)). The fresh water produced by our unit measured less than 95 ppm TDS and less than 0.05 mg/l hydrocarbon. Table 3 shows the total cost to treat 6,000 gallons-per-day produced brine (80 ppm oil) with a mobile water treatment unit (including capital cost, operating cost, and maintenance cost) is less than $0.01 cent per gallon ($0.50 per barrel).

Table 3 - Operating cost for water treatment for 14,000 and 6,000 gpd. The produced water was 11,000 ppm TDS field brine containing residual crude oil.

Flow rate (Produced Water)	14,000 gpd (9.72 gpm)		6,000 gpd (9.72 gpm)	
Treated Water (Permeate) Flow rate	7,000 gpd (4.86 gpm)		3,000 gpd (2.08 gpm)	
TOC in Produced Water (pretreated)	30 ppm C	80 ppm C	30 ppm C	80 ppm C
Total Operating Cost	**0.3109 $/bbl**	**0.4511 $/bbl perm**	**0.3614 $/bbl perm**	**0.5016 $/bbl perm**

The operating cost to desalinate the water depends upon (a) the salinity of the produced water, (b) the design and efficiency of the pretreatment of the water, and (c) the effectiveness of the semipermeable RO membranes. Unless designed properly, pretreatment costs will increase the overall cost of the unit and lower the quantity of fresh water recovered.

Improvements Planned

There was clearly a need for an R&D program to improve the efficiency of membrane-based filters used for produced water, brackish ground water treatment, and desalination. Experience has shown that sub-standard operating efficiency and membrane replacement are significant operating expenses of water treatment facilities.

The research designed by A&M included the development of new cleaning agents and processes for membrane filters used in produced water desalination and in wastewater treatment. Our goal has been to improve operating efficiency by 50% over current practices. Our program utilizes environmentally friendly materials so that the water from the treatment process will meet EPA drinking water standards. Chemical agents developed are based upon technology developed by Arco Alaska for cleaning water injection wells in the Prudhoe Bay Field on the North Slope. This project is an extension of a successful Texas A&M University program funded by the U.S. Department of Energy (DE-FC26-03NT15427). Our project has run concurrently with the existing program and has the same completion date in 2007.

We expect that new cleaning methods for water treatment membrane filtration systems will result in higher operating efficiency and lower operating costs of water treatment units. Lowering the cost to manage produced water will lower the overall production costs to operators in West Texas and other areas of the country, and prolong the lifetimes of existing fields.

DEVELOPMENT OF NEW CHEMICAL CLEANING

Produced water can cause all four types of membrane fouling but typically will cause fouling by mineral and oil deposits. The mineral and oil deposits on the membrane is the primary concern since they will occur from every produced water source and require a different cleaning approach than biological fouling. Particulate fouling will also typically occur but can be cleaning using physical cleaning or high flow rates to strip the layers from the membrane surface.

Chemical Cleanup of Flowlines and Wells in Prudhoe Bay, Alaska

In oil and gas operations, effective cleanout operations are important during drilling or workover of an oil or gas well. This also applies to acidizing treatments of a geological formation or to create an effective bond between a cement composition and a wellbore wall or tubing or casing to avoid undesirable results in oil and gas well operations. By way of example, an ineffective cleanout operation during drilling or workover of an oil well can result in damage where contamination and even plugging occurs at the formation from which there is intention to produce fluids.

Similarly, where an acidizing treatment of a formation is intended to increase the productivity of the formation, in the case that oil-based contaminants are not removed from the wellbore zone adjacent to the formation interval, there can be a reduction in the effectiveness of the acidizing treatment. Moreover, poor cleaning of the wellbore wall, casing, liner or tubing string, can reduce the quality of the cement bonding during cementing operations. This can permit undesirable flow of fluids along the wellbore, undesirable interconnection between separate formations zones, undesirable fluid flow around the casing, or a failure to stabilize the casing in the wellbore. Remedial action for any of the above-mentioned problems or resulting contamination of a formation interval can incur substantial costs in both onshore and offshore well operations.

Pellizollon et al., describe in U.S. Patent 6672388 that for cleaning regimes where a cleaning agent flows over a surface to be cleaned, such as the displacement of a drilling fluid with a spacer fluid, turbulent flow usually has the advantage of increasing the cleaning efficiency [36]. To promote a turbulent flow regime, those skilled in the art normally use commercially available cleaning agents, diluted with locally available water, which is viscosified by addition of suitable polysaccharide-based or other viscosifiers.

In recent years alkylpolyglycoside-based surfactants have increased in importance because they are made from renewable raw materials, they have a good environmental profile and excellent surfactant properties. They have become especially important in detergent compositions, primarily for household cleaning products. Anionic derivatives of alkylpolyglycosides are known in literature. Their advantages have led to their use in other fields, such as application in compositions for agrochemical preparations. Synergism between the alkylpolyglycosides and the anionic surfactants is commonly exploited in the personal care and detergent sectors.

In practice, some weight ratios of binary mixtures of alkylpolyglycosides with anionic surfactants show synergic behavior for some fundamental surfactant properties, such as lowering critical micelle concentration, interfacial tension, and the like, for some important applicative parameters including increases in foaming, wetting, dishwashing performance, and the like. The use of combinations of alkylpolyglycosides with traditional (non alkylpolyglycoside-based) anionic surfactants are widely described [37]. It is possible to find descriptions of many compositions and processes related to the use of alkylpolyglycoside-based surfactants for well bore cleaning. For example, the following U.S. Pat. Nos. 5,977,032, 5,996,692, and 6,112,814 all disclose such applications [38, 39, 40].

Solutions of alkylpolyglycoside-based synergic surfactant mixtures are effective in removing water and oil based drilling fluids, thread sealant and lubricating materials, and oil-based contaminants commonly found in well bores. These include diesel oil, mineral oil, synthetic oils, crude oil, and naturally occurring hydrocarbon substances. Alkylpolyglycoside-based surfactant mixtures can be used as wetting, dispersing and/or emulsifying agents in caustic environments, such as in contact with cement slurries, remaining surface active at relatively high pH. Chan suggested the use of traditional anionics as cosurfactants in alkylpolyglycoside cleaning compositions for oil and gas well operations, but does not mention the use of the anionic derivatives of alkylpolyglycosides.

Membrane Cleanup after Produced Water Desalination

We note the similarity of the plugging phenomena in oil field flow lines and wellbores, such as Prudhoe Bay, with the fouling problems of membrane filter systems. Our research shows that the same cleaning process may be applied to membrane cleaning.

Membrane filtration has been utilized in various industries for the treatment of water and wastewater. These membrane systems are design for treatment of a specific known water source and remove the desired contaminants to meet environmental regulations or desired water quality for industrial use. These contaminants can have a wide range of characteristics that will allow them to be separated through membrane technology. The concern with using membranes in the treatment of wastewater is to increase efficiency of the treatment system by minimizing the fouling and to efficiently clean the membranes after fouling.

To efficiently clean membrane fouling, the fouling type cause by the wastewater should be known. This factor heavily influences the type and amount of cleaning that need to be performed to get the fouling layers removed. Also for a remote filtration unit for well site, high temperature is an important parameter for cleaning membranes efficiently, and heat may not be readily available. These remote locations need a cleaning solution that will work at ambient conditions and not require adding heat to improve economic feasibility. The fouling type is related to the wastewater characteristics and the amount of filtration desired. In typical membrane application the wastewater characteristics are almost constant and have known concentrations, but for produced water treatment the water characteristics will vary from well to well and over time causing additional concerns when developing a cleaning protocol.

As explained earlier, produced water can cause all four types of membrane fouling but typically will cause fouling by mineral and oil deposits. The mineral and oil deposits on the membrane is the primary concern since they will occur from every produced water source and require a different cleaning approach than biological fouling. Particulate fouling will also typically occur but can be cleaning using physical cleaning or high flow rates to strip the layers from the membrane surface. Surface active agents were used in this study to form a micelle cleaning solution for cleaning of produced water fouled UF membranes. These surface active agents form micelles that react with the mineral and oil droplets to form larger particles that are then removed by the high flow rate. This study tested the feasibility of using such a micelle solution to clean the membrane fouling that occur during operation.

Solid surfactant compositions are formed by combining solid surfactants, such as alpha-olefin sulfonates, with an organic base fluid, such as diesel. Solid surfactant suspensions may be combined with an aqueous carrier fluid to form surfactant-containing fluids suitable for, among other things, forming foams or for water wetting surfaces. Solid surfactant suspensions may also be combined with additive materials, such as polymer particles, to form a dispersion or emulsion. Polymer-containing solid surfactant suspensions may also be combined with aqueous carrier fluids to form, for example, viscosified, gelled, or foamed fluids. Concentration of solid surfactant materials contained in a solid surfactant suspension may be varied to affect the function the solid surfactant suspension. For example, the solid surfactant material may function as a polymer surface wetting agent, an emulsifier, a dispersant, a viscosifier, and/or a foamer in well completion and remedial and/or workover fluids.

The specific goal of this research has been to examine the feasibility of using micelle chemical solutions with different levels of oil and water solubility characteristics for membrane cleaning of produced water fouled UF membranes. The research tested the performance of microemulsion solutions in cleaning cycles at ambient condition can provide better performance the standard cleaning procedures. The research evaluated the use of the micelle solution on polyvinyl difluoride UF membranes from various manufactures used in produced water treatment and to determine whether physical conditions of cleaning time, flow rates, and rinse times affect the cleaning performance to optimize the micellar cleaning solution for these UF membranes.

TESTS OF CLEANING AGENTS ON MEMBRANES

Materials and Methods

Fouling of Membrane Samples

With membrane technology, produced water can be treated onsite to provide necessary water quality for treatment by RO. UF membranes are used in the **GPRI Designs™** pretreatment to RO desalination. The appropriate UF membranes demonstrated good performance with oily water. The best UF membranes provide better separation without causing higher capital cost due to higher operation pressures.

The cleanup of both UF and RO membranes is critical to longevity of a field unit. Commercially available UF membranes were selected that provided the desired reduction in both suspended solids and oil content of the produced water.

Microfiltration Membranes

Membrane manufacturers were contacted for UF membrane recommendations for use in oily water separations. These recommendations then were reduced to three by membrane configuration type or whether they are compatible with reduced foot print spiral configuration, molecular weight cutoff (MWCO), and their compatibility with the micelle solution. Flat sheet samples were obtained of each selected membrane and cut for use with the Sepa unit (described in the next section) and the 140 cm^2 test area. The three types are classified and referred to as JW, 5k, and BN.

Experimental Setup and Equipment

The experiments are performed using the GE Sepa™ CF II Med/High Foulant System (GE, YCFHFSYS01) for membrane testing designed for 140 cm^2 flat sheet membranes. The apparatus also consists of a 15 liter feed tank, pulse dampener, high pressure pump with variable speed control, and pressure and temperature gauges to monitor inlet and outlet conditions. The diagram (Figure 4) indicates location of instrumentation and flow control valves for different operating conditions that were investigated

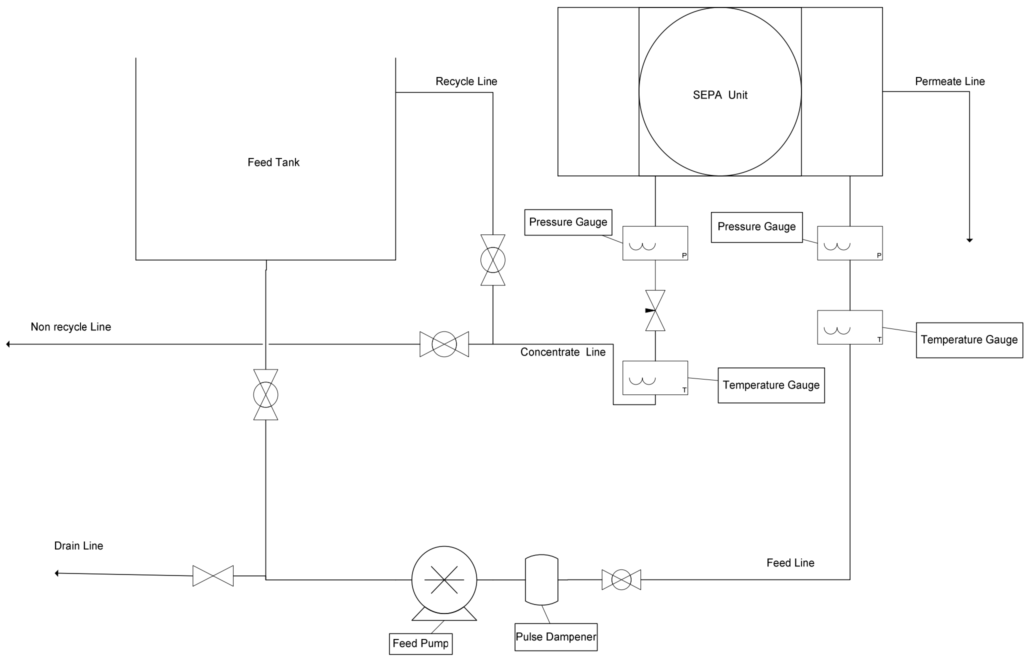

Figure 4 shows a schematic of the membrane work station used for small sample testing and membrane selection.

Each membrane type obtained was tested for produced water treatment under two operational factors of pressure and flow rate under a 3X2 factorial design with no replication based on the membrane specification provided by the membrane manufacture. The membrane specifications for the three UF membranes suggested an operational pressure of about 100 psi. This pressure indicated experimentally set levels of 138, 207, and 276 kPa for the factorial design experiment were appropriate. Limits on flow rates recommended by the Sepa System lab equipment indicated a maximum flow rate of approximately 7.6 liters per minute (Lpm) for high fouling tests provided for flow rate operation levels of 1.6 and 3.8 Lpm in the factorial design. Each experiment was monitored for temperature, flow rates, pressures, pH, operation time, and feed and permeates quality.

The membranes were fouled by using random samples of different produced water obtained from a local disposal well with unknown oil and suspended solids concentrations. The produced water sample obtained is then filtered by a 5 micron depth filter to remove large particles. The membranes are fouled by a 7-liter filtered produced water sample by operating the experimental apparatus for 2 hours with concentrated recycle under different operating conditions that are shown in Table 4. Approximately 30 milliliter (mL) feed samples were taken before and after the two hours to monitor the change in feed conditions during testing. Inlet and outlet pressure were constantly monitored and adjusted during the experiment to maintain a transmembrane pressure (TMP) at the specified level. Temperature, permeate flow rate, and pressure measurements were taken every 30 minutes to verify changes in efficiency. Also, approximately 30 mL permeate samples were collected every 30 minutes to measure water quality achieved by the membrane. Finally pH was monitored throughout the duration of the experiment for any major change in pH for the produced water feed.

Table 4 Fouling Conditions

Fouling Condition	Feed Flow Rate (Lpm)	Transmembrane Pressure (kPa)
1A	1.6	138
1B	1.6	207
1C	1.6	276
2A	3.8	138
2B	3.8	207
2C	3.8	276

The effect of fouling conditions were assumed to be negligible on cleaning effectiveness. The effect of the conditions under which the membranes were fouled should have no appreciable effect on cleaning the surface of the membranes since the cleaning solution were being design to clean heavily fouled oily membranes. These heavily fouled membranes have a limit on the degreed to which they are fouled and can add foulant layers only to the limiting factor of the flow rate of the feed across the membrane.

Flux measurements were temperature adjusted to a common temperature of 298 K and reported as liters per square meter per hour (LMH). The data collected during each of the runs along were analyzed and computed to provide direct comparisons between the different membranes through plots: average flux vs. trans membrane pressure (TMP), and flux vs. time or fouling curve for direct comparison of the data for each membrane under the same operating conditions. The classification and selection of the best was based on the high flux, lowest TMP, and high rejection characteristics of the membrane obtained.

Produced Water Samples

Produced water sample analyses consisted of two measurements -- turbidity and oil content. Turbidity analyses were conducted using a Hach 2100p turbidity meter calibrated with factory standards. Oil analyses were conducted using the TD500 oil-in-water meter developed by Turner Designs Hydrocarbon Instruments, Inc. The TD-500 oil in water meter employs an easy-to-use solvent extraction procedure with high accuracy and repeatability and correlates to EPA and other industry accepted laboratory methods. Each sample collected during an experiment was tested three times and averaged to calculate the turbidity and oil content. The two feed sample averages and the five permeate sample averages were then averaged for a combine feed average and permeate average for both the turbidity and oil content. The average values were used to calculate removal percentages as follows in (*Eq. 1)*.

$$Percent\ \ \mathrm{Re}\,moval\ \ (\%) = \left(1 - \frac{permeate\ \ average}{feed\ \ \ average}\right) * 100 \qquad \text{(Eq. 1)}$$

Table 5 Water quality results

Experiment parameters	Feed Turbidity Average (NTU)	Permeate Turbidity Average (NTU)	Turbidity % Removal	Feed Oil content Average (ppm Oil)	Permeate Oil Content Average (ppm Oil)	Oil content % Removal
JW: 1.6Lpm/138kPa	627.8	2.5	99.60%	364	35	90.43%
JW: 1.6Lpm/207kPa	412.2	1.6	99.61%	1928	573	70.26%
JW: 1.6Lpm/276kPa	238.2	1.7	99.27%	1509	188.1	87.53%
JW: 3.8Lpm/138kPa	252.3	1.1	99.57%	28	11.3	59.52%
JW: 3.8Lpm/207kPa	1000.0	1.3	99.87%	204.3	47.73	76.64%
JW: 3.8Lpm/276kPa	1000.0	1.9	99.81%	156.3	26.867	82.81%
5k: 1.6Lpm/138kPa	365.8	3.7	98.99%	44	16	64.41%
5k: 1.6Lpm/207kPa	868.7	1.6	99.82%	48	8	83.61%
5k: 1.6Lpm/276kPa	1000.0	2.4	99.76%	63	8	87.27%
5k: 3.8Lpm/138kPa	565.2	2.6	99.55%	76	26	65.44%
5k: 3.8Lpm/207kPa	954.7	8.8	99.07%	192	31	83.94%
5k: 3.8Lpm/276kPa	832.8	35.4	95.75%	44	23	47.32%
BN: 1.6Lpm/138kPa	1000.0	1.8	99.82%	136	8	94.31%
BN: 1.6Lpm/207kPa	875.8	2.5	99.71%	62	8	87.60%
BN: 1.6Lpm/276kPa	922.5	2.3	99.75%	98	8	91.92%
BN: 3.8Lpm/138kPa	1000.0	1.8	99.82%	121	7	93.94%
BN: 3.8Lpm/207kPa	1000.0	1.8	99.82%	77	9	87.94%
BN: 3.8Lpm/276kPa	974.0	1.8	99.81%	43	9	78.20%

Table 5 shows that the turbidity and the oil content of the feed was different for each experiment but within the range for produced water. Table 5 displays that turbidity of the permeate water samples typically calculated below 5 NTU. The removal percentage for the turbidity ranged from 95.75% to 99.87%. Table 5 shows also that the oil content of the water samples were influenced by the feed concentrations. The oil removal percentages for the experiments ranged from 47.32% to 94.31%. The results indicated that all three membranes achieved the suspended solids separation necessary before RO desalination. The table also shows that the oil removal percentages were the best for the BN membrane and that the permeate oil content was the lowest achieved by the membranes and averaged below 10 ppm. Finally results indicated that increased TMP or feed flow rates did not improve the oil content separation removal percentages or obtained oil content concentration characteristics of three membranes.

Cleaning of Fouled Membranes

The micelle solutions were prepared using rRO water and precise amounts of surfactants and salt concentration to provide the desired variation in oil and water solubility characteristics and micro emulsion stability.

A cleaning experiment test procedure consisted of taking a fouled membrane and using the experimental apparatus diagram in Figure 4 and running the step-by-step procedure below:

1. Add RO water to feed tank. Flush membrane system (no recycle) with clean RO water specified rinse flow rate for *t* minutes and minimum pressure (no back pressure). Record average temperature and pH over specified time.
2. Flush membrane system (concentrate recycle) with clean RO water specified rinse flow rate for *t* minutes and minimum pressure. Record average temperature and pH over specified time.
3. Drain system.
4. Add RO water to feed tank. Run system taking clean water flux data over range of pressures at 1.0 gpm flow minimum.
5. Record flux data and plot with temperature correction.
6. Drain system.
7. Add 2L of cleaning solution to feed tank. Run cleaning chemical solution over system (concentrate recycle) for *t* min at specified operating flow rate and minimum pressure. Record average temperature and pH over specified time.
8. Drain system.
9. Add RO water to feed tank. Flush system (no recycle) for *t* minutes with clean RO water at specified rinse flow rate and minimum pressure.
10. Flush system (concentrate recycle) for *t* minutes at cleaning flow rate and minimum pressure.
11. Drain system.
12. Add RO water to feed tank. Run system taking clean water flux test over range of pressures at 1.0 gpm flow.
13. Record flux data and plot with temperature correction and compare to new clean flux data and to Step 4.

Step 1 is done without any recycling of the RO water to reduce mixing of fouling water or cleaning solution. Step 2 is done with concentrate recycle specifying the time and flow rate while monitoring pH and temperature. Then, Step 4 and 12 were completed by using a stopwatch and graduated cylinder over a range of at least 3 TMP pressures suggested by the membrane manufacturers from 69 to 345 kPa at 3.8 (Lpm feed flow rate and recorded along with pH and inlet and outlet temperatures.

Analysis of Cleaning Effectiveness

The cleaning effectiveness was determined by comparing the uncleaned flux to the cleaned flux, since the fouling conditions are assumed not to be a factor. To calculate the flux, the permeate flow rate is divided by the membrane area. After that initial flux calculation, the flux is adjusted or corrected to a specified temperature of 298° K by viscosity for the comparisons. Simple linear regressions were used to analyze the corrected flux curves and to calculate average ratios of clean flux to unclean flux, unclean flux to new clean flux, and cleaning effectiveness calculated according to (Eq. 2).

$$Cleaning\ \ Effectiveness\ \ (\%) = \left(1 - \frac{used\ \ flux}{cleaned\ \ flux}\right) * 100 \qquad (\text{Eq. 2})$$

The cleaning effectiveness percentage calculated improvement provided by the cleaning procedure neglecting any effect of the fouling conditions.

Effect of Micelle Solution Formulation

The first series of cleaning tests, Experiments 1-9, were testing the differences between the micelle micro-emulsion solutions. This series is conducted using the above procedure with each test being conducted on the same membrane under the identical cleaning parameters of flow rates and time as indicated in Table 6.

Table 6 Micelle solution test conditions

Experiment Test	1	2	3	4	5	6	7	8	9
Micelle formula	50406A	50406B	50928A	50928B	50928C	50928D	50928E	50929F	50929G
No recycle Rinse before Cleaning Cycle duration (min)	1	1	1	1	1	1	1	1	1
Recycling Rinse before Cleaning duration (min)	5	5	5	5	5	5	5	5	5
Rinse Solution Flow Rate (Lpm)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
Cleaning Cycle duration (min)	15	15	15	15	15	15	15	15	15
Cleaning Solution Flow rate (Lpm)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
No recycle Rinse after Cleaning Cycle duration (min)	1	1	1	1	1	1	1	1	1
Recycling Rinse after Cleaning Cycle duration (min)	5	5	5	5	5	5	5	5	5

Flow Rate Experiments

The next series of experiments, Experiments 10-18, (Table 7) consisted of using the best two micelle solutions from the first test series and performing three sets of three flow experiments tests. The first set changes the flow rate of the cleaning solution within the set. The second set changes flow rate and membrane.The third set changes flow rate, cleaning formula, and membrane with all other cleaning parameters the same as the first test series as shown in Table 7. This set of experiments tests the effects of shear stress on cleaning solution effectiveness. This series of tests also considered whether the different formulas had different or corresponding effect on cleaning performance and flow rate effect and whether the different membranes showed similar performance trends.

Table 7 Flow rate experiments parameters

Experiment Test	10	11	12	13	14	15	16	17	18
Micelle formula	50928A	50928A	50928A	50928A	50928A	50928A	50406B	50406B	50406B
No recycle Rinse before Cleaning Cycle duration (min)	1	1	1	1	1	1	1	1	1

Recycling Rinse before Cleaning Cycle duration (min)	5	5	5	5	5	5	5	5	5
Rinse Solution Flow Rate (Lpm)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
Cleaning Cycle duration (min)	15	15	15	15	15	15	15	15	15
Cleaning Solution Flow rate (Lpm)	1.6	3.8	7.6	1.6	3.8	7.6	1.6	3.8	7.6
No recycle Rinse after Cleaning Cycle duration (min)	1	1	1	1	1	1	1	1	1
Recycling Rinse after Cleaning Cycle duration (min)	5	5	5	5	5	5	5	5	5
Membrane	JW	JW	JW	5k	5k	5k	5k	5k	5k

Contact Time Experiments

The next series of tests consisted of two additional cleaning experiments, Experiment 19 and 20, that tested the cleaning solution contact time or duration. The tests evaluated whether time of cleaning solution contact is a factor and can improve performance. The tests were performed following the cleaning procedure and under the same parameters in Experiment 2 shown in Table 4 except with a 30 minute cleaning time. The testwas repeated. The contact time could cause an increase in effectiveness by increasing the chemical solubilization of the fouling layers. (No tabular data is given for these experiments).

Water Rinsing Experiments

The last series of cleaning tests conducted evaluated changing the rinse duration and flow rates to determine if any effect was seen on the microemulsion solution being maintained on the membrane and reducing the actual effectiveness of the cleaning cycle. The tests were conducted to form sets of experiments to coincide with previous tests with similar conditions for comparison. The experiments in Table 8 tested whether doubling the rinse time and flow rate before and after the cleaning cycle added any notable effect on performance.

Table 8 Water rinsing experimental test conditions

Experiment Test	17	18	21	22	23	24	25	26	27	28
Micelle formula	50406 B	50406 B	50406 B	50406 B	50406 B	50406 B	50928 C	50928 C	50928 C	50928 C
No recycle Rinse before Cleaning Cycle duration (min)	1	1	1	1	1	2	1	1	2	2
Recycling Rinse before Cleaning Cycle duration (min)	5	5	5	5	5	10	5	5	10	10
Rinse Solution Flow Rate (Lpm)	3.8	3.8	7.6	7.6	3.8	3.8	3.8	7.6	3.8	7.6

Cleaning Cycle duration (min)	15	15	15	15	15	15	15	15	15	15
Cleaning Solution Flow rate (Lpm)	3.8	7.6	3.8	7.6	3.8	3.8	3.8	3.8	3.8	3.8
No recycle Rinse after Cleaning Cycle duration (min)	1	1	1	1	1	2	1	1	2	2
Recycling Rinse after Cleaning Cycle duration (min)	5	5	5	5	5	10	5	5	10	10
Membrane	5k	5k	5k	5k	BN	BN	BN	BN	BN	BN

The different sets consists of changing one other variable along rinse flow rate or time to make direct comparisons on performance changes and to notice any trends or slight variation on the rinse effect to the other parameters.

Membrane Type and Cleaning Effectiveness

The last set of experiments and analysis consists of analyzing the data to make comparison on which membrane type was cleaned more effectively. The set of experiments consisted of the baseline test conditions of Experiments 1-9 with changing only the membrane type and utilizing the same micelle solution. The analysis also evaluated whether different membranes showed different effects for rinsing or cleaning flow rates. This analysis tested the suitability of the micelle solution for wide varieties of polyvinyl difluoride UF membranes. The analysis also examines the cleaning solution temperature provided by ambient conditions.

ASPECTS OF MICELLAR CLEANING

The results of the experiments are discussed below. Each major factor that would affect cleaning effectiveness, (micellar formulation, TMP, cleaning agent flow rate, contact time, water rinse time) was determined independently. From these results, an estimate could be made of the optimum conditions for performing cleaning tests.

Micelle Solution Test Series

The flux measurement results from Experiment 1 are shown below:

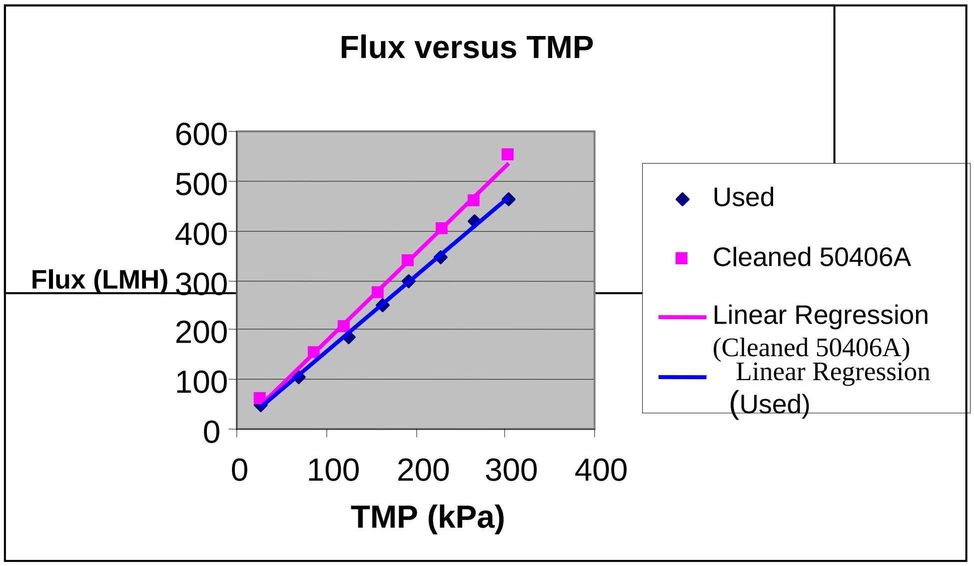

Figure 5 Experiment 1 Pure water flux curves. The flux measurements were measured and adjusted to 298K.

Graphs similar to Figure 5 were utilized to compare and analyze each individual experiment and to calculate the average ratios of cleaned to used, cleaned to new, used to new, and cleaning effectiveness as percentage of unclean to clean. The ratios are averaged over the 3 different points on the flux curve and provided in Table 9.

Table 9 Micelle formula results summary

Experiment Test	1	2	3	4	5	6	7	8	9
Micelle formula	50406A	50406B	50928A	50928B	50928C	50928D	50928E	50929F	50929G
Clean flux/ Used flux	1.15	4.86	7.53	2.16	2.78	1.32	2.16	1.34	1.3
Clean flux/ New flux	1.44	1.68	1.62	1.46	0.98	0.96	0.52	0.31	0.62
Used flux/ New flux	1.25	0.35	0.21	0.68	0.36	0.77	0.25	0.25	0.48
Cleaning Effectiveness (%)	12.9	79.3	86.7	53.6	63.8	20.6	52.5	19.4	23.2

Cleaning Solution Flow Rate Test Series

The results of the cleaning flow rates tests for formula 50406B and 50928A are summarized in Table 10 based on linear regression flux curves and averaged ratios as done previously. Table 10 also shows the affect of different membrane types on the micelle solution performance.

Table 10 Cleaning flow rate effect on performance results

Experiment Test	10	11	12	13	14	15	16	17	18
Micelle formula	50928A	50928A	50928A	50928A	50928A	50928A	50406B	50406B	50406B
Cleaning flow Rate (gpm)	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
Membrane	JW	JW	JW	5k	5k	5k	5k	5k	5k
Clean flux/ Used flux	1.26	1.64	1.72	1.13	1.00	1.00	1.10	1.33	0.92
Clean flux/ New flux	0.63	0.59	0.70	0.30	0.46	0.28	0.34	0.39	0.35
Used flux/ New flux	0.50	0.36	0.41	0.27	0.46	0.28	0.32	0.30	0.38
Cleaning Effectiveness (%)	20.6	38.9	41.7	11.3	0.0	-0.4	7.8	24.1	-9.1

` Contact Time Test Series

Experiments 19 and 20 measured cleaning effectiveness with double the contact time for the cleaning micelle solution and under Experiment 2 parameters. Testing resulted in 82.7% and 77.2 %, cleanup respectively. The clean flux to uncleaned flux ratios were 5.77 and 4.40, respectively. The clean-to-new flux ratios for the set were 1.38 and 2.80. The unclean to new flux ratios for experiment 19 and 20 were 0.24 and 0.64, respectively. No Table for these two experiments has been prepared.

Water Rinse Test Series

Water rinse effects on cleaning results are shown in Table 11.

Table 11 Rinse water quality affects cleanup performance

Experiment Test	17	18	21	22	23	24	25	26	27	28
Micelle formula	50406 B	50406 B	50406 B	50406 B	50406 B	50406 B	50928 C	50928 C	50928C	50928C
Cleaning Solution Flow rate (Lpm)	3.8	7.6	3.8	7.6	3.8	3.8	3.8	3.8	3.8	3.8
Rinse Solution Flow Rate (Lpm)	3.8	3.8	7.6	7.6	3.8	3.8	3.8	7.6	3.8	7.6
Rinse solution Total Contact time (min)	12	12	12	12	12	24	12	12	24	24
Membrane	5k	5k	5k	5k	BN	BN	BN	BN	BN	BN
Clean flux/ Used flux	1.33	0.92	0.98	1.24	3.62	2.10	2.71	1.95	3.02	2.87

Clean flux/ New flux	0.39	0.35	0.34	0.31	0.87	0.47	0.61	0.87	0.58	0.58
Used flux/ New flux	0.30	0.38	0.35	0.25	0.24	0.23	0.23	0.45	0.19	0.25
Cleaning Effectivenes s (%)	24.1	-9.1	-2.2	18.4	71.7	50.5	62.5	48.6	65.9	58.2

Cleaning rate does not necessarily translate into increased flux as shown. Total contact time affects cleanup to a degree but not dramatically. Best cleaning effectiveness resulted in an almost 72% increase in flow efficiency.

DISCUSSION

Micelle Solution Test Series

The results from the first series of tests were shown in Table 9 and indicate that Experiment 2 and 3 showed the best results with highest cleaning effectiveness percentage and cleaned-to-uncleaned flux ratios. In 1994, Lindau and Jonsson reported acid and basic cleaning of oily water membranes cleaned-to-uncleaned flux ratio of 1.3 and 1.4, respectively [16].The data in Table 9 indicates that the performance of the micelle solution in Experiments 2, 3, and 5 were significantly better than for acid or basic solution cleaning of oily water fouled membranes.

Micelle formulas 50406B, 50928A, and 50928C chemically reacted to the oilfield brine-fouled membrane and achieved better cleaning effectiveness by dissolving the oil particulates on the surface of the fouled membrane into the micelle solution. The data show that cleaning of produced water fouled UF membranes with micelle is feasible and more effective than reported in the literature for standard acid and basic cleaning of such fouled membranes. The results also indicate the micelle solution can be optimized to obtain the desired oil and water properties to enhance the performance of the solution.

Cleaning Solution Flow Rate Test Series

The results of Experiments 10-18 indicate that there is a maximum or optimum effective cleaning flow rate for the micelle solution. The change in cleaning effectiveness indicated that increasing cleaning flow rate improves performance for Experiments 10-12 but only to a point shown by Experiments 13-15 for micelle solution 50928A. Solution 50406B and Experiments 16-18 also show the increased flow rate improves performance to a point, beyond which performance is reduced. These experiments indicate the point at which cleaning flow maximizes cleaning effectiveness is dependent on the specific membrane and the micelle solution formula. The membranes affect the cleaning flow rate by how tight the membrane is and whether the micelle solution penetrates within the membrane by the increased flow rate.

Experiments 11 and 12 for the micelle solution also indicate that increasing the cleaning flow rate above the rates of the fouling solution flow rates (see Table 10) show only marginal cleaning effectiveness improvement from 38.9% to 41.7%. This result along with Experiments 15 and 18 indicates that increasing micelle solution cleaning above the operation flow is not necessary or significantly beneficial to cleaning effectiveness.

Micelle Solution Contact Time Test Series

Experiments 19 and 20 when compared to Experiment 2 indicate that doubling the contact time of the micelle solution shows no significant effect on the cleaning performance. Cleaning effectiveness of 82.7%, 77.2%, 79.3% for the three experiments show little if any change in effectiveness that would not be expected for repeated experiments. The set of three experiments show the reaction time of the micelle solution is not the limiting factor on the cleaning effectiveness. The experiments indicated the cleaning flow rate described earlier has a greater effect on performance than contact time.

Water Rinse Test Series

Comparison of results obtained between Experiments 17 and 21, 18 and 22, and between Experiment 25 and 26 indicates the effect of doubling the rinse water flow rates from 3.8 Lpm to 7.6 Lpm. The data indicates that doubling the water rinse flow rate for the cleaning cycle greatly reduces the effectiveness of the cleaning solution unless the micelle solution flow rate was also doubled. Previous experimental series data indicate that increasing the cleaning solution flow rate above the operational condition of fouling was not beneficial. The combined effect of these facts indicate that for the micelle solution, the cleaning flow rate and the rinse flow rate should be the same for the most effective cleaning cycle. The micelle solution cleaning cycle flow rate should be determined by the membrane specification on size or by the separation flow rate used during operation of the membrane.

Experimental data comparison shows that rinse cycle flow rate does have an effect on the cleaning effectiveness shown in Figure 6.

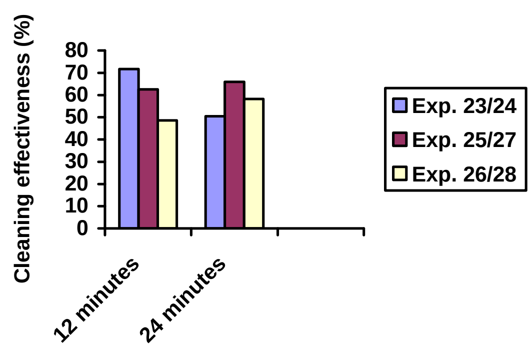

Figure 6 Rinse time comparisons

Figure 6 shows that for the micelle solution the rinse contact time effect depends on the specific micelle formulation and on the actual rinse flow rate. The comparison indicates that for higher rinse flow rates the effect of doubling the duration of the rinse increases the improvement on the cleaning effectiveness. The reduced effectiveness shown for the data indicates that the longer rinse times generally provide better cleaning effectiveness through reducing the fouling layers before introduction of the cleaning solution and reducing the cleaning solution residual left on the membrane surface.

Comparison of Micelle Solution General Effectiveness on Different Membranes

The micelle solution was effective on all membranes tested. The general cleaning performance was better than the standard cleaning with heated acidic and basic solutions. The micelle solution showed better performance on higher MWCO UF membranes. The micelle solutions worked the best on the BN and JW membranes with an approximately 30,000 MWCO. The data showed that micelle solution generally behaved the same for each membrane type. The only effect that was indicated by the different membranes was the limit on cleaning flow rate for the tighter membranes tested.

The average temperature of the micelle solution during cleaning for all experiments was monitored. The temperature of the cleaning solution, a factor in cleaning performance, was not controlled and dictated by ambient test conditions, and heat added due to the pump and line friction was within the MWCO range 5K for all tests conducted.

Conclusions

The results indicate a micelle solution is a feasible method to effectively clean oily water-fouled UF membranes. The results indicate that the micelle solution can be customized to perform better on the fouled membranes according to oil and water solubility. The results also indicate that the micelle solution performs better on UF membrane with 30,000 MWCO. The micelle solution cleaning parameters that should be used to in cleaning cycle optimization are the cleaning flow rate determined by the MWCO and rinse duration. The micelle solution formulation had the most effect on performance with the cleaning flow rate and water rinse duration showing significant improvement on the base level of cleaning effectiveness of the solution.

The micelle solution provides greatly improved cleaning performance for produced water or oily water fouled membranes over the standard cleaning solution of acid and basic solution typically employed by the membrane industry. The experiments showed that a micelle solution can be formulated to operate at ambient conditions and to eliminate the requirement of a heat source for an onsite membrane unit. With optimization, a micelle cleaning solution can provide a very cost-effective solution to cleaning oily water fouled membranes at ambient temperature.

FIELD TESTS OF CLEANING AGENTS

To test cleaning agents in the field, project tests were scheduled along with membrane testing using A&M developed desalination units. Figure 7 shows project sponsors viewing one of the RO units used for field demonstrations of the **GPRI Designs ™ Desalination Technology**. The A&M unit shown in Figure 7 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 7 shows a demonstration of the GPRI Designs TM Desalination Technology. Source: J. Veil, Argonne National Laboratory.

Experience has shown that membranes can be effective pretreatment 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.

Testing A&M Field Unit in Waste Water Application- Brayton Firefighter Training School

Figure 8 shows the GPRI desalination trailer at the water treatment plant on the A&M campus.

Filter efficiency and filter cleanup was measured for a number of agents, and oil/water systems with the mobile unit. Cleanup tests at the water treatment center removed oil content (residual diesel and combustion products) more than 90%. Data from the meters indicated that the electrical power required to perform the water conditioning (pretreatment steps) was less than ($.02 per barrel of fresh water ($0.50 per 1,000 gallons). Subsequent cleanup of the microfilters achieved a 100% flow efficiency regain.

Membrane cleaning was conducted after a series of waste water filtration experiments at the campus Brayton Firefighter training school (Figure 8). Membranes used included a PTI and Dow membranes. Oil content was characterized by diesel oil (used as a fire accelerant at the training school). Contaminants removed included a surface active foaming agent, anti-corrosion chemicals, and friction reduction agents.

As shown, the A&M Mobile Desalination Unit was used to test both pretreatment by membranes and RO desalination at field sites. Different types of membranes were tested. 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 12 shows a comparison of the cost of pretreatment with UF and for RO for different types of brine based on the single pass configuration used in the A&M demonstration unit.

Table 12 Comparison of Desalination Operating Costs –A&M Unit

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 12, for onsite desalination 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.

Neumann Field Test

The A&M unit was used in a field test in the summer of 2006 in Washington County, Texas at Anadarko’s Neumann field site. Membranes used for pretreatment was a “PTI” 10k cutoff membrane followed by a Dow low pressure D-1 RO filter. Characteristics of the oil content in the raw water feed are shown in the following Table.

Table 13 Neumann Well Oil Characteristics

Description of Brine Source	**Raw Water**	**RO Concentrate**	**RO Permeate,**
TDS	--		17 mg/L
Hydrocarbons	67.6 mg/L (tph)	1.0 mg/L (benzene)	85ug/L (benzene)
Arsenic		ND	0.005mg/L
Nitrogen (nitrates)			<0.1 mg/L

Recovery efficiency was found to be greater than 30% fresh (potable) water from the producing well. Cleaning afterward resulted in 100% regain in flow efficiency as shown by the chart depicted in Figure 9. The red line represented the original flow rate across the membrane after cleaning.

Both the microfilter and the RO filter were restored to full flow capacity. Prototype micellar cleaning agents performed better and used less clean water than alternate systems. While not yet optimized, the new system restored essentially complete membrane flux and separation efficiency after cleaning. Significantly the amount of desalinated water that was required to clean the membranes is reduced by more than 75%.

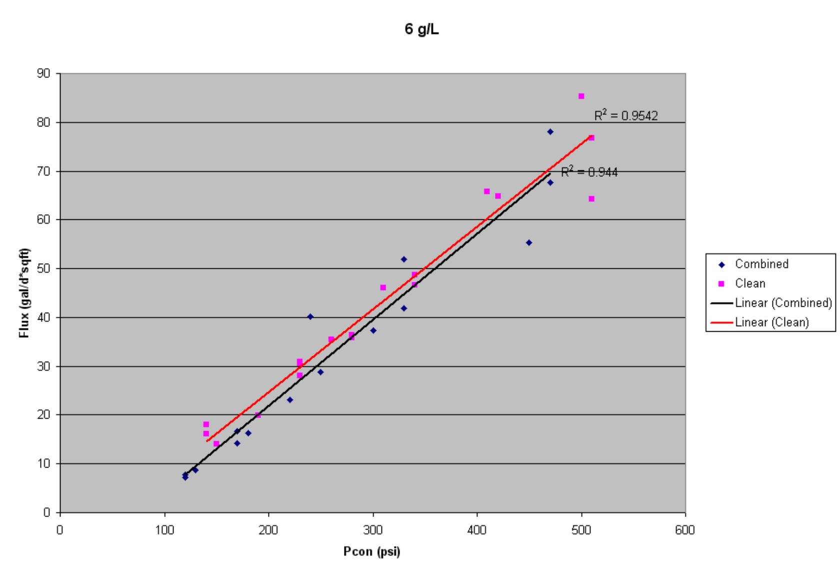

Figure 9 Neumann well regained flow rate across the membrane after cleaning.

Darst Field

The Darst Field is one of the oldest continuously producing oil fields in central Texas; first production originated in the late 1920s and continues to this day. In addition to several thousand barrels of oil the field produces approximately 300,000 barrels of brackish water a day. Given the location and quantity of water produced a large scale desalinization plant would provide a large sustainable supply of potable water to the I-35 corridor between San Antonio and Austin. The proposed sight of the desalinization facility is approximately 22 miles from downtown New Braunfels and San Marcos or 55 miles from downtown Austin and San Antonio. In addition to the close geographic proximity to population centers preliminary tests indicate that the water, which is currently being disposed of through deep pressurized injection wells, is of sufficient quality to cost effectively desalinate. The goal of the project would be to produce approximately 30 acre-feet per day of potable water to sell into the municipal markets along the I-35 corridor.

The proposed project would include a desalinization plant on the surface of El Capote Ranch approximately co-located with the largest injection well in the Darst field. The injection well would continue to operate to provide an outlet for the disposal of brine water. The project develoed a partnership with a commercial water services firm to create the necessary distribution network so that the water may be effectively marketed.

Revenue streams will come from two sources: First, the project company will charge the oilfield operator, Vintage Petroleum, a fee for managing its oilfield waste water. Second, the treated potable water will be sold to municipalities at market rates under long term contracts. Over time the relationship of these two streams would be expected to change but currently they are expected to be about equal. This project represents a novel way to solve both the problem of oilfield water disposal and the dwindling supply of potable water in central using technology current technology.

Testing on the El Capote Ranch brine indicated that an effective membrane treatment process would results in potable water that would meet EPA specifications for potable use. The cleaning agent 50406B was selected as compatible with the high salinity brine and crude oil characteristics Subsequent cleaning of the membranes with the chemical agent afforded 100% cleanup of the membranes at the pilot plant after field water desalination.

Table 15 Darst Field Brine Characteristics

Description of Brine Source	Raw Water	RO Concentrate	RO Permeate,
TDS	26,780 mg/L	31,720 mg/L	1,215 mg/L
Hydrocarbons	5.24 mg/L (tph)	0.311 mg/L (benzene)	< 1.1 ,g/L (tph)
Arsenic	--	ND	ND

DTE Field Site

From September 14-24, 2007, GeoPure Water Technologies, LLC conducted an onsite field test to determine the technical and economic feasibility of purifying and recycling fracturing fluid. The test was conducted at a DTE well site near Jacksboro, Texas.

Figure 10 GeoPure Water Technologies, LLC field unit on location in Oregon

Wastewater Resources, Inc. contributed their pretreatment technology to the process for removal of suspended solids, and GeoPure Water Technologies, LLC provided the membrane system for removal of residual colloidal solids, residual organics, and dissolved solids. A photograph of the GeoPure unit is shown in Figure 10.

Table 16 Field Results GeoPure Unit

September 20 Testing:	Feed chlorides – 17,000 ppm
Average UF membrane inlet pressure	32 psi
Water Temperature	86-90 degrees F
Average UF permeate rate	13 GPM
Average UF reject rate	1.0 GPM (7%)
RO membrane pressure	490-552 psi
RO feed pH	5.5-6.0
RO permeate rate	6.5 GPM (50% recovery rate)
RO permeate conductivity	not measured
RO permeate chlorides	123

Field results of the test are shown in Table 16. Assuming 50% fresh water recovery @ 17,000 ppm chlorides, and $1.65/barrel disposal cost, the waste disposal stream cost is $0.66/barrel as shown in the following Table.

Table 17 Operating cost summary

Chlorides (ppm)	**Chemicals**	**Electricity**	**Consumables & Maintenance**	**Recovery Rate**	**Disposal of brine**	**Opex Total**
7,000	$0.59	$0.085	$0.01	*70%	$0.50	$1.19
17,000	$0.68	$0.085	$0.01	60%	$0.66	$1.44

* estimated

Farmington New Mexico (ConocoPhillips)

A&M personnel operated a small-scale membrane filtration unit (Osmonics plate filter), and a larger mobile filtration test unit for test and demonstration purposes in support for a Los Alamos National Laboratory prefiltration project for ConocoPhillips The equipment was used to evaluate the filterability of the discharge water coming from the pretreatment filtration unit operated by Los Alamos personnel.

The results indicated that pretreatment through the system developed by the Los Alamos/UT/NMT team was effective in conditioning the water for membrane filtration. Detrimental effects from biofouling were minor, but in extended duration experiments, it would necessary to introduce biological control agents.

Fresh water produced from RO filtration would likely meet drinking water standards for the city of Farmington, New Mexico. The cost of producing fresh water with this technology is greater than water purchased from the municipal fresh water plant but less than the cost of buying, then transporting water to a field site to be used for drilling operations[5]. Testing on our larger desalination system showed the relative operating cost

[5] On August 20th, 2007 the cost of a barrel of fresh water to be delivered to a field site was $20 per truck (80bbls). Trucking costs to transport the water were $68 per hour, including a diesel cost surcharge. (Burnett private discussion).

to be less than $0.26 per barrel of fresh water permeate discharged. (Cost figures based on UF pretreatment and a 30,000 TDS oil field brine.)

Chemical cleaning of the microfilter membrane surfaces and the RO membrane used for treatment resulted in a 100% regain in flow efficiency. The results are shown in the summary table.

Texas A&M supported researchers from New Mexico Tech, University of Texas at Austin, and Los Alamos National Laboratory in this project. The photographs in the following figures shoe the field site.

<table>
<tr><td></td><td>Figure 11 ConocoPhillips McGrath salt water disposal site. An overhead door allowed loading/unloading of lab equipment. The lab was fully equipped and air conditioned.

A&M brought 100 gallons of fresh water to be used for equipment cleaning, and membrane test startup.</td></tr>
<tr><td></td><td>The small Osmonics membrane filtration unit is being unloaded at the site. In addition to the small scale unit (approximately 1 ft^2 of membrane area) A&M had available a larger unit configured to provide a membrane with approximately 40 ft^2 of surface area.</td></tr>
</table>

	A&M Separation Scientist Carl Vavra is shown operating the Osmonics unit at the field site. The input feed water for the Osmonics was the sample discharged water collected from the Los Alamos/NMT/UT Austin pre-treatment unit. Both inlet and discharged water were measured for turbidity, pH and salinity (TDS).
	ConocoPhillips field foreman showing "before" and "after" samples of produced water.

Canal Development

Tests were conducted with waste water from a mine tailings pond located out of state. The tests were to determine the filtration efficiency and the fouling tendencies of microfilters used to remove solids from the waste water. Testing was conducted with a GE polyamide filter. Turbidity before the test was approximately 4 NTU. Final clarity of the solution indicated that more than 99% of the TSS were removed from the waste water. The fouling characteristic was found to be 0.014, considered a low value.

Subsequent cleanup of the membrane at the A&M pilot plant restored 100% of the flow efficiency across the membrane.

RESULTS & CONCLUSIONS

The brine results show removal efficiency between 95.7% to 99.8% for all three membranes and under all experimental conditions. Oil removal ranged from 47.3% to

97.3% and is heavily influenced by TMP and flow rate. The cleaning experiments show that the chemical composition has the most influence on the effectiveness, with formulas 50406B, 50928A, and 50928C showing best results. They also indicate the increasing cleaning flow rate improved performance until the cleaning solution starting fouling the membrane. Increasing rinse flow rate had little effect and rinse flow time improved effectiveness slightly. A summary of the results is shown in the following Table.

Table 18 Summary of Results of Chemical Cleaning

Cleaning Run	Membrane	Cleaning Time/flow rate	Total Rinse Time/flow rate	Cleaning effectiveness %
1C-50406B-30	JW	30min/1.5 gpm	12min/1.0gpm	82.7
1C-50406B-30	JW	30min/1.0 gpm	12min/1.0gpm	77.2
1C-50406A-15	JW	15min/1.0 gpm	12min/1.0gpm	12.9
1C-50406B-15	JW	15min/1.0 gpm	12min/1.0gpm	79.3
1C-50928A-15	JW	15min/1.0 gpm	12min/1.0gpm	86.7
1C-50928B-15	JW	15min/1.0 gpm	12min/1.0gpm	53.6
1C-50928C-15	JW	15min/1.0 gpm	12min/1.0gpm	63.8
1C-50928D-15	JW	15min/1.0 gpm	12min/1.0gpm	20.6
1C-50928E-15	JW	15min/1.0 gpm	12min/1.0gpm	52.5
1C-50929F-15	JW	15min/1.0 gpm	12min/1.0gpm	19.4
1C-50929G-15	JW	15min/1.0 gpm	12min/1.0gpm	23.2
.5C-50928A-15	JW	15min/.5 gpm	12min/1.0gpm	20.6
1C-50928A-15	JW	15min/1.0 gpm	12min/1.0gpm	38.9
2C-50928A-15	JW	15min/2.0 gpm	12min/1.0gpm	41.7
.5C-50928A-15	PTI 5k	15min/.5 gpm	12min/1.0gpm	11.3
1C-50928A-15	PTI 5k	15min/1.0 gpm	12min/1.0gpm	0.0
2C-50928A-15	PTI 5k	15min/2.0 gpm	12min/1.0gpm	-.4
.5C-50406B-15	PTI 5k	15min/.5 gpm	12min/1.0gpm	7.8
1C-50406B-15	PTI 5k	15min/1.0 gpm	12min/1.0gpm	24.1
2C-50406B-15	PTI 5k	15min/2.0 gpm	12min/1.0gpm	-9.1
1D-50406B-15	PTI 5k	15min/1.0 gpm	12min/2.0gpm	-2.2
2D-50406B-15	PTI 5k	15min/2.0 gpm	12min/2.0gpm	18.4
1C-50406B-15	BN	15min/1.0 gpm	12min/1.0gpm	71.7
1E-50406B-15	BN	15min/1.0 gpm	24min/1.0gpm	50.5
1C-50928C-15	BN	15min/1.0 gpm	12min/1.0gpm	62.5
1D-50928C-15	BN	15min/1.0gpm	12min/2.0gpm	48.6
1E-50928C-15	BN	15min/1.0 gpm	24min/1.0gpm	65.9
1F-50928C-15	BN	15min/1.0gpm	24min/2.0gpm	58.2

The brine results indicate that BN membrane performed best for removal efficiency and flux and the PTI membrane performed better at lower flow rates for a specific transmembrane pressure. The cleaning solution provides efficient cleaning, but controlling temperature above 20 °C will be necessary for most efficient operation.

The data showed that the use of the new type of cleaning agent was a feasible alternative to traditional means of restoring flux in membrane systems. Specifically the data showed that a micelle solution to clean the produced water-fouled membranes was a feasible and effective method. The study shows that the micelle solution performed better than acidic and basic solutions reported in the literature for this type of foulant. The study also showed with further adjustment of the micelle solution the cleaning effectiveness could be optimized for an ambient temperature cleaning of membranes.

An additional objective was to determine the effect of operational parameters on the performance of the micellar solution. The study consisted of sets of similar experiments to show if any of the parameters changed the micelle effectiveness. The parameters were the membrane type or size, cleaning flow rate, cleaning duration, rinse flow rate, and rinse duration. The studies showed that for the micelle solution the effectiveness of cleaning was not affected by cleaning duration or the rinse flow rate. The study demonstrated that the cleaning flow rate improved performance but is limited by membrane type or MWCO. The results also indicated that increasing the duration of the rinse before and after cleaning improved the overall effectiveness of the micelle solution cleaning of the produced water fouled membranes. The study also indicated that the micelle solution would also be effective on nanofiltration and RO membranes.

Table 19 Summary of Field Cleaning Operations

Field Site	Treatment	Produced Water Characteristics	Membrane	Beginning Flux	After Cleaning	% Flow Recovered
A&M Fire Training School	UF	Waste Water	PTI UF	11 gpm	11	100%
Neumann #1	UF, RO	68 ppm tph	UF, RO (1)	7.5	7.5	100%
Darst Field	UF RO	26,000 tds, 5.24 ppm tph	PTI UF	9.5 gpm	9.4	98%
DTE Site		17,000 ppm chlorides	UF, RO (1)	6.5 gpm (RO)	6.0 gpm (2)	92%
Farmington , NM	RO		RO	0.5	0.5 (3)	100%
Canal Development	UF, RO		Dow Low Psi RO			
	(1) commerical pre-treatment used at site					
	(2) Unit Cleaned at pilot plant after field testing					
	(3) Small membrane test					

A final objective was to test the chemical cleaning process in field applications. Cleaning agents were tested on both UF and RO membranes under a number of field conditions. Several of the cleaning tests were performed at the pilot plant after testing and return of the membranes from the field. A summary of the results is shown in Table 19.

As this specific project reaches its finish, more work is planned to further develop the new cleaning technology and to provide its advantages to commercial facilities in the public sector.

ACKNOWLEDGEMENTS

This project report contains the significant work of Mr. Scott Beech, a graduate research assistant who performed the majority of the laboratory work. Dr. Albert Chan, Mr. Peter Cartwright and Mr. John Veil were key contributors to the project. John, in particular contributed significantly to final report.

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